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PROCESS AND APPARATUS FOR THE CONTINUOUS SPINNING OF FILAMENTS AND RIBBONS FROM QUARTZ AND OTHER REFRACTORY OXIDES

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Fig.1

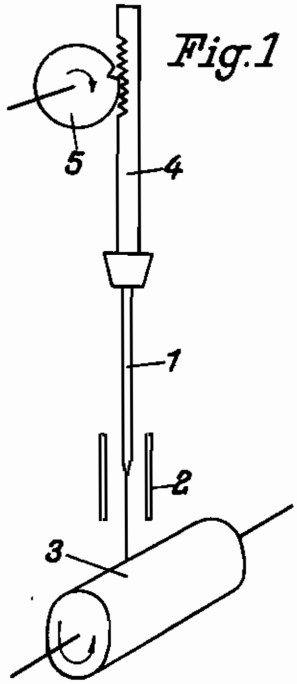


Fig.3

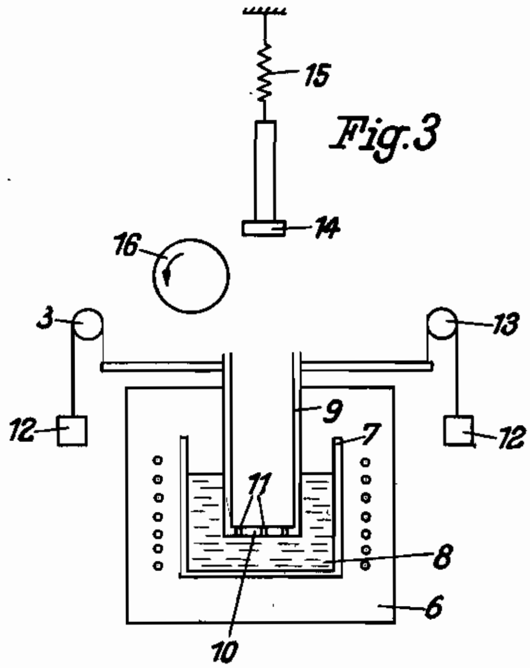


Fig.2

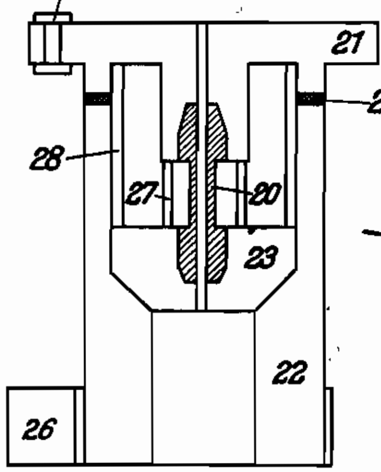
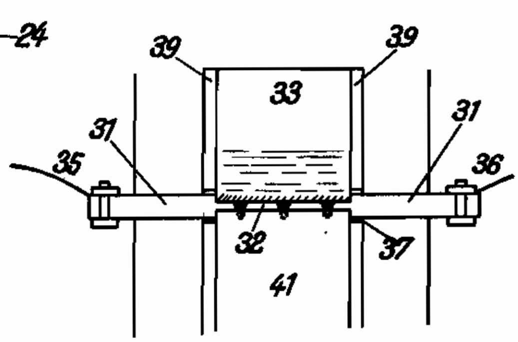


Fig.4



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PROCESS AND APPARATUS FOR THE CONTINUOUS SPINNING OF FILAMENTS AND RIBBONS FROM QUARTZ AND OTHER REFRACTORY OXIDES

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The manufacture of filaments and ribbons from quartz and other refractory oxides offers great difficulties owing to the high melting point of these materials and, hitherto, it was only by means of a discontinuous process that quartz filaments of a few metres' length could be produced. According to that process, a quartz rod subjected to tensile stress was at one place heated up to its melting point. In consequence of this the fused piece of quartz was flung away, at the same time carrying with it a quartz filament from the place of fusion.

