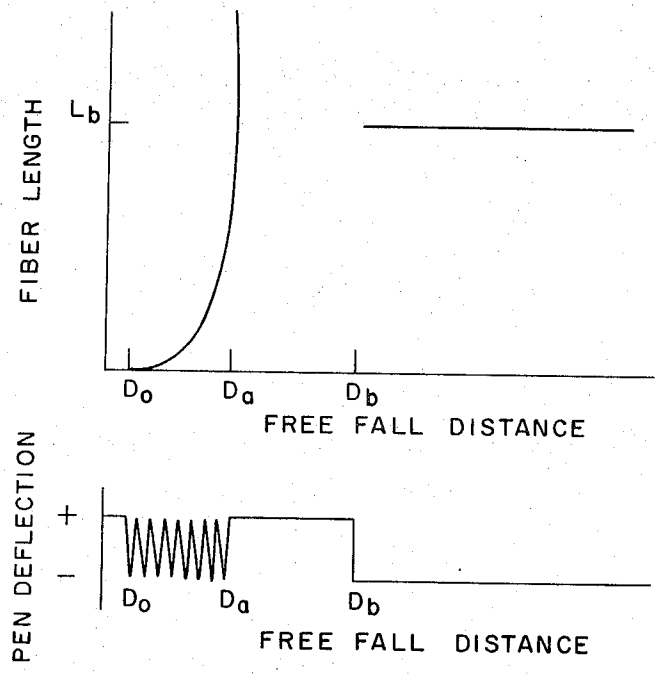
Dec. 18, 1973 W. J. PRIVOTT, JR., ET AL 3,780,153

LOW VISCOSITY MELT SPINNING PROCESS

Filed Oct. 2, 1969 3 Sheets-Sheet 1

FIG. 1.



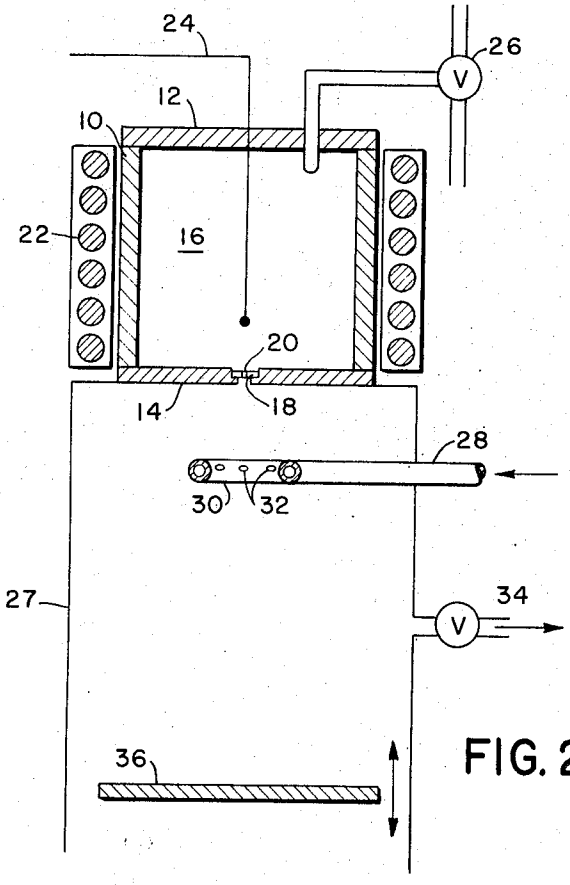


FIG. 2.

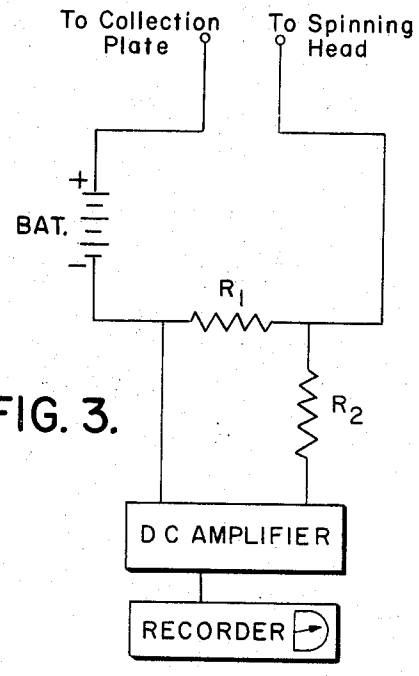


FIG. 3.

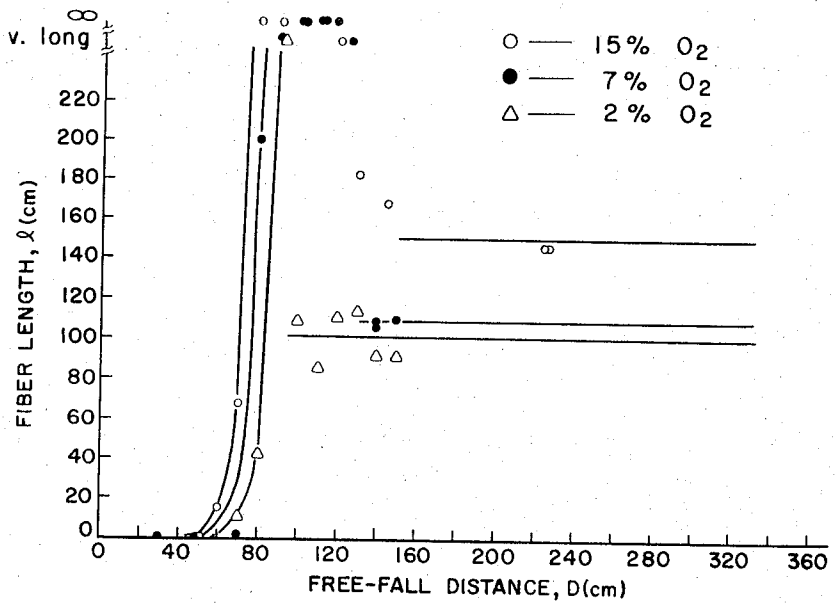

v. long
FIBER LENGTH, ℓ (cm)
220
200
180
160
140
120
100
80
60
40
20
0
0
40
80
120
160
200
240
280
320
360
FREE-FALL DISTANCE, D(cm)
15% O2
7% O2
2% O2

FIG. 4.

