April 21, 1959 W. C. SAEMAN 2,883,273

CRYSTALLIZATION

Original Filed March 4, 1954 2 Sheets-Sheet 1

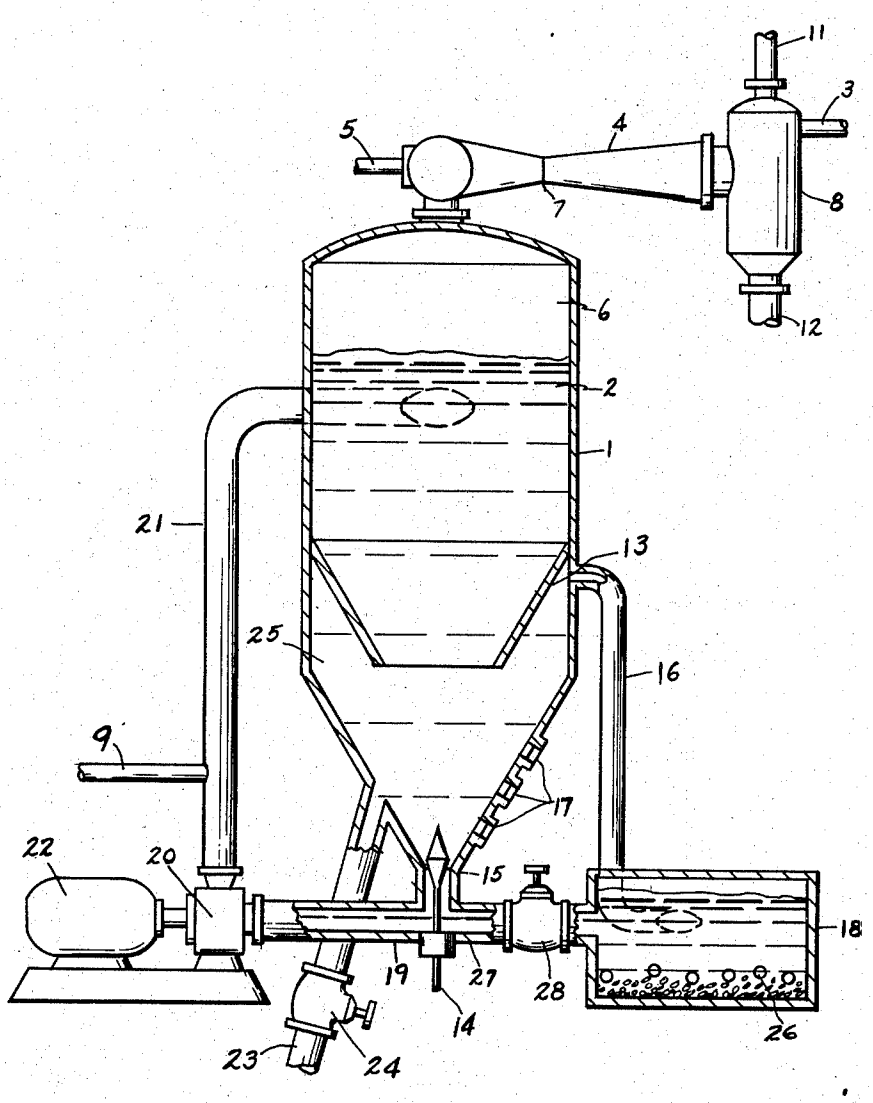

FIG - 1

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CRYSTALLIZATION

Original Filed March 4, 1954 2 Sheets-Sheet 2

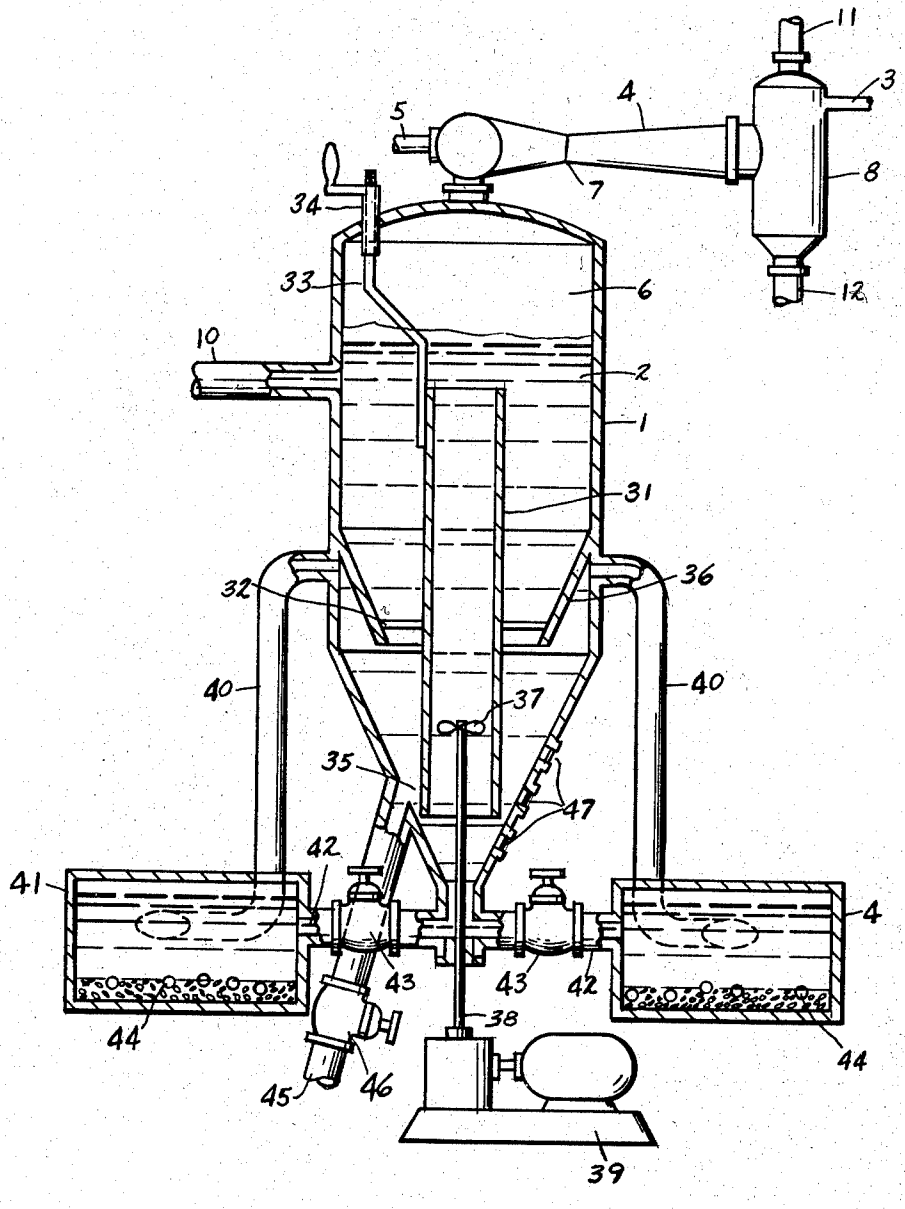

FIG - 2

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2,883,273

CRYSTALLIZATION

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Original application March 4, 1954, Serial No. 414,192, now Patent No. 2,827,366, dated March 18, 1958. Divided and this application February 14, 1957, Serial No. 643,907

2 Claims. (Cl. 23—295)

This invention relates to a crystallization process and apparatus for producing large crystalline material from turbulent suspensions under controlled conditions of operation. More particularly this invention relates to a crystallization process and apparatus in which a control is exerted over the existence time and number of fine crystals in the turbulent suspension of the process in such manner that an unexpectedly high yield of large product crystals is produced. Furthermore, the control is so formulated as to enable the economical reuse of matter contained in the undesired fine crystals with a minimum unbalance of the optimum crystallizing conditions that exist.

Heretofore, standard commercial procedures of the turbulent type for obtaining product crystals of large size involved only a means for growing and selectively removing crystals after they have reached a certain size. They in effect were only procedures in which a control was exerted over the selective removal, no importance being given to the effect of the number of fine crystals existing in the turbulent suspension upon which growth of material will occur. In so failing to exert a control over the number of fine crystals existing in the suspension, an economical and optimum production of coarse crystalline material could not result.

Only one disclosure found which attempts to effect such a control of a turbulent type crystallization process was U.S. 1,845,742. But the process and apparatus disclosed in this patent has been found to be impractical for commercial operation. For example, its use of a screen to separate out unwanted seed crystals is attended with frequent clogging and crusting. Also its use of one auxiliary stream for performing three independent functions is impractical because it combines three streams which require three different flow velocities; namely, (1) the stream which withdraws excess seed crystals from the suspension requires a high flow rate so that there is prompt removal of the excess seed crystals in as small a size as possible, preferably when they can still be considered nuclei crystals, (2) the flow rate through the dissolving tank must be relatively low to permit crystallized material in the tank to be dissolved with a minimum amount of overheating or overdilution so that upon return of the solution to the crystal growth circuit, there will be no unbalance of the optimum crystallizing conditions existing therein, and (3) the flow rate through the elutriation column for the selective removal of product crystals must also be independently controlled so that an efficient regulation of the removal of the product crystal of certain sizes is effected. It has been found that this flow rate should be intermediate the rates discussed above.

