Feb. 28, 1939. D. C. STOCKBARGER 2,149,076

METHOD FOR THE MANUFACTURE OF CRYSTALLINE BODIES

Filed Oct. 18, 1935 3 Sheets-Sheet 1

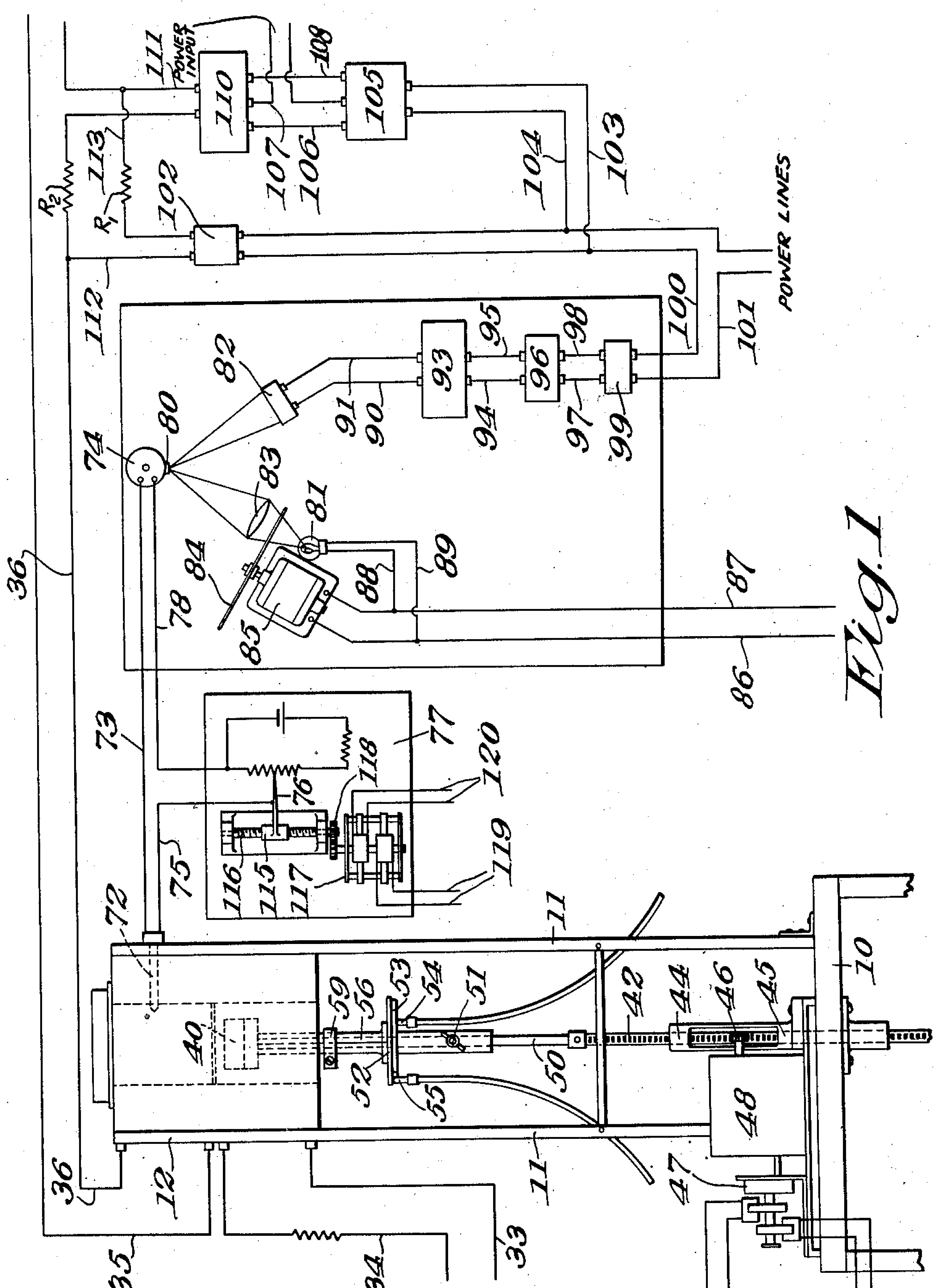