According to the present invention fibres or ribbons of any thickness and in practically unlimited length can be produced. According to the invention the primary material after being fused or plastified by heat is continuously drawn-off from the place of fusion at a great speed in a stretch spinning process, care being taken that the primary material is delivered to the place of drawing-off at a greatly reduced speed, as compared with the spinning speed, and with a much larger cross section, as compared with the cross section of the filaments.

In addition to quartz in its transparent and opaque form, other refractory oxides having glass forming properties, such as zirconium oxide, or mixtures of various refractory oxides can be used for the process. In the process according to the invention the primary material must not necessarily be in form of glass. Furthermore, it is not necessary for the primary materials to be heated till they are fluid; on the contrary, in many cases it will be sufficient to heat the material somewhat above its softening point, so that it just exhibits plastic properties.

According to the cross section exhibited by the primary material at the place of melting, or according to the cross section given to the fused primary material at this place, there can be obtained filaments of the most varied cross sectional shapes, such as ribbon-shaped filaments which incidentally exhibit particularly good mechanical properties. Hollow filaments and hollow ribbons can also be obtained if the primary material, as conveyed to the place of drawing-off, exhibits a corresponding cross section.

Filaments with a ribbon-shaped cross section, however, can also be obtained by rolling out filaments of somewhat larger circular cross section, for example, of 100μ, preferably while they are still in a plastic state. Thereby, the filament of larger diameter obtained in a first stretch spinning operation is introduced into the rolling device either directly, i. e. while still in a plastic condition, or after being heated once more until becoming soft.

In lieu of smooth rolls, fluted or engraved rolls can also be used which impart a desired surface design to the surface of the ribbon to be produced.

The filaments or ribbons obtained according to the process of the invention being very flexible, elastic, and of great tensile strength, they can be twisted and worked into fabrics by weaving and knitting according to the usual methods of the textile industry.

In order to produce ribbons or foils of any width, the filaments or ribbons obtained are cut, for example, worked into staple filaments and felted. The felted mass is shaped into ribbons or foils. By means of rolls it can be rolled out to any desired width or thickness. Subsequently, the mass is heated in a kiln, while at the same time pressing or rolling it, whereby the individual filaments are welded together at their places of contact.

It is more advantageous to mix the felted quartz wool with an organic binder, such as dissolved nitrocellulose, and to mould the plastic mass thus obtained into a ribbon by rolling or pressing. During or after the moulding, the plastic ribbon is solidified by a hardening or drying process till it can be reeled or piled up. Subsequently, the ribbon is passed through a furnace, wherein the binder is burned and the filaments are welded together under pressure.

In an embodiment of the process, by way of example, quartz staple filaments are mixed with an organic binding agent. The felted and solidified mass is continuously passed through a rolling mill and rolled out to a thickness about ten times the thickness of the finished ribbon. Preferably the rolling is carried out at about 150°C. The temperature depends on the solvent used. The solvent evaporates and the rolled ribbon becomes so strong that it can be manipulated. The solidified ribbon is then passed through the burning chamber proper, for example, an electric furnace, wherein the binder is burned, and the felted quartz filaments are welded together by pressure. One may proceed in such a manner that the ribbon, immediately beyond the highest zone of heating, is passed through a pair of rolls which welds the filaments together by pressing, while they are still plastic.

It is particularly advantageous to pass the ribbon through electrically heated rolls. Owing to the radiation of the rolls which are heated to about 1000–1700°C and more when quartz is to be worked into filaments, the binding agent burns off before the ribbon enters the rolls. The ribbon thus produced, directly after the rolling cools down sufficiently, so that permanent changes of shape by the stress of the reeling-up will be prevented.

By special shaping of the rolls, any desired cross section of the ribbons can be obtained. Thus, cylindrical rolls produce a more rectangular cross section, while curved rolls produce a more elliptical cross section.