An object of this invention, therefore, is a crystallization process and apparatus which efficiently exerts a control over the existence of fine crystals present in the turbulent suspension so as to prevent growth upon an unduly large number of such crystals. Another object of this invention is a crystallization process and apparatus which economically and continuously utilizes the material contained in such undesired fine crystals for further crystal growth upon other "desired" fine crystals. A still further object of this invention is a crystallization process and apparatus of the turbulent suspension type which will operate continuously and which will produce unexpectedly large crystals. Other objects will become apparent to those skilled in the art upon reading the following disclosure.

Generally speaking, in accordance with this invention, the foregoing objects as well as others which will become apparent from the following description are accomplished by providing an apparatus and method for substantially immediately removing undesired fine crystals from the turbulent suspension circulating in the crystallizing bath. This is accomplished by elutriating the undesired fine crystals from the suspension. To conserve the material contained in these extracted undesired fine crystals, the crystals may be redissolved in a separate quiescent chamber either by heat, by adding additional solvent, or by other solvating means, and the resulting solution returned to the main body of the liquid preferably at a flow rate, temperature and concentration substantially equalling the conditions existing in the main body, thereby avoiding any abrupt changes in the overall system.

The accompanying drawings which show a certain method of carrying out the invention are not to be considered restrictive and are shown for illustrative purposes only in which:

Figure 1 is one embodiment of an evaporation-type crystallizer used in this invention having an "outside" circulatory system, and

Figure 2 is another embodiment of an evaporation-type crystallizer used in this invention having an "inside" circulatory system.

In Figures 1 and 2, the main crystallization process occurs in crystallizer tank 1. A body of saturated or supersaturated liquid 2, containing suspended crystalline material contained within this crystallizer tank, is constantly being circulated as more fully described hereinafter and subjected either to concentration by an evaporation process using diminished pressure and heat (illustrated in the diagrams) or else to cooling so that a deposition of crystalline material results.

Where the crystallization is effected by an evaporation process (illustrated in the drawings) the diminished pressure is preferably maintained partly by a vacuum line 3 and partly by the use of a steam ejector 4, which utilizes high pressure steam introduced at inlet 5, to sweep out vapors and gases 6, that exist above the body of liquid 2, through the top outlet of the crystallizer tank and through a venturi-type throat 7, into condenser 8. The suspension is preferably kept heated by using only a hot feed (9 in Figure 1, and 10 in Figure 2), or else by using heating elements in the various inlet and outlet pipes hereinafter enumerated. Other diminished pressure-maintaining and heat-maintaining means obviously may also be used. The vapor 6, that is swept out by the steam ejector is condensed by the use of cold condenser spray water or similar spray condensing media introduced into the barometric condenser 8, at inlet 11 and expelled through outlet 12. Alternatively a surface condenser can also be used in which case the condensed papors are taken off in a separate outlet. Such condensed vapors may be reused again if desired either as a solvent for dissolving undesired seed crystals or for dissolving raw crystalline matter.

Where the crystallization is effected by a cooling process the crystallizer tank need not be equipped with a pressure diminishing means. Therefore, the crystallizer tank shown in either Figure 1 or 2 may be closed at its

uppermost region. The cooling is effected preferably by the use of a cold inlet solution coupled with cooling means contained in the various inlet and outlet pipes hereinafter enumerated.

In the embodiment shown in Figure 1, the suspension 2 is circulated from the upper chamber of the crystallizer tank down through a conical "false bottom" 13, attached at an intermediate point of the inner walls of the tank, and into the lower chamber which has a funnel-shaped bottom. A crystal suspension throttling valve 14, varies the size of the funnel-shaped opening 15, for the purpose of regulating the rate of flow through side outlet 16 by its relationship to the main circulating flow. Sight glasses 17, permit observation of this flow through the bottom outlet thereby facilitating adjustment of the throttling valve. With the valve wide open the flow to the circulating pump will pass essentially all through the bottom outlet in view of the greater density of suspension over that of solution. As the valve is closed a greater portion of the circulating stream will emerge through the side outlet 16, and reach the pump via settling tank 18. In practice it is generally found that the valve should be maintained intermediate its full open position and its closed position, its exact position depending upon the size product crystal desired. In this manner, undesired fine crystals are continuously removed from the turbulent suspension as the crystallization process proceeds. They are redissolved in the settling tank and the solution recirculated to the main circulatory body at a rate insufficient to upset the optimum crystallizing conditions existing in the main circulatory system.

