Jan. 25, 1949. C. J. CHRISTENSEN ET AL 2,459,869

CRYSTAL GROWING APPARATUS

Filed Aug. 10, 1946 4 Sheets-Sheet 1

FIG. 1

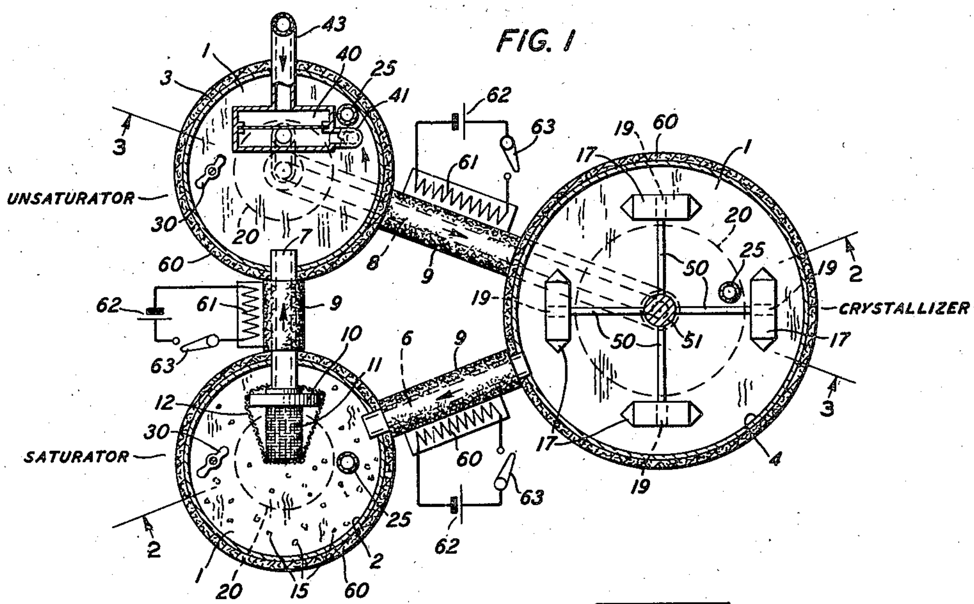

FIG. 2

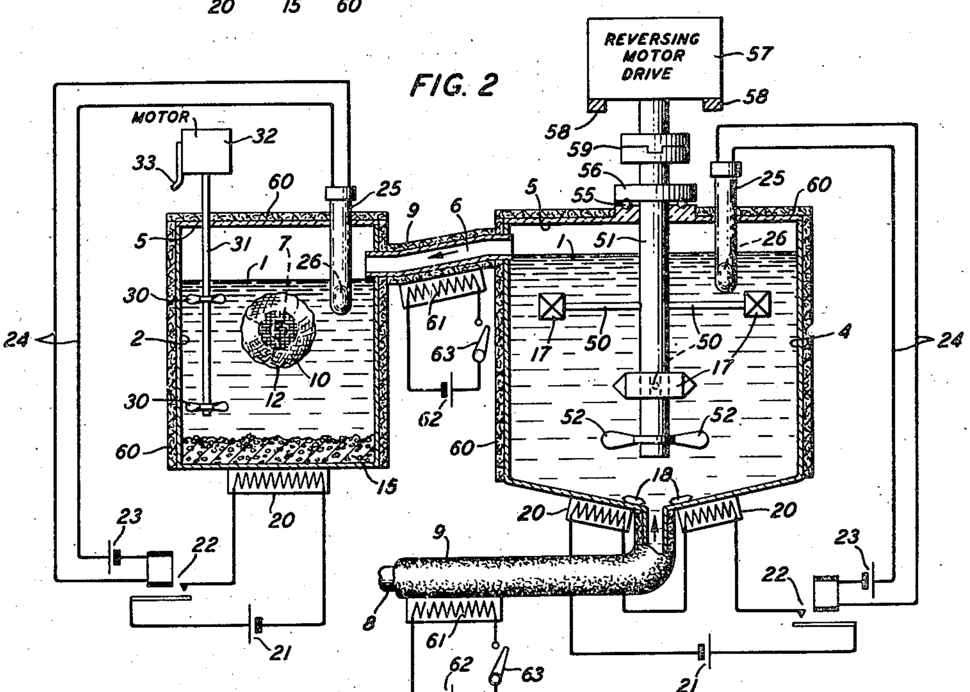

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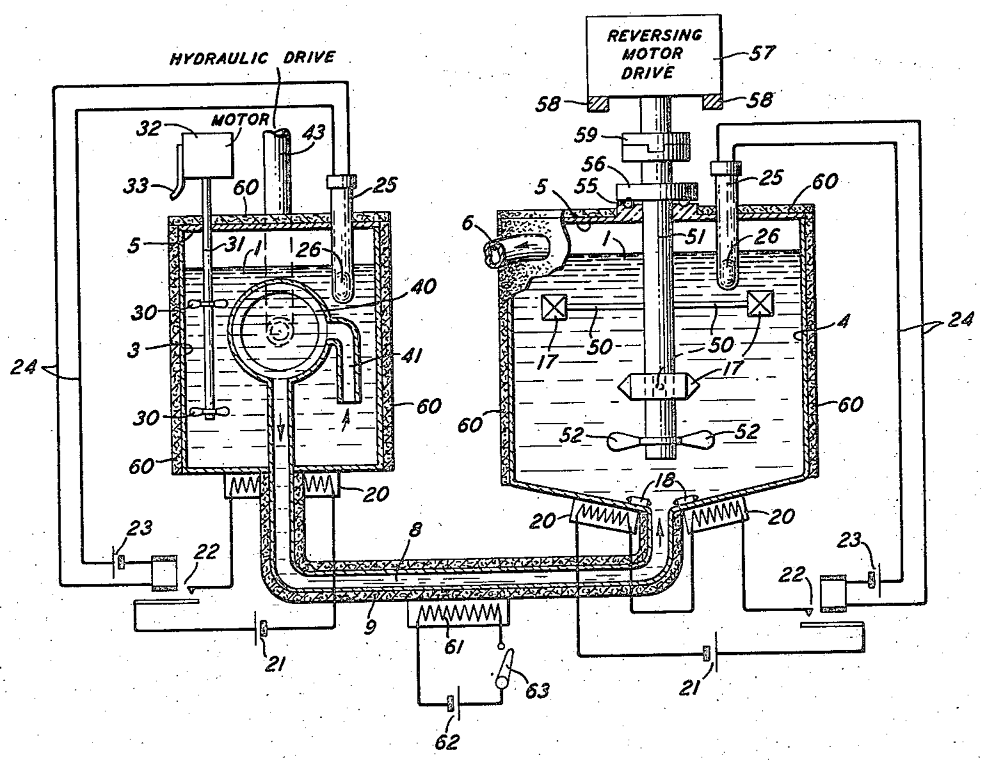
FIG. 3



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Filed Aug. 10, 1946 4 Sheets-Sheet 3