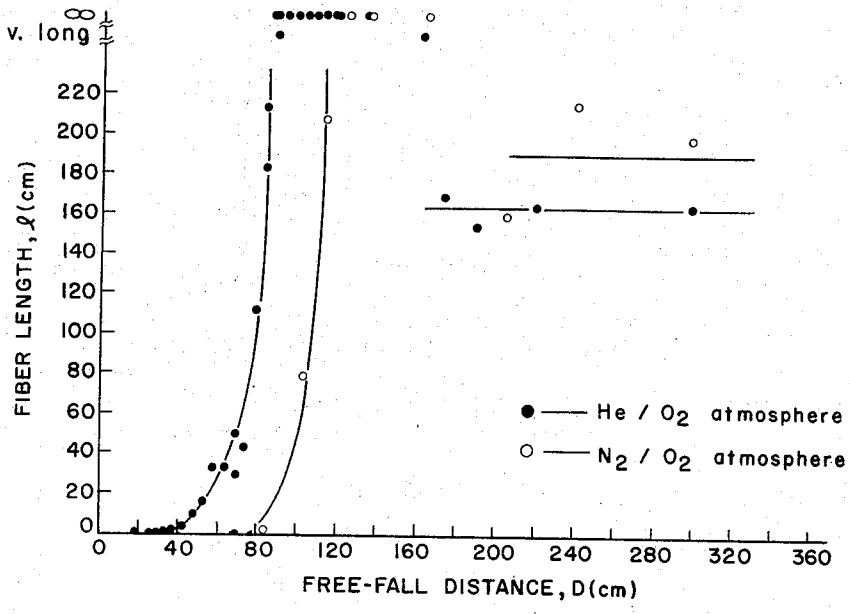

v. long
FIBER LENGTH, ℓ (cm)
220
200
180
160
140
120
100
80
60
40
20
0
0
40
80
120
160
200
240
280
320
360
FREE-FALL DISTANCE, D(cm)
He / O2 atmosphere
N2 / O2 atmosphere

FIG. 5.

LOW VISCOSITY MELT SPINNING PROCESS

Filed Oct. 2, 1969 3 Sheets-Sheet 3

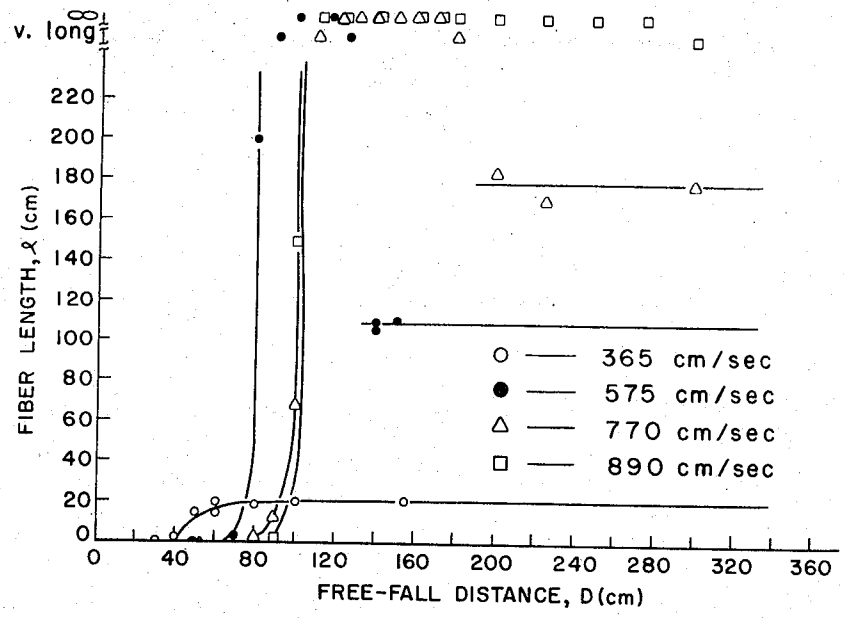


FIG. 6.

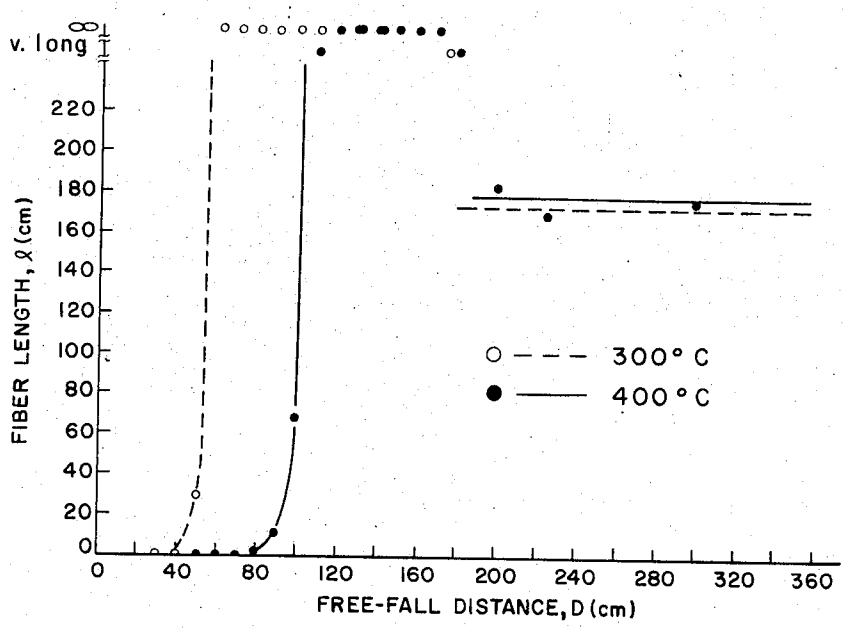


FIG. 7.

United States Patent Office 3,780,153 Patented Dec. 18, 1973

3,780,153

LOW VISCOSITY MELT SPINNING PROCESS

Wilbur J. Privott, Jr., and Robert E. Cunningham, Raleigh, N.C., assignors to Monsanto Company, St. Louis, Mo.