Fig. 1

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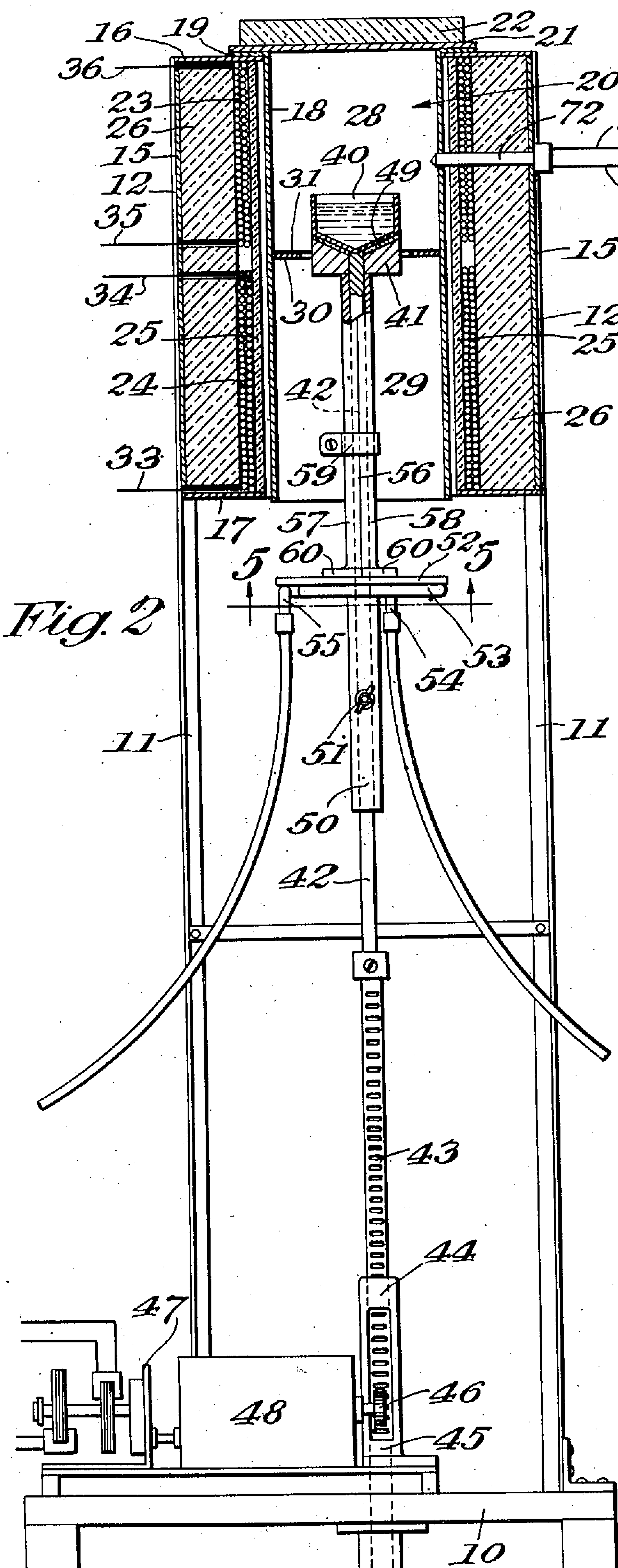
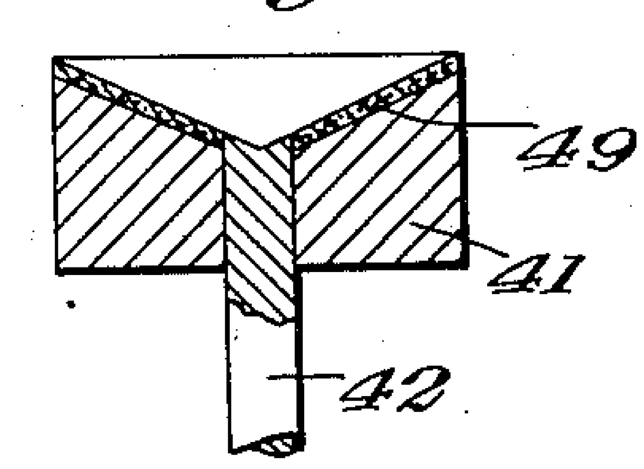


