Feb. 27, 1968 J. L. TORGESEN ET AL 3,371,036
METHOD AND APPARATUS FOR GROWING SINGLE CRYSTALS
OF SLIGHTLY SOLUBLE SUBSTANCES
Filed Oct. 20, 1965 2 Sheets-Sheet 1

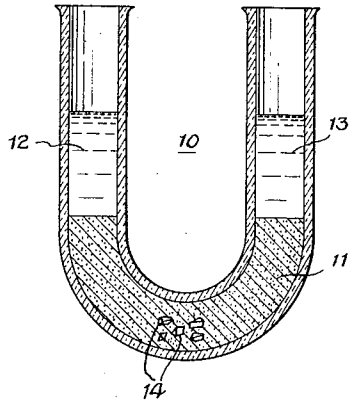

Fig. 1
PRIOR ART

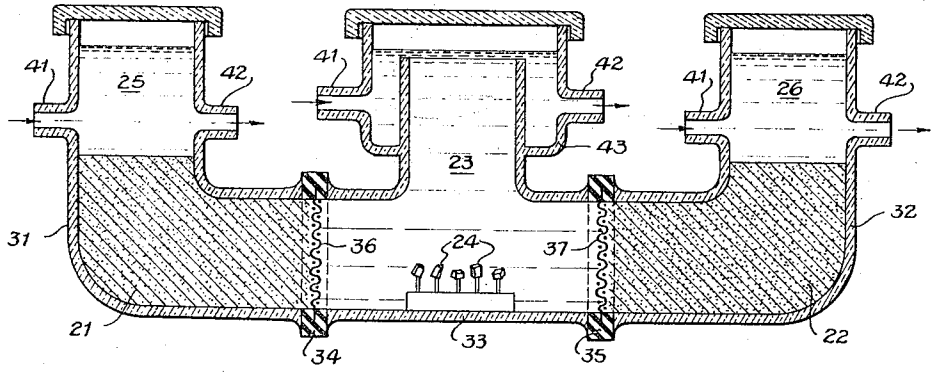

Fig. 2

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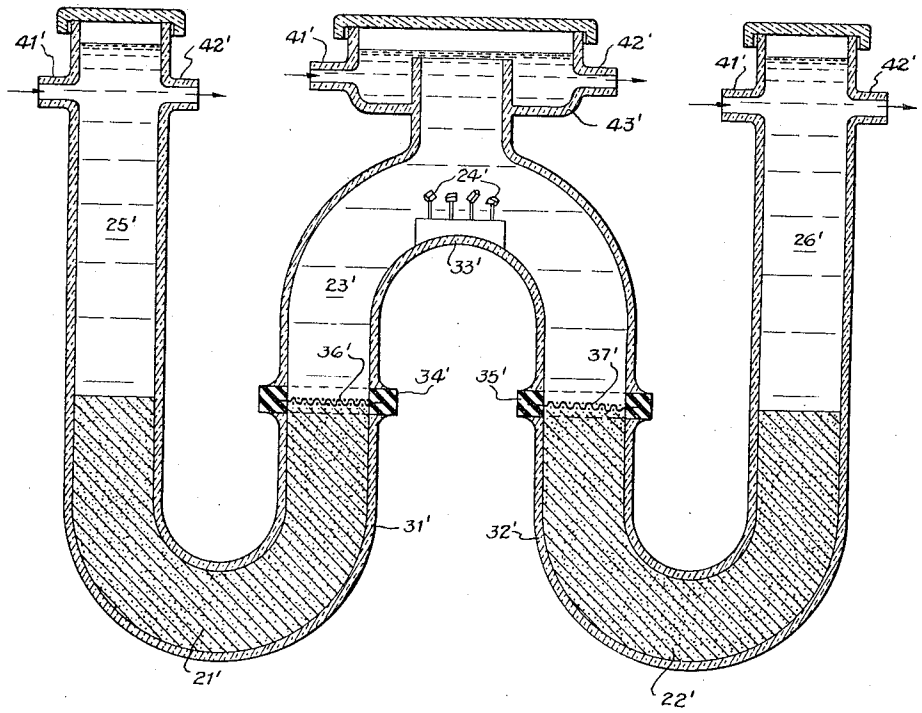

