Oct. 16, 1951 R. K. LADISCH 2,571,457

METHOD OF SPINNING FILAMENTS

Filed Oct. 23, 1950 4 Sheets-Sheet 1

Fig. 1

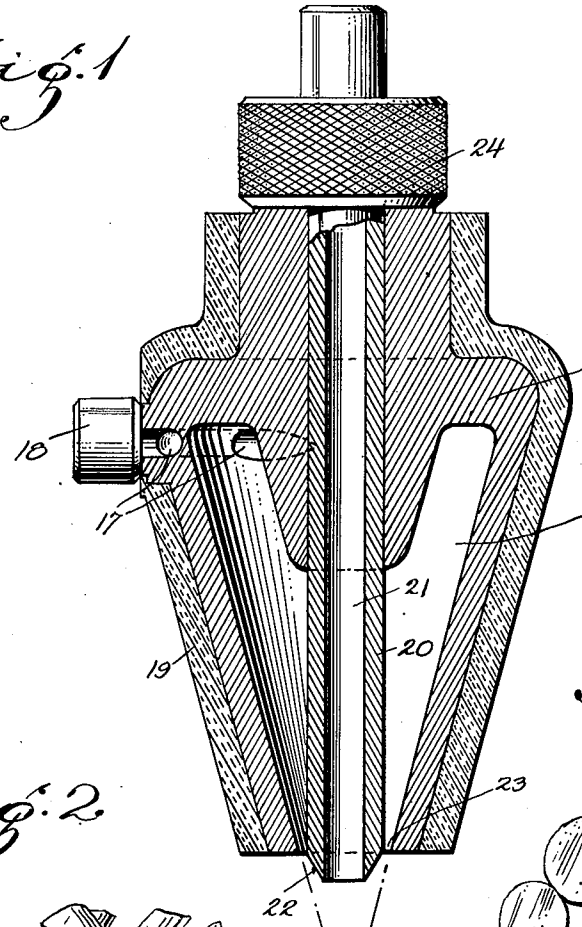


Fig. 3

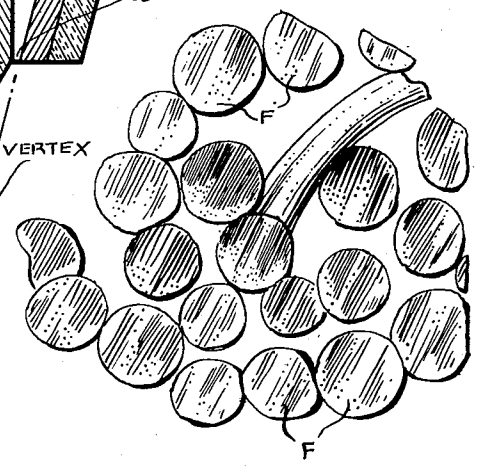
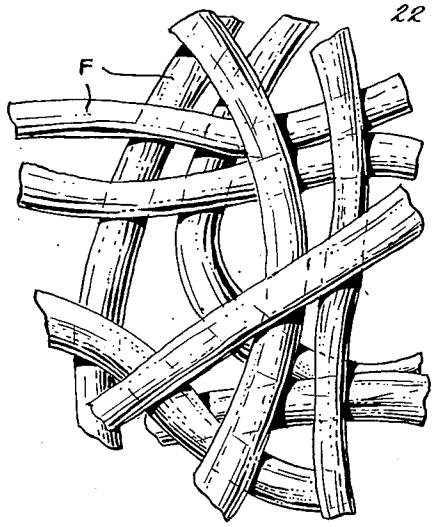


Fig. 2



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Oct. 16, 1951 R. K. LADISCH 2,571,457

METHOD OF SPINNING FILAMENTS

Filed Oct. 23, 1950 4 Sheets-Sheet 2

Fig. 4

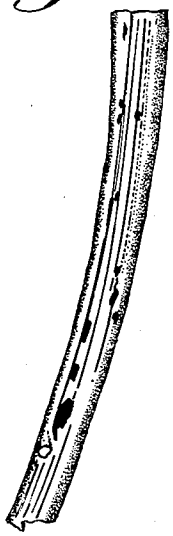


Fig. 5

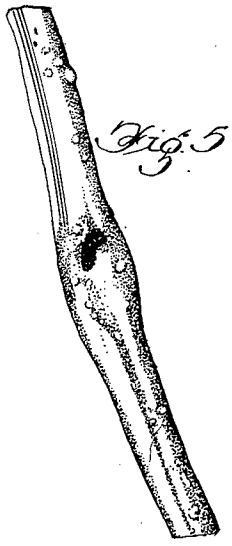


Fig. 10

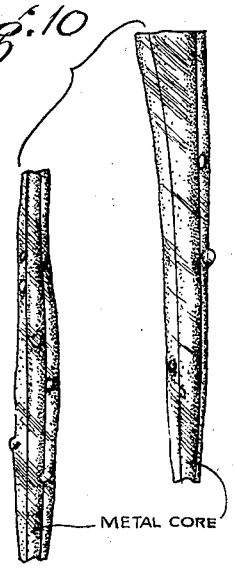


Fig. 6

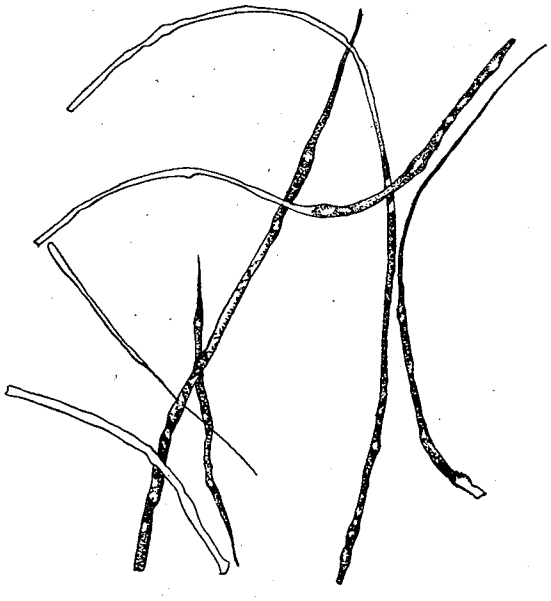
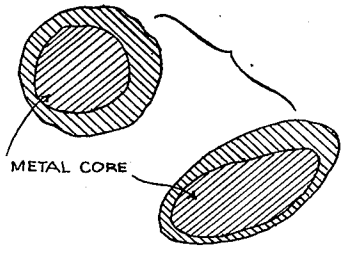


Fig. 11



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Oct. 16, 1951 R. K. LADISCH 2,571,457