The downward flowing suspension is circulated through conduit 19, through pump 20, and then upward through conduit 21, back into the crystallizer tank 1. The pump is operated by motor 22. Other similar flow inducing devices such as a motor driven propeller blade obviously may also be used.

Into the circulatory fluid system, feed solution is introduced at inlet 9, either to make up for the evaporation losses through steam ejector 4 when an evaporation process is being used or else to make up the losses due to the intermittent opening of product crystal outlet 23. The feed solution is introduced at such rate and under such temperature conditions that the suspension will be induced to remain in a condition substantially matching the crystallizing conditions existing in the tank. Product crystals are removed from the crystallizer through product outlet 23 containing valve 24 for intermittent operation either manually or automatically.

The space beneath the conical false-bottom 11, communicates with a side outlet 16, so that the undesired fine crystals may be removed by an elutriation method, the size being determined by the rate of upward flow of the elutriating zone 25, that exists immediately underneath the conical false-bottom 13, and the walls of the crystallizer tank 1. By the term "elutriation" is meant the separation of fine particles from coarse particles by passing an upward flow of fluid through said mixture at a rate that induces the smaller size particles to be in a more upward position of the flow than the coarse particles. Separating said zones will cause a separation of the fine particles from the coarse particles. The undesired fine crystals taken off by this elutriation are deposited in one or more fine crystal settling tanks 18 (only one of which is shown) wherein the crystals settle to the bottom and the mother liquor is then returned to the main circulatory system. More than one settling tank is desired so that while one settling tank is "on stream" for the purpose of settling out undesired fine crystals the other tank or tanks containing fine crystals and mother liquor is preferably being heated to a slight extent by steam coils 26, so that small crystals will be redissolved in the mother liquor. When redissolved the tank is again placed "on stream," manually or automatically, and the liquor is thereby returned to the main suspension by conduit 27 to again take part in the crystallizing process thereby avoiding loss of solid matter to fine crystal formation. Several valves 28 (only one shown) contained in conduits 27 (also only one shown), are used to place these tanks "on" and "off stream" as the need arises. The undesired fine crystals obviously may also be dissolved in the mother liquor by other means such as by the addition of solvent to the settling tank while it is "off stream." This "off stream"-"on stream" technique avoids the undue upsetting of the crystallizing condition that would occur if only one settling tank were held "on stream" at all times.

In the embodiment shown in Figure 2, the suspension 2, is circulated upwardly through tubular conduit 31, which is located axially within the crystallizer tank 1, and held in place by several supporting members 32 (only two shown) and by a vertically adjustable bracket 33. Depending upon the needs of the process, this tubular conduit can be raised or lowered thereby regulating opening 35 by means of screwcrank 34, located outside of the crystallizer tank at the upper end of adjustable bracket 33. When the upward flowing suspension reaches the top it flows over the edges of the tubular conduit and then downward through a conical false-bottom 36, located intermediate the crystallizer tank into the lowermost funnel-shaped chamber of the tank. After passing through controllable opening 35, it again flows upwardly through axially located conduit 31, thereby causing an "inner" circulatory system. To effect the circulation, an upward directing propeller 37, axially located in conduit 31 is driven by propeller shaft 38, and motor assembly 39. Other means for effecting the circulatory system obviously may also be used without departing from the spirit and scope of this invention.

Undesired fine crystals are removed from this "inner" circulatory system by elutriating the undesired fine crystals upwardly between the conical false bottom 36, and the walls of the crystallization tank 1, and then into either of the fine crystal outlet conduits 40, depending upon which is "on stream" as more fully described below. With conduit 31 raised to allow the free flow of suspension through opening 35, the flow through fine crystal outlet 40, will be small and only very fine crystals will be carried into the settling tank 41. As conduit 31 is lowered, the proportion of circulating suspension through the fine crystal settling tank 41, increases thereby carrying more fine crystals of increasing size out of the crystal suspension. In practice, it is generally found that the tubular conduit should be maintained intermediate its lowermost position and its uppermost position, its exact position depending upon the size of product crystal desired. In this manner, undesired fine crystals are continuously removed from the turbulent suspension as the crystallization process proceeds.

