July 7, 1942. W. H. ALLEN ET AL 2,288,667

METHOD OF CRYSTALLIZING SUBSTANCES FROM SOLUTION

Filed Aug. 15, 1938 2 Sheets-Sheet 1

Fig. 1

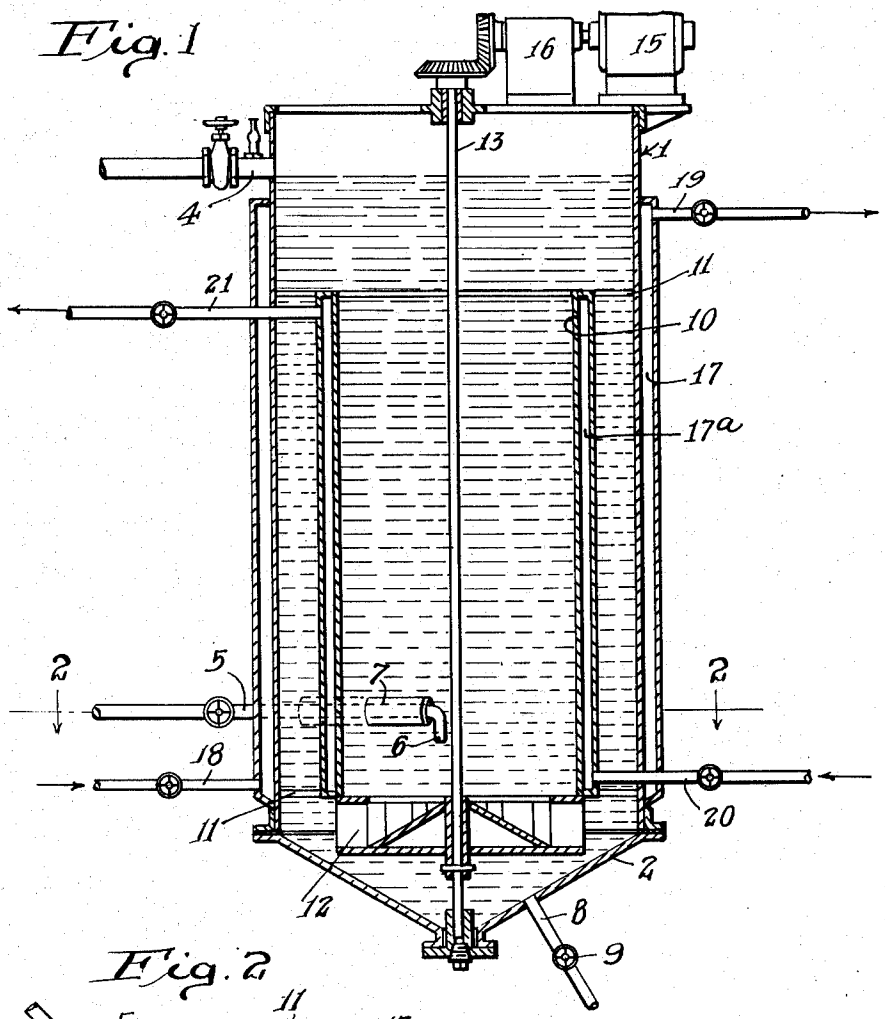
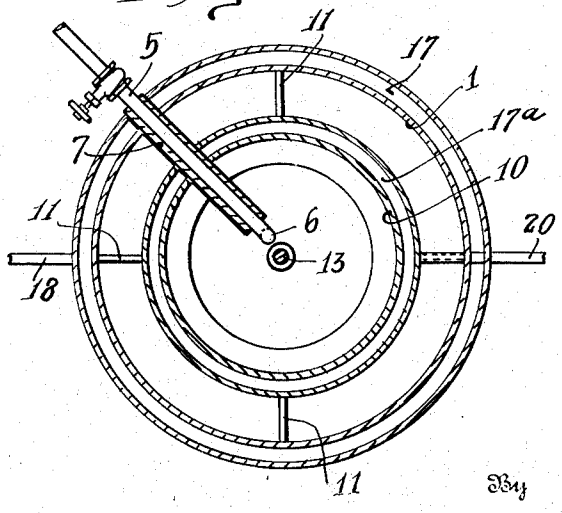