If very thin ribbons or foils are to be rolled, it is preferred to card the staple filaments or the wool, prior to or after the treatment with the binding agent. Hereby, a more or less parallel orientation of the filament pieces is achieved. As an example, a rotating carding machine cards a thin fleece of quartz wool which is continuously lifted from the carding machine and passed through the binding agent. The fleece impregnated with the binder then passes through a preliminary wringer whereby the excess of the binding agent is removed; then through a preliminary drying device, if desired, which by partial evaporation of the solvent imparts to the ribbon a more consistent quality; then through the rolling device proper wherein the ribbon is rolled to measure. Then the ribbon passes through the drying stove where the remainder of the solvent is evaporated entirely. Therefore, the ribbon reaches the kiln where the binder is burned and the filaments are welded together under pressure. On leaving this furnace the ribbon is reeled-up, passing through cutting machines, if desired.

According to the method of carding, ribbons of widely differing degrees of density are obtained. It is possible to produce both porous and practically imporous ribbons.

The ribbons obtained are translucent to transparent. When having a corresponding thickness they are exceedingly flexible. If, for example, vitreous quartz filaments of a diameter of 1μ are used and a thickness of 5μ is chosen for the ribbon, such ribbons are readily suitable to be wound round very fine wires without risk of breaking. The length of the individual filaments, when staple filaments are being used, may range from a few mm to many cm.

The connection of the ends or edges of the ribbons and foils is best effected by welding. For special purposes, for example, electrical purposes, foils or ribbons can be provided on one or on both sides, wholly or partly, with a metal layer, for example, by means of the cathode sphuttering process.

It is particularly advantageous to impregnate the ribbons or foils produced according to the present invention, when they are to be used for electrical purposes, with preferably organic insulating materials, such as higher saturated hydrocarbons, paraffins, ceresins, cholesterines, styrols, polymerisation products of the most varied kind, cellulose derivatives, and the like. As an example, highly porous finished ribbons are dipped into liquid ceresin, while taking the precautions customary in impregnating. After the ribbon has imbibed the impregnating agent and the excess of the impregnating agent has been removed, for example, by means of a wringer, the ribbon is dried and can readily be used as an insulating covering for cables.

In lieu of immersing the whole ribbon in the impregnating agent, one can treat it, on one or both sides, with the impregnating agent by means of a distributing roller. If the impregnating agent is applied to one side only, the other side of the ribbon can be coated with metal.

The great technical advantage of these ribbons resides in their high strength and in the good electrical properties of the organic insulating materials.

In the following examples we have set forth the stretch spinning process according to the invention and devices for carrying it out, but they are presented only for purposes of illustration and we do not wish to limit ourselves in respect of the devices illustrated in the examples.

Figure 1 illustrates diagrammatically a stretch-spinning device for producing quartz filaments.

Figure 2 shows the furnace used, by way of example, for heating the raw material.

Figures 3 and 4 illustrate modified embodiments of stretch-spinning devices.

According to Figure 1 of the accompanying drawings the end of the quartz rod 1 is brought to softening temperature in a closely confined heating zone of the smelting furnace 2, and the quartz filament drawn off from the end of the rod is wound round a rotating winding device, for example, the roller 3. In proportion to the quartz filament being spun from the end of the quartz rod, the rod is passed into the smelting furnace by means of a feeding device consisting of the rack 4 in which the rod is secured by means of a chuck, and the cog-wheel 5. The higher the speed of rotation of the winding device 3, the more material is drawn off from the end of the rod and the more quickly must the feeding device feed the rod. The thickness of the drawn-off quartz filament, at a given feed of the material to be spun, depends upon the speed of the rotating winding device, it being necessary, in the case of a very high speed, for the raw material to be highly softened accordingly, with a view to obtaining sufficient fluidity, so that the filament will not break off.

If a quartz rod circular in cross-section is being used, the spun quartz filaments will exhibit a cross-section of the same kind. If the quartz rod used is rectangular or elliptical in cross-section, a quartz ribbon is obtained. When quartz tubes are used hollow filaments or ribbons are obtained. The quartz rod may consist of transparent or opaque vitreous quartz. Moreover, a quartz rod produced by means of any sintering process may likewise be used.

