

Oct. 7, 1952

R. K. LADISCH

2,612,679

FILAMENTS CONTAINING FILLERS

Filed Aug. 21, 1951

2 SHEETS—SHEET 1

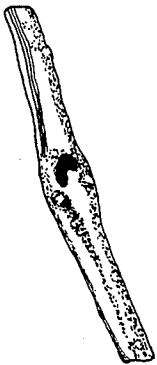


Fig. 3



Fig. 2

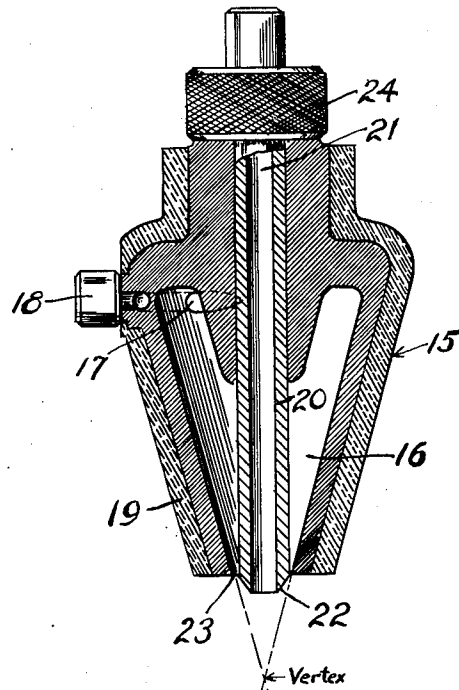


Fig. 1

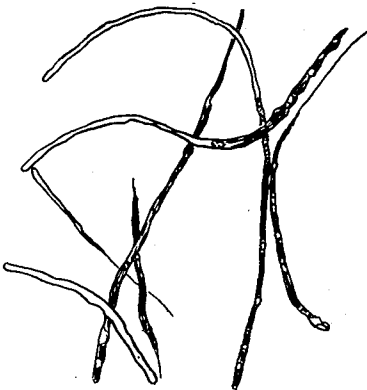


Fig. 4

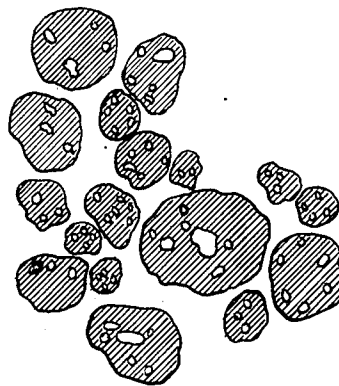


Fig. 5

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2 SHEETS—SHEET 2

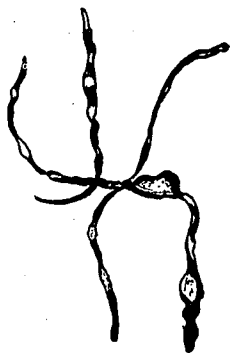


Fig. 7

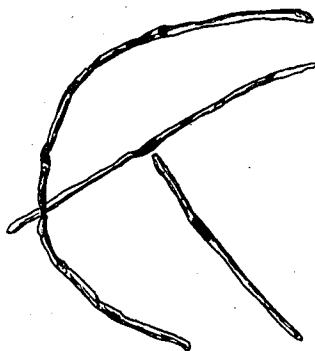


Fig. 6



Fig. 8

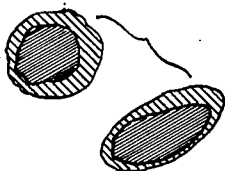


Fig. 9

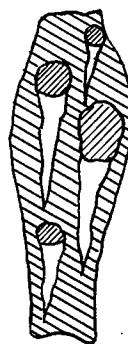


Fig. 10

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2,612,679

FILAMENTS CONTAINING FILLERS

Rolf Karl Ladisch, Drexel Hill, Pa.

Original application October 23, 1950, Serial No. 191,672. Divided and this application August 21, 1951, Serial No. 242,972

11 Claims. (Cl. 28—82)

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

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

This invention relates to artificial fibers or filaments containing solid fillers.