Fig. 2



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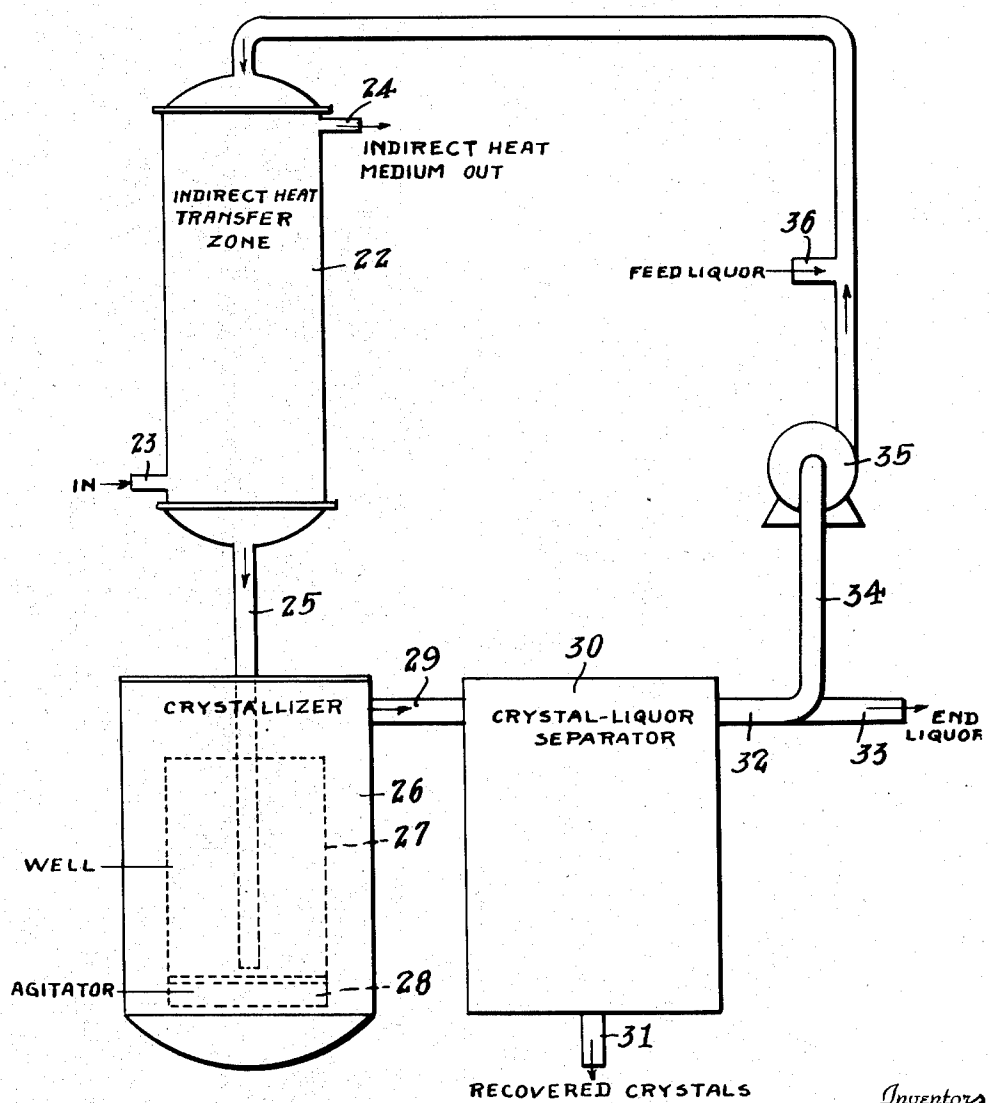
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Filed Aug. 15, 1938 2 Sheets-Sheet 2

Fig. 3



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Patented July 7, 1942 2,288,667

UNITED STATES PATENT OFFICE

2,288,667

METHOD OF CRYSTALLIZING SUBSTANCES FROM SOLUTION

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Application August 15, 1938, Serial No. 224,960

7 Claims. (Cl. 23—295)

This invention relates to a method of crystallizing a substance from solution, and is applicable generally to the crystallization of all substances from solution. The method may be used for crystallizing both inorganic salts and compounds and also organic substances from solution.

It is the general object of the present invention to provide a method of crystallizing substances from solution without evaporation of the solution, which method may be carried out so as to secure an increased rate of crystallization and a relatively large yield from the apparatus employed, while at the same time producing crystals of good and uniform shape and of a desired size.