The solution containing the unwanted fine crystals enters the fine crystal setting tank 41, wherein the crystals settle to the bottom while the mother liquor leaves the tank to return to the main circulating body through conduit 42. When the fine crystal settling tank contains sufficient fine crystalline matter, it is placed "off stream" by closing valve 43 either manually or automatically. The fine crystals are then redissolved preferably by heating the contents of the tank with the use of heating coils 44, contained in the base of the tank. Other means of dissolving fine crystals, such as by adding additional solvent may be employed also. When the undesired fine crystals are redissolved, the tank is again placed "on stream" by manual or automatic operation so that the saturated solution containing dissolved crystalline matter might be re-used most economically.

Produce crystalline matter is removed from the crystallizer tank by means of product outlet 45, which is opened intermittently with the use of valve 46, depending

upon the size of crystalline matter desired. This opening of valve 46 may be automatically performed to effect a totally continuous process. Use of sight glasses 47, contained in the funnel-shaped portion of the crystallizer tank enables the determination of this desired size.

The apparatus described above is used in accordance with the following procedure. A heated solution or suspension of material is introduced into the crystallizer tank at the start of the process and whenever the liquid level is deplenished beyond operability by evaporative losses or by product crystal removed by means of feed inlets 9 and 10. If the heat introduced with the solution is insufficient for evaporating the solvent from the solution, auxiliary sources of heat connected with the apparatus are used.

It is to be again noted here that the apparatus described above may be modified for a crystallization process by cooling. In such event, the solution is preferably introduced in a cooled state and subsequently further cooled by cooling means located in the inlet and outlet conduits of the apparatus or else by a cooling jacket.

The solution is caused to circulate through the "outside" or the "inside" type of circulatory system depending upon the apparatus used, the velocity being regulated for the most efficient crystallizing conditions, by means of the appropriate regulating devices shown in the drawings. Such velocity regulation is influenced by the following factors; namely, strong agitation aggravates the formation of excess nuclei while weak agitation allows an excessive accumulation of crystals to settle out on the bottom thereby obstructing the circulation of suspension.

As the suspension circulates, crystals are either deposited out of solution, or are in the growing stage in which more crystalline matter deposits upon the surface of existing crystals. For the purpose of definition the following terms are used in referring to the various crystals existing in the suspension; namely crystal nuclei are those bodies which have just been deposited out of solution, seed or fine crystal are either crystal nuclei or crystal nuclei having additional matter deposited upon their surface by reason of their relatively short existence in the suspension, and product crystals are those crystals which have grown to the size desired as the end product. In stages of growth the above crystal definitions fall into the following order: First, there comes into being a crystal nucleus. It then grows until it is a fine crystal. If this crystal is allowed to remain in the suspension and grow still further it is termed a seed crystal. This seed crystal eventually becomes a product crystal, the end result of the process.

During the crystal deposition undesired fine crystals are constantly removed by an elutriating stream located below the conical false-bottom contained in the crystallizer tank. These crystals are transported to a fine crystal settling tank where they settle out while the mother liquor is returned to the main circulatory system. The tank, when sufficiently filled with deposited fine crystals is preferably placed "off stream" and then the settled crystals are redissolved, either by the use of heat, by the use of additional solvent, or other similar solvating means. The resulting solution is then returned to the main circulating stream so that there is an efficient use of all crystalline matter.

As the crystallization process proceeds, the product crystals that are produced, are removed intermittently either manually or automatically by opening the product outlet. The product crystals are filtered off and the remaining suspension may either be discarded or returned to the crystallizer tank. An explanation for the success of this invention follows hereinafter, but it should be noted that this discussion is only a discussion of what is believed to be correct. Other more plausible explanations may be later discovered and therefore this invention should not be limited by the herein offered explanation.

According to an article in Chemical Engineer's Handbook, third edition, pages 1058 and 1059 (1950), McGraw-Hill Book Co., New York, N.Y., the size of product crystals from a continuous crystallization appears to be dependent upon at least the following four principles:

(1) The rate of crystal growth under turbulent conditions is directly proportional to the supersaturation of the solution.

(2) The rate of crystal growth is proportional to the area of crystal surface exposed to the solution.