METHOD OF SPINNING FILAMENTS

Filed Oct. 23, 1950 4 Sheets-Sheet 3

Fig. 7

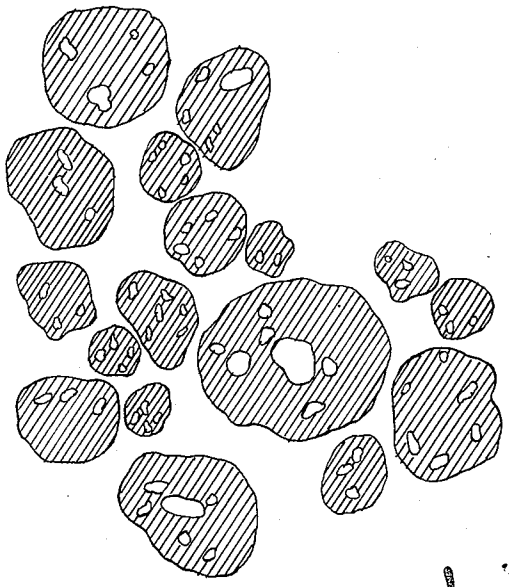


Fig. 8

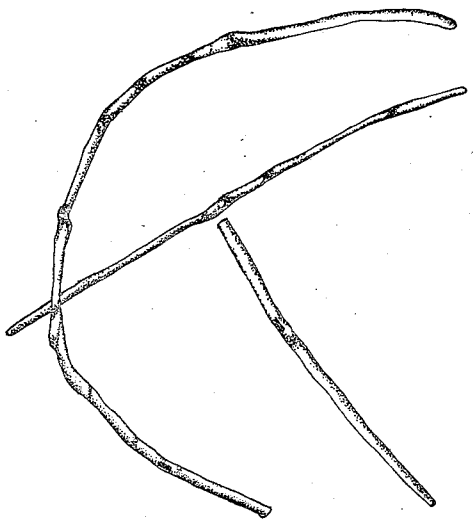
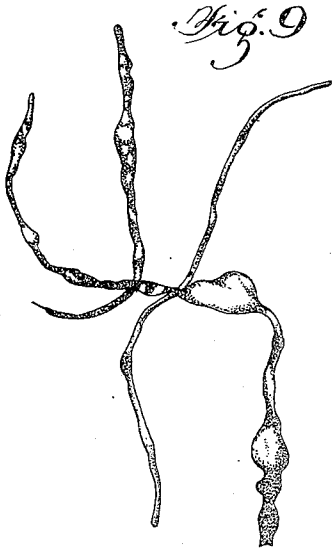


Fig. 9



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Oct. 16, 1951 R. K. LADISCH 2,571,457

METHOD OF SPINNING FILAMENTS

Filed Oct. 23, 1950 4 Sheets-Sheet 4

Fig. 13

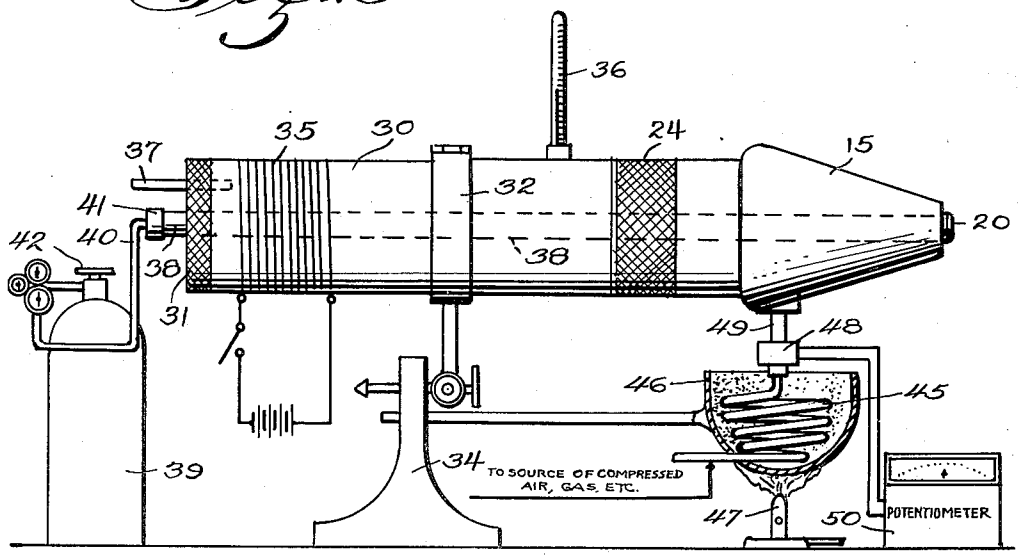


Fig. 14

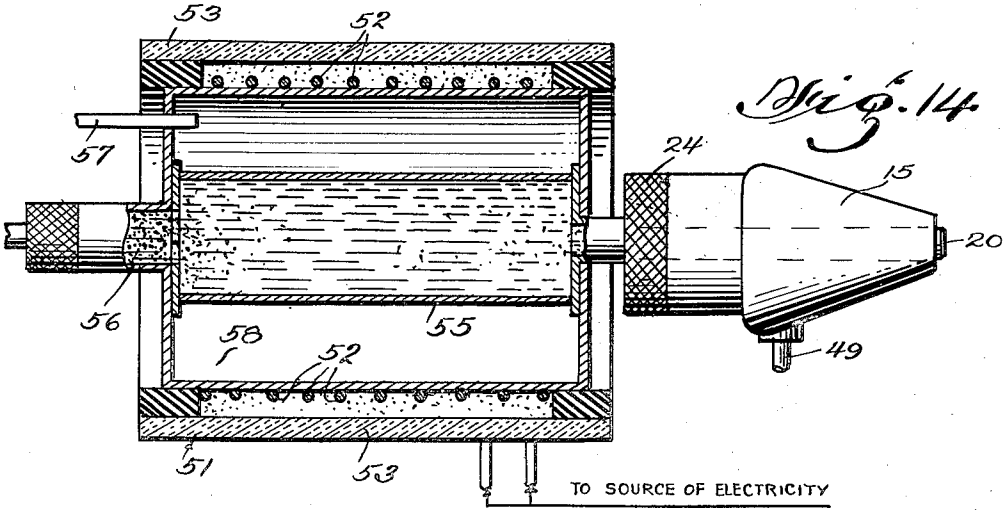
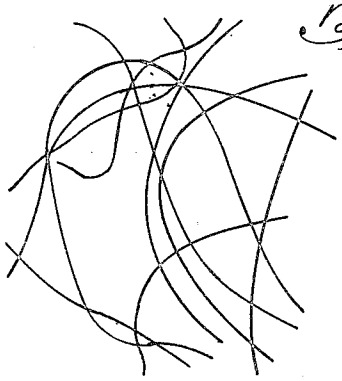


Fig. 12



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2,571,457

UNITED STATES PATENT OFFICE

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METHOD OF SPINNING FILAMENTS

Rolf Karl Ladisch, Drexel Hill, Pa.

Application October 23, 1950, Serial No. 191,672

16 Claims. (Cl. 18—54)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

1

The invention described herein, if patented, may be manufactured by or for the Government for governmental purposes without the payment to me of any royalty thereon.

This application is a continuation-in-part of my application Serial No. 89,776, filed April 26, 1949, and is also a continuation-in-part of my pending application Serial No. 110,371, filed August 15, 1949; Serial No. 110,372, filed August 15, 1949; and Serial No. 122,343, filed October 19, 1949.

This invention relates to a new method of making artificial fibers, filaments and the like from "filament-forming liquids," as fully explained hereinafter. The method departs from the use of a spinneret as conventionally employed for manufacturing fibers and filaments from various sources of fiber-forming materials, and eliminates, therefore, the high cost of spinnerets, their operation and maintenance. The method avoids discontinuities and irregularities inherent in the process of spinneret spinning, which are caused by foreign solid particles even of minute size either being present in the filament-forming raw material or originating during the spinning process as a consequence of partial decomposition of the raw material. The method does not require auxiliary equipment as used in spinneret spinning such as means for clarifying the raw material and special filter packs. The method is distinguished by its simplicity from other non-spinneret processes, such as the production of "Polyfibre" from a solution of polystyrene in isopropyl benzene by means of rather complicated apparatus containing numerous moving parts.

The invention is distinguishable from known methods in that (*a*) a relatively small amount of energy put into an elastic fluid is rapidly concentrated to a theoretically infinite value per space unit by causing said flow of elastic fluid to spiral towards the vertex of a cone; (*b*) a filament-forming material flows to this location of high energy concentration at or near the vertex; (*c*) the conduit for the filament-forming material is unconventionally large in diameter, that is, is scores or hundreds of times larger than the apertures in spinnerets; and (*d*) the process of filament formation occurs near the vertex in the midst of surrounding elastic fluid, unobstructed by apparatus, with violent force and at a rate of production not known heretofore with comparably simple apparatus and low input of energy.