Our new method is based upon an improvement in the type of agitation or circulation employed to maintain the solution and crystals in movement relative to each other during crystallization. It is known to improve crystal size and habit by keeping the solution in movement past the crystal particles so as to continuously present fresh solution to contact with the crystal particles and thereby increase their size. The solution, for example, has been moved continuously past the crystals placed in the form of a stationary bed, the solution motion causing the crystal particles to be agitated but not to move out of the bed. Also, a body of solution containing crystals has been agitated more or less disorderly by means of impellers which create a suspension of the crystals in a zone about the impeller but allow the crystals to settle in other parts of the solution. While such methods are an improvement, they have left much still to be desired, as the rates of crystallizing must be greatly below desired rates when large sized crystals are desired. The desirability of continuously supplying crystal particles to a zone in which supersaturation is produced has also previously been enunciated; but, no practicable method has been offered by which this desideratum has been utilized to produce good-sized crystals of clean habit, at a high production rate. Our purpose has been to provide an improved circulation method which will produce satisfactory crystals at higher rates of crystallization.

In our application for United States patent, Serial No. 433,984, Patent No. 2,130,065, issued September 13, 1938, we have set forth an improved crystallization process, in which a special method of circulating the solution and crystals is applied to evaporative crystallization processes. It has been found that uniform, coarse-grained crystals could be produced in a rapid evaporation process if the circulation produces and maintains a uniform suspension of the crystals in the liquor, or solution being crystallized, and continuously moves that suspension through the surface zone at which evaporation takes place. This result was accomplished by moving all of the solution and crystals to and from the surface at a rate substantially in excess of the settling rate of the crystals. With this type of circulation, sufficient crystal surface area is always present in the surface zone where supersaturation is produced to absorb any appreciable degree of supersaturation and also the liquor in that zone is continuously being replaced by fresh liquor. As a result, higher rates of providing supersaturation may be employed without exceeding the metastable supersaturation range and forming undesired quantities of excess, fine crystals, i. e., "false seed." The supersaturation is largely expended essentially almost as soon as it is produced. Continuous replacement of the solution at the surface avoids labile supersaturation and assures a uniform temperature throughout the body of the solution, since all parts of the solution are continuously treated at the surface.

We have now found that this same type of circulation may be advantageously applied to crystallization processes in which no evaporation occurs, the supersaturation being produced simply by a change of temperature, and whether or not there is a marked zone in which the supersaturation is produced, corresponding to the surface zone in an evaporation process. The provision of a circulation which maintains all of the solution and crystals undergoing movement producing a uniform suspension of the crystals in the liquor increases the rate at which supersaturation may be produced without forming an undesired quantity of excess fine crystals. This process differs from previous procedures not only in that all the crystals are kept in movement, but the entire body of solution is uniformly moved at a high rate. Also, the rate of movement of both solution and crystals is many times the rates heretofore used or considered. For example, in crystallizers in which the solution was moved at the previously high rate of 300 gallons per minute, it was found that the advantages of the present invention were derivable only when the rate of motion was increased to about 30,000 gallons per minute and the type of circulation was such that all of the liquor moved continuously and uniformly.

To secure the desired uniform suspension of crystals in the solution, the solution must move in one continuously moving stream with all por-

tions traveling at a substantially uniform rate in excess of the settling rate of the crystals. Such movement will occur when the solution moves through a cyclic path which includes all portions of the zone of the crystallizer in which the solution is held. For example, movement of the solution and crystals to and from the surface, or down and around a vertical well within the crystallizer, can be employed to carry the solution through a cyclic path so that all portions of the solution are in movement.

We prefer to employ a system in which the solution and crystals are moved through a path from the bottom of the crystallizer to the surface of the body of the solution and back, as then the entire crystallizing system is retained within the crystallizer, per se, throughout the crystallization process. A path of this type can be provided by means of partitions of various types which divide the crystallizer into two parts, one for upward movement and the other for downward motion of the solution. The two sections are preferably made of essentially equal cross-sectional area so that the rate of flow will be uniform throughout the path. In this way, there is no increase or decrease in the velocity of the liquor undergoing circulation. These proportions may be varied considerably, however, without materially affecting the efficiency of the process or apparatus, so long as the upward rate of flow is above the settling rate of the crystals.

