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W. C. SAEMAN
CRYSTALLIZATION

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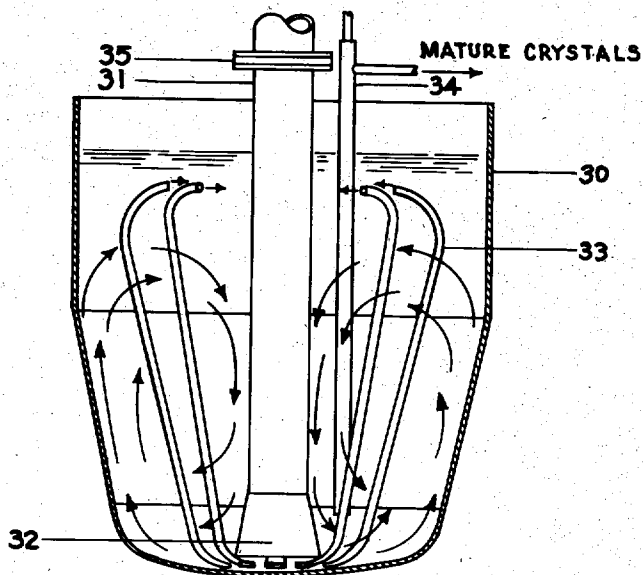


Fig. 2

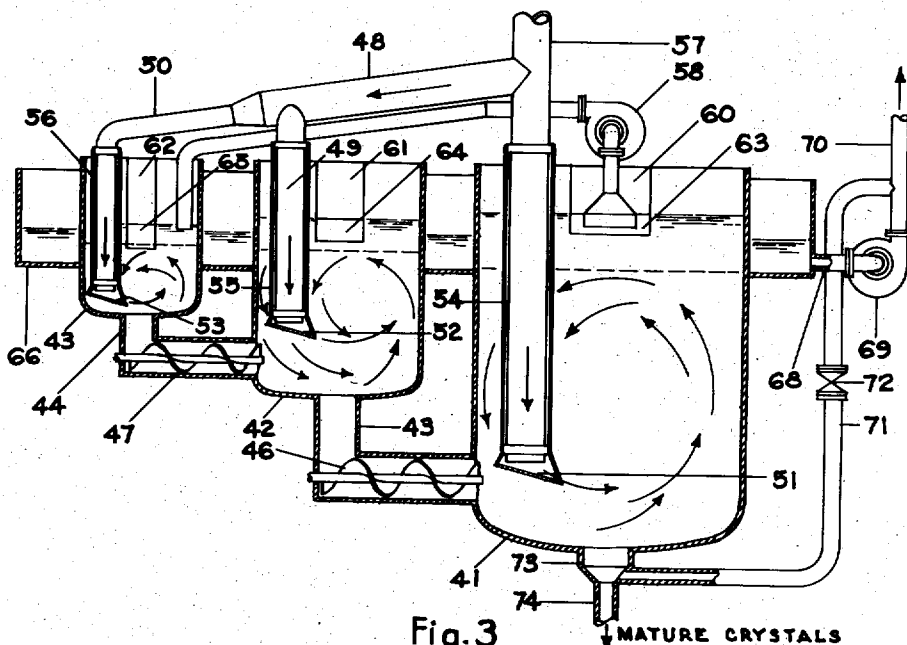


Fig. 3

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CRYSTALLIZATION

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6 Claims. (Cl. 23—302)

(Granted under the act of March 3, 1883, as
amended April 30, 1928; 370 O. G. 757)

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The invention herein described may be manufactured and used by or for the Government for governmental purposes without payment to me of any royalty thereon.

This invention relates to improvements in methods and apparatus for the crystallization of substances characterized by rapid crystal growth. In one particular application it relates to improvements in methods and apparatus for the crystallization of ammonium nitrate.

This application is a continuation-in-part of my copending application Serial No. 654,490 filed March 14, 1946, now abandoned.