The lower the viscosity of the "filament-forming liquid," the farther removed from the vertex the disrupture into filaments will occur. The higher the viscosity of the "filament-forming liquid," the nearer to the vertex the disrupture into filaments will occur. However, disrupture of the "filament-forming liquid" into filaments will in all cases be outside of the conduit for the "filament-forming liquid" and within the cone-shaped figure bounded by the spirally rotating elastic fluid. It will be evident from this that the inventive idea facilitates the mass production of fibers, filaments, and the like under unusually simple and economical conditions.

2

In consideration of this type of spinning the process may be termed "cyclone-spinning," and the products obtained according to this invention may be termed "cyclone-spun" products.

The products obtained by this method are, in general, inherently curled entangled fibers and/or filaments capable of forming yarns, or mats, or batts, or wool-like masses, or mere shapeless piles useful in various ways in the arts. Fibers and/or filaments of varying diameter may be produced solely by changing conditions of operation when employing standard apparatus. Ultrafine fibers having diameters around one micron and even smaller may be manufactured easily in contradistinction to known commercial processes where such an attempt meets prohibitive production costs.

Among other objects, the invention aims to provide an economical method of preparing said fibers and/or filaments, yarns, mats or matting, batts, wool-like masses, shapeless piles and the like from "filament-forming liquids" as hereinafter defined. A number of the products thus obtained because of their extreme light weight combined with their high heat-insulating effect are believed to be valuable for stuffing or lining articles of clothing, sleeping bags, heating pads, electric blankets, comforters, pillows, cushions, seat pads and upholstery, mattresses, life preservers, shock or crash pads and the like, also for insulating the walls of refrigerators and refrigerator cars and trucks, passenger cars, airplanes, ships and other vehicles, houses and industrial buildings, and portable shelters for military and other use. In one example of the method the material formed had a specific gravity of only 0.005, as explained below. Some of the products of the invention may have such insulating qualities as to be useful in acoustics and/or in the insulation of articles subjected to electrical stresses. A number of products obtained according to the invention consist of ex-

tremely fine and curly fibers and are believed to be particularly suitable for gas masks, industrial air filters, air conditioning equipment, air filters in engines of passenger cars and trucks, and the like. Also woven or knitted fabrics may be made from threads drawn or twisted from several of the filaments. Insulating mats or woven fabrics made from filaments formed in accordance with the invention may be incorporated in clothing and other articles subjected to flexure to give a pronounced heat-insulating effect without being destroyed or rendered valueless by repeated bending, folding or twisting. Additionally, the products of the invention may be relatively inexpensive and in certain cases are readily adaptable to coloring as by conventional means.

In another aspect of this invention cyclone-spun fibers and filaments of polymers have finely divided solids physically incorporated therein at spaced intervals, the discrete solid particles always being enveloped by a tubular polymeric casing. Substantially similar products are obtained from solutions of polymers having finely divided solids mixed therein prior to spinning from the nozzle. Some or all of these solid particles may have diamaters or lateral dimensions materially greater than the normal internal diameter of the surrounding tubular envelope, yet the polymer will completely encase the particles, which being spaced apart longitudinally of the envelope will form spaced bulbous swellings or bulges: an advantageous characteristic for some uses of the products. In other cases the solid particles are so close together within the envelope as to form what is visually a continuous core, which may be non-metallic as well as metallic; and if preferred, the filaments so formed may have relatively large cores so as to be predominantly metallic in structure and characteristics, while having thin walls of the pure polymer, or the polymer united with plasticizer. In some products of the invention the fibers or filaments each have interior cavities or voids at frequent intervals, these cavities apparently being partially evacuated by the action of the solid particles which move at high velocity during formation of the filaments, the exterior walls of the filaments, however, sealing off the cavities and remaining smooth and unbroken. This aspect of the invention effects the combining of a polymer or copolymer or polymeric mixture with metals, metalloids, and other solids which may be too coarse to pass through a spinneret, and results in filaments which may be of increased resilience and flexibility, and when matted may form filter bodies giving improved results. The electrostatic, magnetic and insulating qualities and the weight, "feel," curliness and other physical characteristics of the filaments may be materially changed by following this aspect of the invention, to effect considerable improvements over filaments made from the pure polymer, copolymer or polymeric mixture with or without a plasticizer. In the claims, for convenience, I use the term "polymer" to include not only true polymers but also copolymers, mixed melts of polymers and/or copolymers, solutions of polymers and copolymers, and plasticized polymers and copolymers and mixed melts as aforesaid.

I made these surprising and economically important discoveries as referred to above in general and as fully explained hereinafter in experiments with the so-called "Nubilosa" nozzle. The design of this type of nozzle has been generally disclosed by C. Ladisch in German Patent No. 411,948, ausgegeben April 9, 1925, and the corresponding U. S. Patent No. 1,811,637, issued June 23, 1931. Numerous variants of this nozzle are well known in the art of atomizing liquids. The nozzle delivers a rotating flow of elastic fluid which travels at high velocity and may attain supersonic velocity, towards a point outside the nozzle termed the "Vertex," and near this "Vertex" "filament-forming liquids," as fully explained hereinafter, are readily disrupted and drawn out to form fibers and/or filaments of varying lengths and degrees of fineness.

Turning now to the "filament-forming liquids" useful for practicing this invention, it should be explained that this category includes any liquid capable of forming a fiber or a filament when permitted to fall freely as a stream through an elastic fluid, said liquid being generally limited to those materials which exhibit a transformation interval; such liquids will generally produce fibers or filaments having a substantially amorphous character immediately after the formation of said fibers or filaments. It is to be understood that such a liquid may be, but does not have to be, a pure substance; it may be a single molten material or a molten mixture, and may contain other ingredients such as solvents, plasticizers, or solid fillers. It may consist of any combination of the aforesaid or equivalent constituents. It is further to be understood that the expression "to fall freely as a stream" means that the material in the liquid state is able to fall solely under the influence of gravity. The above mentioned elastic fluid may be heated or cooled; it may be under a partial vacuum or under pressure; and in general, it will have those physical conditions which facilitate fiber or filament formation. The elastic fluid may be air, nitrogen, carbon dioxide, steam, a volatilized organic solvent, or any other gas or vapor or combination of gases and/or vapors which will facilitate the formation of fibers or filaments from such liquids falling freely as a stream through said gas or vapor. In further explanation, a fiber or filament formed in free fall from said liquid according to previous explanation is considered to be of practical value if its physical and chemical characteristics meet, or can be made to meet after forming of said filamentous material, the requirements necessary for whatever purpose such filamentous material might be intended.

Bearing the foregoing in mind, this invention relates, therefore, to a method of making fibers and/or filaments from a category of materials exhibiting definite physical properties. Among the materials forming such filamentous masses belong many artificial resins, such as cellulose propionate, polyamides of the nylon type, polystyrene, polyvinyl acetate, and cellulose acetate; natural resins, such as shellac and colophonium; some inorganic glasses; organic glasses, such as sucrose octa-acetate ($C_{28}H_{38}O_{19}$); glassy chemicals, such as boron trioxide (B_2O_3), and sodium metaphosphate $(NaPO_3)_n$; other vitreous materials, such as certain types of candy; and metalloids such as selenium. The members of this group, although departing from each other often widely in their chemical nature, are related closely by their rheological properties. Scientifically, resins have been termed organic glasses, while glasses have been considered to be inorganic resins. Most members of said group are plastic solids at ordinary temperatures; and most members of said group have been proven to possess polymeric structure.