Movement of the solution through the path must be attained by means which do not subject the liquor to excessive mechanical stimulus, as the allowable limit of metastable supersaturation, below which the liquor must be held to avoid new nucleus formation, is reduced by shock, abrasion, and other mechanical stimulus. In general, any pumping means capable of handling a large volume of liquor at slow speed will be sufficiently free of such effects for our purposes. Paddles, screw type pump impellers, and centrifugal pump impellers, for example, are adapted for use in circulating the solution and crystals around a central baffle or partition. The arrangement of impeller or circulating means with respect to other parts of the equipment should be chosen so that there is sufficient clearance to avoid forcing the liquor and crystals sharply against rigid parts, and rubbing surfaces between which crystal abrasion may take place should be avoided.

The advantages of our invention will be better appreciated from a consideration of the mechanics of the crystallization process. In any crystallizer, the crystallization process occurs as a result of treatment of the solution which causes it to become supersaturated. When a solution is being continuously subjected to treatment causing it to become supersaturated, the supersaturation will be expended or released through deposition on and growth of existing crystal particles, through formation of fresh quantities of fine crystals or as a result of both processes. The release of supersaturation occurs solely by growth of existing crystals if the crystal surface area available is sufficient to absorb the supersaturation and hold it within the metastable field. Lack of sufficient surface area will allow the supersaturation to enter the labile field and spontaneously form fine crystals. If large crystals are desired, spontaneous formation of new crystals must be limited to the relatively small number needed for replacement of those withdrawn as completed product. By circulating the solution and crystals so as to form an essentially homogeneous suspension, the degree of supersaturation throughout the body of the solution is more nearly uniform, and all of the solution is continuously contacted with available crystal surfaces. Differences in temperature and composition throughout the body of the solution are thus maintained small, and the crystal particles are continuously in motion with all of the liquor. As a consequence, it is possible to more closely control the degree of supersaturation throughout the system and to avoid the occurrence of localized zones in which the supersaturation becomes labile.

Any non-evaporative type of crystallization process may be improved by this process of our invention. In general, the temperature change producing supersaturation will be produced directly within the crystallization chamber by use of cooling coils or other heat transfer means, but the invention is also useful with equipment in which the supersaturation is produced in one unit and the crystallization occurs largely elsewhere in the manner hereafter described in connection with figure 3 of the drawings. We also will describe the application of our invention to a crystallizer in which the supersaturation is produced by cooling jackets placed around and within the crystallizer as illustrated in Figures 1 and 2.

The present invention, together with various objects and advantages thereof, will best be understood from a description of preferred forms of processes embodying the invention. For this purpose, we will hereinafter describe such examples, the description being given in reference to the accompanying drawings, in which—

Figure 1 is a diagrammatic view in elevation of a crystallizer with cooling jackets to which the process of the invention has been applied.

Figure 2 is a horizontal section, taken on the line 2—2 in Figure 1.

Figure 3 is a diagrammatic view in elevation illustrating the operation of the process in which separate crystallizing and supersaturating zones are used.

We have chosen to illustrate our invention by reference to a tank crystallizer in which the supersaturation is produced by a cooling jacket, but it will be appreciated that the description is given without prejudice to our rights to the use of the invention with other non-evaporative type processes with which it provides advantages.

Referring now to Figure 1 of the drawings, the crystallizer comprises a tank 1 having a dished bottom enclosure 2. Preferably, the crystallizer is maintained in operation filled to the height of an overflow pipe 4. Solution to be crystallized is admitted to the crystallizer through a suitable line 5 which may terminate at the shell 1 or may extend within the shell as indicated in the drawing. In the latter case, the inner end of the inlet pipe 5 is provided with a turned-down spout 6 and an insulation covering 7. At the bottom of the crystallizer is provided an outlet line 8, with a valve 9, for emptying the contents of the crystallizer

Within the tank, and below the overflow outlet 4, is provided a circulation well 10 which forms the partition for forming the circulation path for the solution and crystals. The well 10 simulates a large section of pipe and is fixed concentrically within the tank 1 by suitable means. Preferably, such means include rectifying vanes 11 which extend vertically between the wall of the crystallizer

and the well 10 and are indicated as four in number. The vanes 11 serve the dual purpose of preventing swirling of the contents of the crystallizer and of holding the well 10 in place. The diameter of the well should preferably be such that the cross-section area of the crystallizer will be divided into two equal parts. These proportions may, however, be varied considerably in practice without departing from the spirit or the effectiveness of the invention. We prefer to keep the surfaces bounding the circulation path smooth and thereby avoid subjecting the solution to serious mechanical stimulus.