In an example carried out in practice, a quartz bar circular in cross-section and of 3 mm diameter was used; the rate at which the quartz rod was fed into the device, was 1 cm per minute and the rate of winding round the roller was 900 m per minute. Thus, the ratio of the rate at which the raw material was fed, to the spinning rate was 1:90,000; this involves a reduction in cross-section by $\sqrt{90,000}=300$. The cross-section of the quartz filament obtained was obut 7 μ, accordingly. As winding devices that rotate still more rapidly, can readily be operated, it is possible to produce considerably thinner filaments such as filaments having a cross-section of only ½ μ or less.

For producing exceedingly fine filaments the work may be carried out in stages; thus at first a fairly thick thread is produced, then this thread is fixed in the feeding device and drawn out to form a very fine thread. In all these embodiments of the invention, but also when rods are being used, a number of threads or ribbons can be spun simultaneously, if desired, by employing one winding device, whereby one furnace as well as several furnaces may be used.

Figure 3 illustrates in some detail another advantageous embodiment of the invention. In the high frequency furnace 6 employed by way of example the receptacle 7 made of a highly refractory material, such as graphite or carbon, and containing the fused quartz 8 is employed. Dipping into the fused quartz is the tube 9 (made of graphite, carbon, thorium oxide, and the like) with the plate 10, which is provided with nozzles 11. Part of the static weight of the tube 9 is balanced by counterweights 12, which are suspended over pulleys 13. The remaining weight of the tube causes the plate 10 to sink into the melt to a certain depth only. The hydrostatic pressure of the melt then forces the molten quartz through the holes in the plate 10 into the interior of the tube 9. At the commencement of the manufacturing process the quartz plunger 14, which is secured in a metal tube suspended from the spring 15, is brought into contact with the threads entering the tube 9, by bending the spring; as soon as contact is made between the plunger 14 and the inflowing quartz mass the spring 15 is caused to leap up, whereby the threads extruded from the nozzles are drawn out. These threads are then laid over the winding device 16 and reeled up thereon.

Threads of different diameter are obtained according to the speed with which the winding device 16 is moved. Reeling speeds of from 500 to 3,600 m per minute and more were employed. By suitably adjusting the weights 12 it can be attained that the tube 9 with the nozzle plate 10 will sink into the melt in proportion to the spinning of threads from said melt, so that there is a constant hydrostatic pressure at the nozzle openings.

The diameters of the nozzles are many times larger than the thickness of the quartz filaments produced, for example, 3 mm as compared with a diameter of the filaments of 3 μ. The thickness of the threads is not determined by the apertures of the nozzle plate but by the stretching operation. The spun quartz filaments may be given a great variety of cross-sectional shapes by shaping the nozzles accordingly; hollow threads or ribbons, for example, may thus be obtained.

In the embodiment of the invention according to Figure 3 a plurality of threads is spun from the melt simultaneously, according to the number of nozzles provided.

In the apparatus according to Figure 1 as well as in that according to Figure 3 a feeding device is used which conveys the raw material to the place of drawing-off at a rate that is considerably lower than the drawing-off speed of the filaments, and furthermore there is employed a rotary drawing-off device such as a reel whose speed determines the thickness of thread and which is destined to receive the spun filament. In both devices the cross-section of the raw material which is determined in the device according to Figure 1 by the cross-section of the quartz rod used, and in the device according to Figure 3 by the cross-section of the apertures of the nozzle plate, is considerably greater than the cross-section of the quartz filaments produced.

Figure 4 illustrates a modified construction of the stretch-spinning device. The fused quartz is forced under pressure through a nozzle plate 3 (spinneret), made of carbon, tungsten carbide, graphite, or a similar refractory material which, however, is an electric conductor, the nozzle plate itself being used as heating element. For this purpose current supply leads 35 and 36 are provided. In order to utilize the heat effectively, only that part of the quartz mass to be spun is fused or plastified by heating which is nearest to the nozzle plate. This part of the quartz mass is extruded through the nozzles by pressure, for example by the pressure of the quartz mass with which it is weighted. The plastic or liquid parts of the quartz mass extruded from the nozzles are drawn off by means of a deviee such as shown in Figure 3 and wound round the roller. It will be seen from Figure 4 that the graphite plate 31 is substantially thinner at the point 32, whereby the electrical heating energy is concentrated at this point. Part 32 is provided with holes that are advantageously from 2 to 4 mm in diameter, and forms the spinneret of the apparatus. Above 32 in the chamber 33 quartz sand, for example, is placed, protected by a heat insulation 39 or an electrical insulation 37. If the electrical circuit is closed, the spinneret will be heated to a temperature corresponding to the voltage applied, and, if said temperature is high enough, it will fuse the quartz sand in the chamber 33 just above 32. Owing to the static pressure exerted on the melt by the quartz sand above it, the melt passes through the nozzles of the plate 32 and enters the chamber 41; in this chamber the quartz that is forced through is grasped by any suitable device, drawn off, and wound on a drum.