This application is a division of my pending application Serial No. 191,672, filed October 23, 1950, entitled "Method of Spinning Filaments," now Patent No. 2,571,457, dated October 16, 1951. According to the novel method of said parent application, a relatively small amount of energy put into an elastic fluid is rapidly concentrated to a theoretically infinite value per space unit by causing the elastic fluid to spiral towards the vertex of a hollow cone; a "filament-forming liquid," as hereafter defined, flows to this location of high energy concentration; the conduit for the "filament-forming liquid" is unconventionally large in diameter, that is, it may be scores or hundreds of times larger than the apertures in conventional spinnerets; and the 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 disruption into filaments will occur. The higher the viscosity of the "filament-forming liquid," the nearer to the vertex the disruption into filaments will occur. However, such disruption will in all cases be outside of the conduit through which the "filament-forming liquid" flows but within the cone-shaped figure bounded by the spiraling elastic fluid. The elastic fluid may be heated or cooled; it will be under pressure; and, in general, it will have those physical conditions which facilitate fiber formation. In consideration of this type of spinning, the method may be termed "cyclone-spinning" and the products of the invention may be termed "cyclone-spun" products.

The expression "filament-forming liquid" includes any liquid capable of forming a fiber or 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 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 molten mixture, and may contain other ingre-

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dients, such as solvents, plasticizers, and solid fillers. It may consist of any combination of the aforesaid or equivalent constituents. The expression "to fall freely as a stream" means that the material in the liquid state is able to fall solely under the action of gravity. To the category of "filament-forming liquids" 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 octaacetate ($C_{28}H_{38}O_{19}$); 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.

According to one aspect of this invention, cyclone-spun polymeric fibers and filaments have finely divided solids physically incorporated therein at spaced intervals, the discrete solid particles always being enveloped by a tubular polymeric casing. Some or all of these solid particles may have diameters 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 another aspect of the invention, the solid particles within the envelope are so close together as to form what is visually a continuous core, which may be non-metallic or metallic, and, if preferred, the filaments so formed may have relatively large cores so as to be predominantly metallic or metalloid in structure and characteristics, while having thin, continuous, unbroken walls of the pure polymer, or the polymer united with a plasticizer. In other cases 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, remaining smooth and unbroken and sealing off the cavities, as well as the solid particles adjoining the ends of the cavities.

Among other objects, the invention aims to provide fibers or filaments suitable for making threads, yarns, mats or matting, batts, wool-like

masses, woven or unwoven sheets, panels, and the like. A number of the products of the invention because of their extreme light weight combined with their high heat-insulating quality will 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, portable shelters, houses, and industrial buildings. 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. Other products of the invention consist of extremely fine and curly fibers and are believed to be particularly suitable for gas masks, industrial air filters, air conditioning equipment, etc. Also, woven or knitted fabrics suitable for certain articles of clothing may be made from threads drawn or twisted from several of the filaments. Insulating mats or woven fabrics made from the filaments may form linings or paddings within 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. Filaments of the invention 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 may be materially changed by the addition of properly selected solid particles, to effect considerable improvements over filaments made from a pure polymer, copolymer, or polymeric mixture.

In the accompanying drawings forming a part of this specification—

Fig. 1 is a longitudinal section through a nozzle useful for making the fibers or filaments of the invention, the scale being nearly full size;

Fig. 2 is a reproduction of part of a photomicrograph of cellulose propionate filament containing 4% by weight of iron powder, magnification about 150:1;

Fig. 3 is a reproduction of part of a photomicrograph of cellulose propionate filament containing 2% silica gel powder, magnification about 150:1;

Fig. 4 is a reproduction of part of a photomicrograph of several cellulose propionate filaments containing the same silica gel as in Fig. 3, the magnification being about 20:1;

Fig. 5 is a reproduction of part of a photomicrograph showing the filaments of Fig. 4 in cross section, the magnification being about 315:1;

Fig. 6 is a reproduction of part of photomicrograph showing polyvinyl acetate filaments combined with 5% by weight of iron powder, the magnification being about 90:1;

Fig. 7 is a reproduction of part of a photomicrograph showing a few nylon filaments combined with 2.5% by weight of iron powder, the magnification being about 90:1;

Fig. 8 is a reproduction of a photomicrograph of two cellulose propionate fibers having continuous tin cores, the magnification being about 85:1;

Fig. 9 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. 10 is a greatly enlarged fragmentary longitudinal section through one of the filaments of Figs. 4 and 5, showing several of the longitudinally extending cavities and solid particles of silica gel at the larger ends of said cavities.