The well divides the crystallizer into two paths in which the solution and crystals may be circulated to form a substantially homogeneous suspension of crystals in the solution throughout the body of the crystallizer. To this end, the well extends downward close to the bottom of the crystallizer and upward to a distance somewhat below the overflow outlet 4 so that all of the solution will be maintained in circulation.

At some point in the continuous liquor path formed by the well 10, we provide suitable means for producing a movement of the solution and crystals through the path at a rate which will form a substantially homogeneous suspension of the crystals in the solution. Such means is preferably some form of large volume, slow speed impeller or pump which may move the solution either up through the well and down the sides thereof or in the opposite direction. We have found the impeller of U. S. Patent No. 1,997,277 well adapted for this purpose and the impeller 12 illustrated at the bottom of the well is of that design. The impeller is mounted on a shaft 13 which is concentric with the well 10. The impeller is rotated by a motor 15 connected to the shaft 13 through the gear box 16.

The diameter of the impeller is approximately equal to that of the well 10 and the cross-sectional areas of the intake and exhaust ports of the impeller are made as nearly equal to that of the well 10 as possible, so that the path of the liquor through the impeller is essentially the same as that through the well. It is preferable that the space left between the lower extremity of the impeller 12 and the bottom of the crystallizer should be comparatively small since such constitutes a dead space. In this way, the danger of accumulation of crystals in this space is lessened. If desired, the well 10 may be mounted with impeller 12 on the shaft 13.

Crystallization takes place within the crystallizer shell 1 when a heat transfer medium is circulated through jackets 17 and 17a which form the outer walls of the tank 1 and the well 10. Inlet and outlet conduit pairs, 18—19 and 20—21, permit circulation of the medium through the jackets. Such medium will generally be a cooling medium or refrigerant, but with substances having invert solubilities and also in some applications a heating medium may be required to maintain the desired temperature of crystallization.

The heat transfer may also be effected with other types of heat transfer devices, such as a cooling coil immersed in the liquor or surrounding the tank 1.

In Figure 3 of the drawings there is diagrammatically illustrated a form of apparatus in which supersaturation is produced in one unit and crystallization in another unit. In Figure 3 of the drawings 22 indicates any suitable apparatus for supersaturating the solution to be crystallized, such as an indirect heat transfer cooler having an inlet 23 and an outlet 24 for a cooling medium. The cooler 22 is provided with a line 25 for introducing the cooled and supersaturated liquor into the crystallizer 26. It is to be understood that the crystallizer 26 should be identical with that of Figures 1 and 2 of the drawings, except that it may omit the jacket 17 and 17a. It should include a vertical well 27 and an impeller diagrammatically indicated at 28. From the crystallizer 26 an overflow line 29 is provided for carrying the admixture of solution and crystals to a suitable crystal-liquor separator 30, from the bottom of which at 31 are withdrawn the recovered crystals which thereafter are retained separated from the liquor, whereas the liquor is withdrawn from the line 32 and may be discharged in whole or in part through line 33 or returned in whole or in part through line 34 and pump 35 to the cooler 22. The fresh solution may be introduced through the inlet 36.

Having thus described the construction of a suitable apparatus in which the method of the present invention may be carried out, we will now describe the method as it is applied to the crystallizing of a substance from solution.

The crystallization of any substance from a solution thereof can be improved by the use of the present invention. We mention, by way of example, the crystallization of borax, boric acid, glauber salt, sodium chloride, sodium sulfate anhydrous, potassium chloride, oxalic acid dihydrate, barium chloride dihydrate, copper sulfate pentahydrate, etc. The different materials crystallized by the process of the present invention may have many differences in their manner of crystallization. Thus, for example, borax and glauber salt both have a substantial tendency to produce supersaturated solutions, although borax has a slow rate of crystal growth while glauber salt crystallizes very rapidly once crystallization begins. Sodium and potassium chlorides exhibit very little tendency to supersaturate, while boric acid may be said to be an average material exhibiting a moderate degree of supersaturation and a fair rate of crystal growth. Barium chloride, copper sulfate and oxalic acids are materials mentioned for the reason that they are examples representing a heavy compound, a common metal salt, and an organic compound, respectively. Each of such materials will, of course, require somewhat different temperature conditions for the operation of the process and apparatus in crystallizing the same. Crystallization begins only after supersaturation has been incurred, so that it is necessary in the crystallization process first to produce a solution which will become supersaturated during the cooling and then introduce it into the zone or zones where it is to be treated to induce supersaturation and crystallization. For the application of the process on any particular substance it is necessary, therefore, only to examine the handbooks to determine the conditions under which such a substance reaches saturation and introduce the solution into the cooling zone at a concentration such that saturation will be exceeded during the cooling.