Fig. 2

Fig. 3



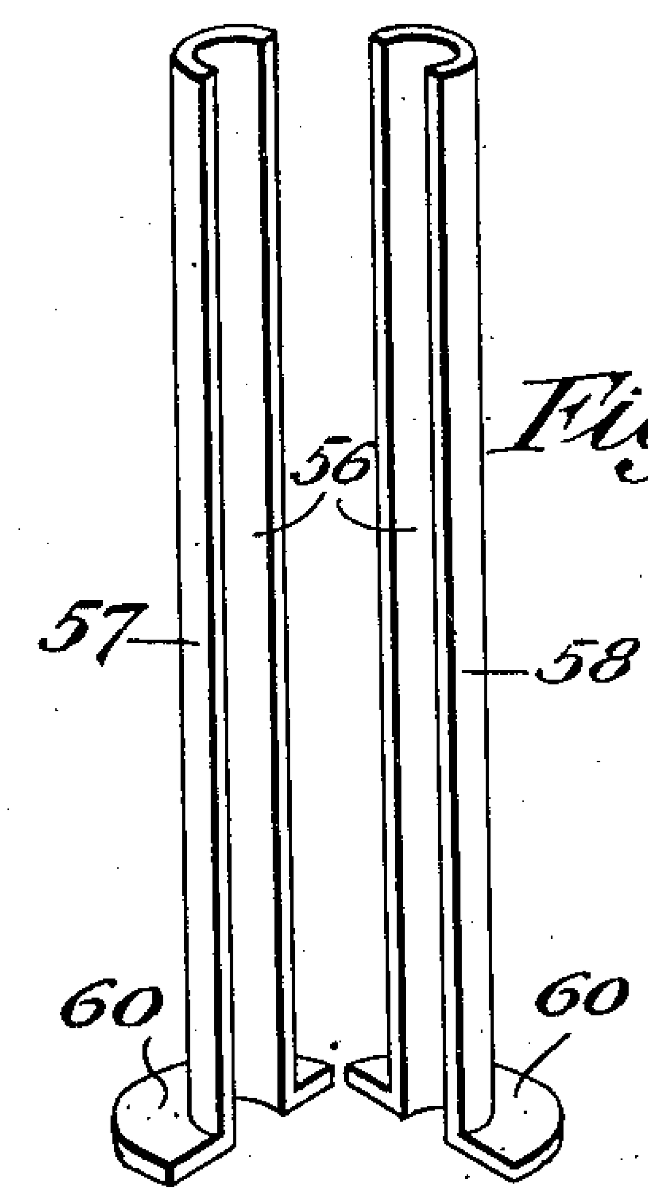


Fig. 4

Fig. 5

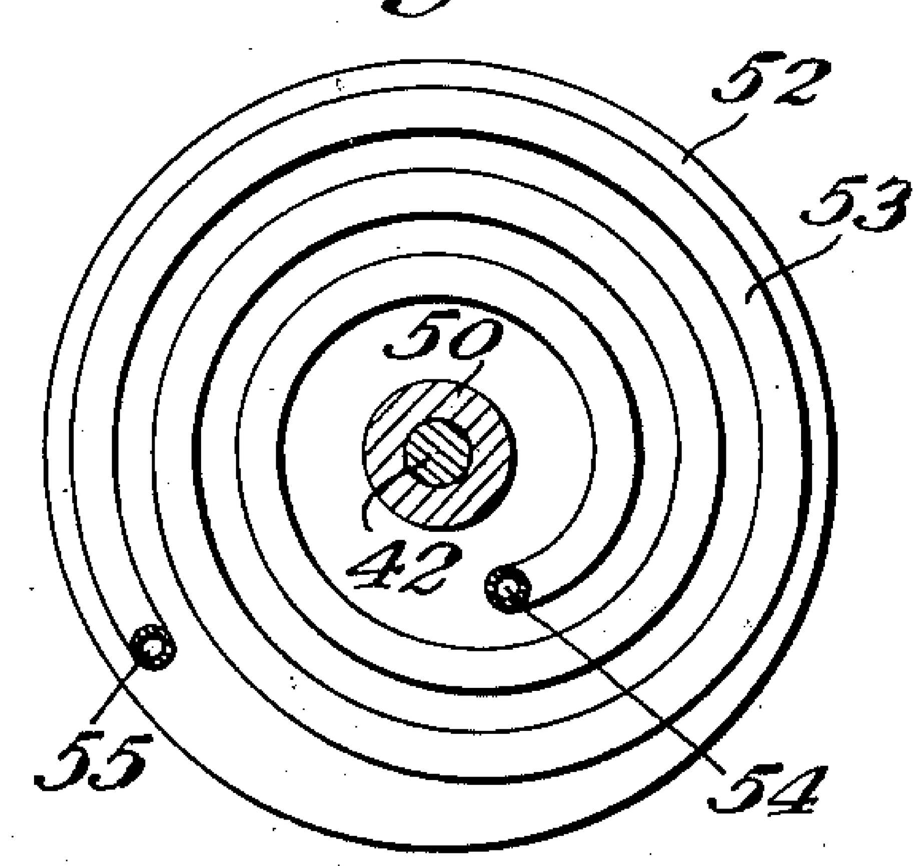


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Fig. 6

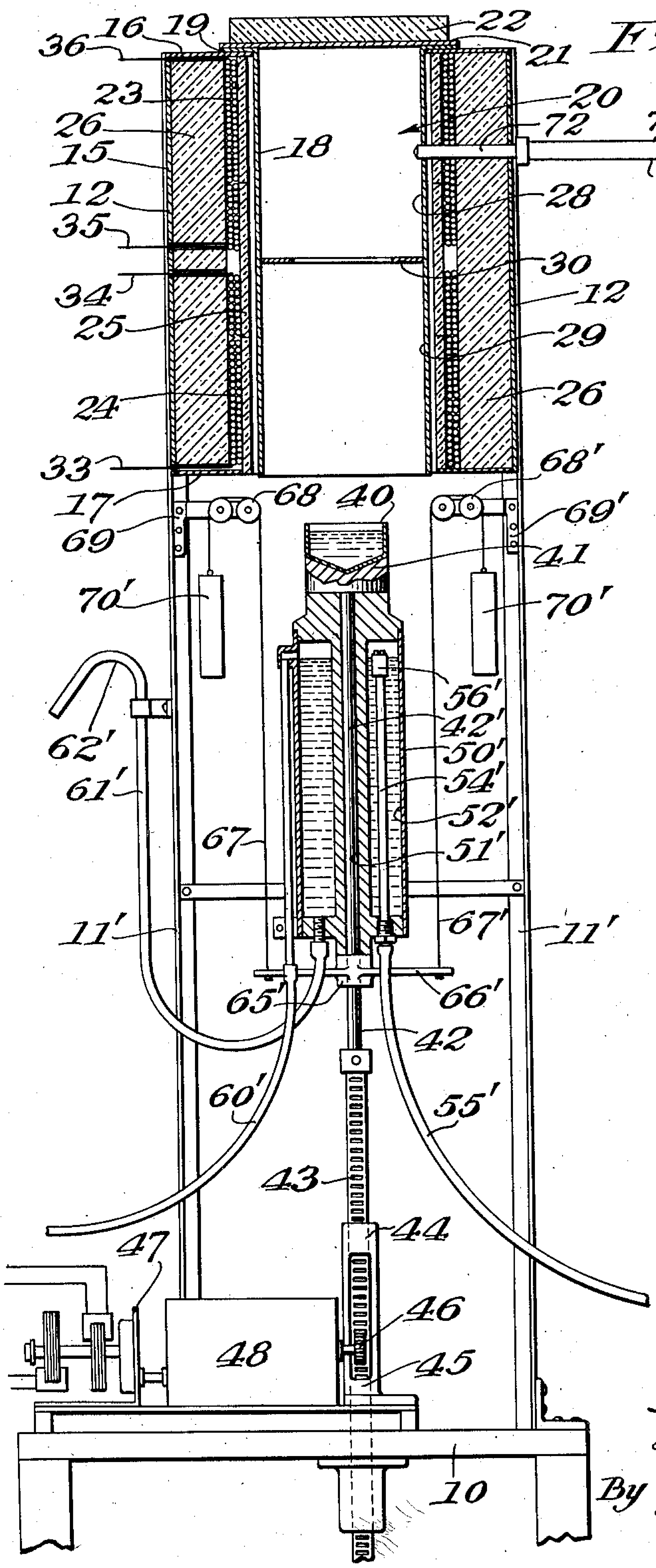
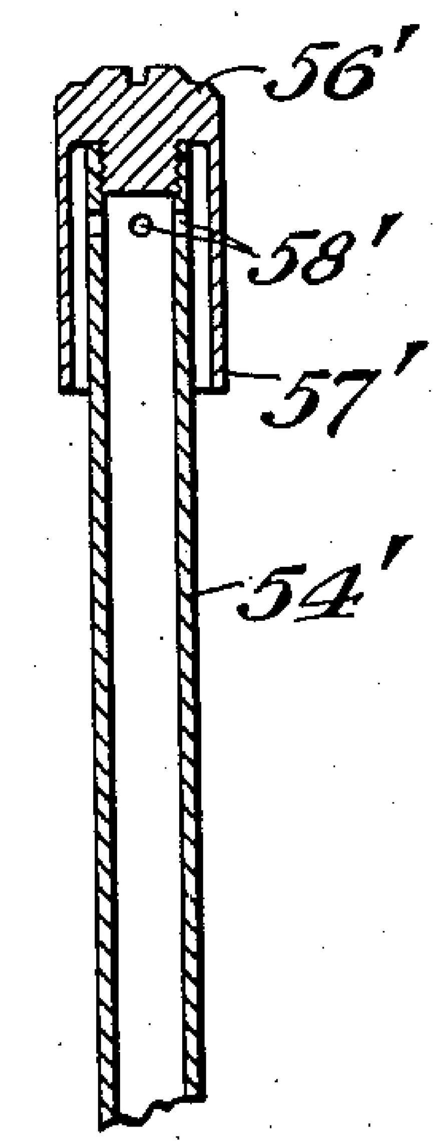


Fig. 7



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UNITED STATES PATENT OFFICE

2,149,076

METHOD FOR THE MANUFACTURE OF CRYSTALLINE BODIES

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Application October 18, 1935, Serial No. 45,613

5 Claims. (Cl. 23—88)

This invention relates to the manufacture of crystalline bodies from fused material and has for its object the production of strong crystalline bodies of great purity and of desired size. The invention makes possible the production of a new article of manufacture heretofore unknown.