In the accompanying drawings forming a part of this specification,

Fig. 1 is a longitudinal section through a nozzle useful for practicing the method of the invention, the scale being approximately full size;

Fig. 2 is a reproduction of part of a photomicrograph of resinous (cellulose propionate) filaments made by the invention, the enlargement being about 100:1;

Fig. 3 is a reproduction of part of a photomicrograph of resinous (cellulose propionate) filaments shown in cross section, the enlargement being about 146:1;

Fig. 4 is a reproduction of part of a photomicrograph of cellulose propionate filament containing iron powder, 4% by weight, the magnification being about 150:1;

Fig. 5 is a reproduction of part of a photomicrograph of a cellulose propionate filament containing 2% silica gel powder, magnification about 150:1;

Fig. 6 is a reproduction of part of a photomicrograph of several cellulose propionate filaments containing the same silica gel as in Fig. 5, the magnification being about 20:1;

Fig. 7 is a reproduction of part of a photomicrograph showing the filaments of Fig. 6 in cross section, the magnification being about 315:1;

Fig. 8 is a reproduction of part of a photomicrograph showing polyvinyl acetate filaments combined with 5% iron powder, the magnification being about 90:1;

Fig. 9 is a reproduction of part of a photomicrograph showing a few nylon filaments combined with 2.5% iron powder, the magnification being about 90:1;

Fig. 10 is a reproduction of a photomicrograph of two cellulose propionate and tin fibers, the magnification about 85:1;

Fig. 11 is a reproduction of a photomicrograph of cellulose propionate fibers with solid cores of tin shown in cross section, the magnification being about 625:1;

Fig. 12 is a reproduction of a photomicrograph of a number of polyvinyl acetate filaments combined with molten selenium, magnification about 60:1;

Fig. 13 is a side elevation, partly in section showing diagrammatically apparatus useful for cyclone-spinning fiber-forming "liquids" of relatively low viscosities; and

Fig. 14 is a diagrammatic sectional elevation of apparatus suitable for cyclone-spinning fiber-forming liquids of higher viscosities, those parts which are also shown in Fig. 13 being mostly omitted.

Referring to Figure 1, the preferred nozzle comprises a generally frusto-conical body **15** having a hollow frusto-conical chamber **16** on the inside and having an inlet **17** for an elastic fluid opening tangentially at the larger end of said chamber, with a coupling **18** to couple a supply pipe of elastic fluid (not shown) to the nozzle. The elastic fluid supplied may be compressed atmospheric air, steam, nitrogen, carbon dioxide or other gas or vapor, or a mixture of any or all of such gases or vapors, which does not interfere chemically with the process of fiber and/or filament formation from "filament-forming liquids," under the conditions obtaining. Generally the elastic fluid will be, and in many cases it must be, heated. A layer of insulation **19** is shown surrounding the nozzle to minimize heat losses. At higher operating temperatures of the nozzle a heating element, consisting of electrical heating wires or other means for heating, is preferred to, and is used in place of, the insulation **19**. Arranged coaxially of the nozzle is a straight feeding tube or conduit **20** having a smooth bore **21** of uniform diameter and having its discharge end beveled as at **22** and projecting slightly beyond the discharge opening **23** in the nozzle. Discharge opening **23** is a narrow annular opening defined by the inside walls of the body **15** at its smaller end and the outer walls of tube **20**. It will be noted that this discharge opening is directed toward a point outside the nozzle marked "Vertex" which is the vertex of the cone that coincides with the inner frusto-conical walls of chamber **16**. The opposite end of tube **20** is to be connected with a vessel, pipe or conduit feeding a supply of "filament-forming liquids." Bore **21** has a diameter which is extremely large in comparison with the passageways provided in spinnerets or other extrusion apparatus; this diameter may exceed one-fourth of an inch and in many cases is large enough to permit free gravity flow of the "filament-forming liquid" by merely directing the nozzle downwardly. This large feeding tube presents a solid stream of said liquid which in comparison with the portion of said cone that lies outside the nozzle is very massive, being usually of a diameter exceeding one-half the base diameter of the cone which is outside of the nozzle. Nut **24** threaded on tube **20** and swiveled on the nozzle body may be used to adjust the size of the discharge opening **23** by shifting the position of the slidable tube **20** longitudinally.

Having described the nozzle, it will be apparent that the nozzle may be modified in a number of ways without departing from the spirit and scope of this invention. As is well understood in the prior art, the feeding tube **20** of said nozzle may be shaped on its outside substantially similar to the frusto-conical chamber **16** in somewhat smaller dimensions. The bore of feeding tube **20** may be constructed near its lower end, or it may extend funnel-like toward the discharge end of said feeding tube. The discharge end of feeding tube **20** may be substantially flat or squared off instead of being beveled, and this opening may be at substantially the same height as discharge opening **23**. The "filament-forming liquid" is disrupted and drawn into fibers and/or filaments near the "Vertex." It will be understood that this phase "near the vertex" includes any and all points within the cone having its tip at the "Vertex" and its base at the discharge opening **23** (as shown in Fig. 1) where contact is made between the "filament-forming liquid" and the spiraline elastic fluid.

Referring to Fig. 13, the apparatus there shown includes a retort or vessel **30** in which the "filament-forming liquid" is prepared or into which it is poured, a nozzle **15** by which the "filament-forming liquid" is cyclone-spun, and a source of compressed elastic fluid (not shown) discharging into the nozzle as will be described. To support the vessel **30**, which may be tubular, a clamp **32** is provided and is adjustably secured to a standard **34**. This clamp is so made as to permit swinging the vessel **30** into a vertical position with nozzle **15** directed downwardly. To heat the vessel a heating element in the form of coils of resistance wire **35** may be wrapped around the vessel for any desired fraction of its length, with a connection to a conventional source of electricity as indicated. A thermometer **36** may have its bulb end

within the interior of the vessel, which is hollow and closed to the atmosphere except at its ends, one of which (31) has a small air vent tube 37. Coaxial with the tubular vessel 30 is a pipe 38 which is either removable from the vessel to be filled with the "filament-forming liquid," or is filled from one end while in the vessel, for instance by means of a funnel, not shown. The "filament-forming liquid" placed in pipe 38 is melted by convection currents of air within the vessel. The air vent tube 37 and openings (not shown) at the opposite end prevent the interior of the vessel from becoming too hot at one point, which might cause decomposition of the "filament-forming liquid." Obviously heat insulating material may be wrapped around the heating element and vessel if desired; however, with "filament-forming liquids" having a low temperature transformation interval insulation will not usually be necessary. To impose pressure on the "filament-forming liquid" to feed it to the nozzle 15, a pressure source such as a cylinder 39 of compressed nitrogen may be coupled by a tube 40 and clamp 41 with the inlet end of pipe 38. When valve 42 on the top of the cylinder is opened, the "filament-forming liquid" will be pushed or pressed into the feed tube 20 of the nozzle. In lieu of a nitrogen cylinder, a CO_2 cylinder or (in some cases) a source of steam under low pressure may be employed as a source of energy to cause feeding of the "filament-forming liquid." If said liquid is not subject to oxidation under the temperatures obtaining in pipe 38, the nitrogen cylinder may be replaced by a compressed air cylinder (not shown). The clamp 41 permits quick detachment of pipe 38 from the pressure source, so that the pipe may be refilled or replaced by a pipe filled with "filament-forming liquid"; however, under other conditions usually a large container for said liquid (not shown) will hold a sufficient amount of it for one "run" of the apparatus, and feeding to the nozzle will be continuous for the "run."