The above described stretch-spinning device renders it possible to attain, under economic conditions, a particularly high drawing-off rate, (for example 4,000 m per minute and more).

The filling up with quartz sand in this embodiment is particularly simple as the quartz sand can be poured into the chamber 33 from above by means of suitable devices, the level being kept constant as near as possible.

In order to reduce as much as possible the loss by radiation in the spinneret on the side not facing the melt, it is advantageous to build up the spinneret of two or more layers of different materials that are electric conductors, such as carbon and graphite, in such manner that the layer nearest to the fusing mass is a better electric conductor than the outer layer. Hence, a stronger electric current will flow through this layer, and make it hotter than the side opposite to the fusing mass. It is particularly advantageous to provide the side of the spinneret opposite to the fusing mass with a layer of a heat insulator such as zirconium silicate.

It is preferred to work in a neutral atmosphere, for example, by passing nitrogen into the chamber 33 and 41.

Whereas in the device according to Figure 1 the raw material is heated to just above softening point and is in a viscous state, in the embodiment according to Figures 3 and 4 the melt is comparatively fluid.

For softening or fusing the raw material smelting furnaces are used which permit of being adjusted to a correspondingly high temperature and easily regulated. For example, there may be employed electric resistance furnaces, high frequency furnaces, coal dust furnaces, rod furnaces, Tammann furnaces, and furnaces heated by a oxyhydrogen or oxygen blowpipe.

Sometimes it may be advisable, particularly when using coal burning furnaces, to pass nitrogen, argon or other inert gases through the furnace in order to protect the furnace materials, or it may be advisable to cover or impregnate the structural parts exposed to high temperatures and to the air with protective substances.

Figure 2 illustrates by way of example the construction of an electric furnace that can with advantage be used in conjunction with the device according to Figure 1.

To the burner 20 made of graphite or carbon current is supplied, on the one hand through the head 21 of the furnace, and on the other hand through the jacket of the furnace that consists of the tube 22 of carbon or graphite, and through the intermediate member 23. The two current supply leads are electrically insulated from each other by the porcelain or asbestos insulation ring 24. Current is supplied to the head-piece 21 through the copper bolt 25 and to the jacket 22 through the copper clamp 26. The burner 20, the head-piece 21 and the intermediate member 23 are perforated to allow the passage of the quartz rod from which the quartz thread is to be spun. If the quartz rod is inserted from the top such a distance that its end extends a little way beyond the hottest part of the heating zone, the end of the quartz rod extending beyond the hottest zone will fuse immediately the current is switched on, whereupon it drops, taking a thread with it, and in this way commences the spinning operation.

In order to avoid losses by radiation and for the purpose of protecting the carbon parts of the furnace the interior of the heating chamber 2 is provided with porcelain tubes 27 and 28 which at the same time prevent the access of atmospheric oxygen.

At a given cross-section and length of the nozzles there is given for each temperature of the melt a drawing-off rate calculable from Poiseuille's equation. When this drawing-off rate is adjusted accordingly, the viscosity of the melt has to be constant, if the apparatus is to work perfectly, since otherwise, in the event of the viscosity increasing, too little of the melt would flow through the nozzle, and the threads would become thinner and thinner, and finally snap off. Likewise, in the event of the viscosity dropping (i. e. the temperature rising) there would be derangements, as increasingly more of the melt would be delivered than is required with the fixed drawing-off rate and the diameter of filament desired. Two conditions may arise: Either the diameter of the filament becomes greater or there appear in the thread, in the event of sudden sharp changes in viscosity, so called "fishes" (short, much thickened portions of thread). In both cases a rational spinning manufacture would be subject to undesirable stoppages.