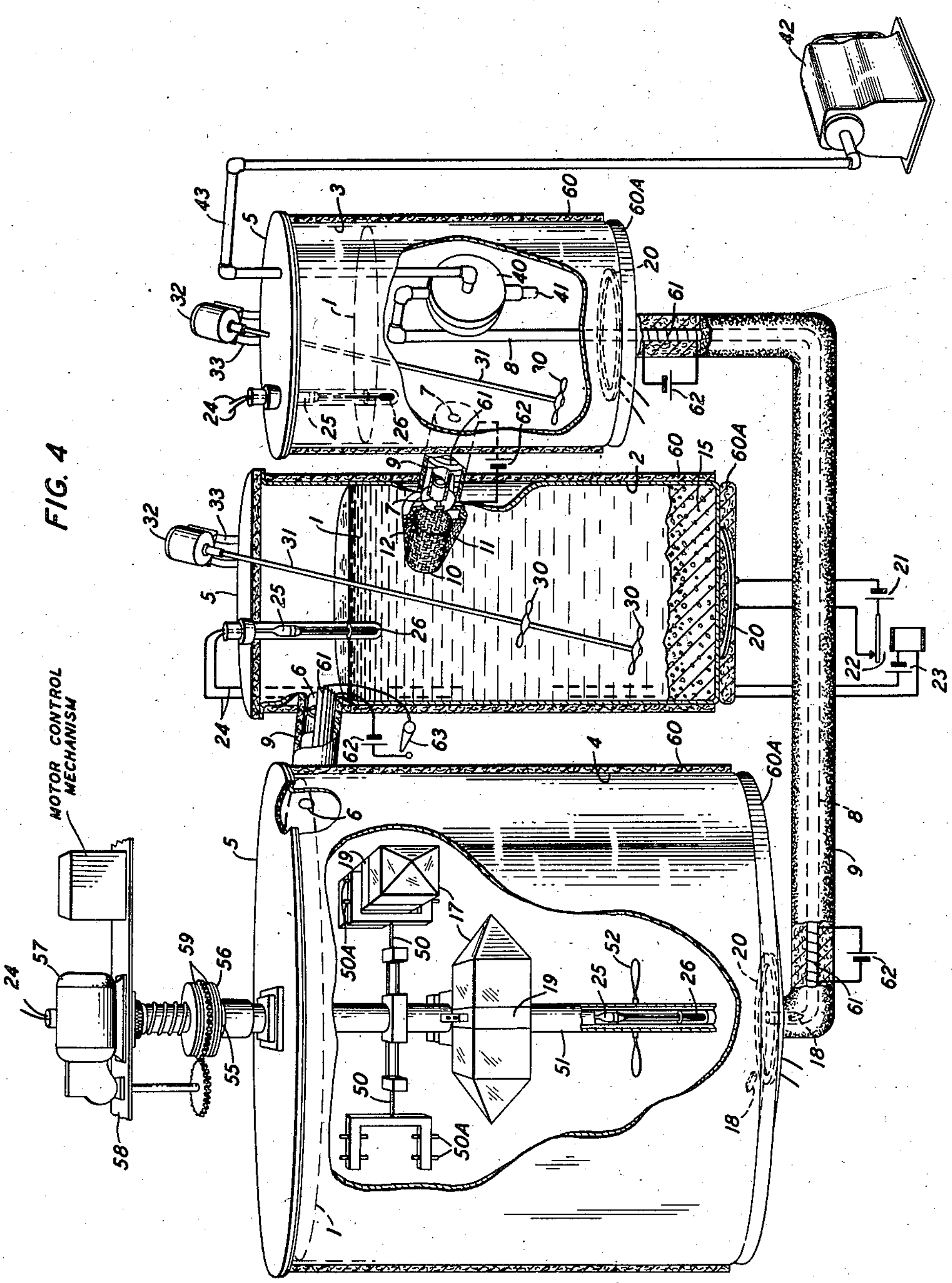

FIG. 4

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FIG. 5

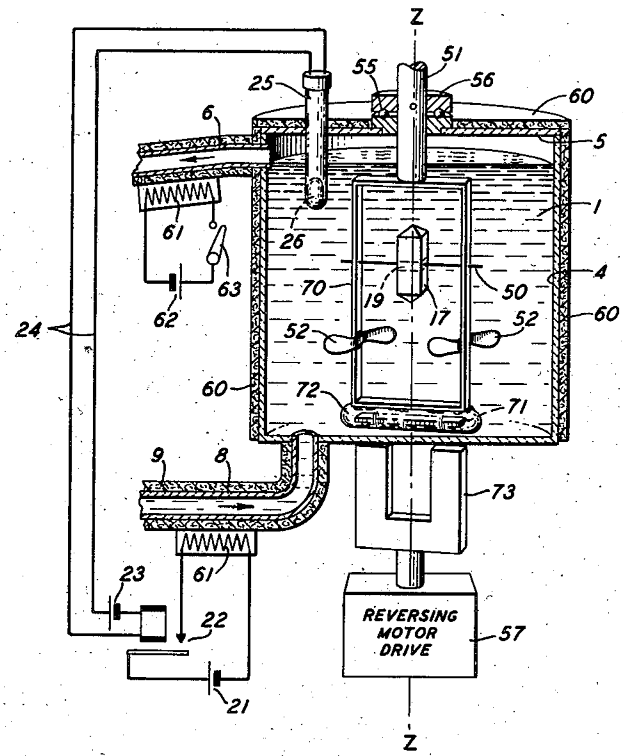
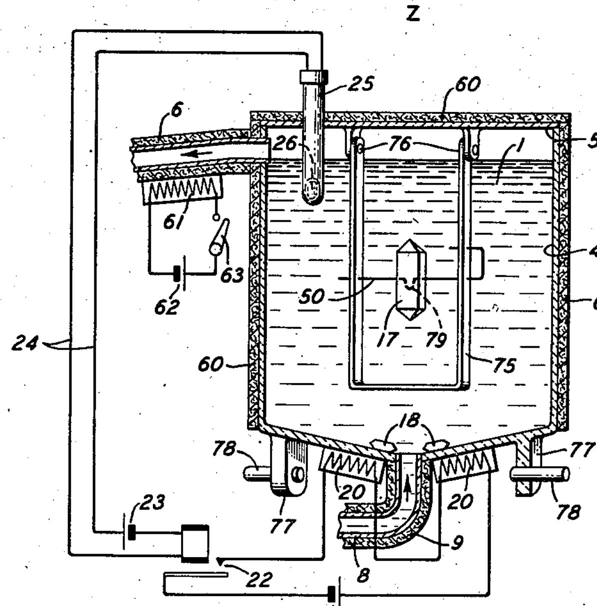


FIG. 6



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CRYSTAL GROWING APPARATUS

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Application August 10, 1946, Serial No. 689,672

6 Claims. (Cl. 23—273)

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This invention relates to apparatus for growing crystals from a nutrient solution and particularly to crystallizer systems of the circulating solution type which may be utilized for growing large single crystals in a supersaturated nutrient solution at a constant temperature. Such artificial crystals may comprise such crystalline substances as ammonium dihydrogen phosphate, ethylenediamine tartrate, dipotassium tartrate, Rochelle salt or other crystal substances, from which elements may be cut for use as circuit elements in such systems as electric wave filter systems, oscillation generator systems and other electrical systems.

