Dec. 9, 1958 C. J. CHRISTENSEN 2,863,740

CRYSTAL GROWING SYSTEM

Filed April 25, 1957

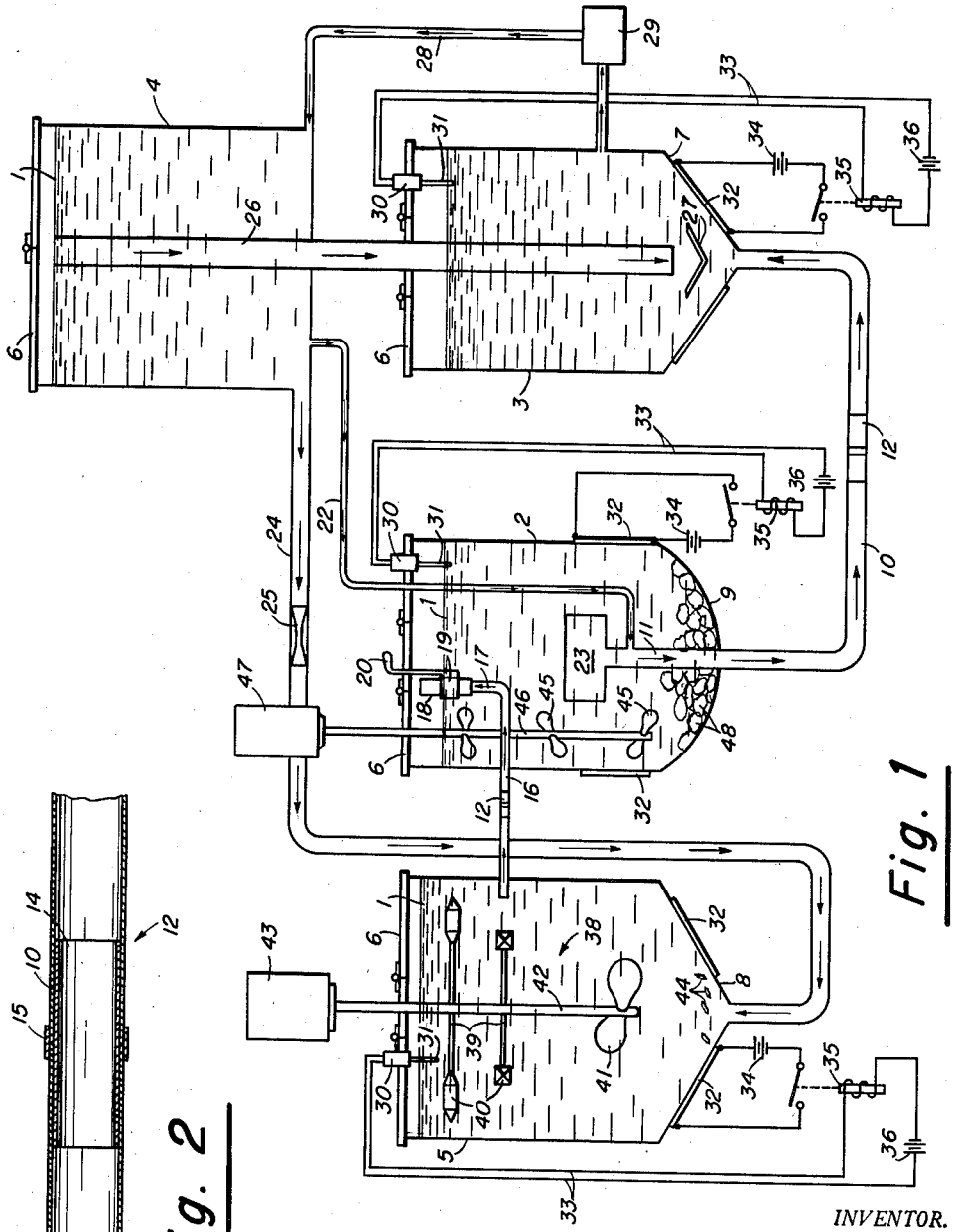


Fig. 1

Fig. 2

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United States Patent Office 2,863,740 Patented Dec. 9, 1958

2,863,740

CRYSTAL GROWING SYSTEM

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Application April 25, 1957, Serial No. 655,163

9 Claims. (Cl. 23—301)

This invention is an improvement over Patent No. 2,459,869, granted to Carl J. Christensen et al. and relating 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.

While it has been possible to grow satisfactory crystals with the patented apparatus, it has been found that accumulation of and plugging by spurious seed crystals occurred in the conduit due to cooling of the saturated solution therein. This is overcome in the apparatus of the present invention by using a crystal growth inhibiting material for the conduits and by additional circulation of the unsaturated solution.