All these difficulties can be avoided by carefully controlling the amount of heat (electrical energy) supplied and/or the drawing-off rate and/or the pressure exerted on the melt. The refractory oxides, more especially quartz, show sometimes very undesirable property, viz. an extremely high temperature sensitiveness of the viscosity, particularly in that range of temperature in which the work is carried out on economical grounds. Spinning experiments bear this out very clearly. There is always an endeavour to employ as low temperatures as possible because, apart from the not unconsiderable technical difficulties involved in employing a temperature that is only 100°C higher than is absolutely necessary (in the high range of about 2,000°C and over) the loss of heat increases very rapidly. The lower the temperatures at which spinning can still be carried out, the greater are the changes in viscosity with the temperature, so that to spin economically special attention must be given to temperature and drawing-off rate. Further, on grounds of economy, the nozzle constants, the viscosity (temperature), the pressure and the drawing-off rate must be adjusted to optimum conditions.

For this purpose different steps may be taken. Since generally the electric resistance of the electric heating element employed in the different stretch-spinning devices increases continuously, the electric energy must, if a constant voltage is used, be altered in accordance with the alteration of the electrical resistance of the heating element. Arrangements can be made either so to control the current that it is constant; then only in the first approximation is the same effect obtained. Or better still, the energy itself is controlled. In the first case an ammeter is coupled with a control motor through a relay in such manner that when the current drops the control motor causes a main control device that acts for example on a step transformer, to furnish a higher voltage, and vice versa. In the second case, a watt-meter is used instead of an ammeter.

It is also possible, by means of the ammeter or watt meter through relays or other devices to influence the speed of rotation of the winding machine. The rate of the influence required can be deduced from Poiseuille's equation.

Finally, the pressure can be controlled by which the melt is forced through the nozzles. The simplest manner of controlling is to put the receptacle containing the melt under the pressure for example, of a gas cylinder provided with a reducing valve. Since in practice in nearly all processes nitrogen is used as rinsing gas, it is advisable to keep the receptacle containing the melt under the pressure of a nitrogen atmosphere. It is then possible to control the reducing valve through relays by means of the ammeter or wattmeter, i. e. to increase the pressure with a decreasing supply of electrical energy, and vice versa. As it is not possible to go beyond a certain pressure, it is advisable, beyond a certain pressure, to control the drawing-off rate that has hitherto been constant.

It will be understood that still other combinations of controlling are possible. Thus, for example, it is possible to regulate to a constant current intensity and to a certain gas pressure. Finally it is possible, up to a certain limit, to regulate to a constant electric energy supplied, whereupon the pressure is regulated up to a further limit and finally the drawing-off speed is also regulated.

Since the filaments produced by the process according to the invention are often charged electrostatically it is advisable to discharge them before they are wound; this can be effected, for example, by passing them through a bath of an electrolyte.

As already explained, the filaments produced are remarkable by high elasticity and tensile strength. They can without difficulty be twisted to threads by all the methods customary in the textile industry. Filaments with a diameter of less than 5μ show considerable knotting strength.

As quartz has a very low dielectric loss ($tg\delta$ about 1×10^{-6}), the quartz filaments, ribbons and foils produced according to the invention are very suitable for insulating wires and cables and particularly for insulating conductors of high frequency currents. They are furthermore suitable as dielectric in condensers. Quartz ribbons, such as can readily be produced by the process of the invention in cross-sectional ratios of from 1:2 to 1:100 and over, are particularly useful. Such quartz ribbons are far superior to the materials hitherto used for this purpose such as silk, ethyl cellulose, polystyrol, and the like.

As the new quartz filaments and ribbons may be produced in any length desired and are very elastic they can be readily woven into fabrics to be used for the most varied purposes, for example, fabrics in which particular importance is attached to their being permeable to ultra-violet rays, acid-proof, fire-proof, etc.

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