One of the objects of this invention is to grow large single crystals.

Another object of this invention is to grow crystals continuously without interference from spurious or spontaneous seeding in the nutrient solution.

Another object of this invention is to grow crystals more rapidly.

Another object of this invention is to grow crystals at constant temperature.

Crystallizers may be utilized for producing synthetic crystals of piezoelectric quality. This involves the preparation of a suitable nutrient solution and the seed crystals, and the manner of growing the full size crystals therefrom. The general principle is that of circulating past the growing surfaces of the crystal a supersaturated nutrient solution and maintaining it in supersaturated condition. The growing crystal continuously removes salt from the nutrient solution and this loss in salt is most frequently compensated for by adding additional solute in amount sufficient to make up for the salt taken in growing the crystal and to maintain the nutrient solution in supersaturated condition. In general and within limits, the higher the supersaturation of the nutrient solution, the faster will be the rate of growth of the crystal. However, at the relatively higher supersaturations, spurious crystals tend to form spontaneously in the solution. The spontaneously formed crystals reduce the amount of salt available for the growth of the desired crystal, and unless removed, eventually will obstruct its desired growth. By utilizing means for destroying such spurious crystals and for maintaining good solution circulating conditions with respect to the growing surfaces of the crystal to be grown, it has been found possible to grow large clear crystals at a relatively rapid rate in a supersaturated nutrient solution.

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A reciprocating rotary gyrator type of crystallizer may be conveniently utilized for growing the crystals in the supersaturated nutrient solution which may be contained in a suitable crystallizer tank. The gyrator may be mounted coaxially with respect to the axis of the crystallizer tank and may consist of a rotatable shaft carrying one or more crystals mounted thereon by means of stainless steel wires or pins, for example, inserted in the crystal and carried by the rotatable shaft. Heat may be supplied to the nutrient solution from a heating resistance coil mounted immediately beneath the outside bottom surface of the crystallizer tank, the heat being applied mainly at or near the center of the cone or dish-shaped bottom only of the crystallizer tank. The rotation of the gyrator forms a vortex in the solution along the axis of the tank and the spurious or spontaneously formed seeds are concentrated in the center of this vortex and drop to the center of the tank bottom or slide down the sloping bottom to the lower central point or inlet where the heat supplied at this location may cause such spurious seeds there located to dissolve, while the crystal mounted on the gyrator shaft continues to grow in the upper supersaturated region of the nutrient solution.

Certain crystals may be grown more satisfactorily in a solution held at some specific constant temperature, rather than over a range of gradually lowered values of temperature. To adopt the crystallizer to a constant temperature growing schedule, the solution may be made to flow in a cycle from and back to the crystallizer through the following units: A saturator held at a slightly higher solution temperature than that of the crystallizer tank solution, a filter to remove all but the microcrystalline material from the solution received from the saturator, a heater tank to raise the solution slightly above the saturation temperature and dissolve all microcrystalline material, and a pump to deliver the clear refortified solution to the bottom of the crystallizer tank. The spent solution may flow by gravity from the top region of the crystallizer tank back into the saturator. The several connecting links and tanks may be suitably heat-insulated to prevent spurious seeding. The foregoing description is in terms of a solute with a positive temperature coefficient of solubility. For solutes with a negative temperature coefficient of solubility appropriate adjustments can be made in the relative temperatures of the various parts of the crystallizer apparatus and the surrounding ambient conditions.

When the nutrient solution in the crystallizer vessel is adapted to the constant temperature growing schedule at a suitable temperature, the solution may be kept in supersaturated condition at that temperature by introducing refortified solution into the bottom of the crystallizer tank and permitting the spent or used solution therein to overflow through an outlet near the top of the crystallizer tank into the saturator tank where the solution is resaturated with additional salt before being returned through the unsaturator vessel to the crystallizer tank. Connecting conduit pipes and apparatus between the three vessels mentioned may be heat insulated and also may be additionally heated by suitable means in order to prevent undesired crystallization in the circulating fluid.

The apparatus may continuously supply a solution of the nutrient material for growing crystals at constant temperature, and it is particularly suitable for use with salts having unusual temperature-solubility relations and those highly susceptible to internal crystal strains occurring with temperature changes. Also much larger crystals or more crystals may be grown in a single operation because the amount of available salt for the crystal growth is relatively unlimited. The apparatus may employ three main units, namely, a crystallizer utilizing the principle of moving the growing crystal through the solution, a saturator to replenish used salt, and a heater to raise the freshly saturated or refortified salt solution to a temperature above the saturation point temperature so as to avoid the carrying of extraneous seed crystals into the crystallizer as the solution enters it after having been in the saturator with its multiplicity of small crystals, many of microscopic dimensions. The solution flows in a cycle from the crystallizer to the saturator, to the unsaturator and back to the crystallizer, additional salt being dissolved in the saturator to compensate for the crystalline solute removed in the crystallizer.

The crystallizer apparatus is useful in growing large crystals, is relatively inexpensive to construct, requires relatively little power to operate, is simple in control and operation, is reliable in results when dependable control and actuating equipment are used in its construction, has the ability to destroy spurious and spontaneous seeds in the nutrient solution, and the results of the process may be easily observed at all stages.

For a clearer understanding of the nature of this invention and the additional advantages, features and objects thereof, reference is made to the following description taken in connection with the accompanying drawing, in which like reference characters represent like or similar parts, and in which:

Figs. 1 to 3 are simplified views in section illustrating a crystallizer system comprising a crystallizer, a saturator and an unsaturator, Fig. 1 being a top or plan view, Fig. 2 being an elevational view of the crystallizer and saturator taken approximately on the line 2—2 of Fig. 1, and Fig. 3 being an elevational view of the crystallizer and unsaturator taken approximately on the line 3—3 of Fig. 1.

Fig. 4 is a more detailed view of the system illustrated in Figs. 1 to 3;

Figs. 5 and 6 are elevational views illustrating modifications in crystallizers.

Referring to the drawing, Figs. 1 to 3 and 4 are simplified views illustrating a circulating type crystallizer system comprising three interconnected vessels each containing the circulating nutrient solution 1 and consisting of a saturator tank 2, an unsaturator tank 3 and a crystallizer tank 4. The tanks 2, 3 and 4 may be tanks composed of stainless steel or other suitable material and provided with glass or other suitable covers 5. Suitable conduit piping such as stainless steel pipes 6, 7 and 8 covered with siutable heat insulating material 9 may be utilized to interconnect the three tanks 2, 3, and 4. The nutrient solution 1 flows in a cycle from the saturator tank 2 to the unsaturated tank 3, to the crystallizer tank 4 and back to the saturator tank 2, as indicated by the arrows shown in the drawing.