The solution to be crystallized is introduced into the crystallizer through line 5. When the crystallizer has been filled to the level of the overflow outlet 4, the impeller is started and is rotated at a rate to produce an essentially homogeneous suspension of the crystals formed by the cooling in the solution. In a batch process the

cooling is continued without further addition of liquor until the solution has been cooled to the final low temperature desired. The crystallizer is then emptied and the process repeated on a further batch of solution. If the operation is to be continuous a batch of liquor is first cooled and then additional liquor is continuously introduced through inlet 5 and cooled sludge withdrawn through outlet 4. The crystals produced during the cooling are recovered from the cooled sludge of solution and crystals by any suitable solid-liquor separating means, such as filters, settlers, etc.

The movement of solution should be such as will cause it to move continuously, uniformly, and rapidly throughout the entire crystallizing zone so that distribution of supersaturated liquor is essentially uniform throughout the body of the solution. The rate of upward flow of liquor should be several times as great as the settling rate of the large crystals in the system if the full advantage of our invention is to be realized. It is not merely sufficient to create a flow or disturbance which will keep the crystals from settling on the bottom of the crystallizer. The flow must be great enough to cause the crystals to flow with the liquor over the well, so that there is a more or less uniform distribution of crystals throughout the body of the liquor. Too low rates of flow will be accompanied by an accumulation of crystals suspended in the liquor just above the impeller. Somewhat higher rates will decrease the density of this accumulation or bed of crystals, but rates in excess of the settling rates of the crystals present are necessary to avoid excessive concentration of the crystals in localized zones.

Illustrative of the relative magnitude of our volume of circulation and size of circulating equipment, we will give dimensions for a crystallizer 8 feet in diameter, adapted to hold 5,500 gallons of liquor to be crystallized. The well 10 and impeller 12 are about 5 feet 4 inches in diameter and the impeller is rotated about 27 revolutions per minute. This creates a liquor flow of about 3 feet per second, equivalent to a flow of about 30,000 to 35,000 gallons per minute. In comparison, ordinary impellers rarely exceed a foot in diameter and low speed fluid pumps operate generally at rates of 400 to 500 R. P. M. Ordinary liquor flows in crystallizer operation seldom exceed 300 to 400 gallons per minute, which is higher than average operation.

The rates we have set forth, 30,000 to 35,000 gallons per minute in a 5,500 gallon crystallizer or about 2 to 3 feet per second, are sufficient to maintain crystals of most substances of 10 mesh size (about 2 millimeters of side or diameter) well distributed throughout the liquor and will prevent undue concentration of crystals in the lower extremity of the vessel. Representative settling rates of the larger screen cuts of crystals of the commercial forms of several substances will illustrate the sufficiency of these rates. The free settling rate of borax crystals of 10 mesh size in a saturated borax solution at 100° F. is approximately 21 to 22 feet per minute, which is only about ⅛ to ⅙ of the rates noted. Sodium chloride crystals of about 20 mesh size settle at the rate of 12 feet per minute in saturated sodium chloride solutions at 72° F., as compared with our rates of 2 to 3 feet per second. Potassium chloride crystals of 20 mesh size settle at the rate of about 9 feet per minute. Barium chloride dihydrate crystals of 20 mesh size have a free settling rate of about 25 feet per minute. $CuSO_4.5H_2O$ and oxalic acid, two dissimilar materials, settle at similar rates, the rate for the former being about 11 feet per minute and for the latter about 10 feet per minute in their saturated solutions at about 72° F. While the speed of circulation, as herein described, is substantially above the settling rate of the crystals present, it is to be understood that in operation of the process there may be under the law of probability a minor portion of the crystals which grow to such size as will not be carried with the solution but will settle to the bottom of the apparatus. Any accumulation of such settled crystals at the bottom of the apparatus may be conveniently removed when the apparatus is washed out to remove crystal deposits from the walls, etc. Such deposits will seldom amount to more than a fraction of 1% of the total product of the apparatus.

While the particular process herein described is well adapted to carry out the objects of the invention, it is to be understood that various modifications and changes may be made, all coming within the scope of the appended claims.