Continuation-in-part of application Ser. No. 599,539, Dec. 6, 1966. This application Oct. 2, 1969, Ser. No. 863,311

The portion of the term of the patent subsequent to Feb. 6, 1990, has been disclaimed

Int. Cl. B28b 3/20

U.S. Cl. 264—176 F 12 Claims

ABSTRACT OF THE DISCLOSURE

Continuous length fibers are formed from inorganic molten materials of low melt viscosity. The continuous fibers are obtained by extruding a free-falling stream, film-stabilizing the stream against the disruptive effects of surface tension pending solidification, and decelerating the solidified stream at a selected point intermediate of a first point (D_a) upstream of which an imposed stream decelerating force causes disruptions in the stream continuity and a second point (D_b) downstream of which the net tensional force acting upon stream results in substantially uniform finite length fibers.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending and commonly assigned application Ser. No. 599,539, filed Dec. 6, 1966, now abandoned. This application is also related to the other copending and commonly assigned applications of: S. A. Dunn, L. F. Rakestraw and R. E. Cunningham, application Ser. No. 829,216, filed June 2, 1969; S. A. Dunn, L. F. Rakestraw and R. E. Cunningham, application Ser. No. 838,603 filed July 2, 1969; and S. A. Dunn, L. F. Rakestraw, R. E. Cunningham, application Ser. No. 596,286, filed Nov. 22, 1966, now abandoned.

FIELD OF THE INVENTION

The present invention relates generally to the formation of shaped articles from materials of low melt viscosity and, more particularly, to the formation of shaped articles of indefinite length directly from streaming low viscosity melts.

BACKGROUND OF THE INVENTION

Many workers in the spinning art have expended considerable effort in attempts to answer the long recognized needs for practical and economical methods of fabricating continuous fibers from materials of such low viscosity as to defy any practical application of the conventional spinning techniques commonly employed in the spinning of materials having significant viscosities in the molten state as typified by the glasses, organic polymers, and materials of large molecular size.

Until recently, attempts to produce indefinite length metal fibers has been limited to such techniques as reducing relatively large diameter wire through successively smaller drawing dies until the desired diameter is achieved, or by encasing the low viscosity melt material within a vitreous sheath during attenuation. In general, such approaches have been found particularly impractical for the fabrication of continuous, small diameter-fibers.

Therefore, the present invention is primarily concerned with the manufacture of continuous fibers of less than 100 mils and provides a particularly attractive technique for making fine diameter, continuous wire and other fibers

of less than about 35 mils in diameter from inorganic melts of low viscosity.

BRIEF STATEMENT OF THE INVENTION

In attempting to form shaped articles directly from streaming melts of low viscosity, the problem initially encountered is one of stabilizing the liquidous portion of such streams, pending their solidification, against an intrinsic tendency to undergo local fluid mass transfers due to surface tension which, if unchecked, normally culminate in stream disruption. The above referenced applications Ser. No. 829,216 and Ser. No. 838,603 together with U.S. Pat. 3,216,076 issued to Alber et al. on Nov. 9, 1965, are addressed to the multifaceted aspects of this problem. Moreover, these references disclose a unique and practical approach to solving the problem. In quite general terms, these approaches involve the concept of film-stabilized melt spinning wherein a low viscosity melt is free-streamed under carefully controlled conditions through selected atmospheres productive of a rapid film formation about the stream to thereby stabilize same against surface tension-induced breakup pending solidification by normal heat transfer phenomena.

In addition to the inability of low viscosity streams to withstand surface tension-induced disruptions while in the liquid state, they are also highly susceptible to disruption by forces engendered by the impact or deceleration incident to taking up the streaming body after solidification. The forces generated during such deceleration often result in shearing rupture or deformation of the stream.

A recognition of the fragile, substantially non-extendable nature of low viscosity melts generated in the form of free streams has brought the realization that such streams, however initially stabilized pending their solidification, must be conveyed under carefully controlled conditions to minimize stream disturbing forces if indefinite length production of suitable quality is to be achieved. As herein disclosed, it has now been discovered that a critical interrelationship between the forces imposed upon a low viscosity stream at a given point and the stress capacity of the stream at points upstream thereof must be mainained if stream continuity is to be preserved. More precisely, we have now discovered that, in the case of low viscosity streams, there is a point (D_a), as measured from the stream origin, above which any given deceleration of the stream results in repeated disruptions. Also, there exists a point (D_b), as measured from the stream origin, above which the stream must be decelerated if repeated tensile breaking is to be avoided. Further, if stream continuity is to be preserved, the conditions under which the stream is transported from its origin must be so manipulated as to maintain the point D_a upstream of the point D_b for a given mode of deceleration and such deceleration must be applied at a point intermediate the points D_a and D_b.

By virtue of such manipulation of the force system acting upon the stream at given points therealong, a low stress spinning operation may be established wherein the fragile, low strength upper regions of a low viscosity stream, initially stabilized against disruption due to mass transfer within the liquid regions, is effectively isolated from disrupting forces that would otherwise be imposed. As will be disclosed, the location of points D_a and D_b along the stream may realily be varied, both relatively and absolutely, by judicious manipulation of one or more spinning conditions to thereby facilitate preferred operating conditions and results.

In the instant invention the materials employed to form continuous fibers and filaments are those normally solid inorganic materials (solid at 25°) having melt viscosities approximately 10 poises or less. Among such materials

are the metals, alloys thereof, intermetallic compounds, ceramics, metalloids, and various salts.

Among the metals which can be spun are beryllium, cobalt, aluminum, thorium, nickel, iron, copper, gold, uranium, zinc, manganese, magnesium, tin and the alloys of such metals. Representative of the low melt viscosity ceramics which may be suitably employed for spinning are alumina, calcia, magnesia, zirconia and mixtures of these and other oxides wherein such mixtures exhibit low melt viscosities, i.e., equal to or less than about 10 poises. Metalloids, such as boron and silicon, salts such as potassium chloride and a variety of the other normally solid inorganic materials with low melt viscosities are capable of being spun into continuous filaments according to this invention.