The saturator may comprise a suitable tank 2 having an inlet opening connected with the conduit 6 disposed adjacent the top level of the nutrient solution 1 contained in the saturator tank 2, as illustrated in Figs. 1, 2 and 4; and having an outlet opening connected with the conduit 7 disposed below the top level of the nutrient solution 1 contained in the saturator tank 2 as illustrated in Figs. 1, 2, and 4. The overflow solution 1 may flow under the influence of gravity from the outlet opening in the crystallizer tank 4 through the inlet opening in the saturator tank 2 by way of the inclined conduit pipe 6 which interconnects the two vessels 2 and 4, and the solution 1 in the saturator tank 2 may flow into the unsaturator tank 3 by way of the conduit pipe 7 which interconnects the two vessels 2 and 3. A filter 10 which may comprise an inner fine screen 11 surrounded by a covering cloth 12 may be placed in the saturator tank 2 over the inlet to the pipe 7 in order to filter the nutrient solution 1 entering the unsaturator tank 3 from the saturator tank 2. A quantity of excess solid salt 15 may be maintained in the bottom region of the saturator tank 2 in contact with the nutrient solution 1 therein in order that the nutrient solution 1 may be provided with additional solute for making up for the loss of salt as taken from the nutrient solution 1 in the process of growing the crystals 17 in the crystallizer tank 4. In order that the nutrient solution 1 contained in the saturator tank 2 may take into solution a sufficient additional quantity of the excess solid salt 15, the solution 1 in the saturator tank 2 may be continuously maintained at a suitable elevated temperature by means of a suitable heater 20 which may be disposed adjacent the outside bottom surface of the saturator tank 2 in the central region thereof, as illustrated in Figs. 1, 2 and 4.

The heater 20 may comprise a resistance coil type electric heater of suitable wattage heated by a suitable source of current supply 21 and controlled by a suitable relay 22, power supply source 23, conductive connections 24 and thermostat 25 having its heat sensitive element 26 disposed in the nutrient solution 1 in order to maintain the temperature thereof at a suitable value which may be a constant or nearly constant value of temperature. As an illustrative example, the thermostat 25 and heater 20 may be set to maintain the temperature of the solution 1 in the saturator tank 2 at a temperature of the order of about 38° C. for a solution of ammonium dihydrogen phosphate, and of the order of about 28° C. for a solution ethylene diamine tartrate. It will be understood that the most suitable differential in temperature for the solution 1 between the saturator tank 2 and the crystallizer tank 4 will be determined according to the nature of the solution 1, and of the crystal 17 to be grown, and the degree of supersaturation of the solution 1 in tank 4 which can be tolerated without causing disorderly crystal growth in crystal 17 or the occurrence of spontaneous seeding in the crystallizer tank 4.

One or more propeller blades 30 may be disposed in the nutrient solution 1 in saturator tank 2 for stirring the solution 1 continuously in contact with the excess salt 15. The propellers 30 may be secured to a revolving shaft 31 and conveniently driven by a suitable electric motor 32 which may be clamped or otherwise attached to the saturator tank 2 as by a bracket 33. The saturator tank 2 may be provided with a suitable cover or lid 5 which may conveniently be composed of glass or other suitable transparent material that will permit inspection of the contents of the tank 2. The conduit pipe 7 surrounded by suitable heat insulating material 9 connects the filtered solution outlet of the saturator tank 2 with the unsaturator tank 3.

As illustrated in Figs. 1, 3 and 4, the unsaturator or superheat tank 3 may comprise a suitable tank 3 having a solution inlet opening connected with the horizontal conduit pipe 7 disposed at the side of the unsaturator tank 3 that is adjacent the saturator tank 2. The filtered and resaturated solution 1 from the saturator tank 2 flows through the interconnecting conduit pipe 7 into the unsaturator tank 3, the direction of flow of the solution 1 being indicated by the arrow.

A suitable diaphragm type pump 40 submerged in the solution 1 in the unsaturator tank 3, as illustrated in Figs. 1, 3 and 4, may receive the nutrient solution 1 through an open-ended inlet pipe 41 and pump the nutrient solution 1 therein through the solution outlet conduit pipe 8 extending through the bottom of the unsaturator tank 3 into the crystallizer tank 4. The diaphragm pump 40 may be operated by suitable hydraulic drive means 42 applied thereto through the pipe 43. One or more motor-driven propeller blades 30 may be disposed in the nutrient solution 1 in the unsaturator tank 3 for stirring the solution 1 therein continuously.

In order that the solution 1 contained in the unsaturator tank 3 may be maintained in an unsaturated condition with respect to the solute therein and so that all seed crystals which may have passed with the saturated solution from the saturator 2 through the filter 10 will be destroyed, the temperature of the solution 1 may be maintained at a suitable value by means of a suitable heater 20 disposed adjacent the outer bottom surface of the unsaturator tank 3 in the central region thereof. The heater 20 may comprise a wire type resistor of suitable wattage heated by a source of current 21 and controlled by a thermostat regulator 25 having its heat sensitive element 26 disposed in the nutrient solution 1.

The crystallizer may comprise a tank 4 as illustrated in Figs. 1, 2, 3 and 4, the tank 4 having a solution inlet opening in the central portion of the bottom thereof, the inlet opening being connected with the heat-insulated conduit pipe 8 leading from the output of the pump 40 which is disposed in the unsaturator tank 3 and which pumps the nutrient solution 1 at a suitable rate of flow into the crystallizer tank 4. The outlet opening of the crystallizer tank 4 is disposed adjacent the upper level of the solution 1 therein where the overflow solution 1 may flow under the influence of gravity through the inclined heat-insulated conduit pipe 6 back into the saturator tank 2.

The crystallizer tank 4 may be provided with a cone-shaped or dish-shaped bottom having such a suitable inclination or slope that any spurious seeds 18 formed in the solution 1 in the crystallizer tank 4 may fall and gather in the region of the center of the bottom of the crystallizer tank 4, or in the opening of inlet pipe 8, where they may be redissolved into the unsaturated solution 1 entering from the unsaturator 3 through pipe 8, or by means of the unsaturated conduction layer of solution adjacent to the heaters 20. The heaters 20 may be disposed adjacent the central portion of the bottom of the crystallizer tank 4 and may provide sufficient heat to raise the temperature of the conduction layer of the solution 1 adjacent to the heaters 20 to an unsaturated condition, while leaving the upper regions of the solution 1 in a supersaturated condition for growing therein the planted crystals 17 disposed in contact therewith. The heater 20 may comprise a resistance wire coil or coils heated by a source of current 21 and controlled by a thermostat regulator 25 having its heat sensitive element 26 disposed in the supersaturated nutrient solution 1 in order to maintain the temperature thereof continuously at a suitable constant temperature.