(3) Each face of a crystal is characterized by a rate of growth coefficient which determines the geometric shape of the crystal. Corollaries of this are that the geometric shape of a crystal essentially remains unchanged as the crystal grows and that the interfacial angles of a crystal remain constant.

(4) The size of each crystal is determined by the rate and time of growth.

From these four principles, one can derive from mathematical calculations the cumulative weight of crystals contained in a suspension in terms of its seed rate and linear size; namely,

$$W \sim nL^4$$

or

$$W = anL^4$$

where:

W=cumulative weight
a=constant
n=seed rate
L=linear size of a crystal

From this relationship one can see that the cumulative weight of crystals up to a given size varies as the fourth power of the crystal size. Using this fourth power relationship, the cumulative weight of relatively small seed crystals in a turbulent suspension is found to be generally negligible as compared to the weight of the product crystals. For example, crystals smaller than half size constitute only $\frac{1}{2}^4$ or $\frac{1}{16}$ of the total weight of crystals in suspension. It can, therefore, be seen that heretofore used commercial processes were too concerned with selective separation rather than other factors. The minor proportion of undersized crystals is actually such a minor proportion of the total that they can generally be disregarded. Items of more importance however would appear to reside in the "n," the seed rate of the relationship. The seed rate n must be controlled to realize the desired crystal size L in the weight of product W; for example, if n is very large for a given weight of product the size L will be comparatively small, whereas a low seed rate n will yield comparatively larger crystals for the same weight of product. Therefore, complete size control in a crystallizer cannot be effected without controlling the seed rate n and if no means are provided for doing this the average crystal size L will correspond to the natural seed rate of the system.

In accordance with this invention it has been found that in turbulent suspension type crystallizations removing undesired fine crystals substantially as fast as they are formed effects the seed rate, n, in such manner that the size L is proportionally greater than heretofore obtained. The only patent that discloses such a technique is U.S. 1,845,742 but in view of the discussion given previously of the manner of operation used, it can be seen that commercial exploitation of this patent was impossible. The process herein disclosed is, however, readily adaptable to commercial operation in view of its novel mode of operation and its novel apparatus.

Among the crystals which may be readily produced by the herein disclosed process and apparatus the following are typical: Ammonium nitrate, ammonium sulfate, sodium sulfate, sodium chloride, potassium sulfate, and other similar-type crystalline-producing compounds. However,

the invention is obviously not to be limited by a recitation of crystalline-producing material for its breadth rests upon the method and apparatus rather than the specific crystal being produced.

It is to be noted that in the operation of this invention the control over the seed rate may be varied. Should extremely large crystals be desired the seed rate should be kept at a low rate by increasing the rate of destruction of fine crystals. The throttling valve of Figure 1 or the suspended conduit of Figure 2 in this case should be kept so that its opening is small. If small product crystals are desired the fine crystal destroying rate should be kept at a minimum. The opening of the crystal growth inducing circuit (#15 of Figure 1 and 35 of Figure 2) should be large.

While a detailed description of the invention has been provided, it is realized that those skilled in the art may make modifications in and adaptations of the process and apparatus described above without departing from the spirit and scope of this invention. It is, therefore, to be specifically understood that such obvious modifications are considered within the scope of the herein described process and apparatus.

This application is a division of application Serial No. 414,192 filed March 4, 1954, now Patent No. 2,827,366.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. In a crystallization process occurring in a single, vertical reaction vessel wherein there is a suspension of product size and fine crystals normally mixed together in a turbulent solution, a method of eliminating excessive fine crystals from said mixed suspension comprising the steps of establishing an internal quiescent zone within said suspension, said zone falling within the intermediate region of the vessel, directing said fine crystals out of the mixed suspension towards said quiescent zone, withdrawing said fine crystals together with solution from the zone, eliminating the withdrawn fine crystals from the solution and returning the solution, substantially free of fine crystals, to the main body of the suspension.

2. In a crystallization process occurring in a single vertical reaction vessel wherein there is a suspension of product size and fine crystals normally mixed together in a turbulent solution, a method of eliminating excessive fine crystals from said mixed suspension comprising the steps of establishing an internal quiescent zone within said suspension, said zone falling within the intermediate region of the vessel, establishing a distinct current within said suspension, directing said fine crystals out of the mixed suspension towards said quiescent zone, utilizing said current as a conveyor, withdrawing said fine crystals together with solution from the zone, eliminating the withdrawn fine crystals from the solution, returning clear solution substantially free of fine crystals to the main body of the suspension and dissolving said fines and returning the resulting solution to the main body of the suspension.

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