One object of this invention is to provide new and improved apparatus for growing crystals.

Another object is to grow large single crystals continuously and rapidly at constant temperature without interference from spurious or spontaneous seeding in the nutrient solution.

Another object is to provide new and improved crystal growth inhibiting conduits.

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 can be 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 at the fixed temperature of the crystallizer. 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 are spontaneously nucleated 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.

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. The proper agitation of the growing crystals in the solution is very important. 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 of the crystallized 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 adapt 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 solution, a filter to remove all but the microcrystalline material from the solution received from the saturator, an unsaturator to raise the solution slightly above the saturation temperature and dissolve all microcrystalline material, a pump to deliver the clear refortified solution to a feed tank from which the solution is delivered to the bottom of the crystallizer. The spent solution may flow from the crystallizer at a point well below the level of the solution therein to the saturator. The several connecting conduits are fashioned from Tygon or similar crystal growth inhibiting material to minimize spurious seeding and to readily observe spurious crystal growth which can be quickly eliminated by opening the conduits to allow a momentary flow of solution which quickly flushes out the offending crystal growth. Solution from the feed tank is allowed to flow to the exit side of the filter in the saturator which controls crystal growth in the conduit from the saturator to the unsaturator. 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 and feed tank to the crystallizer tank.

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 occuring 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 an unsaturator to raise the freshly saturated or refortified salt solution to a temperature above the saturation 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 to the feed tank 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 drawings, in which like reference characters represent like or similar parts, wherein:

Fig. 1 is a schematic showing of the crystal growing system; and

Fig. 2 is a detail of the conduit couplings of Fig. 1.

Referring to Fig. 1 wherein there is illustrated the crystal growing system of the present invention which has four inter-connected tanks, each containing the circulating nutrient 1 and consisting of a saturator 2, unsaturator 3, feed 4, and crystallizer 5. The tanks may be fashioned out of stainless steel or other like material and provided with covers 6 made of glass or other suitable material. The unsaturator 3 and crystallizer 5 may have a cone shaped bottom 7, 8, respectively.

The saturator 2 has a hemispherical bottom 9 to which is connected an outlet conduit 10 having one end portion 11 disposed within the saturator 2, the other end being connected to the bottom of unsaturator 3. The conduit 10, made of Tygon or similar crystal growth inhibiting material, has a coupling 12, as shown in detail in Fig. 2, formed out of a glass tube 14 inserted within the conduit 10 and sealed with Tygon tape 15 for the purpose of opening up the conduit 10 to allow outflow of solution which quickly and cleanly flushes out any undesirable spurious crystal growth.

A conduit 16 has one end connected to the crystallizer 5 below the level of solution 1 in the crystallizer 5, the other end formed into a bent portion 17 which is connected to the saturator 2 such that the bent portion 17 is vertically disposed within the saturator 2. The bent portion 17 is provided with a telescopic end member 18 having a clamp 19 to which is attached a handle 20 that can be manually manipulated tao adjust the disired level of solution 1 in the crystallizer 5. The solution in saturator 2 must always be maintained at a level below the solution level in crystallizer 5, otherwise, the solution may flow from saturator 2 to crystallizer 5, which would seed the crystallizer 5 with unwanted crystals. Conduit 22 is connected to the feed tank 4 and joins conduit 10 at end portion 11 just below filter 23 which is located in the saturator 2 over the end portion 11 of conduit 10. Unsaturated solution is allowed to flow from feed tank 4 to conduit 10 so that the solution mixture from the filter 23 and feed tank 4 is unsaturated and no crystal will grow in conduit 10. The filter 23 may be made of fine screen or other similar material.

The feed tank 4 is connected to the lower part of the crystallizer 5 by a conduit 24 having a capillary 25 of suitable size to allow about one gallon per minute of flow. Feed tank 4 has an overflow pipe 26 mounted in the center and extending down through the unsaturator 3 to a point just above the baffle 27 located in the bottom 7 in the vicinity of the inlet of conduit 10. The unsaturator 3 is connected to the feed tank 4 by conduit 28 which has a pump arrangement 29 for conveying the solution 1 to the feed tank 4.

The saturator 2, unsaturator 3, and crystallizer 5 have independent temperature controlling thermostats 30 having a sensitive element 31 disposed within solution 1 and connected to the heaters 32 located on the lower portions of the tanks by conductive wires 33. The heaters 32 may be of any type heating element such as a resistance coil heated by any appropriate power source 34 and controlled by relay 35 operated by power supply source 36.