The thermostat temperature of the solution 1 in the crystallizer tank 4 may correspond to a fixed value that renders the solution 1 supersaturated with respect to the solute therein. For growing ammonium dihydrogen phosphate crystals 17 such a temperature may be of the order of about 38.0° C. for example, with correspondingly higher solution temperatures in the saturator tank 2 and the unsaturator tank 3 such as, for example, solution temperatures of about 40° C. and 43° C. in the saturator and unsaturator tanks 2 and 3, respectively.

The crystal bars 17 are grown in the crystallizer tank 4 by moving the crystal through the supersaturated solution 1 thereby taking salt from the supersaturated solution 1 and depositing it in crystalline form on the outer surfaces of the crystal bars 17. In order to move the crystal bars 17 in the supersaturated solution 1, they may be rotated about a vertical axis first in one direction of rotation and then in the opposite direction of rotation. Such rotation tends to produce a vertical vortex in the solution 1 and the vortex tends to gather any spurious seed crystals 18 at the central part of the bottom of the crystallizer tank 4 where such undesired seeds 18 may be redissolved into the solution by the heater 20 or by the hot solution entering the inlet from tube 8. The crystals to be grown into larger size bars 17 may be mounted on one or more wires or supports 50 carried by a reciprocating rotary shaft 51. A propeller type stirrer 52 may be mounted on the lower end of the rotary shaft 51.

More particularly, the crystallizer 4 illustrated in Figs. 1, 2, 3 and 4 is a reciprocating gyrator type of crystallizer which may be used for growing a planted seed crystal 19 into a larger sized crystal 17 from a supersaturated nutrient solution 1 contained in the glass or metal tank 4 or other suitable container. The container 4 as illustrated in Figs. 1, 2, 3 and 4 may comprise a tank 4 having cylindrical side walls and a cone or dish-shaped bottom, and provided with a suitable cover 5 which may be a glass cover 5. The crystals 17 are carried in contact with the supersaturated nutrient solution 1 by means of radial type supports 50 secured to the centrally located and vertically disposed gyrator shaft 51, the upper portion of which may extend through a central opening in the container cover 5 and be there carried by a suitable bearing such as a ball bearing 55 and flange 56. The rotary gyrator shaft 51 may be driven by any suitable actuating means such as, for example, a reversing electric motor 57 carried by a supporting frame 58 and connected to the shaft 51 through a clutch 59, the motor 57 being geared or otherwise coupled to the gyrator shaft 51 so that the shaft 51 may rotate at a suitable speed such as, for example, four or more revolutions per minute, the direction of rotation of the shaft 51 being reversed every one, two or more of its revolutions, as desired. The power capacity required of the motor 57 is sufficient to overcome the viscous drag effect of the crystals 17 moving through the nutrient solution 1. A ball bearing type of mounting 55 may be utilized when it is desired to reduce friction at points 56 where the gyrator 51 is hung.

The reciprocating rotary gyrator shaft 51 may be mounted coaxially with respect to the axis of the cylindrical tank 4 and may consist of a pipe or rod of methylmethacrylate resin, stainless steel or other suitable material of the order of one inch, more or less, in diameter. To the shaft there may be attached a number of radial or other type supports 50 upon which the growing crystals 17 may be mounted by the stainless steel wires or pins 56 or 50A extending into holes provided in the body of each of the crystals 17. The supports 50 may take various forms as illustrated in the drawing.

The rotary motion of the gyrator 51 creates a vortex in the solution 1 which bunches extraneous crystal seeds 18 at the bottom of the crystallizer tank 4 where they may be redissolved into solution in the thin layer of unsaturated solution locally produced along the bottom part only of the solution by a locally increased temperature produced by the heater 20 or 61. The unsaturated layer of the solution 1 is confined mainly to a location immediately above the heaters 20 where the spurious seed crystals 18 are aggregated. Only a limited amount of heat is applied from the heaters 20 to a limited area on the central bottom of the crystallizer tank 4 where spurious seed crystals 18 spontaneously formed in the solution 1 may be concentrated and destroyed, while at the same time the planted crystals 17 mounted above the bottom region of the tank 4 will grow in contact with the supersaturated nutrient solution 1. This useful condition comes about by raising the temperature above the saturation temperature only at the extreme bottom portion of the crystallizer tank 4 and by introducing suitably heated solution through the inlet pipe 8 at the lowest point of the cone-shaped bottom of the tank 4.

The crystallizer container 4 may be composed of a stainless steel or glass capable of withstanding heat applied to the bottom thereof and producing no unfavorable chemical reaction with the nutrient solution 1 contained therein. The diameter and height of the crystallizer tank 4 may be of any suitable values such as of the order of three feet or more for example. The cylindrical sides and the flat cover 5 of the tanks 2, 3 or 4 may be protected with a layer of felt or other suitable heat-insulating material 60. Depending upon the size of the crystallizer tank 4, a large number of planted crystals 17 may be grown simultaneously in a single crystallizer tank 4. Moreover, a number of such crystallizer tanks 4 may be arranged for operation in bank. While in the drawing only one crystallizer tank 4 has been illustrated, it will be understood that an additional crystallizer tank 4 or tanks 4 may be served in the same manner from the same saturator and unsaturator tanks 2 and 3, thus obtaining a system in which two or more crystallizing tanks 4 are supplied from a single set of saturator and unsaturator tanks 2 and 3.

The temperature of the nutrient solution 1 may be automatically regulated by a suitable thermoregulator 25 having its heat-sensitive element 26 extending into the nutrient solution 1. The automatic heat control and temperature regulating equipment 20 to 26 may comprise any suitable type of thermoregulator 25, relay 22 and heater 20. The thermoregulator 25 may be for example of the standard mercury-in-glass type, the temperature sensitive end 26 of which is inserted in thermal contact with the nutrient solution 1. The thermoregulator 25 may be connected by conductive wires 24 with a suitable power supply source 23 for operating a relay 22 having a contact which is connected in circuit with a power supply source 21 suitable for heating the heater resistors 20. The heaters 20 may be any suitable heaters, such as resistance wire coils 20 having a heat energy capacity which is relatively small with respect to that of the nutrient solution 1. One or more heaters 20 may be utilized in any given location and as may be required to maintain the desired temperature for the adjacent nutrient solution 1.

While a particular form of temperature control equipment 20 to 25 has been illustrated, it will be understood that any suitable temperature control apparatus may be used that is dependable in operation over a continuous crystal growing period which may be of the order of some weeks or months. A continuous program of uniform temperature control is ideal and requires good temperature control equipment. If desired, the entire equipment may be operated in a temperature controlled room.