It has been customary in the art to accomplish continuous crystallization by suspending a body of crystals in a rising current of liquid generated by introducing a stream of supersaturated solution into a crystallizing vessel near the bottom thereof. As the supersaturated solution rises in contact with the body of crystals solute is deposited on the crystals and the resulting desupersaturated solution is withdrawn from an upper part of the vessel. The introduction of a stream of supersaturated solution near the bottom of a crystallizing vessel has been employed to impart a swirling motion to the suspension so that the crystals pass repeatedly through the solution as it is desupersaturated and growth is thus distributed evenly among the crystals in suspension. It is customary to control the rate of upward flow of solution through the crystallizing vessel to allow the larger crystals to settle to the bottom from whence they are removed, and to prevent the smaller crystals from being carried out of the top of the vessel by the overflow.

The known methods for continuous crystallization may be divided into two broad classes, namely, those in which new seed crystals are supplied from an outside source and those in which fresh nuclei are generated and grown along with the maturing crystals. United States patents covering processes of the first class are those of Isaachsen, Nos. 1,478,337 and 1,693,786 and of Howard, No. 1,559,703. Jeremiassen's U. S. Patents Nos. 1,704,611; 1,860,741; 2,042,661; 2,164,111; 2,164,112; and 2,375,922 are directed to the second class although several of these patents describe both types of operation. However, the primary object of most known methods is to grow coarse crystals of desired size from seed crystals and little attention has been directed to the generation and control of growth of seed crystals.

In continuous processes crystals in suspension remain mobile at all times and numerous small fragments may be broken off by attrition and collision to serve as nuclei for new crystals. Other fresh nuclei may be produced in supersaturated solution because of the inoculating

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effect of existing crystals. The number of nuclei from both of these sources can be regulated to some degree by varying the degree of agitation, the density of crystal suspension in the crystallizing vessel, and the degree of supersaturation. If excess nuclei are produced they may be separated from the suspension and are usually dissolved and recycled. If a sufficient number of new nuclei is not generated seed crystals must be supplied from an outside source.

In order to maintain efficient, continuous operation of a crystallizer producing coarse granules, it is essential that only as many nuclei be retained as are required to equal the number of mature crystals withdrawn since each of the retained nuclei must be developed into a fully grown crystal.

The necessary balance of growth between large and small crystals has been accomplished in the prior art in the following three ways:

1. The small crystals remain incorporated in a suspension of larger crystals at all times and thereby share with them the conditions favoring crystal growth.

2. The rate of desupersaturation of the supersaturated solution entering the suspension is sufficiently slow that crystal growth is distributed widely throughout the suspension and therefore affects both large and small crystals even if the large and small crystals are segregated at various levels in the crystallizer.

3. The smaller crystals are caused to circulate through the supersaturated liquor circuit and therefore have an advantage in opportunity for growth over the larger crystals which are retained in the crystallization vessel at all times.

These known methods for the generation and development of nuclei are adequate for the crystallization of substances characterized by slow rate of crystal growth, as such crystals can be produced in desired size and quality without very close control of the various factors involved. However, when it is desired to produce strong, smooth, coarse crystals of a substance characterized by rapid crystal growth, such as ammonium nitrate, sodium thiosulfate, or calcium nitrate, in large crystallizing vessels and at high production rate the methods of the prior art are very unsatisfactory.

The mere use of large crystallizing vessels introduces problems into the crystallization of such substances. Because of the rapid crystal growth, only those crystals in the immediate vicinity of the point of introduction of supersaturated solution grow. All available solute is deposited upon crystals in this location. In addition there is a tendency of crystals in suspension in a large vessel to accumulate in regions of greater crystal concentration thus leaving regions of lesser crystal concentration or

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"wells" extending upward through the solution. Since the incoming fluid has a tendency to follow the line of least resistance, it tends to flow upward through such regions of low crystal concentration and crystals in these regions grow at the expense of other crystals. Isaachsen in U. S. Patent No. 1,573,716 has proposed the use of various diffusion elements in the path of the incoming solution of such nature that the resistance to flow of the solution through the element is sufficiently in excess of the resistance to flow through the suspension so that the effect of minor variation in crystal density is minimized. In conjunction with these diffusion elements deflectors may also be used to impart horizontal velocity components to the solution which will sweep any static bed of crystals that tends to settle out into the incipient wells in the suspension, thereby filling them with crystals and counteracting the initial condition which tended to form the wells.