DESCRIPTION OF THE DRAWINGS

In undertaking a more detailed discussion of the present invention and the manner of its practice, reference shall be had to the accompanying drawings as being illustrative, but not limitative, thereof and in which:

FIG. 1 is a diagrammatic graph depicting the typical interrelationship of fiber length with stream free-fall distance;

FIG. 2 is a vertical, partially sectionalized view of a simplified apparatus which may be employed in the practice of the instant process;

FIG. 3 is a schematic circuit diagram of conventional make-up which may be employed to electrically monitor and record the stream continuity; and

FIGS. 4–7 are graphical presentations of pertinent data obtained in carrying out the reported examples which show the effect of variations in selected spinning parameters upon the interrelationship of fiber length with stream free-fall distance.

DESCRIPTION

Though the following discussion has particular reference to the production of filamentary-like articles, it is to be understood articles of other shapes, such as tubes, rods, films, ribbons and wires of any desired size and cross-sectional configuration, are as well contemplated where their formation from free-streaming low viscosity melt is attended by problems analogous to those of filamentary formation, insofar as such problems are overcome according to the concepts and practices herein disclosed and their equivalents.

As previously mentioned, the problem initially encountered in the streaming of low viscosity melts is one of stabilizing the liquid region of the stream against a surface tension-driven mass transfer mechanism. Although it is contemplated that such liquid region stabilization may be accomplished by the application of magnetic, electrostatic, or hydrodynamic systems, a preferred mode is to employ the concept of film stabilizing the surface of the liquid region. As set forth in the above-referenced copending applications Ser. Nos. 829,216 and 838,603, it has recently been discovered that breakup of the jet prior to solidification may successfully be suppressed by the generation of a stabilizing film of minute thickness about the nascent stream prior to its disruption and pending solidification by normal heat transfer phenomena. Briefly, this has come about through an appreciation of the following considerations: (1) if the stream velocity of a low viscosity material is not sufficient, surface tension-driven amplification and propagation of normally unavoidable, though initially minor, stream disturbances prevent the formation of an efficient jet; and (2) at intermediate velocities, the jet is disrupted by varicose breakup, wherein slightly attenuated portions of a liquid cylinder tend to further attenuate which results in ultimate disruption under the urge of surface tension forces. With increasing velocity, sinuous breakup and undue aerodynamic deceleration (in which the stream becomes contorted by interaction with the spinning atmosphere) become the limiting considerations. Such disturbances are resisted by stream inertia and viscosity, but the viscosity of the materials of interest herein is negligible to the point that undue breakup of the stream normally occurs well before it can be solidified in the form of indefinite lengths.

According to the teachings of the above-identified applications and the Alber patent, the liquid portion of such low viscosity streams may be successfully film-stabilized by spinning into suitable atmospheres which, either by reaction, decomposition or deposition, result in the rapid formation of thin films about the nascent stream to thereby suppress the above referred to disruptive forces and provide shaped articles having aspect ratios greatly exceeding those previously obtainable via unstabilized free-stream spinning of low viscosity melts.

It has further been ascertained that optimum production, as regards product length and cross-sectional uniformity, may be thwarted by disruption or attenuation of the stabilizing film prior to sufficient solidification of the stream. Such film attenuation ofttimes results in total breakup of the stream; short of this, film strength may become so non-uniformly weakened as to result in undesired variations in stream cross-section. As taught in application Ser. No. 838,603 such film disruption may be minimized, for example, by passing the melt through a "short-bore" orifice to thereby provide the stream with a relatively flat velocity profile. The result is to minimize a viscosity-driven velocity relaxation mechanism towards the attainment of plug flow which can only be accommodated by an acceleration or expansion of the stream surface.

As herein employed, the term "short-bore" orifice has reference to one whose configuration is essentially characterized by a minimum cross sectional area which extends over a maximum distance, as measured in the direction of flow through said orifice, of less than about 5 times the major dimension of said minimum cross sectional area. For example, a capillary of circular cross-section having a ratio of length/diameter (L/D) of greater than 5/1 has been found to result in a stream which undergoes undue surface expansion as it progresses from the orifice, resulting in a reduction of film uniformity and a consequent reduction in product uniformity and length. In many instances the disrupting influence of stream surface expansion up the film is so extensive as to result in total breakup of the stream itself, wherein only shot or extremely short length fibers could be obtained.

The term "major dimension of the minimum cross-sectional orifice area" is employed herein to denote the maximum straight-line distance measurable over the minimum orifice cross section. It has been discovered that use of an orifice wherein the minimum cross sectional area extends over a distance, measured in the direction of flow, greater than approximately 5 times the distance of such major dimension, results in the issuance of a stream having such a pronounced parabolic flow profile as to result in at least partial disruption or weakening of the stabilizing film being formed upon the surface of the stream. Though it may be possible to otherwise overcome the deleterious effects of such film disruption, as by increasing the richness or rate of the reactivity of the film-forming atmosphere, it has been found that production of a high order of uniformity is attainable only where the film is maintained substantially intact pending solidification. At extremely high rates of film formation, it is possible that the film structure may be renewed sufficiently rapidly to overcome the effects of incipient film disruption, but such is not normally the case. In any event, in most instances, diameter uniformity deteriorates and filament length otherwise obtainable become severely foreshortened. Thus, qualitatively, the essence of the flow velocity profile aspect lies in the discovery that, contrary to considerations attending the streaming of non-film-stabilized jets, film-stabilized spinning from low viscosity melts improves significantly, particularly as regards product cross-sectional uniformity and

length, as the initial portion of the jet is caused to approach plug flow.

Another closely interrelated aspect of film-stabilized spinning practice relative to velocity profile considerations resides in velocity control of the free-streaming melt. It should be controlled to lie within such limits that the dimensionless quantity $V\sqrt{\rho D/\gamma}$ which quantity is the square root of the well known Weber Number and shall hereinafter be termed the Rayleigh parameter, wherein V is stream velocity and D, ρ and γ are stream diameter, density and surface tension, respectively has a value within the range of 1 to 50, preferably within the range of 2 to 25. It has been discovered that, where the velocity of extrusion fails to satisfy this condition, the breakup time of the jet becomes so shortened that effective stabilization, either by the film technique or some other mode, is not likely to be established, even in the presence of an accetpable velocity profile at the point of stream issuance. For a given melt composition of a known surface tension and density extruded as a free stream at a given diameter, the optimum velocity lying within the Rayleigh parameter range of 1 to 50 will normally by determined experimentally, primary consideration being given to the density of the melt relative to that of the atmosphere into which extrusion takes place, as well as the temperature of extrusion relative to the temperature of the spin chamber. For example, given a melt with a density of 4 gms./cm.^{3}, a surface tension of 1000 dynes/cm., and a stream diameter of 0.03 cm., it is necessary to have a stream velocity between approximately 90 to 4500 cm./sec. to be within a Rayleigh parameter range of 1 to 50.