In accordance with the invention, the molten mass to be crystallized is moved at a controlled rate from a region hotter than the solidification temperature of the mass to a region cooler than the solidification temperature of the mass. At the same time a sharply localized zone of steep temperature gradient is maintained between the relatively hot and cool regions. Consequently, the temperature of the edge portion of successive layers of the mass corresponds to the solidification temperature of the mass as these edge portions reach a substantially fixed location in the path of travel of the mass and solidification begins and progresses inwardly. Purer crystals are obtained when this temperature gradient is maintained as steep as possible, and better crystals are obtained when the zone of solidification approximates a plane. In certain instances, such as when the thermal conductivity of the mass being solidified is small or the size of the crystal being produced is large, it is desirable to control the rate of heat flow through the inner portion of the mass from the hotter to the cooler region. Thus, if the rate of heat flow through the inner portion of the mass is too slow, the zone of solidification tends to be concave. By properly controlling the rate of heat flow through the inner portion of the mass, the zone of solidification may approximate a plane.

Substances which heretofore could not be crystallized to provide bodies of sufficient strength and purity to make them available for practical scientific and commercial uses may be crystallized by the practice of the invention to provide crystalline bodies of commercial size and of such strength and purity that they may be shaped and used for various purposes. Thus, the invention makes possible the production of strong crystalline bodies of substances which have heretofore been available only as natural crystals and of substances which do not occur in the form of natural crystals and which are relatively free of inclusions. Fused lithium fluoride is an example of a material which may be crystallized in accordance with the invention to provide bodies of desired size and of such quality that they may be shaped to render them valuable for practical scientific and commercial uses. Crystals made in accordance with this invention have a high degree of purity which increases their value. Other materials may be crystallized by the practice of the invention, such as sodium chloride.

Crystalline bodies of lithium fluoride produced by the practice of my invention are themselves new and are characterized by optical properties not possessed by any other known optically useful solid material obtainable in practical size. Such bodies are characterized by unusually low dispersion in the visible region and by transmission of ultra-violet radiation or ultra-violet light rays having a wave length at least as short as 0.11 micron. The difference in index of refraction for any two wave lengths, which is a measure of the dispersion for these wave lengths, is small for lithium fluoride. In the trade the dispersive power of any optical substance is expressed as

$$\frac{1}{\nu}$$

Where

$$\nu=\frac{N_D-1}{N_F-N_C}$$

N_F=index of refraction for light of wave length 0.4861 micron;

N_D=index of refraction for light of wave length 0.5893 micron;*

N_C=index of refraction for light of wave length 0.6563 micron;

*Mean wave length for the doublet.

The quantity N_F—N_C is known as the mean dispersion.

(Ref: Hardy and Perrin, "The Principles of Optics", pp. 113, 117, and 118.)

ν for lithium fluoride produced by the practice of my invention is found to lie between 99 and 100.

ν for optical glass may lie between 20 and 70, depending on the composition of the glass.

The invention will be more clearly understood from the following description in conjunction with the accompanying drawings: in which,

Fig. 1 is a diagrammatic view of a suitable apparatus for the practice of the invention;

Fig. 2 is an elevational view, partly in section, of a portion of the apparatus;

Fig. 3 is a detail sectional view of one of the parts of the apparatus;

Fig. 4 is a detail perspective view of another portion of the apparatus;

Fig. 5 is a sectional view taken upon the line 5—5 of Fig. 2;

Fig. 6 is an elevational view, partly in section, of a modified construction of a portion of the apparatus corresponding to the portion illustrated in Fig. 2; and

Fig. 7 is a detailed sectional view of one of the parts of the apparatus shown in Fig. 6.

Before explaining in detail the present invention it is to be understood that the invention is not limited in its application to the details of construction and arrangement of parts illustrated in the accompanying drawings, since the invention is capable of other embodiments and of being practiced or carried out in various ways. Also it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation, and it is not intended to limit the invention claimed herein beyond the requirements of the prior art.

A suitable apparatus for use in practice of the invention is illustrated in the accompanying drawings and comprises a support 10 carrying a frame 11 for supporting a furnace 12. The furnace 12 comprises an annular casing having an outer cylindrical wall 15, top wall 16, bottom wall 17 and an inner cylindrical wall 18 which is supported in position by a flange 19 extending outwardly from its upper end and resting upon the top wall 16. The inner wall 18 defines the outer limit of the chamber 20 within the furnace which is closed at its upper end by a cover plate 21 which may carry suitable insulation 22. Heating coils 23 and 24 surround a tubular core 25 and are separated from the outer cylindrical wall 15 by suitable insulation 26. The chamber 20 is divided into an upper chamber 28 and a lower chamber 29 by an annular metallic ring 30 carried by the inner wall 18 and positioned in the plane between the adjacent ends of the coils 23 and 24. Preferably, the upper surface of the annular ring 30 is covered with a thin polished platinum sheet 31 to deflect heat and maintain a sharp temperature gradient at the plane of division between the two chambers of the furnace. The coil 24 is connected through leads 33 and 34 to a suitable source of electrical energy and the coil 23 is connected by leads 35 and 36 to a suitable source of electrical energy.