The crystallizer tank 5 is equipped with a support 38 having radial members 39 for mounting crystals 40 and a stirring means 41, mounted on shaft 42. A motor 43 operates the support 38 in a reciprocating action, moving about 30 seconds in each direction before it is reversed. This action tends to produce a vertical vortex in the solution 1 which gathers any spurious seed crystals 44 at the central part of the bottom of the crystallizer 5 where heat is supplied by heaters 32 and more important where the undersaturated solution enters from the feed tank at a higher temperature causing the spurious seeds to dissolve. The saturator 2 is equipped with stirring means 45 mounted on shaft 46 which is operated by motor 47. The salt 48 is agitated by the vigorous stirring of paddles 45 so that the solution in the saturator 2 is saturated with respect to the salt 48.

The conduits 10, 16, 22, and 24 are made of crystal growth inhibiting material such as Tygon for several reasons:

(1) It is easily washed free from solutions which might otherwise form spurious seed crystals 44 that would anchor in pores of other types of conduits such as stainless steel;

(2) If spurious crystals 44 should begin to grow in the tubing, they never attach to the walls of the tubing and hence can be readily observed and removed; and

(3) It is easy to work with Tygon such as adding the coupling 12 and capillary 25. Conduit 28 may be of any material such as stainless steel, not necessarily Tygon.

The heater 32 is placed on the side of the saturator instead of on the bottom 9 so that heat will not develop in the solution 1 under a layer of salt 48 which might collect in regions on the bottom of the tank. This is very important, since any trapped solution in the interstices of the aggregate of crystal fragments then become saturated at a higher temperature than that desired. Intermittently this solution would be released by a "bump" and a sizeable quantity of dissolved salt would be carried into the solution. This would lead to a fluctuation in the saturation of the solution which in turn would affect the crystal growing process.

To place the system in operation, the saturator 2, unsaturator 3 and feed tank 4 are filled with deionized water and salt 48 added to the saturator 2 until they are filled with the nutrient solution 1 saturated at the temperature of the saturator. Seed crystals 40 are suitably secured on radial members 39 in the empty crystallizer 5 and then heated to the solution temperature, so that they do not crack in heat shock on adding the saturated solution 1. The circulation of solution 1 from the feed tank 4 to the crystallizer 5, thence to the saturator 2 is established and the temperature in the tanks adjusted to the growing condition desired. Solution 1 from the feed tank 4 is admitted to the crystallizer tank 5 at the bottom at a temperature about 2° C. above the saturator temperature. This solution being unsaturated acts to dissolve the

spurious seed crystals always incident to the mounting of the seed crystals on the support. The unsaturated solution in the crystallizer is then caused to cool to a supersaturated solution in about two hours. The feed tank and saturator are then coupled to the crystallizer and the circulation of the solution in the facility commenced. The outflow of solution from the crystallizer to the saturator is taken at a point below the level of the solution in the crystallizer to minimize the growth of spurious crystals which would inevitably form in the outflow conduit **16**, it having been found that tube **26** always becomes clogged with salt crystallizing out of the solution flowing through it if the tube is not completely filled with solution.

Very excellent mixing is achieved by the stirrer **41** which keeps the temperature of the solution in contact with the growing crystals **40** very uniform and is maintained constant by heat from heater **32** located on the bottom **8**.

The solution **1** in the saturator **2** is kept saturated by efficient mixing with stirring means **45** and heater **32**. Salt **48** is replenished as required. The saturated solution flows from the saturator **2** to the unsaturator **3** through filter **23** which strains out any undissolved salt except the very smallest fragments.

Another critical point in maintaining the proper temperature control is at the filter **23**. By permitting a flow of the unsaturated solution **1** from the feed tank **4** through conduit **22**, to enter the end portion **11** of conduit **10** just below the filter **23** compensates for the slight cooling of the saturated solution after passing through the filter **23**. Otherwise this cooling off of the solution would result in the accumulation of very fine spurious crystals coming through the filter **23** that could cement together to form a solid aggregate.

The solution **1** in the unsaturator **3** and feed tank **4** is kept about 2° C. above the temperature of the saturator **2** so that all seed crystals are eliminated from the circulating solution, otherwise the entire system would continuously be seeded with microscopic seed crystals from the saturator **2**.

The solution **1** from the unsaturator tank **3** is continuously pumped into the feed tank **4** by a pump arrangement **29** in excess of that needed to feed the crystallizer **5** and that portion routed below filter **23**. This excess flows back to the unsaturator **3** through overflow pipe **26** at a substantial rate so that the temperature of the solution **1** in the feed tank **4** remains the same as that in the unsaturator **3**.