To break up the "filament-forming liquid," the energy of a compressed elastic fluid is employed, such elastic fluids as air, CO_2, nitrogen or superheated steam being most likely to be used. Pressures of between approximately 15 p. s. i. and 60 p. s. i. above atmospheric pressure have been employed; with commercial compressed gas cylinders, reducing valves will be used. In the case of air, CO_2, or nitrogen, preheating may be necessary, and in the illustrative apparatus, Fig. 13, a coil of pipe 45 connected with the gas source is surrounded by a sand bath 46, with a source of heat such as Bunsen burner 47 under the sand bath. A thermocouple 48 is on the discharge pipe 49 which leads to the nozzle, and a potentiometer 50 is connected with the thermocouple to indicate the temperature of the elastic fluid as it enters the nozzle. Good results have been obtained with the temperature of the elastic fluid between 110° C. and 700° C., with temperatures of the "filament-forming liquids" ranging between 95° C. and 680° C. In most runs the temperature differential between the "filament-forming liquid" and the elastic fluid did not exceed 50° C. Fig. 14 discloses modified apparatus for use where the "filament-forming liquid" has a transformation interval at a higher temperature. The nozzle 15 is the same, and the sources of heated elastic fluid and of pressure for feeding the "filament-forming liquid" may be considered the same. The differences reside in the construction of the retort or vessel 51 per se, which in this instance is shorter and of larger diameter than vessel 30, is surrounded by a resistance coil 52 (connected to a source of electricity, not shown) and has insulation 53 enclosing the heating coil. Instead of a resistance coil, induction or other means of heating may be employed. Within the vessel 51 is a tube or pipe 55 which receives the "filament-forming liquid" 56 at one end and discharges it at a suitable degree of fluidity at the other end, where nozzle 15 is mounted. An air inlet tube 57 may be provided to let atmospheric air into the hollow interior 58 of the vessel. The action is the same as in the apparatus of Fig. 13. In both forms of the apparatus the nozzle is shown directed horizontally; however, in actual practice, it may point directly downwardly or at an angle of 45° to the horizontal or at any other angle. Good results have been obtained with the 45° angle when making matting. Forming of the filaments F (see Figs. 2 and 3) may take place in atmospheric air, or in a chamber filled with nitrogen or other non-oxidizing elastic fluid. For convenience I use the term "mid-air" to denote any atmosphere of elastic fluid into which the described nozzle discharges the described spiralling elastic fluid and the "filament-forming liquid."

Turning to Fig. 1, the "filament-forming liquid" flows out of feed tube 20 either by gravity or under pressure. The nozzle will discharge a rotating flow of heated elastic fluid at discharge opening 23, as has been explained previously. Said "filament-forming liquid" and said rotating flow of heated air will meet just outside the nozzle in mid-air inside the imaginary cone having its vertex at the point marked "Vertex" and its base at discharge opening 23. This meeting of said "filament-forming liquid" and said gas disrupts and apparently draws out the "filament-forming liquid" into fibers and/or filaments which may be deposited on a moving belt (not shown) or within a chamber (not shown) until a sufficient mass is collected, after which the mass may be removed for other processing.

Referring to Figs. 13 and 14, it will be understood that the invention has been explained in connection with apparatus acceptable in a laboratory for practicing the method. Obviously the present invention is not limited to the particular apparatus and procedures described herein. In commercial practice the apparatus as described may be superseded by widely different apparatus. For instance, it may be advantageous to place the nozzle and cause it to form the fibers and/or filaments within a chamber whose temperature is automatically controlled to any practical and useful height, or to arrange a battery of such nozzles in one production unit, all of the nozzles being fed from a common source of "filament-forming liquid," or to use large nozzles of high delivering capacity, or to prepare the "filament-forming liquid" for cyclone-spinning by efficient economical means of heating well known in the art.

Having indicated the nature of the invention and having described apparatus useful for practicing the inventive method, the following examples will further illustrate this novel method of cyclone-spinning and the products obtained by this method.

Filaments of Artificial Resins

Among the artificial resins which may be cyclone-spnn in accordance with the inventive method are the following: polystyrene, polyamides of the nylon type, polyvinyl acetate, cellulose acetate, cellulose propionate, and cellulose nitrate. Frequently, a plasticizer will be added

in small amounts, say 5–10%. Filaments have been formed under widely varying conditions, some of which are set forth in Table I.

Table I

Sample No.	Compound	Air Temp. °C.	Polymer Temp. °C.	Nozzle Pressure, p. s. i.	Tube Pressure (p. s. i. above Atmospheric)	Filament Diameter (microns)	Cc.[1] per gm.	Fiber Appearance
1	Cellulose Propionate plus plasticizer.	230	(2)	60	0	0–30	73	Short, curled, entangled. Formed ½ inch mat.
2	do	250	255	40	16	48–86	180	Long, curled, entangled. Good resilience.
3	do	250	255	40	10	68–82	190	Do.
4	do	250	255	40	4	32–54	200	Do.
5	do	250	255	20	16	70–98	70	Do.
6	80% Cellulose Propionate, 10% Polystyrene, 10% plasticizer.	300	255	30	4	22–86	43	Curled, entangled. About 50 cm. long. Not brittle.
7	Polystyrene	290–320	(2)	60	0	8–22	41	Short, curled, entangled. Formed ½ inch mat.
8	do	300	315	60	7.5	24–70	30	Short, slightly curled, entangled. Brittle.
9	do	300	315	60	2.5	50–84	50	Fairly long, curled, entangled; slightly brittle.
10	do	300	315	60	0	18–40	60	Curled, entangled, approx. 25 cm. long. Not brittle.
11	do	330	300	50	10	80–108	40	Short, curled, entangled. Brittle.
12	do	330	300	30	10	244–274	130	Do.
13	do	260	(2)	30	10	152–168	40	Do.
14	do	260	(2)	30	5	70–130	35	Do.
15	do	320	(2)	30	0	6–22	40	Curled, entangled, short. Slightly brittle.
16	Polyvinyl Acetate	270	260	20	15	386	(2)	Long, straight, continuous filament. Brittle.
17	do	200	235	90	20	58–74	22	Short, straight, entangled. Brittle.

[1] Empirical values, correct to ± 10%.
[2] Not recorded.

The cellulose propionate of samples 1 to 6 inclusive of Table I is known to the trade as "Forticel No. 28102" and contains 9% of a long chain aliphatic ester type plasticizer. The polystyrene (samples 7 to 15 inclusive) had the trade name of "Koppers 5110 P8 Pellets," while the polyvinyl acetate (samples 16 and 17) was "Mowilith 50."

A study of the above table shows among other things that (1) filament length was reduced by increasing the pressure of the air fed to the nozzle, and increased by reducing such pressure; (2) when resin temperature was reduced concomitantly with increase in nozzle pressure, the filament was very short but was of much finer diameter (samples 16 and 17); (3) the finest filaments were obtained with zero pressure on the resin, that is, with gravity feed (samples 1, 7, 10 and 15); the filamentous masses of lightest weight were formed from plasticized cellulose propionate (samples 2, 3 and 4). Figs. 2 and 3 reproduce some cellulose propionate filaments on a greatly enlarged scale, this product being part of sample No. 2.