Referring to Fig. 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, the inlet opening tangentially at the larger end of said chamber, said nozzle having a coupling 18 to couple a supply pipe of elastic fluid (not shown). The elastic fluid will usually be air, but it may be 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 "filament-forming liquids." 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 material-feeding tube or conduit 20 connected with a vessel, pipe, or conduit (not shown) feeding a supply of "filament-forming liquid," said tube 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 of 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 "filament-forming liquid" is disrupted and drawn into fibers and/or filaments near this "Vertex." It will be understood that the phrase "near the Vertex" includes any and all points within the hollow cone having its tip at the "Vertex" and its base coinciding with the outer edges of discharge opening 23, in which cone contact is made between the "filament-forming liquid" and the spiraling elastic fluid.

The bore 21 of the feeding tube has a diameter which is extremely large in comparison with the passageways provided in spinnerets or other conventional extrusion apparatus; this diameter may exceed one-fourth of an inch and frequently 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 the "filament-forming liquid" which in comparison with the portion of the aforesaid cone that lies outside the nozzle is very massive, being usually of a diameter exceeding one-half the base diameter of that cone portion. A 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 slidable tube 20 longitudinally. Other apparatus used with the nozzle is disclosed in the aforesaid R. K. Ladisch patent.

The described nozzle may be modified in a number of ways, for example, the feeding tube 20 may be shaped on its outside substantially similar to the frusto-conical chamber 16 though in smaller dimensions. The bore 21 may be con-

stricted near its lower end, or it may extend funnel-like toward the discharge end. Instead of being beveled as at 22, the discharge end of tube 20 may be squared off, and its opening maybe in substantially the same plane as discharge opening 23. Instead of pointing directly downwardly, the nozzle may point downwardly 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. Usually even when the nozzle is pointed directly downwardly low pressure will be employed to force the "filament-forming liquid" out of the feed tube. Forming of the filaments may take place in atmospheric air, or in a chamber filled with nitrogen or other non-oxidizing elastic fluid. The nozzle discharges a spiraling flow of elastic fluid from discharge opening 23 and this spiraling fluid encounters the solid stream of "filament-forming liquid" outside the nozzle or in mid-air, between the nozzle and the "Vertex." This meeting of the "filament-forming liquid" and the elastic fluid, which builds up in velocity until it attains supersonic velocity near the "Vertex," disrupts and draws out the "filament-forming liquid" into fibers and/or filaments which may be deposited on a moving belt or within a chamber (not shown) until a sufficient mass is collected, after which the layer or mass may be removed for other processing.

To incorporate solid particles in the filaments formed by the described nozzle, powdered silica gel, or powdered "frozen" solids, such as aluminum, copper, iron, nickel, cobalt, and tin, are added in small amounts to the "filament-forming liquid" prior to feeding it to the nozzle. In lieu of powdered "frozen" 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 a molten resin. Due to the peculiar nozzle construction, no clogging is possible if the heat is maintained to prevent solidification, and relatively coarse particles may be added which will cause very pronounced bulges in the filament, if present in small percentages (0.5 to 10% by weight).

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

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	28-88
11	do	Silica gel, 2.0%, 250 to 300 mesh	70	16-98
12	do	Silica gel, 4.0%, 250 to 300 mesh	60	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 are believed to be accurate to $\pm 10\%$, and were determined by filling a vessel of known volume and weight with the entangled filaments and ascertaining the weight of the filamentous mass, which was not compressed except by its own weight.

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 apparently distributed evenly along the lengths of the fibers. There was no noticeable change in the fiber texture as compared with cellulose propionate free of 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 iron, and felt more slippery, while the color ranged from light grey (2%) to dark grey (10%). See Fig. 2 (magnification 150:1) for the approximate appearance of the product of Run No. 8 (4% iron). The sample containing 10% iron was brittle. Tin particles gave the fibers a slippery feel and changed the color to grey. The silica gel was distributed as beads along the fibers, see Fig. 3 (magnification 150:1) while the fibers themselves varied considerably in diameter as shown in Fig. 4 (magnification 20:1). Fig. 5 shows how fibers incorporating silica gel particles 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 when picked up by the spiraling air jet. In longitudinal section, these voids were elongated, misshapen cones, as viewed under the microscope, with the large end of each cone adjacent to a solid particle. See Fig. 10. Cross sections through these voids therefore varied greatly in diameter, as Fig. 5 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 metal-

lic iron or steel particles encased 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 as filter cloths 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 strong magnet close to it. This technique will be desirable in cases where the filter is very fragile or where it should not be touched for some reason while on its support.