A crucible 40, adapted to contain the liquid to be crystallized, is carried by a support 41 which is fixed upon a rod 42, the lower end of which is suitably secured to a rack bar 43 longitudinally movable in suitable guides 44 and 45 fixed upon the support 10. The passage in the annular ring 30 is such as to permit the crucible 40 and the support 41 to move therethrough without excessive clearance. The rack bar 43 is engaged by a pinion 46 which is actuated by a synchronous clock motor 47 through speed reduction gearing 48. The crucible 40 should be made of material having a low thermal conduction and not attacked by the substance being crystallized and may have any desired shape to correspond to that of the crystalline body to be produced. However, the bottom of the crucible should be tapered to a point at which the crystallization begins, and the top surface of the support 41 is preferably of shape complementary to that of the bottom of the crucible and is coated with a layer 49 of alundum cement, through which the upper end of the rod 42 extends to engage the point of the crucible 40.

A sleeve 50 is adjustably mounted upon the rod 42 and is held in desired position thereon by a clamp 51. A disk 52, having a hole through which the rod 42 extends, is fixed upon the upper end of the sleeve 50. The disk 52 may be brass and its upper surface, preferably, is blackened. A pancake cooling coil 53 is soldered to the lower surface of the disk 52 and is provided with a water inlet 54 and outlet 55. In order to control the rate of flow of heat through the inner portion of the mass in the crucible and to cool the upper portion of the rod 42 and provide a cold spot at the tip of the crucible, a heat conducting split tube 56 having complementary portions 57 and 58 is held upon the rod 42 by a clamp 59. The portions 57 and 58 of the split tube 56 are provided each with an outwardly extending flange 60 adapted to rest upon the disk 52.

In the practice of the invention power is supplied to the coils 23 and 24 so as to maintain the upper chamber 28 at a temperature above the solidification temperature of the liquid to be crystallized and to maintain the temperature of the chamber 29 below the solidification temperature of the liquid to be crystallized. In order to control and maintain the desired temperature within the chamber 28 a temperature regulator may be provided comprising a thermal couple 72 projecting into the chamber and electrically connected by a lead 73 to one terminal of a galvanometer 74 and by a lead 75 to the slide wire 76 of a potentiometer 77. The other terminal of the galvanometer 74 is connected by a lead 78 to the potentiometer 77. The galvanometer 74 is provided with a mirror 80 adapted to reflect light rays from a lamp 81 on or off a photronic cell 82 depending upon the position of the galvanometer mirror. A lens 83 is interposed between the lamp 81 and the mirror 80 so as to concentrate the rays upon the latter. A light chopper 84 in the form of a perforated disk is interposed between the lens 83 and the lamp 81 and is carried upon the armature shaft of a motor 85 which is connected through the leads 86 and 87 to a source of electrical energy. The lamp 81 is connected by leads 88 and 89 to the leads 87 and 86 respectively. The photronic cell 82 is connected by leads 90 and 91 to an amplifier 93 which in turn is connected by leads 94 and 95 to a rectifier 96. The rectifier 96 is connected by leads 97 and 98 to a master relay 99 which is connected by leads 100 and 101 to the terminals of a single relay 102. The leads 100 and 101 are connected by leads 103 and 104 respectively to a double relay 105. The relay 105 is connected by leads 106, 107, and 108 to a demand regulator 110. The lead 36 from the coil 23 is connected to the demand regulator which in turn is connected by a lead 111 to a source of electrical energy for heating the coil 23. The relay 102 is connected by leads 112 and 113 to the lead 36 and lead 111 respectively.

In order to permit the temperature within the chamber 28 to be increased or decreased, the slide wire 76 of the potentiometer is movably carried by a sleeve 115 threaded upon a screw shaft 116 and which is rotated by a synchronous motor 117 through suitable reduction gearing 118. The synchronous motor 117 is connected by leads 119 and 120 to a suitable source of electrical energy.

The potentiometer 77 is set so that the galvanometer mirror 80 reflects light from the lamp 81 on the light-sensitive cell 82 when the temperature of the couple 72 is adjusted as desired. Because of the intermittent character of the light reaching the cell 82, due to the action of the light chopper 84, the electrical response of the cell 82 contains an alternating current component which is amplified by the amplifier 93 to produce alternating current power. This power is suitable, after rectification by the rectifier 96, for operating the master relay 99. The master relay 99 controls the operation of the relays 102 and 105. The relay 105 controls the direction of motion of a motor-driven rheostat called "demand regulator" 110 in such a manner that when no chopped light falls on the cell 82, the demand regulator 110 slowly decreases the amount of current flowing through the heating coil 23; whereas, when a predetermined amount of chopped light falls on the cell 82, the current flowing through the coil 23 is slowly increased. The relay 102 acts with the demand regulator 110 to decrease or increase the current flowing through the coil 23 by disconnecting or connecting, respectively, a suitable resistance R_1 across the combination comprising the demand regulator 110 and the series resistance R_2. The action of the relay 102 is nearly instantaneous so that practically as soon as the galvanometer mirror 80 has deflected sufficiently to send a small amount of chopped light to the cell 82 the current flowing through the coil 23 is increased thereby raising the temperature of the furnace. The said increase in temperature produces an increase in the electrical response of the couple 72 so that the galvanometer mirror 80 deflects in the opposite direction thereby decreasing the amount of chopped light reaching the cell 82 to the extent that the relay 102 causes less current to flow through the coil 23. The consequent decrease in furnace temperature produces a decrease in the electrical response of the couple 72 so that the galvanometer mirror 80 deflects in the direction to increase the amount of chopped light reaching the cell 82, and so on.