The crystals **40** are grown in the crystallizer **5** by moving the crystals 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 crystals **40**.

The rate of the crystals growth in the crystallizer **5** can be adjusted by varying the temperature of the solution in the crystallizer **5** relative to that of the saturator **2**. The following temperatures in the various tanks of the system have been found to be satisfactory for proper growth of crystals:

Ambient temperature≷25° C.
Saturator temperature=40.0±.1° C.
Unsaturator temperature=42.±0.3° C.
Feed tank temperature=42.0±3° C.
Crystallizer temperature=39.4±.1° C.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A crystallizer system comprising a saturator vessel, an unsaturator vessel, a feed vessel, a crystallizer vessel, conduits cyclically connecting said vessels in the order from said saturator vessel to said unsaturator vessel and from said unsaturator vessel to said feed vessel and from said feed vessel to said crystallizer vessel and from said crystallizer vessel back to said saturator vessel, temperature sensitive devices independently responsive to predetermined temperature values disposed in said saturator, unsaturator and crystallizer vessels respectively, heaters electrically connected to said temperature sensitive devices and disposed adjacent said saturator, unsaturator and crystallizer vessels respectively, crystal support means disposed within said crystallizer vessel, an overflow conduit connected from said feed vessel to said unsaturator vessel, and a conduit connected from said feed vessel to an end portion of said conduit connected from said saturator vessel to said unsaturator vessel, said end portion being disposed within said saturator vessel.

2. A crystallizer system as set forth in claim 1, said conduits being formed from crystal growth inhibiting material.

3. A crystallizer system as set forth in claim 1, said conduits connecting from said saturator vessel to said unsaturator vessel and from said crystallizer vessel to said saturator and from said feed vessel to said unsaturator each having a coupling.

4. A crystallized system as set forth in claim 1, said conduit from said crystallizer vessel to said saturator vessel having mean for adjusting the level of a solution in said crystallizer vessel.

5. A crystallizer system comprising a saturator vessel having a hemispherical bottom, an unsaturator having a cone-shaped bottom, a feed vessel, a crystallizer vessel having a cone-shaped bottom, conduits cyclically connecting said vessels in the order from said saturator vessel bottom to said unsaturator vessel bottom and from said unsaturator vessel to said feed vessel bottom and from said feed vessel bottom to said crystallizer vessel bottom and from aid crystallizer vessel back to said saturator vessel, temperature sensitive devices independently responsive to predetermined temperature values disposed in said saturator, unsaturator and crystallizer vessels respectively, heaters electrically connected to said temperature sensitive devices and disposed adjacent the bottoms of said saturator, unsaturator and crystallizer vessels, respectively, crystal support means disposed within said crystallizer vessel, an overflow conduit connected from said feed vessel to said unsaturator vessel, means in said conduit from said crystallizer vessel to said saturator vessel for adjusting the level of a solution in said crystallizer vessel, means for stirring a solution in said crystallizer and saturator vessels, and a conduit connected from the bottom of said feed vessel to an end portion of said conduit connected from the bottom of said saturator vessel to the bottom of said unsaturator vessel, said end portion being disposed within said saturator vessel.

6. A crystallizer system as set forth in claim 5 wherein said end portion has a filtering means thereon.

7. 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, an unsaturator stage, a feed stage and a crystallizer stage comprising the steps of 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 feed stage, from the feed 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 salt 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 from the unsaturator stage to the feed stage, moving the heated solution from the feed stage into the bottom of the crystallizer stage at a rate of flow sufficient to replenish used solute removed from the solution by crystallization in the crystallizer stage, moving a portion of the heated solution in the feed stage into the path of travel of the solution between the saturator stage and the unsaturator stage to curtail spurious crystal growth therein, heating the lowest part 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.

8. 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, an unsaturator stage, a feed stage and a crystallizer stage comprising the steps of 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 feed stage, from the feed stage to the crystallizer stage and from the crystallizer stage back to 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, 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 to the feed stage, moving the heated solution from the feed stage into the bottom of 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 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 crystals therein, and moving the heated solution from a point substantially below the level of solution in the crystallizer to the saturator stage to curtail spurious crystal growth during movement of the heated solution from the crystallizer stage to the saturator stage.

9. The method of growing crystals as set forth in claim 8 further including the step of moving a portion of the heater solution in the feed stage into the path of travel of the solution between the saturator stage and the unsaturator stage to curtail spurious crystal growth therein.

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