In further runs, I found that fillers amounting to as much as 80% of the total weight of the resinous filaments may be added without clogging the nozzle or preventing the formation of tube-like filaments. Thus the described process makes possible for the first time the formation of filaments heavily laden with a metallic or metalloid core or content, so that the filaments are more metallic or metalloid in their characteristics than 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. The selenium was such a large proportion 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 metalloid 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 continuous core sheathed by the resin.

Fig. 8 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 indicated air pressure of 15 p. s. i. and 3 p. s. i. 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. 8 shows, and some were as short as 2 mm., while others were 50 mm. long. Fig. 9 (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.

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

Thus, polyvinyl acetate (Mowilith 30) was dissolved in 15% acetone (the 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. (super-

atmospheric). 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, are shown in Fig. 6, which omits the finest filaments because no details of their structure were apparent from the photomicrograph.

Again, nylon molding powder (duPont Code 10001) was dissolved in 70% formic acid (the percentage being based on the total weight of the solution) and 2.5% by weight of iron powder 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 in diameter were obtained, with a volume-weight ratio, as explained above, of 15. Several of the coarser nylon filaments produced under these conditions as shown in a photomicrograph (90:1) are reproduced in Fig. 7. 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.

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 Serial 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. Molten glass, whose temperature is at least 250° higher than its softening point, is fed into the feed tube 20 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 relatively large feed tube 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 small or larger than the average diameters of the glass filaments; if larger, the glass filaments will form envelopes having spaced bulbous enlargements like the polymeric filaments disclosed in the foregoing. Of course, the size of the filler particles must never equal the diameter of the passageway 21 of the feed tube.

Substantially pure selenium may also be cyclone-spun by the described nozzle, as is disclosed in the pending application of R. G. H. Siu, Serial No. 127,479, filed November 15, 1949. Selenium powder (Elmer & Amend, S-137) was melted in an open porcelain crucible and was fed into the feed tube of the nozzle. Air at 20 p. s. i. was employed as the gas. The nozzle was heated to 240° C. and was directed vertically downward. The molten selenium was disrupted readily by the spiraling jet of air 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, with a considerable proportion 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 two mixtures were separately cyclone-spun. In each case the iron particles were encased with-

in 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 with powdered selenium to the extent of 5% by weight, and the mixture was cyclone-spun, obtaining dark brownish-grey filaments with no appreciable metallic sheen but with the silica gel appearing as glistening beads having a metallic appearance because of the enveloping selenium. All of the described selenium products were curly.

What I claim is:

1. Artificial filaments containing solid particles which lie wholly on the inside of the filament, many of said solid particles being larger than the diameter of the filament.

2. Artificial filaments each consisting of a polymer and solid particles mixed therein and located on the inside of the filament, the solid particles being separated along the length of each filament and being larger than the diameter of the filament.

3. An artificial filament which is composed of a polymer of indefinite length and of generally uniform diameter except at certain spaced points along its length, the filament walls being greatly enlarged or bulged out and inclosing or sheathing a particle of a solid material at each of said spaced points.

4. The invention defined in claim 3, wherein the particle of solid material is metallic.

5. The invention defined in claim 3, wherein the particle of solid material is silica gel.

6. An artificial filament consisting of continuous unbroken walls of a polymer having bulbous enlargements at frequent intervals along its length, and a solid particle within each of the bulbous enlargements.

7. The invention defined in claim 6, wherein the major proportion of the solid particles are

each adjoining the larger end of an elongated cavity wholly within the filament.

8. Artificial filaments each composed of a generally tubular envelope formed from a filament-forming liquid and encasing a plurality of spaced solid particles, at least some of which are larger than the average diameter of the tubular envelope so that they cause the walls of the envelope to bulge out.

9. The invention defined in claim 8, wherein the solid particles are present in the range of 0.5% to 10% by weight of the encasing tubular envelope.

10. The invention defined in claim 9, wherein the solid particles are metallic.

11. The invention defined in claim 9, wherein the solid particles are silica gel.

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