It is clear that the hereinbefore described performance of the temperature regulator is such that the furnace temperature cannot wander greatly as long as conditions are nearly constant, e. g., when the room temperature and line voltage do not change much. If, however, conditions are not sufficiently nearly constant, the demand regulator 110 plays an important role. During successive steps of the hereinbefore described performance the reversible motor of the demand regulator 110 acts alternately to decrease and increase slowly the amount of resistance connected in series with the coil 23 and this action is initiated in each case at t he time of operation of the relay 102 since the relays 102 and 105 are both controlled by the master relay 99. Under nearly constant conditions the average increases and decreases of the resistance in the demand regulator 110 are practically equal so that the action is similar to that of the relay 102. When there is demand for more power due to a drop in line voltage, for example the "on" times of the relay 102 exceed the "off" times, and hence the motor of the demand regulator 110 runs on the average more in the direction to reduce the amount of series resistance than it runs in the opposite direction. Similarly, the series resistance is increased when the line voltage is too high.

It is now clear that the temperature regulator is capable of maintaining practically constant furnace temperature even when the average power required to do so is not constant.

In the practice of the invention, the support 41 is raised into the chamber 28 and the crucible 40 containing the liquid to be crystallized is positioned thereon. When lithium fluoride is being crystallized, a metallic crucible, such as platinum, is used, the outer surface of which may be darkened as by copper plating which is subsequently oxidized. If, for example, it is desired to produce a crystalline body of lithium fluoride, the salt in granular or other solid form is placed in the crucible 40 and melted. When the desired quantity of material to be crystallized, e. g., lithium fluoride, has been melted and brought to the desired temperature which, preferably, should be substantially above the fusion point, the motor 47 is started to move the support 41 downwardly at a slow rate. The motor 47 and the reduction gearing 48 may be so arranged so as to impart any desired rate of movement to the support 41. Good results have been obtained by moving the support 41 downwardly at the rate of about one inch in twenty hours. When the lowest point of the crucible 40 substantially coincides with the plane of division between the chambers 28 and 29 crystallization of the liquid begins and successive layers of the liquid are progressively crystallized as these successive layers are progressively brought substantially into the plane of division between the chambers 28 and 29. Excellent results have been obtained when maintaining the temperatures of the chambers 28 and 29 such that the temperature just above the partition 30 is about 930° C. and the temperature just below the partition is about 810° C., the melting point of lithium fluoride being about 850° C. Under such conditions, the thickness of the partition 30 being about 0.10 mm, a temperature gradient of about 1000° C. millimeter is obtained. The maintenance of a high temperature gradient at the partition 30 is favored by the use of a temperature in chamber 28 which is substantially, e. g., 100 to 200° C. above the melting point of the mass. Storage of the solidified mass in chamber 29 at a high temperature serves to avoid shattering of the crystal such as would occur if it were rapidly cooled to atmospheric temperature.

There appears to be a relationship between the temperature gradient dividing the hotter and cooler regions and the rate at which the mass is moved from the hotter to the cooler region. Thus, when the temperature gradient is less than that stated, the rate of movement of the mass must be less than that stated in order to produce a crystal approaching the quality desired. While no accurate limits of minimum temperature gradient or maximum and minimum rate of movement of the mass have been established, a temperature gradient as low as 1° C. per millimeter is impractical.

At the beginning of the crystallization process the point of the crucible bottom is chilled by contact with the end of the support rod 42 with the result that a small crystal is formed there. This small crystal acts as a nucleus so that no seed crystal is required and it also insures that no supercooling of the liquid can take place. It is, of course, recognized that during the subsequent solidification of the material in the conical bottom part of the crucible, which occurs as the crucible is lowered, the high temperature gradient is of relatively small effect because here the crucible is enveloped by the support 41 and the alundum cement 49. The steep temperature gradient comes into full play as soon as the conical bottom part of the crucible has passed down through the annular ring 30.