In each of the "runs" tabulated above the filaments were transparent or semi-transparent, circular or approximately circular in cross section, glossy and curly. Referring to Fig. 3, the lines appearing in the sections of the individual filaments approximately reproduce the lines seen in the photomicrograph of the cut filaments. If a perfectly clean cut of the filaments had been made, these lines doubtless would not appear. Glass fibers are straight in short lengths, as photomicrographs clearly show, and when subjected to flexure, such fibers break uniformly along the plane of flexure, thus forming an opening or break in the mass of fibers which will permit the rapid escape of heat through the opening or break. This makes glass fibers, however light in weight, impractical for insulating clothing and other articles subjected to repeated flexure. On the other hand, the non-brittle filaments listed above are entirely practicable for insulating clothing, and even the filaments noted in Table I as being brittle are far more resilient and less likely to break than glass fibers of comparable fineness.

Under the conditions specified in Table I, there was no noticeable decomposition of the resins except a slight darkening of the cellulose propionate at 230° C., which suggests the use of an atmosphere of nitrogen or other non-oxidizing gas or vapor instead of air, in the event this darkening is considered undesirable. When the resinous wool is to be used for lining articles such as clothing it will be out of sight and a slight darkening will not matter.

To introduce plasticizer into the resin, the latter was melted in an open vessel whose temperature was maintained at a previously determined point. When the resin became soft enough, about 10% of a plasticizer such as Paraplex G–25 (Resinous Products and Chemical Co.) was stirred in and then the mixture was transferred rapidly to the inner pipe or chamber 38 or 55. Sample No. 17, however, was cyclone-spun directly after melting, without the addition of plasticizer. Cyclone-spinning of the resin into the open air causes such rapid cooling that the curly product may be collected at a short distance from the nozzle, e. g., one to three meters, and is then ready for further processing or use.

In explanation of the column headed "Cc. per gm.," these values were determined by placing the entangled filaments in a vessel of known volume and weight and ascertaining the weight of the filamentous mass, which was not compressed except by its own weight. In explanation of the values in the column headed "Nozzle pressure, p. s. i.," these were obtained by employing a manometer attached to the pressure line in the laboratory, from which the air passed through a heating coil to the inlet of the nozzle. In later experiments a second manometer was attached directly to the inlet of the nozzle. It was then discovered that the pressures listed in Table I were too high by 30–40%; evidently the resist-

ance of the heating coil reduced the pressure of the compressed air to this extent.

The filaments may be allowed to form a pile of no particular shape or may form a well defined mat or matting one-half inch thick or even thicker, looking something like cotton wool but not so white and having more of a sheen due to the higher reflectivity of the individual filaments, which in many cases are translucent or semi-transparent.

Solutions of various resins may be spun into filaments by the described nozzle, as disclosed in my pending application Ser. No. 123,343 filed October 19, 1949. Thus a solution of polyvinyl acetate in acetone (15% of the total weight of the solution) was prepared by the usual method, and the solution was introduced into the central feed tube **20** of the nozzle. Preheating was not necessary. The nozzle temperature was 300° C. and the air pressure was 15 p. s. i. Transparent filaments were obtained whose diameter varied between 4 and 30 microns, while the volume per weight ratio (cc. per gm.) was determined as 65 by the method described above, with an error of ±10%. The polyvinyl acetate was "Mowilith 30." Again, nylon molding powder (Du Pont Code 10001) was dissolved in formic acid (70% by weight of the total weight of the solution) and this solution was introduced into the central feed tube **20** of the nozzle, again without preheating. The nozzle temperature was 70° C. and the air pressure was 15 p. s. i. Very fine filaments ranging between 1 and 12 microns in diameter were obtained, with a volume per weight ratio (cc. per gm.) of 25 (±10%).

For each of the resins listed above there is at least one well known solvent which can be employed in practicing the invention. It is believed to be unnecessary to list all the known solvents for the named resins.

Filaments of Artificial Resins With Fillers

If the addition of fillers is desirable, powdered metal, powdered metal alloys or other powdered or finely divided solids are added in small amounts to the resin prior to feeding it to the described nozzle. Such "frozen" metals as aluminum, copper, iron, nickel, cobalt and tin may be added in powder form. In lieu of powdered metals, molten metals of low melting points, such as tin, metalloids such as selenium, and low melting alloys such as soft solder and Wood's metal may be added in small amounts to the molten resin, with the heat maintained to prevent solidification. Non-metallic powders such as silica gel may also be added in small percentages. Due to the peculiar nozzle construction, no slogging is possible if the mixture is kept molten until spun, and relatively coarse powders may be added which will cause very pronounced bulges in the filament, if present in small percentages (0.5 to 10% by weight).

Table II, below, shows the results obtained during twelve runs during which cellulose propionate was cyclone-spun alone and then mixed successively with aluminum, copper, iron and tin powders and silica gel powder and cyclone-spun, the feeding pressure within the tube **20** being 3 p. s. i., the temperature of said tube being about 250° C., the temperature of the gas (atmospheric air) being about 270° C., and its pressure being about 15 p. s. i. (superatmospheric) measured at the nozzle inlet.

Table II

Run No.	Resin	Substance Added, Amt. and Particle Size	Fiber, Volume per wgt. (cc./gm.)	Fiber Diameter (microns)
1	Cellulose propionate	none	280	34–68
2	do	Aluminum 0.5%; Passes 140 mesh	190	38–64
3	do	Aluminum 1.0%; Passes 140 mesh	200	22–92
4	do	Aluminum 2.0%; Passes 140 mesh	100	18–76
5	do	Copper, 2.0%; Passes 250 mesh	200	36–46
6	do	Copper, 4.0%; Passes 250 mesh	140	22–66
7	do	Iron, 2.0%; Passes 250 mesh	110	24–30
8	do	Iron, 4.0%; Passes 250 mesh	130	28–60
9	do	Iron, 10.0%; Passes 250 mesh	70	38–76
10	do	Tin, 5.0%; Passes 325 mesh	150	28–86
11	do	Silica gel, 2.0%; 250 to 300 mesh	70	16–96
12	do	Silica gel, 4.0%; 250 to 300 mesh	50	18–70

The cellulose propionate was the variety known to the trade as "Forticel 28102" and contained 9% plasticizer of unknown composition, being pre-melted at 230° C. before mixing with the powdered materials. The aluminum powder was "Mallinckrodt 3116"; the copper powder was "Eimer & Amend, H. Reduced, C. P."; the iron powder was "Mallinckrodt 5304, Degreased"; the tin was "Eimer & Amend, T–129, Finest Powder, Pure"; and the silica gel was "Eimer & Amend, S.–156" dried at 500° C. for eight hours to expel practically all moisture. The volume per weight ratios were determined empirically, as explained above in connection with Table I, and are believed accurate to ±10%.

When more than 1% of aluminum powder was added, resiliency and flexibility of the filaments were reduced. The color of all three aluminum-containing filaments was silvery grey. With 1% aluminum added, the filament had a slippery feel. Copper powder (2–4%) imparted a faint reddish tinge to the filaments and enhanced their heat-insulating efficiency. This powder was distributed evenly along the lengths of the fibers. There was no noticeable change in the fiber texture as compared with cellulose propionate without filler (run No. 1). Iron powder occurred as individual particles of irregular size and shape spaced at almost regular intervals along the fiber lengths. The fibers were made more curly by the presence of the iron, and felt more slippery. The color ranged from light grey (2%) to dark grey (10%). See Fig. 4 (magnification 150:1) for the approximate appearance of the product of run No. 8 (4% iron). The sample containing 10% iron was brittle. The tin gave the fiber a slippery feel and changed its color to grey. The silica gel was distributed as beads along the fibers; see Fig. 5 (magnification 150:1). The fibers themselves varied considerably in diameter as shown in Fig. 6 (magnification 20:1). Fig. 7 shows how the fibers incorporating silica gel looked in cross section (magnification 315:1), the open areas being voids or partially evacuated areas apparently formed because of the bullet-like

velocity of the solid particles. In longitudinal section these voids were elongated, misshapen cones, as viewed under the microscope, with the larger ends adjacent to the solid particles. Cross sections through these voids therefrom varied greatly in diameter, as Fig. 7 indicates.