In general, propagation of varicose breakup determines the lower limit of the Rayleigh parameter range, while either sinuous breakup or aerodynamic deceleration determine its upper limits. The upper limit of the range is increased as the density of the melt relative to the spin atmosphere increases; i.e. the greater the density of the melt and/or the less the density of the spin atmosphere, the higher the Rayleigh parameter value (taken as a measure of extrusion velocity) at which successful spinning may be accomplished, though optimum performance may dictate a somewhat lower level.

Though the above described film-stabilization technique is the preferred mode of initially stabilizing the liquid region of the stream, it is again emphasized that other modes of accomplishing initial stabilization of the liquid region are as well contemplated in the practice of the instant low stress spinning process in that its principles are equally applicable to low viscosity streaming regardless of the mode of initial jet stabilization. In other words, practice of the instant process presumes effective stabilization in the liquid region and is concerned with the preservation of such region from those disrupting forces normally encountered during further progress of the now solidified stream. For example, the liquid jet may also be stabilized under the influence of a magnetic or electrostatic field of such intensity and direction as to counteract those forces tending toward fluid mass transfer. It is also possible that the liquid jet may be stabilized by hydrodynamic control. Experience has indicated, however, that the above-referenced film stabilization technique is to be preferred for its greater reliability and simplicity of execution, once the relevant factors are understood in their proper relationship.

As employed herein, the term stream shall be taken to denote both the liquid and solid regions of a free-streaming body and, absent a contrary connotation, to include the filamentary shapes issuing from the streaming body. Where a film is employed as the mode of initially stabilizing the liquid region, the term stream has reference both to the extruded melt and the applied film as a single entity. The term freeze point of the stream shall be taken in the pragmatic sense to denote that point along a solidifying stream at which discrete particles (shot) having an aspect ratio greater than unity are obtained on intercepting the stream at that point; thus, interception at any upstream point by a chosen mode of deceleration results, by this pragmatic definition, in an indiscrete, as opposed to a particalized, mass. The term stream breaking strength shall be taken in the conventional sense as denoting that force beyond which stream discontinuities occur. As a practical matter, the properties characteristic of the molten region of a low viscosity stream are such that its yield and ultimate (or breaking) strengths are of the same, low magnitude. This follows from the fact that the incipient attenuation of a low viscosity melt stream accompanying a force exceeding what would conventionally be termed its yield strength rapidly culminates in a surface tension-driven breakup of the stream without a further increase in the applied force. Thus the breaking strength of a low viscosity stream may, for all practical purposes, be equated to its yield strength. The term indefinite length is employed herein to connote extruded shaped articles of possible continuous length, that is, lengths which are not necessarily limited by the process of their formation.

In exemplifying the practice of the present invention, a simplified spinning assembly, as schematically depicted in FIG. 2, was employed. As there indicated, such an apparatus essentially comprises a melt crucible **10** which, in the case of the examples which follow, was fabricated from stainless steel. The crucible is provided with an upper header plate **12** and a lower orifice plate **14**, both of which are maintained in sealing engagement with crucible **10** to provide a gas-tight melt chamber **16**. The orifice plate **14** has seated centrally thereof a watch-sized jewel **18** formed of any suitable material chemically compatible with the melt being processed; the jewel is drilled to provide a suitable spinning orifice **20**. In the examples which follow, a ruby jewel having an orifice diameter of 100 microns and a length/diameter ratio of unity was employed. Melting of the spin charge within chamber **16** was accomplished by means of electrical resistance heating elements **22** and charge temperature was monitored by means of a thermocouple arrangement **24**. Preferably, the spinning charge was melted under a vacuum prior to effecting extrusion under an inert gas pressure; this may readily be accomplished by the two-way valve and conduit arrangement indicated at **26**, whereby chamber **16** may be alternately evacuated and pressurized to effect the desired extrusion rate. In order to confine the various reactant and cooling gas mixtures employed, a glass (Pyrex) spinning column **27** is arranged to receive the stream extruded through orifice **20**. The spin gas mixture is supplied through conduit **28** to be gently deployed throughout the spinning column by means of a gas distribution ring **30** provided with equi-spaced gas orifices **32**. Prior to extrusion into the desired gas mixture, the spinning column is preferably evacuated under vacuum, which may be provided by means of a valved connection **34**. Of course, during evacuation, the lower end of the spinning column may be temporarily sealed by means of any suitable plate arrangement, not shown. The extruded stream was collected as selected distances down the column by means of a collection surface **36**, which may take the form of a metal plate. As indicated by the two-way arrow heads, the collection surface **36** is adjustable in the vertical direction to establish the desired catch distance. Normally, the plate was maintained horizontal, but we have found that it may be inclined at widely varying angles without any substantial effect upon the fiber lengths obtained.

It is to be understood that the above-describing spinning assembly merely represents a typical apparatus which may be employed in the practice of the present invention, which latter is in no way limited to the details of the apparatus. For example, where it is desired to spin high melting point materials, an induction-heated spinning assembly would be found preferable, if not essential.

In the following discussion and examples, the term free-fall distance shall be taken to denote that vertical distance between the spinning orifice and the collection

surface. However, it is to be emphasized that free-fall distance is not necessarily defined by the position of a solid collection surface such as depicted in FIG. 2. Such a surface is merely to be taken as symbolic of that point below the orifice at which a decelerating force is brought to bear upon the stream. This force may arise by the sudden impact of the stream upon a solid surface or a more gradual stream deceleration, such as may be effected by causing the stream to pass through a significantly denser and/or counterflowing spin atmosphere; similarly, a more gradual stream deceleration may be achieved by the imposition of a suitable electrostatic field. It is only in service of simplicity that the following discussion is made largely in terms of effecting stream deceleration by collection upon a solid surface.