We claim:

1. The process of crystallization which comprises changing the temperature of the solution to be crystallized by transfer of heat through a heat transfer medium while avoiding appreciable evaporation and rendering said solution supersaturated primarily as a result of the temperature change, continuously passing said solution into a crystallizing zone, therein subjecting said solution and crystals produced therein to a continuous circulation to and from the surface of the body of such solution at a rate in excess of the settling rate of the crystals present, continuously withdrawing an unclassified mixture of larger crystals and solution from said zone, separating all of the crystals and solution which crystals are thereafter maintained separated from the crystallizing zone, transferring said solution to the supersaturating zone, returning said solution from said supersaturating zone to the crystallizing zone, and recovering the crystals produced.

2. The process of crystallization, which comprises passing a solution to be crystallized into a crystallizing zone, therein subjecting said solution to continuous circulation at a relatively uniform linear velocity whereby there is produced and maintained within said zone a substantially homogeneous mixture of all of the crystals and solution, subjecting said solution to a temperature change by transfer of heat in the direction of decreasing solubility and rendering said solution supersaturated while avoiding evaporation of solution within said zone, withdrawing an unclassified portion of the mixture of crystals and solution from said crystallizing zone, separating all of the crystals from the solution, and maintaining all of such crystals thereafter separate from the crystallizing zone.

3. The process of crystallization, which comprises passing a solution to be crystallized into a crystallizing zone, therein maintaining the body of solution and crystals undergoing circulation through a cyclical circulation path to and from the surface of said body of solution at a rate substantially in excess of the settling rate of all of the crystals, changing the temperature of such solution and rendering it supersaturated primarily as a result of the temperature change by transfer of heat between a medium while avoiding evaporation of the solution within said

zone, withdrawing an unclassified mixture of the crystals and solution from said crystallizing zone, and separating all of the crystals from the solution and maintaining said crystals thereafter separated from the crystallizing zone.

4. The process of crystallization, which comprises passing a solution to be crystallized into a crystallizing zone, maintaining the solution and crystals produced during crystallization in continuous circulation to and from the surface of the body of solution in said zone at a rate substantially in excess of the settling rate of all of the crystals present, changing the temperature of said solution and rendering it supersaturated primarily as a result of the temperature change by a transfer of heat between a medium and said solution while avoiding evaporation of solution within said zone, and withdrawing from the crystallizing zone an unclassified mixture of the crystals and solution, separating all of the crystals from the solution, and maintaining thereafter all of said separated crystals separated from the crystallizing zone.

5. The process of crystallization, which comprises passing a solution to be crystallized into a crystallizing zone, maintaining the solution and crystals produced during crystallization in continuous circulation to and from the surface of the body of solution in said zone at a uniform linear velocity substantially in excess of the settling rate of all of the crystals present, changing the temperature of said solution and rendering it supersaturated primarily as a result of the temperature change by a transfer of heat between a medium and said solution while avoiding evaporation of solution within said zone, separating from the crystallizing zone an unclassified mixture of crystals and solution, separating all of the crystals from said solution, and maintaining said crystals thereafter separated from the crystallizing zone.

6. The process of crystallization, which comprises passing a solution to be crystallized into a crystallizing zone, maintaining the solution and crystals produced during crystallization undergoing circulation around and through a vertical well under the impetus of a large-volume slow-speed pump at a rate in excess of the settling rate of all of the crystals present, changing the temperature of said solution and rendering it supersaturated primarily as a result of the temperature change by transfer of heat between a medium and said solution while avoiding evaporation of said solution within said zone, withdrawing from the crystallizing zone an unclassified mixture of the crystals and solution, separating all of the crystals from the solution, and maintaining thereafter all of said crystals separated from the crystallizing zone.

7. The process of crystallization, which comprises passing a solution to be crystallized into a crystallizing zone, therein subjecting said solution to continuous circulation to and from the surface of the body of solution at a uniform rate in excess of the settling rate of all of the crystals present, withdrawing unclassified sludge of mother liquor and crystals from said zone, permanently separating all of said crystals from said mother liquor and from the crystallizing solution, changing the temperature of said clarified solution outside of said crystallizing zone without appreciable evaporation and rendering it supersaturated primarily as the result of the evaporation-free temperature change, returning said supersaturated solution to the crystallizing zone, and recovering the permanently separated crystals.

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