It will be noted that in the crystallizer system illustrated in Figs. 1 to 4 the nutrient solution 1 which may be a solution of ammonium dihydrogen phosphate, or other salt solution, may be saturated in the saturator tank 2 at a fixed temperature, by stirring excess salt 15 in contact with the agitated solution 1 in the saturator tank 2. The solution filters, by gravity feed, for example, through the cloth covered filter 10 disposed in the saturator tank 2, into the unsaturator tank 3 where it is heated above the saturation temperature in order to prevent spurious seeding and to dissolve any small seed crystals which may have passed through the filter 10. The solution 1 is then pumped by the pump 40 at an unsaturated temperature from the unsaturator tank 3 into the crystallizer tank 4 at a rate of flow which is sufficient to provide additional salt as may be needed during the crystallization of the salt on the crystals 17 in the crystallizer tank 4. The rate of flow may correspond to a value sufficient for the purpose mentioned such as for example 10 to 50 liters per hour, and will be dependent upon the temperature differential between the solution 1 in the saturator tank 2 and the crystallizer tank 4. Each of the three tanks 2, 3 and 4 has an independent temperature controlling thermostat 25 and heater 20 for independently controlling the temperature of the solution 1 therein. As an illustrative example, the solution 1 in the saturator tank 2 may be controlled by its thermostat 25 at about 40° C., the solution in the unsaturator tank 3 may be controlled by its thermostat 25 at any convenient temperature above the 40° C. mentioned, such as a temperature from 42° to 46° C., and the solution 1 in the crystallizer tank 4 may be controlled by the thermostat 25 at a suitable crystal growing temperature below the 40° C. value mentioned, such as, for example, a value of 38.0° or 39.0° C., the latter being a temperature value that corresponds to a supersaturated condition for the solution 1 in the crystallizer tank 4.

In addition to the heaters 20, heaters 61 in the form of resistance wire coils 61 may be applied around and along parts or along the whole of the piping 6, 7 and 8 connected between the saturator tank 2, the unsaturator tank 3 and crystallizing tank 4, in order to maintain the temperature of the solution 1 in the pipes 6, 7 and 8 above the saturation temperature of the solution 1 thereby to prevent crystallization of salt therein. The heater coils 61 may be energized by any suitable power supply 62 and control means 63.

It will be noted that the apparatus illustrated in Figs. 1 to 4 may be used for growing large single crystals 17 from the nutrient solution 1 and may consist broadly of three interconnected vessels, namely, the saturator 2 where additional solute is added to the solution 1, the unsaturator 3 where the solution 1 is brought to such a temperature condition that the solution 1 becomes less than saturated with respect to the solute, and the crystallizer 4 wherein the solution 1 is adjusted in temperature so that it becomes supersaturated and wherein seed crystals 19 are planted so that they may grow into large size crystals 17 by taking solute from the nutrient supersaturated solution 1. Means are provided to cause the nutrient solution 1 to flow in the cycle from the saturator 2 to the unsaturator 3 to the crystallizer 4 and back to the saturator 2. Means may be provided to maintain the solution in each of the three vessels 2, 3 and 4 at a predetermined independent temperature. The saturator 3 may be provided with a stirring device 30 for mixing the excess salt 15 with the solution 1 therein and a filter 10 may be fitted over the outlet of the saturator 2 leading to the unsaturator 3. The unsaturator 3 may be provided with a pump 40 the fluid handling part of which may be entirely submerged in the unsaturator tank 3. The crystallizer 4 may have a coned or dished bottom with the unsaturated solution 1 from the unsaturator 3 entering the lowest point at the apex of the cone or the center of the dish. The crystallizer 4 may be equipped with a gyrator the shaft 51 of which is mounted vertically with the axis of the crystallizer tank 4, with means 50 or other suitable supports attached to the gyrator shaft 51 on which seed crystals 19 can be mounted for growing into individual large crystals 17. Suitable means such as an electric motor 57 may actuate the gyrator shaft 51 either in one direction of rotation, or alternatively in opposite directions of rotation at a predetermined time interval. The nutrient solution 1 may be caused to flow at such a rate from the unsaturator 3 to the crystallizer 4 that the supersaturated condition of the solution 1 adjacent to the growing crystals 17 can be maintained.

In connection with temperature control considerations, it has been found that when the entire apparatus is operated in a temperature controlled room, there are several alternative ways of maintaining steady temperature in the solution 1 in the crystallizer 4 other than by means of the mercury thermoregulator 25 and associated external heater 20. To understand this it may be appropriate to note that it is of course necessary to supply sufficient solution from the unsaturator 3 by means of the pump 40 so that the crystals 17 will grow as rapidly as possible. Once this rate of flow of solution has been established as a minimum permissible, and with a suitable constant ambient temperature, it is then possible to maintain a steady crystallizer temperature by three different, but somewhat interrelated methods. One way of accomplishing this is to set the ambient temperature sufficiently low so that with a minimum solution flow to satisfy the crystallizing requirements, the temperature of the solution 1 in the crystallizer 4 will be too low. Then by adjusting the pump rate somewhat higher, it is quite easy to reach a steady state condition so that the extra heat required to overcome the ambient cooling will be provided by the hot entering solution from the unsaturator 3. Another way to control the crystallizer 4 temperature is to have an electric fan blowing on the bare metal wall of the crystallizer 4, and then for a given rate of flow of solution 1 greater than required to balance the heat loss to ambient, to adjust the fan speed to balance heat supply and heat loss. A third way is to supply a small, fixed and continuous heat flow into the tank 4 from a small external heater 20 mounted on the bottom of the tank 4, this amount of heat being just sufficient to offset the heat loss to the ambient, when the pumping rate is insufficient to supply all the heat that is needed. These three alternatives provide a flexibility of control, and a somewhat more steady temperature under certain conditions, than that provided by the mercury thermoregulator 25 and associated external heater 20.

Fig. 5 is a sectional view illustrating another form of crystallizer 4 comprising a magnetic driving arrangement that may be utilized for growing a crystal in a rotary gyrator type of mount. In this arrangement, the growing crystal 17 may be turned or rotated about a longitudinal vertical central axis Z—Z, thereof, the crystal 17 being carried by one or more horizontal wires 50 mounted in the two vertical side plates of a rectangular-shaped stainless steel rotatable frame 70. The frame 70 may be carried by the shaft 51 suspended from a ball bearing 55 associated with the container cover 5. The frame 70 may be rotated by means of the shaft 51 as illustrated in Figs. 1 to 4, or by means of a magnetic clutch arrangement as illustrated in Fig. 5. The magnetic coupling arrangement as shown in Fig. 5 may include a driven magnet bar 71 disposed in an enclosing protective glass tube 72. The glass tube 72 may be secured by cement or other suitable adhesive means to the bottom plate of the rectangular frame gyrator 70. A coaligned motor-driven "Alnico" U-shaped magnet 73 disposed very closely adjacent the outside glass bottom surface of the glass tank 4 may cooperate with the driven magnet bar 71 disposed inside the tank 4 in order to rotate the gyrator 70 and crystal 17 simultaneously. The clearance between the driven magnet bar 71 and the upper faces of the U-shaped driver magnet 73 may be made very small. The rotating gyrator frame 70 functions as a support for the crystal 17 and also as a means for stirring the nutrient supersaturated solution 1 contained in the crystallizer tank 4. If desired, the frame 79 may be equipped with one or more propeller blades 52 disposed on the two vertical sides and the horizontal bottom plate thereof for obtaining an increased and uniform circulation of the nutrient solution 1 in the crystallizer tank 4. As illustrated in Fig. 5, the crystal 17 may be moved in the supersaturated nutrient solution 1 about its own axis with frequent reversals in its direction of rotation by means of the magnetic coupling, operating through the glass bottom of the container 4, to the reversibly driven magnet 73. An economy of power results from moving the crystal 17, rather than moving the combined container 4, liquid 1 and crystal 17. The arrangement involves a uniform circulation of the solution 1 and a movement of the crystal 17 through the body of the nutrient solution 1 by turning in the solution, rather than mainly a movement of the solution 1 around the crystal 17.