In lieu of metallic iron powder as a filler, I contemplate using powdered magnetite or ferrous ferric oxide (Fe_3O_4) in the same proportions as the metallic powders or I may magnetize metallic iron particles in filaments by placing the filaments in a strong magnetic field. The resultant magnetic filaments may be twisted into yarns and the yarns may be woven to form fabrics which may be useful to make filters having a dual function, viz., mechanical filtration and magnetic separation of iron particles too small to be caught upon the meshes of the woven filter fabric. A filter containing a sufficient proportion of magnetized particles may also be desirable because it can be lifted off a support without rupture by bringing a magnet close to it. This technique will be desirable in cases where the filter is fragile or where it should not be touched for some reason while it is on its support.

In further runs with fillers added to resins, I found that as much as 80% of the total weight of the filaments may be added without clogging the nozzle or preventing the formation of tube-like filaments. Thus the described nozzle makes possible for the first time forming of filaments heavily laden with a metallic or metalloidal core or content, so that the filaments are more metallic or metalloidal than they are resinous.

When selenium in finely divided form (100% passing through a 250 mesh sieve) was added to the extent of 80% by weight to polyvinyl acetate (Mowilith 30), with an indicated nozzle temperature of 240° C. and an indicated air pressure of 20 p. s. i., the filaments formed had a volume per weight ratio of 23 and a diameter ranging from 1 to 18 microns. Fig. 12 (magnification about 60:1) is only an approximation of a few of the fibers forming a curly, entangled mass. The selenium was such a large part of the fibers that it imparted a dark brown appearance and gave a rather harsh feel to them, besides making them quite brittle. Each fiber, however, consisted of a continuous thin tubular envelope surrounding the metalloidal core. The mixing of polyvinyl acetate with molten selenium in a 50–50 volume ratio results in a homogeneous viscous mixture at 240° C. which readily forms filaments, again with the metalloid forming a core sheathed by the resin.

Fig. 10 shows the ends of two cellulose propionate fibers containing tin cores, enlarged 85 times. Cellulose propionate (Forticel 28102) was mixed with tin powder passing a 325 mesh sieve, and the mixture was cyclone-spun with an air pressure (indicated) of 15 p. s. i. and 3 p. s. i. pressure in the feed tube. Temperatures were 250° C. in the feed tube and 270° C. for the compressed air. While part of the mixture left the "Vertex" in the form of plain resinous fibers and separate tin pellets, a considerable percentage of plastic tubular fibers with tin cores were formed. These tin cores were not of uniform diameter but varied as Fig. 10 shows, and some were as short as 2 mm., while others were 50 mm. long. Fig. 11 (magnification 625:1) shows in section solid tin cores which were a major part of the fibers, but in some sections the tin cores were so fine they could only be seen under a microscope after dissolving away the resinous envelope with methyl acetate. Microscopic examination failed to disclose a single tin fiber free from an enveloping polymeric sheath or tube. The forms of Figures 10, 11 and 12 are covered in my pending application Ser. No. 110,372, filed Aug. 15, 1949.

Solutions of various polymers mixed with powdered fillers may be spun into filaments, as disclosed in my pending application Ser. No. 122,343 filed October 19, 1949.

Thus polyvinyl acetate (Mowilith 30) was dissolved in 15% acetone (percentage being based on the total weight of the solution) and 5% by weight of iron powder (300 mesh) was added and the mixture thoroughly stirred and then introduced into tube 20. The nozzle temperature was 300° C. and the air pressure 15 p. s. i. (superatmospheric). Filaments of from 8 to 48 microns were obtained, with a volume-weight ratio, as explained above, of 65. Some of the larger filaments, magnified 90 times for a photomicrograph, are shown in Fig. 8, which omits the finest filaments because no details of their structure were apparent from the photomicrograph.

Again, nylon molding powder (Du Pont Code 10001) was dissolved in 70% formic acid (percentage being based on the total weight of the solution) and 2.5% iron passing a 300 mesh sieve was mixed in the solution. The nozzle temperature was 70° C. and the air pressure 15 p. s. i. Filaments ranging from 2 to 12 microns were obtained, with a volume-weight ratio of 15. Several of the coarser nylon filaments produced under these conditions as shown in a photomicrograph (enlarged 90 times) are reproduced in Fig. 9. Better results would be obtained by spinning completely under nitrogen. The filaments in each case were collected and put in a dessicator, which was evacuated by a water injection pump for three days to remove traces of solvent which had not been lost during the spinning process itself.

Filaments of Natural Resins

(1) *Rosin (colophonium)*

Rosin (colophonium), Dark, "Eimer and Amend," was melted at 95° C. and fed in tube 20 of the nozzle. The temperature of the compressed air to operate the nozzle was 110° C., its pressure was 20 p. s. i. Curly, finely crimped fibers ranging in average diameter between 1 and 2 microns were obtained. A substantial portion of the product had fiber diameters below 1 micron. Volume-weight ratio as explained above was 82 cc. per g.

(2) *Shellac*

Brown shellac flakes, an ordinary commercial product, were melted at 170° C. and fed into tube 20 of the nozzle. The nozzle was operated with compressed air (40 p. s. i.) at a temperature of 170° C. Curly filaments having an average diameter of 2 to 5 microns were obtained.

Glass Filaments

Glasses of a number of different compositions may also be cyclone-spun by the described nozzle, as is disclosed in the R. G. H. Siu application Ser. No. 110,663, filed August 16, 1949, and in the Siu continuation-in-part application Ser. No. 180,686, filed August 21, 1950. The result is inherently curly glass filaments of a fineness of less than one micron up to 100 microns, with an average diameter of 6 microns.

The compositions of the glasses disclosed in the

Grimm et al. Patent No. 2,227,082 dated December 31, 1940, which have softening points of between 339° C. and 387° C., are known to be entirely suitable for the process.

The procedure is as follows: Molten glass, whose temperature is at least 250° C. higher than its softening point, is fed into the inner or axial feed tube **20** of the nozzle at low pressure. The temperature of the compressed elastic fluid operating the nozzle should be about 100° C. higher than the temperature of the glass as it enters the feed tube.

The straight axial tube **20** permits the feeding not only of molten glass towards the "Vertex" but also mixtures of molten glass with powdered metals such as platinum (for soft glass), tungsten (for Pyrex glass) and other metals and metallic alloys. These mixtures will form filaments near the "Vertex," provided the metals or alloys have about the same coefficient of expansion as the glass and are not chemically changed thereby. The size of the particles of the filler may be smaller or larger than the average diameters of the filaments; if larger, the filaments will form envelopes with bulbous enlargements like the polymeric filaments disclosed above. Of course the size of the particles of the filler must never equal the diameter of passageway **21** of the feed tube.

Filaments of Organic Glass

Sucrose octa-acetate, $C_{28}H_{38}O_{19}$, whose melting point is 72.3° C., has been spun with the aid of the described nozzle, at a temperature of 75° C., with the compressed air temperature also approximately 75° C., at a pressure (superatmospheric) of 15 p. s. i. The product was a mass of white curly filaments of 2–10 microns diameter.

Filaments of Chemicals

I have also spun, with the aid of the described nozzle, inorganic chemicals in the "glassy" state. Examples follow:

(1) *Boron trioxide*

Boron trioxide, (B_2O_3) C. P., Eimer and Amend, was melted at 680° C. and was fed into the tube **20** of the nozzle, the compressed air temperature being approximately 700° C. and its pressure being 50 p. s. i. A coil of electrical heating wire instead of insulation **19** (Fig. 1) served to maintain the body of the nozzle at this temperature. Filaments of short length having diameters from 5 to 60 microns were obtained.