As before related, the process embodying the present invention is based on the discovery that, in the case of low melt viscosity streams, there is a point D_a above which such streams cannot undergo a given deceleration without disruption and a point D_b below which hte stream will, if not decelerated, undergo tensile breaking; further, the force system imposed upon a low viscosity stream may be so manipulated as to cause the point D_a to be maintained upstream of the point D_b to thereby enable one to decelerate and collect the stream at some intermediate point without provoking stream disruption. The proper interrelationship for indefinite length production is diagrammatically typified by the graph appearing in the upper portion of FIG. 1, wherein the free-fall distance of the stream is plotted against fiber length. As there shown, four distinct regions appear on this curve. For free-fall distances less than the distance D_o (denoting the freeze point of the stream, as hereinbefore defined) the stream is yet molten and any attempt to collect the stream at lesser distances results in but a molten mass. For distances intermediate the points D_o and D_a, fiber length is seen to increase exponentially with increasing free-fall distance. Although the stream is at least partially solid in this region, a disturbance sufficient to disrupt is caused by the sudden deceleration due to impingement upon the collection surface. At free-fall distances intermediate points D_a and D_b, continuous length production may be obtained. When the stream is allowed to fall through distances equal to or greater than D_b, the tensile force due to increasing stream length (and, therefore, weight) is sufficient to cause stream breakage. Thus, at points below D_b, relatively uniform fiber lengths independent of free-fall distances are obtained.

As the examples will illustrate, the reltaive and absolute positions of the points D_o, D_a and D_b may be manipulated as desired by proper variations of the process variables. For example, the points D_a and D_b may occupy relative positions such that D_b occurs upstream of D_a; in such a case, there is no free-fall distance at which continuous length filaments can be collected. Such a circumstance may arise by numerous combinations of factors affecting the force system being imposed upon a stream, but is found to be a particular problem in the case of spinning high density melts, especially in the larger diameter range. In such cases, the force system acting upon the stream must be modified in light of the present teachings such that the point D_b is caused to be shifted downstream relative to the point D_a if indefinite length production is to be obtained.

An effective aid in determining stream continuity relative to free-fall distance may take the form of a very simple electrical continuity tester circuit, such as schematically diagrammed in FIG. 3. As there indicated, such a tester serves to electrically interconnect the collection surface with the melt crucible to thereby sense electrical continuity, or lack of it, between the collection surface and the spinning head where an electrically conducting melt is being processed. Similar determinations are, of course, made by directly measuring the fiber lengths obtained at varying free-fall distances, but use of the continuity tester allows one monitor stream continuity continuously and to modify spinning conditions accordingly.

As previously indicated, the fiber lengths obtained under various process conditions will vary in a characteristic manner with free-fall distance, as shown in FIG. 1. Indications of the mechanism by which stream breakup occurs in the regions above point D_a and below point D_b are obtained by relating fiber length to free-fall distance to indicate where and when stream breakage occurred, while microscopic examination of the ends of broken lengths serve to indicate stream state at the position of break as well as the rapidity of the break. In the lower portion of FIG. 1 is shown a recording of the continuity tester for the typical graph appearing there-above. In relating this recording to the free-fall distance curve, it may be observed that the freeze point D_o of the stream is the point below which fibrous shapes, as opposed to a molten mass, may be collected. Thus, when the stream is caught at distances less than D_o, there is electrical continuity between the collection surface and the spinning head via the liquid stream, as indicated by the continuous positive deflection on the recorder curve. For free-fall distances between D_o and D_a, the on-off shape of the continuity curve indicates that the impingement of the stream upon the collection surface initiates a disturbance sufficient to effect stream breakage at some point upstream of the collection surface. An examination of the fiber ends obtained by collection within this region indicates that stream breakage occurs very rapidly, but after a solidification sufficient to retain a fibrous shape. Thus, the disturbances set up in the stream upon impingement on the collection surface at these free-fall distances are sufficient to physically disrupt the stream and only broken lengths can be obtained.

The exponential increase in fiber length as the point D_a is approached is highly suggestive of a damped disturbance superimposed upon increasing stream strength as it passes downstream, which factors combined to determine the fiber lengths obtainable in the region interemdiate the points D_o and D_a.

As indicated by the graph and recording of FIG. 1, continuous fibers are obtained for free-fall distances between points D_a and D_b; the continuity tester, of course, indicates electrical continuity within this region.

The recorded continuity curve of FIG. 1 clearly illustrates that, for distances greater than D_b, the stream undergoes breakage before impingement upon the collection surface. Because the force due to gravity has, beyond this point, become greater than the sum of stream strength and the drag force generated under the chosen spinning conditions, the stream is caused to break prior to contacting the collection surface; thus, the recording indicates a continuously open circuit. The appearance of the ends on the broken lengths obtained at free-fall distances greater than D_b indicate that they break in a very hot, solid region or in the liquid region; further, the lengths of the resultant fibers indicate that they break very near the freeze point.

For a more detailed understanding of the present invention, reference is now made to the following examples which are illustrative of the effects of the more pertinent spinning parameters upon the force system imposed upon an extruded low melt viscosity stream at varying free-fall distances. In all of the following examples, stream deceleration collection was effected by catching the stream upon a metal plate. The spinning assembly previously described with reference to FIG. 2 was employed and the spinning charge was in the form of a mixture of 62 weight percent lead/38 weight percent tin. The stream was film-stabilized by extrusion into an oxygen-containing atmosphere to form an oxide film. Unless otherwise specified, the spinning conditions were as follows: extrusion pressure of 20 p.s.i.g. argon at an extrusion temperature of 400° C., a reactant/cooling gas mixture of 7 vol. percent oxygen/93 vol. percent helium at room temperature and

atmospheric pressure, extrusion through a 100 micron diameter orifice formed in a watch-sized ruby jewel, the orifice having a L/D ratio of unity, a Pyrex spin column of 6 in. inside diameter and 300 cm., length. The melt crucible was fabricated from stainless steel having an inside diameter of 1¾ in. and a depth of 6 in. Preferably, heating to melt was accomplished under a vacuum of below 100 microns of mercury pressure. Also, extrusion was commenced prior to introducing the spin gas into the spinning column.