It is believed that the improved results obtained by the practice of the invention are due to the sharply localized steep gradient near the surface of the crucible, and an equi-temperature surface which is plane or nearly plane and extends across the crucible and its contents at this level. While the existence and location of the steep gradient region are determined by the annular ring **30** and the difference between the temperatures of the chambers **28** and **29**, the location and shape of the freezing layer are determined by the actual temperatures of the chambers **28** and **29**. If the temperature of the upper chamber **28** is too high relative to the temperature of the lower chamber **29** the freezing layer surface is concave upwards, the layer is too low and an inferior crystal is obtained. If the temperature of the upper chamber **28** is too low relative to the temperature of the lower chamber **29** the freezing layer is convex upwards, the layer is too high and an inferior crystal is obtained. The temperatures of the two chambers **28** and **29** are adjusted by trial until the freezing layer surface is nearly plane and practically coincident with the steep gradient region and under these conditions a good crystal is obtained.

In the practice of the invention each layer starts its growth at the surface of the crucible. Moreover, as the crystal passes slowly downward the timing of new layers is regular. This is because, since the gradient is steep, it remains substantially fixed in space as the crucible moves. Hence the time when a given point in the material passes through the temperature of solidification is determined precisely near the surface of the crucible. If the gradient were not abrupt at this point the casual wanderings of temperature always present in a furnace would cause layers to spring out in an irregular manner, and occasionally in bunches, with inevitable entrapment. The fixed steep gradient with the consequent regular succession of independently growing layers thus prevents entrapment of impurities.

In Fig. 6 another arrangement for controlling the rate of heat flow through the inner portion of the mass being crystallized from the hotter to the cooler region is illustrated. This arrangement includes a cooling device comprising a cylindrical casing **50'** having a central guide passage **51'** adapted to receive the rod **42** and upon which the casing is slidably mounted. The casing **50'** of the cooling device is provided with an annular passage **52'** in which a cooling fluid, such as water, may be circulated. A pipe **54'** is mounted in the bottom of the casing **50'** and is connected with a suitable fluid inlet conduit **55'**. The upper end of the pipe **54'** is provided with an outlet nozzle **56'** having a depending skirt or sleeve **57'** and extending downwardly below outlet openings **58'** near the top of the pipe whereby fluid supplied through the pipe **54'** is directed downwardly along the outer surface of the pipe. A conduit **60'** communicates with the top of the annular passage **52'** to permit the escape therefrom of air or vapor. A fluid outlet conduit **61'** communicates with the annular chamber **52'** and extends upwardly therefrom to a fixed point, as indicated at **62'**, so as to control the level of fluid within the annular chamber **52'**. The casing **50'** is supported upon a ring **65'** which is slidably mounted upon the rod **42'**. The ring **65'** is provided with a pair of arms **66'** to each of which one end of a cable **67'** is secured. Each of the cables **67'** extends upwardly from the arms **66'** over pulleys **68'** rotatably carried by a bracket **69'** fixed to the frame **11'** and is secured at its other end to a counterweight **70'**.

What I claim is:

1. The method of making a crystal from a molten mass which comprises slowly moving the molten mass at a controlled rate from a region hotter than its solidification temperature to a region cooler than its solidification temperature, controlling the relative temperatures of said regions, and maintaining a sharply localized zone of steep temperature gradient between said regions at the boundary of said mass, said zone having a temperature gradient of substantially 1000° C. per millimeter.

2. The method of making a crystal from a molten mass which comprises moving the molten mass at a rate of about 1/20 of an inch per hour from a region hotter than its solidification temperature to a region cooler than its solidification temperature, controlling the relative temperatures of said regions, and maintaining a sharply localized zone of steep temperature gradient between said regions at the boundary of said mass, said zone having a temperature gradient of substantially 1000° C. per millimeter.

3. The method of making a crystal from a molten mass which comprises slowly moving the molten mass from a region of substantially uniform temperature materially above the melting point of the mass into a region of substantially uniform temperature materially below the melting point of the mass but materially above atmospheric temperature through a zone of steep temperature gradient at the boundary of the mass of the order of 1000° C. per millimeter, and regulating the rate of movement of the mass and the rate of heat flow through the interior of the mass so as to maintain an isothermal zone at the crystallizing temperature of the mass substantially in the plane of said zone of steep temperature gradient.

4. The method of crystallizing which comprises slowly moving a molten mass from a region at a substantially uniform temperature materially above the melting point of the mass to a region at a substantially uniform temperature materially below the melting point of the mass but sufficiently elevated to prevent cracking of the crystal due to thermal contraction thereof, through a zone having a temperature gradient adjacent the boundary of the mass of the order of 1000° C. per millimeter and regulating the rate of movement of the mass and the rate of heat flow through the interior thereof so as to maintain the surface of contact of solid and liquid portions of the mass substantially in a plane which coincides with said zone of steep temperature gradient.

5. The method as defined in claim 4 in which the mass consists of lithium fluoride, the temperature of the molten mass above the zone of steep temperature gradient is about 930° C. and the temperature of the mass below said zone of steep temperature gradient is about 810° C.

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