Fig. 3

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METHOD AND APPARATUS FOR GROWING SINGLE CRYSTALS OF SLIGHTLY SOLUBLE SUBSTANCES

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This invention relates to crystal growing, and more particularly to a method and apparatus for growing macroscopic single crystals of slightly soluble substances.

Single crystals of slightly soluble substances that are difficult or impossible to grow from the melt, vapor, or the like often may be grown successfully in silica gels. As is well known, however, the resultant crystals are limited in size and perfection by the presence of the gel.

Accordingly, an object of this invention is to provide an improved method and apparatus for growing, under the control of a gel or the like, single crystals of a desired substance from a solvent in which they are only slightly soluble.

Another object of this invention is to provide a method and apparatus for growing larger, more perfect single crystals of slightly soluble substances than has heretofore been possible.

These and other objects of the present invention will readily be understood when the following description is read in conjunction with the accompanying drawing, in which:

FIG. 1 is a cross-sectional view of the prior art gel apparatus, and

FIGS. 2 and 3 are cross-sectional views of exemplary embodiments of the present invention.

Referring to FIG. 1, it will be seen that a typical prior art apparatus for growing single crystals of slightly soluble substances by a batch process in an aqueous silica gel comprises a glass U-tube **10**, the bend of which is filled with a precipitated silica gel **11**. The arms of the U-tube are partially filled with two solutions **12** and **13**, each comprising a selected reacting substance dissolved in water. The substances react to produce the desired substance, which is only slightly soluble in water. Of course, the reaction may produce other substances or by-products, which generally are water-soluble or gaseous. As will readily be appreciated, if the solutions **12** and **13** were to be mixed directly, the desired sparingly soluble reaction product would not form a few large single crystals, but would precipitate out of solution in finely divided form. By providing the silica gel **11** between the solutions **12** and **13**, the reacting substances slowly diffuse toward each other, and the reaction product is obtained as fairly large single crystals **14**, which grow in contact with the gel **11**.

Unfortunately, the presence of the gel **11** and other reaction products about the crystals **14** tends to limit the ultimate size, purity and perfection of the crystals. This is, in part, due to the mechanical restraint imposed on the crystals by the gel, to the tendency of the gel to become loaded with by-products that change the crystal habit and block the diffusion of additional reacting substances, and to the tendency of the gel to split away from the corners and edges of the growing crystals and thereby unbalance the diffusion rates of the reacting substances to the growth surfaces of the crystals.

In the present invention, the undesirable influences of the gel on the growing crystals are completely avoided, essentially by dividing the gel into two or more portions, filling the space between the portions with solvent, and seeding the free solvent with small crystals of the desired

substance or of other seed material on which the desired crystal can grow epitaxially. Thus, in the illustrative embodiment of the invention shown in FIG. 2, the gel function is provided by a pair of members **21**, **22** that are spaced apart, the space therebetween being filled with a body of solvent **23**, in which seed crystals **24** are planted. The seed crystals **24** are supplied with reacting substances from solutions **25** and **26** disposed over the gel-function members **21** and **22**. Since the crystals **24** grow in the presence of the solvent **23** rather than in the presence of a gel, the crystals tend to be larger and more perfect than was heretofore possible.

The members **21** and **22** may comprise silica or other gels, non-ionic dispersants, packings of glass fibers, glass beads, plastic fibers or beads, sand, or any other mass of material having a network of capillary channels or interconnecting micelles, so that the diffusion of dissolved substances therethrough cannot be perturbed by random environmental influences such as building vibrations, temperature fluctuations, and the like. The members **21** and **22** are conveniently supported by glass or the like elbows **31** and **32** that are connected to an inverted T **33** by means of suitable gaskets **34**, **35** and clamps (not shown). If necessary, the gaskets **34** and **35** may have embedded therein meshes or screens **36**, **37** for retaining the members **21**, **22** in the elbows.