EXAMPLE I

This example illustrates the effect of a variation in the reactant gas concentration upon the fiber length obtainat given free-fall distances. Utilizing the apparatus of FIG. 2, a helium/oxygen spin gas mixture was supplied to the spin column through the gas distribution ring 32 positioned approximately 50 cm. below the orifice, in a manner to effect a gentle gas motion in the vicinity of the orifice. The helium which functions as a coolant gas had a constant flow rate of 2.5 c.f.m. to maintain a relatively constant heat transfer rate, the oxygen flow rate being varied to obtain the desired volume percent oxygen in the mixture. Oxygen functions as the reactant gas in forming an oxide stabilizing film about the lead/tin melt as it is given issue as a free stream through the orifice. The variation in fiber length with free-fall distance was determined at oxygen concentrations of 2, 7 and 15 volume percent, the resultant data being presented in the graph of FIG. 4. As there shown, under the conditions specified, an oxygen concentration of 2% is virtually the minimum level at which indefinite length filaments can be obtained. That is, at a free-fall distance, as measured downstream from the orifice, of approximately 95 cm., substantially continuous lengths are obtainable, whereas a small decrease in free-fall distance (i.e., shifting the collection surface upstream) results in impact breakage of the stream; alternatively, a small increase in free-fall distance is seen to result in tensile breakage. At somewhat lesser oxygen concentrations, the impact and tensile break points D_a and D_b would come to occupy positions wherein the tensile breaking point D_b occurs upstream of the impact breaking point D_a, with the result that continuous lengths would not be obtainable at any free-fall distance. As the oxygen concentration is increased to the levels of 7% and 15%, it is seen that the free-fall range over which continuous lengths may be obtained increases; that is, the distance downstream of the tensile break point D_b from the impact break point D_a increases with increasing reactant gas concentration. It is surmised that, with increasing oxygen concentrations, the stabilizing film is of increasing thickness and, consequently, strength, resulting in both an upstream shift of the impact break point D_a as well as a downstream shift of the tensile break point D_b.

It is possible that, even when employing optimum orifice configurations as above discussed, too high a concentration of reactant gas may result in such an early formation of the stabilizing film that the velocity of the extruding stream has not had sufficient time to relax to a flat profile, with the result that the film is either unduly attenuated or entirely disrupted to thereby prevent the formation of substantially continuous length filaments or, at best, filaments which exhibit a high degree of cross sectional uniformity along their lengths. As shown in the data of FIG. 4, an oxygen concentration of 15% is not sufficient to precipitate stream breakage under the conditions specified. It has been observed however that spinning melts into high reactant gas concentrations (viz. 100% oxygen) results in stream breakage into short lengths, very likely due to premature formation of the stabilizing film.

EXAMPLE II

This example illustrates the effect of coolant gas properties, particularly as regards viscosity, density and coefficient of heat transfer, upon the variation in fiber length with free-fall distance. As graphically recorded in FIG. 5, two series of runs were conducted employing spin gas mixtures of 3.3 c.f.m. helium/0.3 c.f.m. oxygen and 1.7 c.f.m. nitrogen/0.3 c.f.m. oxygen.

The molecular weight of the coolant gas affects the stabilizing film formation through its mass transfer effects on the rate of diffusion of the reactant gas to the stream surface; the freeze point and temperature history of the stream through its heat transfer effects; finally, the force system on the stream through its momentum transfer or viscous drag effects. Nitrogen is not as good a heat transfer agent as helium; it provides a greater viscous drag; finally, it retards the diffusion of oxygen to the stream surface necessary to form the stabilizing film. These effects combine to reflect the data set out in FIG. 5, wherein it is seen that, comparing nitrogen to helium, larger distances are required for freezing the fibers (the freeze point D_o being approximately 20 cm. below the orifice for the helium mixture and approximately 40 cm. for the nitrogen mixture), larger distances are required for disturbances due to impingement upon the collection surface to cease to be detrimental to stream continuity (as indicated by an impact break point D_a of approximately 90 cm. for the helium mixture and 120 cm. for the nitrogen mixture), and, finally, longer lengths of stream are required before tensile breakage occurs due to the difference in stream weight and viscous drag, stream plus film strength being substantially constant in both cases (the tensile break point value D_b being approximately 160 cm. for the helium mixture and 205 cm. for the nitrogen mixture).

It should be pointed out that, for higher melting materials, viz. over 1500–1600° C., heat transfer by radiation becomes more important so that the type of coolant gas will have less effect on the overall heat transfer rate at such higher temperatures.

EXAMPLE III

This example illustrates the effect of spinning velocity upon the interrelationship between fiber length and free-fall distance. The rate at which a low viscosity melt is extruded through an orifice determines the free, unbroken jet length of the stream in the absence of a reactant gas, as well as affecting the viscous drag force and heat transfer of the stabilized stream through its influence upon the relative velocity of the stream with respect to the spinning atmosphere. These factors combine to provide the net result set out in the graph of FIG. 6 when following the procedure and conditions set out in Example I (using a reactant gas of approximately 7% by volume oxygen/93% by volume helium supplied at a rate of approximately 3 c.f.m., extrusion being carried out at a temperature of approximately 400° C.).

It is seen that at an extrusion pressure of 12 p.s.i.g., the resulting stream velocity of 365 cm./sec. is too low to provide continuous lengths under these conditions, probably because of an insufficient free jet length. Further, it is seen that, at least up to extrusion velocities of approximately 900 cm./sec. (under a pressure of approximately 60 p.s.i.g.), signficant increases in the range of free-fall distances over which continuous lengths can be collected is achieved by increasing the extrusion velocity. This is accounted for by an increase in the distance from the orifice of the tensile break point D_b resulting from an increasing viscous drag force on the stream with increasing stream velocity. The freeze points D_o and impact break points D_a are also seen to shift downstream with increasing spinning velocity due to the fact that mass flow rates increase faster than heat transfer rates, while the downstream migration of the tensile break point D_b is greater than that of the impact break point D_a, resulting in the observed increases in the free-fall distance range over which continuous lengths may be collected.