Fig. 6 is a view of another form of crystallizer tank arrangement which may be utilized for growing crystals 17 from a supersaturated nutrient solution 1 by movement of the crystal 17 through the body of the nutrient solution 1. As illustrated in Fig. 6, the crystal 17 is moved through the nutrient solution 1 in a swinging type of motion, the crystal 17 being mounted on a trapeze-like suspension 75 affixed by suitable pivots 76 to the underside of the container cover 5, the suspended trapeze 75 being adapted to swing back and forth within the container 4, thereby swinging the suspended crystal 17 through the supersaturated nutrient solution 1. Suitable reciprocating means may be utilized for actuating the suspension 75, such as means rocking the tank 4 on a tilting table 77 actuated about coaligned shafts 78 by any suitable reciprocating driver means, such as for example that illustrated in Kjellgren Patent Re. 19,697 dated September 10, 1935, Fig. 1 at 17 to 24. By slightly tilting the table 77 to and fro about the common horizontal axis of the shafts 78, the freely swinging trapeze 75 causes the growing crystal 17 to move or swing back and forth through the nutrient solution 1 thereby providing conditions for uniform growth of the crystal 17 with little motion imparted to the solution 1 beyond some desirable circulation. The crystal 17 may be mounted on one or more stainless steel wires 50 which may be of any suitable square or other bent form, such as illustrated at 78 in Fig. 5, in order to prevent twisting of the mounted crystal 17, relative to the supporting wire 50 itself.

While the invention has been described particularly in connection with the growing of crystals 17 from a nutrient solution comprising ammonium dihydrogen phosphate ($NH_4H_2PO_4$), it may also be utilized for growing other types of artificial or synthetic crystals 17 from a suitable corresponding nutrient solution 1 such as, for example, crystals 17 comprising ethylene diamine tartrate or comprising di-potassium tartrate, for example.

Where the crystals 17 comprise di-potassium tartrate, they are of course grown from a suitable supersaturated solution of that salt. It has been noted that nutrient solutions 1 of potassium tartrate when strongly colored by means of decomposed organic tartrate, either through overheating of such solutions or through caramelized burning of the solid potassium tartrate salt in

such solutions, have a highly stabilizing effect on the uniformity and clarity of growth of the crystals 17 grown from supersaturated solutions 1 of such potassium tartrate. Such a solution 1 may be prepared by burning or caramalizing the solid salt, dissolving it into the solution 1, filtering and utilizing it without attempting to remove the soluble colored material which is probably decomposed tartaric acid. Crystals 17 grown from this highly colored solution heal readily and give clear crystalline material.

Where the nutrient solution 1 comprises ammonium dihydrogen phosphate, various substances such as ammonium sulphate, may be added in suitable amount in order to produce various effects on the growth habit of the crystal 17, as described in an application, Serial No. 598,691, filed June 11, 1945, by A. N. Holden.

While in Figs. 1 to 6 various arrangements for the crystallizer 4 have been illustrated, examples of additional forms are given in an application for Crystal growing apparatus, Serial No. 598,691, filed June 11, 1945, by A. N. Holden, and in an application, Serial No. 598,693, filed June 11, 1945, by C. J. Christensen, now United States Patent No. 2,442,755, dated June 8, 1948.

Although this invention has been described and illustrated in relation to specific arrangements, it is to be understood that it is capable of application in other organizations and is therefore not to be limited to the particular embodiments disclosed.

What is claimed is:

1. A crystallizer system comprising a plurality of more than two separate interconnected vessels each having inlet and outlet openings and including a saturator vessel, an unsaturator or superheat vessel, and a crystallizer vessel, and conduits cyclically connecting said vessels in the order from said saturator vessel to said unsaturator vessel and from said unsaturator vessel to said crystallizer vessel and from said crystallizer vessel back to said saturator vessel, said conduits comprising a conduit connecting said outlet opening in said saturator vessel with said inlet opening in said unsaturator vessel, a conduit connecting said outlet opening in said unsaturator vessel to said inlet opening in said crystallizer vessel, said last-mentioned inlet opening being an opening extending through the lowermost part of the bottom of said crystallizer vessel, and a conduit connecting said outlet opening in said crystallizer vessel with said inlet opening in said saturator vessel, a temperature sensitive device disposed in said saturator vessel, a heater electrically connected with said temperature sensitive device and disposed adjacent said saturator vessel, a temperature sensitive device disposed in said unsaturator vessel, a heater electrically connected with said last-mentioned temperature sensitive device and disposed adjacent said unsaturator vessel, said crystallizer vessel having disposed therein work carrying means, a temperature sensitive device disposed in said crystallizer vessel, and a heater electrically connected with said last-mentioned temperature sensitive device and disposed adjacent said bottom inlet opening in said crystallizer vessel, said temperature sensitive devices being independently responsive to predetermined temperature values.

2. A crystallizer system comprising a plurality of more than two separately enclosed interconnected vessels each having inlet and outlet openings and including a saturator vessel, an unsaturator or superheat vessel, and a crystallizer ves-

sel, and conduits cyclically connecting said vessels in the order from said saturator vessel to said unsaturator vessel and from said unsaturator vessel to said crystallizer vessel and from said crystallizer vessel back to said saturator vessel, said conduits comprising a conduit connecting the outlet opening in said saturator vessel with the inlet opening in said unsaturator vessel, a conduit connecting the outlet opening in said unsaturator vessel with the inlet opening in said crystallizer vessel, said last-mentioned inlet opening being an opening extending through the bottom of said crystallizer vessel and said bottom being a dish or cone shaped bottom having downwardly sloping surfaces and having said last-mentioned inlet opening positioned substantially at the apex or lowest point thereof, and a conduit connecting the outlet opening in said crystallizer vessel with the inlet opening in said saturator vessel, a pump connected with one of said conduits, heating means disposed immediately adjacent at least a part of said conduits, heat insulating means covering at least a part of said conduits and vessels, a temperature sensitive device disposed in said saturator vessel, a heater electrically connected with said temperature sensitive device and disposed adjacent said saturator vessel, a temperature sensitive device disposed in said unsaturator vessel, a heater electrically connected with said last-mentioned temperature sensitive device and disposed adjacent said unsaturator vessel, said crystallizer vessel having disposed therein work carrying means, a temperature sensitive device disposed in said crystallizer vessel, a heater electrically connected with said last-mentioned temperature sensitive device and disposed adjacent said bottom inlet opening in said crystallizer vessel, said temperature sensitive devices being independently responsive to predetermined temperature values.