(2) *Sodium metaphosphate*

$(NaPO_3)_n$, C. P., Eimer and Amend, was melted at 600° C. The compressed air operating the nozzle had a temperature of approximately 600° C. and a pressure of a 15 p. s. i. A hearing element for the nozzle as described under (1) was employed. A fluffy mass consisting of curly fibers with average diameter of 1–2 microns was produced.

Filaments of Organic Vitreous Materials

Two parts by weight of sucrose and one part glucose were mixed with a small amount of water. The mixture was slowly heated in a beaker. It was stirred vigorously while heating. A viscous mass was obtained when the temperature had risen to 150° C. The composition was still substantially undecomposed. This mixture was fed into tube **20** of the nozzle as described. The temperature of the compressed air operating the nozzle was 160° C., its pressure was 15 p. s. i. A fluffy mass of fine fibers having an estimated average diameter of 1–3 microns was obtained. The diameters could not be measured microscopically because the fibers were extremely hydroscopic. Obviously the product is a confection generally similar to spun sugar, and could be colored and/or flavored as preferred.

Filaments of Metalloids With or Without Fillers

Substantially pure selenium may also be cyclone-spun by the described nozzle, as is disclosed in the pending application of R. G. H. Siu, Ser. No. 127,479, filed November 15, 1949. The molten selenium was disrupted readily by air at 20 p. s. i. and formed a rapidly moving stream of filaments which collected as a curly mass in the open air below the nozzle. The filaments varied from one to 30 microns in diameter, a considerable proportion being below 10 microns. In color they were dark grey with a metallic sheen when viewed as a mass.

The same selenium powder was mixed with 5% by weight of iron powder (300 mesh), also with iron powder of 45 mesh, and the mixtures were cyclone-spun. The iron particles were encased within the selenium and formed enlargements or bulges spaced along the filaments.

In a further test, silica gel powder (45 mesh, Eimer & Amend, S–156) was mixed to the extent of 5% by weight with powdered selenium, and the mixture was cyclone-spun, obtaining dark brownish-grey filaments with no appreciable metallic sheen but with the silica gel appearing as bulbous enlargements or beads having a metallic appearance because of the enveloping selenium.

The volume per weight ratios (cc. per gm.) of the products of the four cyclone-spinning tests described above were respectively 15, 10, 15 and 16 before the filamentous masses became compacted by settling. All four products were curly.

In General

When working with "filament-forming liquids" of relatively low viscosity the product of the described nozzle is usually a curl or mass of entangled and twisted, inherently curly filaments. This curly mass may be collected and may be used without modification with regard to many compositions belonging in the class of "filament-forming liquids," as fully explained above. Particularly with regard to resins, this curly mass may be formed into a mat which may be compressed with heat to make self-sustaining panels as disclosed in the application of R. G. H. Siu, Ser. No. 138,872, filed January 16, 1950, or to make thin flexible non-woven sheets as disclosed in the application of Mario Pesce, Ser. No. 170,673, filed June 27, 1950; or the curly mass may be further twisted or divided and twisted to make a yarn or yarns, as disclosed in the application of Stanley Backer, Ser. No. 139,110, filed January 17, 1950, and such yarns may be woven into different fabrics. The inherently curly filaments readily form batts or wool-like masses having good to excellent heat-insulating properties and because of their resilience, will make good to excellent linings for clothing, sleeping bags, tents, etc. Also the filaments are less expensive than those fibers which are subjected to an artificial crimping process as described in a number of patents in the prior art.

What I claim is:

1. A method of forming entangled masses of

filaments characterized by causing an elastic fluid to spiral in a path which is in the shape of a hollow cone towards the vertex of the cone at a very high velocity, and causing a filament-forming liquid to flow in a liquid stream toward said vertex in a path coincident with the axis of the cone, said liquid flow being in the same general direction as the progressive movement of the spiraling elastic fluid and the spiraling fluid contacting the liquid stream near the vertex to form the filaments.

2. A method of forming entangled masses of filaments characterized by causing a stream of a filament-forming liquid to flow in a liquid stream towards a point in mid-air, and causing an elastic fluid to flow in a spiral path with a very high and ever increasive velocity towards said point, the spiral path forming a hollow cone surrounding the path of flow of the stream of filament-forming liquid, the vertex of said cone being adjacent said point, and the spiraling fluid contacting the liquid stream near the vertex to form the filaments.

3. The invention defined in claim 2, wherein the velocity of the elastic fluid is supersonic at said point.

4. A method of forming entangled masses of filaments characterized by causing a filament-forming liquid to flow in a liquid stream in a sulstantially straight path out of the member which confines it into mid-air, and causing an elastic fluid to spiral around the path of the filament-forming liquid in a path which is shaped like a hollow cone, the spiraling fluid approaching the vertex of the cone with a very high velocity, the path of the spiraling fluid being controlled so as to contact the filament-forming liquid stream within the confines of the cone, thereby forming filaments.

5. The invention defined in claim 4, wherein the filament-forming liquid is a molten non-metallic material and the elastic fluid attains supersonic velocity at said vertex.

6. The invention defined in claim 4, wherein the filament-forming liquid is a solution and the elastic fluid attains supersonic velocity at said vertex.

7. The invention defined in claim 4, wherein the filament-forming liquid is a molten non-metallic material containing a small proportion of a finely divided solid material which retains its identity in the molten material and also in the individual filaments.

8. The invention defined in claim 4, wherein the filament-forming liquid is a solution containing a small proportion of a finely divided solid material which retains its identity in the solution.

9. The invention defined in claim 4, wherein the filament-forming liquid is a resin.

10. The invention defined in claim 4, wherein the filament-forming liquid is an artificial resin.

11. The invention defined in claim 4, wherein the filament-forming liquid is a natural resin.

12. The invention defined in claim 4, wherein the filament-forming liquid is confined in and flows out of a conduit which is of relatively large diameter so that free gravity flow of said liquid through said conduit may take place and so that a relatively massive stream of liquid is presented to the spiraling elastic fluid.

13. A method of forming entangled masses of filaments characterized by causing an elastic fluid to spiral in a path which is shaped like a hollow cone towards the vertex of the cone at supersonic velocity; causing a relatively massive stream of a filament-forming liquid to flow in a liquid stream towards said vertex in the same general direction as the progressive movement of the spiraling elastic fluid; said massive stream having a width which is a major fraction of the base diameter of said cone, the spiraling fluid contacting the liquid stream near the vertex to form a multiplicity of filaments simultaneously.

14. The invention defined in claim 13, wherein the filament-forming liquid is a molten material containing a small proportion of a finely divided solid material which retains its identity in the molten material.

15. The invention defined in claim 13, wherein the filament-forming liquid is a solution containing a small proportion of a finely divided solid material which retains its identity in the solution.

16. A method of forming entangled masses of filaments with internal substantially continuous cores which consists in mixing a molten core material with a filament-forming liquid, causing the mixture to flow through a nozzle, and subjecting the mixture after it emerges from the nozzle to a spiraling blast of an elastic fluid, said spiraling blast being in the shape of a hollow cone and moving with ever increasing velocity towards a point which is the vertex of the cone and which is outside the nozzle, the spiraling blast surrounding the mixture and encountering the mixture near said vertex, the spiraling blast attaining very high velocity, and contacting the mixture and forming such filaments near the vertex.

ROLF KARL LADISCH.

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