The solutions **25** and **26** correspond to the solutions **12**, **13** of the prior art, and therefore require no elaboration. The body of solvent **23** contained in the T **33** may comprise the solvent used in preparing the solutions **25**, **26**, or a different solvent miscible therewith. If desired, the solutions **25**, **26** and solvent **23** may be continuously or periodically freshened, by introducing fresh material into ports **41** and draining the old material from ports **42**. Since the solvent **23** should not be agitated by the fresh solvent, to avoid precipitating the reacting substances dissolved in the solvent **23**, it is preferable to surround the top of the T **33** with a ring **43**, the ports **41** and **42** being connected to the ring. The levels of solutions **25**, **26** and solvent **23** are typically made identical, as by the use of leveling bulbs on ports **42**, to avoid any hydrostatic heads in the system, and the common level should be adjusted to be slightly above the top of the T **33**. In this manner, a layer of fresh solvent is maintained over the body of solvent **33**, whereby dissolved by-products in the solvent **33** are continually removed by diffusion from the region of the growing crystals **24**.

From the foregoing it will be evident that the present invention enables one to grow single crystals of desired substances from solutions of two (or more) reacting substances, the admixture of the solutions being controlled by diffusion-regulating members, while the crystals grow in the environment of solvent **23**. The crystals thus are grown relatively free of restraints, are readily observable (provided the T **33** is transparent), and are readily accessible for harvesting. The crystal growing region is easily seeded, irradiated if and as expedient, cleaned of undesired substances, or solutes, and provided with crystal dopants, habit modifiers, complexing agents and the like. In addition, the crystal growing region may readily be provided with an electrical field, for example via the (metal) screens **36**, **37**, for accelerating or decelerating the diffusion of the reacting substances or ions into the solvent **23**. Additionally, the screens **36**, **37** may be used as electrodes for measuring the conductance and hence concentration of the substances dissolved in the solvent **23**.

FIG. 3 illustrates a modification of the apparatus shown in FIG. 2, wherein the tubings **31'**, **32'**, and **33'** adjacent gaskets **34'** and **35'** have been "stretched" and bent to render the gaskets **34'**, **35'** horizontal. Thus the diffusion regulating members **21'**, **22'** form a horizontal interface

with the solvent 23', whereby the members 21' and 22' may comprise mechanically weak gels and the like, incapable of being used as vertical interfaces.

Although the invention has been described by way of specific illustrative embodiments, it is intended that the invention be limited only as set forth in the appended claims.

What is claimed is:

1. The method of growing large single crystals, which comprises

(a) providing solutions of two materials which react to produce a crystallizing substance,

(b) providing a body of solvent from which crystals of said substance grow,

(c) connecting each of said solutions to said body of solvent by respective members having a network of capillary channels,

(d) seeding said body of solvent with small crystals of the desired substance,

(e) diffusing the material solutions through their respective network of capillary channels into the body of solvent where they react to form the crystallizing substance,

(f) crystallizing the substance on the seeds provided in the solvent, and

(g) harvesting said crystals after they have grown the desired amount.

2. The method set forth in claim 1, and further comprising,

(a) freshening said solutions and solvent to provide a continuous process.

3. The method set forth in claim 1, and further comprising,

(a) adding crystal dopants, complexing agents, or habit modifiers to said body of solvent.

4. The method set forth in claim 1 wherein the said solutions are connected to said body of solvent by respective members having a network of interconnecting micelles.

5. The method set forth in claim 1 wherein the seeding of said body of solvent is with a desired substance of material upon which the crystals can grow epitaxially.

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