EXAMPLE IV

It is the purpose of this example to demonstrate the effect of spinning temperature upon the variation in fiber length with free-fall distance. The temperature at which a low discosity melt is extruded directly affects the heat transfer requirements necessary to solidify the stream and indirectly affects the rate of formation of the stabilizing film through the temperature-dependence of the film-forming reaction. Following the procedure of Example I, two series of runs were conducted at extrusion temperatures of 300 and 400° C. and an extrusion pressure of 42 p.s.i.g. the results obtained being graphically set forth in FIG. 7. The decrease in heat transfer requirements at the lower temperature are clearly reflected in the significantly lower freeze point D_o and impact break point due to a more rapid increase in stream strength. The change in the rate of formation in the stabilizing film for these two temperatures is apparently not sufficient to cause significant changes in the tensile strength of the film, as reflected by the small changes in tensile break point D_b. It is thus observed that a greater free-fall distance range for collection of continuous lengths obtains at the lower extrusion temperatures.

As may now be appreciated, the position of the tensile break point D_b relative to the orifice is determined by the balance between the force of gravity, on the one hand, and stream strength and the viscous drag force, on the other hand. As disclosed in the previously referenced copending application Ser. No. 596,286, now abandoned, where gravity force is decreased (as by spinning lower density melts and/or smaller diameter streams) and/or the viscous drag force is increased (as by an increase in spin gas density and viscosity, a lower co-current or higher counter-current gas flow, or a higher spinning velocity), a point is reached where the viscous drag force overcomes gravity to the extent that, upon the initiation of normally unavoidable deviations of the stream from a straight-line path, the drag force is sufficient to effect a progressive bending of the stream.

At viscous drag force levels where the rate of such drag-sustained bending exceeds stream velocity, the bending will be caused to migrate upstream relative to the orifice into the hot, weak region of the stream where it becomes arrested by stream disruption or total severance. Thus, it is seen that, though viscous drag-sustained stream deviations may initiate in the solid, relatively higher strength downstream region, it may propagate upstream at a velocity (V_p) greater than the stream velocity (V_s) to result in stream disruption. Where such a stream force system obtains, obviously the tensile breaking point D_b has, for all intents, been shifted an infiinite distance downstream and, where indefinite length production is to be obtained, the force system imposed upon the stream must be modified by reducing the viscous drag force to a level at which the propagation velocity of drag-sustained deviations is less than stream velocity. Under these conditions, the tensile break point D_b will occupy a position of finite distance from the orifice and, if this distance be greater than the distance of the impact break point D_a, deceleration of the stream at an intermediate point may be accomplished without provoking breakage.

It may now be appreciated that there has been herewith disclosed a novel process for spinning indefinite length articles from low viscosity inorganic melts by inter-controlling the force system imposed upon the stream relative to that point to which a predetermined deceleration is brought to bear. Thus enlightened, many obvious variations, modifications and substitutions may readily occur to those skilled in the art. It is to be understood, therefore, that the invention herein set forth, particularly as regards the many alternative process manipulations, is limited only by proper construction of the appended claims.

We claim:

1. A process for the formation of continuous fibers which comprises spinning a free, molten, filamentary stream of a normally solid inorganic material having a melt viscosity of less than ten poises into a gaseous film-forming atmosphere at a velocity such that the dimensionless quantity,

$$V\sqrt{\frac{\rho D}{\gamma}}$$

lies between 1 and 50 where ρ, D and γ represent the density of the molten material, the diameter of the stream, and the surface tension of the molten material, respectively, whereby a stabilizing film is formed on the periphery of said free, molten, filamentary stream, allowing the film-stabilized free filamentary stream to solidify and, thereafter, decelerating the solidified stream at a point intermediate a first point D_a, above which deceleration of the stream causes disruption in the stream continuity, and a second point D_b, below which the net tensional force acting on the stream is sufficient to disrupt stream continuity.

2. The process of claim 1 wherein the inorganic melt is a metal or alloy thereof.

3. The process of claim 2 wherein the metal or alloy thereof is selected from the group consisting of aluminum, beryllium, cobalt, copper, iron, magnesium, nickel and alloys of such metals.

4. The process of claim 1 wherein the inorganic melt is a ceramic.

5. The process of claim 4 wherein the ceramic is aluminum oxide.

6. The process of claim 1 wherein the inorganic melt is a metalloid.

7. The process of claim 6 wherein the metalloid is selected from the group consisting of boron and silicon.

8. The process of claim 1 including inserting a collecting surface intermediate D_a and D_b to cause the solidified stream to collect as continuous fibers.

9. The process of claim 1 including the steps of moving a column of gas counter to the stream movement at a position intermediate of D_a and D_b, causing the solidified stream to decelerate, and collecting said solidified stream as continuous fiber.

10. The process of claim 1 wherein the dimensionless quantity

$$V\sqrt{\frac{\rho D}{\gamma}}$$

has a value between 2 and 25.

11. A process for the formation of continuous wire which comprises spinning a molten metal or alloy thereof as a free filamentary stream into a gaseous oxide film-forming atmosphere at a velocity, V, such that the Rayleigh parameter, equal to the value

$$V\sqrt{\frac{\rho D}{\gamma}},$$

lies between 1 and 50, where ρ, D and γ represent the density of the molten metal, the diameter of the stream and the surface tension of the stream, respectively, whereby the molten filamentary stream is stabilized by the formation of an oxide film on the periphery of said stream and thereafter solidified, the improvement which comprises decelerating the solidified stream at a point intermediate a first point, above which deceleration causes breaks in the solidified stream, and a second point, downstream of which the net tensional force acting on the stream causes breaks in the stream, said first point being upstream of said second point.

12. In a process for the manufacture of continuous wire wherein a molten metal or alloy thereof is spun as a

free filamentary stream into a gaseous atmosphere at a velocity, V, such that the value,

$$V\sqrt{\frac{\rho D}{\gamma}},$$

lies between 2 and 25, where ρ, D and γ represent the density of the molten metal or alloy, the diameter of the molten stream and the surface tension of the molten stream, respectively, and wherein the molten stream is solidified in filamentary form, the improvement which comprises applying a decelerating force to the solidified stream at a point intermediate a first point, above which such decelerating force breakes the continuity of the solidified stream, and a second point, below which the solidified stream breaks because the net downstream tensional forces exceed the strength of the molten stream, said first point being upstream of said second point.

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