3. A crystallizer system comprising a plurality of more than two separately enclosed interconnected vessels each having inlet and outlet openings and including a saturator vessel, an unsaturator or superheat vessel, and a crystallizer vessel, and conduits cyclically connecting said vessels in the order from said saturator vessel to said unsaturator vessel and from said unsaturator vessel to said crystallizer vessel and from said crystallizer vessel back to said saturator vessel, said conduits comprising a conduit connecting the outlet opening of said saturator vessel with the inlet opening in said unsaturator vessel, a conduit connecting the outlet opening in said unsaturator vessel with the inlet opening in said crystallizer vessel, said last-mentioned inlet opening being an opening extending through the bottom of said crystallizer vessel and said bottom being a dish or cone shaped bottom having downwardly sloping surfaces and having said last-mentioned inlet opening positioned substantially centrally at the apex or lowest point thereof, and a conduit connecting the outlet opening in a side of said crystallizer vessel with the inlet opening in said saturator vessel, a pump connected with one of said conduits, heating means comprising electrically heated resistors disposed immediately adjacent at least a part of said conduits, heat insulating means directly covering at least a part of said conduits and vessels, and a stirring device disposed in each of said vessels, said saturator vessel having a filtering screen disposed over said outlet opening thereof, a temperature sensitive device disposed in said saturator vessel, a heater electrically connected with said temperature sensitive device comprising an electrically heated resistor disposed adjacent said saturator vessel, a temperature sensitive device disposed in said unsaturator vessel, a heater electrically connected with said last-mentioned temperature sensitive device and comprising an electrically heated resistor disposed adjacent said unsaturator vessel, said crystallizer vessel having disposed therein a reciprocating gyrator type work carrying means mounted substantially coaxially with respect to the vertical axis of sad crystallizer vessel, a temperature sensitive device disposed in said crystallizer vessel, a heater electrically connected wtih said last-mentioned temperature sensitive device and comprising an electrically heated resistor disposed adjacent said bottom central inlet opening in said crystallizer vessel, said temperature sensitive devices being independently responsive to predetermined and different temperature values.

4. The method of growing crystals from nutrient solution circulating in contact with excess solid salt disposed at a point along the path of travel of the solution passing successively through a saturator stage, a separate superheat or unsaturator stage and a separate crystallizer stage, which consists in circulating the solution cyclically in a continuous path of travel passing successively from the saturator stage to the unsaturator stage, from the unsaturator stage to the crystallizer stage and from the crystallizer stage back to the saturator stage, moving the solution in contact with the excess solid salt in the saturator stage, heating the solution in the saturator stage to a temperature value sufficiently above its saturation point temperature to render it sufficiently unsaturated to add additional solute thereto from the excess solid salt therein, heating the solution in the unsaturator stage to a different temperature value above said temperature value in the saturator stage and sufficiently above its saturation point temperature to render it sufficiently unsaturated with respect to the solute therein to dissolve crystalline material, moving the heated solution received from the unsaturator stage upwardly into the lowest part only of the bottom of the body of solution in the crystallizer stage at a rate of flow sufficient to replenish used solute removed from the solution by crystallization in the crystallizer stage, heating the lowest part only of the body of solution in the crystallizer stage at a temperature suitable to maintain the lowest part only thereof unsaturated at a temperature value sufficiently above saturation point temperature to curtail crystallization and suitable simultaneously to maintain the upper part thereof saturated at a temperature value sufficiently below saturation point temperature to permit crystallization and growth of crystals, and moving the crystals in contact with the saturated upper part of the solution in the crystallizer stage.

5. The method of growing crystals from nutrient solution circulating in contact with excess solid salt disposed at a point along the path of travel of the solution passing successively through a saturator stage, a separate superheat or unsaturator stage and a separate crystallizer stage, which consists in circulating the solution cyclically in a path of travel passing from the saturator stage to the unsaturator stage, from the unsaturator stage to the crystallizer stage and from the crystallizer stage back to the saturator stage, stirring the solution in contact with the excess solid salt in the saturator stage, heating

the solution in the saturator stage to a temperature value sufficiently above its saturation point temperature to render it sufficiently unsaturated to add additional solute thereto from the excess solid salt therein, filtering the solution sufficiently to remove solid crystalline material therefrom in passing from the saturator stage to the unsaturator stage, heating the solution in the unsaturator stage to a different temperature value above said temperature value in the saturator stage and sufficiently above its saturation point temperature to render it sufficiently unsaturated to dissolve crystalline material in the solution passing through the unsaturator stage, moving the heated solution from the unsaturator stage upwardly into the lowest part only of the bottom of the body of solution in the crystallizer stage, heating the lowest part only of the body of solution in the crystallizer stage at a temperature suitable to maintain the upper part thereof saturated at a temperature value sufficiently below saturation point temperature to permit crystallization and growth of the crystals therein, and moving the crystals in contact with the saturated upper part of the solution in the crystallizer stage.

6. The method of growing mounted crystals from nutrient solution circulating in contact with excess solid salt disposed at a point along the path of travel of the solution passing successively through a saturator stage, a separate superheat or unsaturator stage and a separate crystallizer stage, which consists in circulating the solution cyclically in a continuous path of travel passing successively from the saturator stage to the unsaturator stage, from the unsaturator stage to the separate crystallizer stage and from the crystallizer stage back to the saturator stage, stirring the solution in contact with excess solid salt in the saturator stage, heating the solution in the saturator stage to a temperature value sufficiently above its saturation point temperature to render it sufficiently unsaturated to add sufficient additional solute thereto from the excess solid salt therein to replenish used solute removed from the solution by crystallization in the crystallizer stage, filtering the replenished solution sufficiently to remove solid crystalline material therefrom in passing from the saturator stage to the unsaturator stage, stirring the solution in the unsaturator stage, heating the solution in the unsaturator stage to a different temperature value above said temperature value in the saturator stage and sufficiently above its saturation point temperature to render it sufficiently unsaturated with respect to the solute therein to dissolve crystalline material, moving the heated solution from the unsaturator stage upwardly into the lowest part only of the bottom of the body of solution in the crystallizer stage at a rate of flow sufficient to replenish used solute removed from the solution by crystallization in the crystallizer stage, heating the lowest part only of the body of solution in the crystallizer stage at a temperature suitable to maintain the upper part thereof saturated at a temperature value sufficiently below saturation point temperature to permit crystallization and growth of the crystals therein, revolving the crystals in contact with the saturated upper part of the solution in the crystallizer stage, and heating the solution intermediate the unsaturator and crystallizer stages to a temperature value sufficiently above saturation point temperature to render it sufficiently unsaturated to dissolve crystalline material therein.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,353,571	Dreibrodt	Sept. 21, 1920
2,164,112	Jeremiassen	June 27, 1939
2,204,180	Gerlach	June 11, 1940

OTHER REFERENCES

Comptes Rendus (Fr.), vol. 124—1897, p. 400.