In addition, Jeremiassen in U. S. Patent No. 2,164,111 has proposed the use of specific formation of aggregate or crystals in the place of fixed elements to serve as diffusion elements required to obtain uniform distribution of solution.

While the present invention is applicable to crystallization generally, and is especially advantageous in the crystallization of all substances both organic and inorganic which are characterized by rapid crystal growth, it will be described with reference to the crystallization of ammonium nitrate, a material which has been crystallized with difficulty in the past.

When crystallization of ammonium nitrate is attempted by circulating nuclei through an exterior supersaturated liquor circuit and the introduction of the resulting larger crystals into the crystallization vessel proper as seed crystals, the crystals produced are weak, rough, and inferior to those developed and grown in the crystallizer only. As is explained in detail later, the degree of supersaturation necessary to obtain maximum production of finished crystals is such as to cause the small seed crystals to grow too fast while in the exterior circuit and as a result weak, intermediate-size crystals are produced. It is, therefore, apparent that the known methods are not adequate to produce strong, coarse crystals of ammonium nitrate at an economical production rate. For most commercial purposes it is necessary that crystals of ammonium nitrate be strong, coarse and that the production rate be high enough to make the process economical. By the methods of the prior art processes it has been possible to obtain these characteristics when working with crystals such as ammonium sulfate or other substance characterized by slow crystal growth. With ammonium nitrate or other material characterized by very rapid crystal growth, it has been necessary to sacrifice one or more of the desired characteristics in order to obtain the others. Strength of crystals and high production rate can be obtained but the crystals produced are too fine for fertilizer use or for many other commercial uses. Likewise, large crystals can be made at high production rate but they will be rough and weak; and strong, large crystals can be produced only at a low production rate.

It is an object of this invention to provide a method for the rapid production of strong, smooth, coarse crystals of a material characterized by rapid crystal growth.

Another object is to provide a method for

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positive regulating of the growth of crystals at all stages from nuclei to maturity.

Another object is to provide a method for preventing irregular distribution of crystals in a growing zone.

Another object is to provide a method for producing ammonium nitrate crystals suitable for fertilizer use at high production rate.

Still another object is to provide an apparatus for the production of crystals adapted to positively control the growth of crystals at all stages.

Another object is to provide an apparatus for producing ammonium nitrate crystals suitable for fertilizer use at high production rate.

Other objects and advantages will become apparent as this disclosure proceeds.

I have now found that these objects may be easily attained in apparatus embodying principles of my invention by continuously introducing a stream of supersaturated solution of the material to be crystallized into a lower part of a crystallizing vessel; directing said stream at predetermined or controlled velocity to maintain two zones in the resulting body of liquid in the crystallizing vessel, namely, a lower crystallizing zone wherein the liquid is maintained in substantially streamlined, substantially vertical rotation and an upper relatively quiescent zone; introducing seed crystals into said lower crystallizing zone; producing fine crystals in said crystallizing zone by attrition of coarser crystals; withdrawing mature crystals from a lower part of said crystallizing zone; withdrawing said fine crystals produced by attrition into said upper, relatively quiescent zone; contacting said fine crystals with supersaturated solution of the material being crystallized until their size is substantially increased; controlling the degree of supersaturation of said last mentioned supersaturated solution and introducing the resulting crystals of increased size into said crystallizing zone as seed crystals.

The apparatus of my invention comprises in combination a crystallizing vessel; means for continuously introducing a stream of supersaturated solution at predetermined or controlled velocity into a lower part of said vessel; means for directing the entering stream of supersaturated solution operable in conjunction with said means for introducing supersaturated solution to maintain substantially vertical rotation of liquid in substantially streamlined flow in the lower portion of the crystallizing vessel, to maintain a zone of relatively quiescent liquid in the crystallizing vessel above the liquid in vertical rotation and to provide for continuous transfer of liquid from the rotating liquid to the relatively quiescent liquid; means for introducing supersaturated liquid at controlled rate into said upper quiescent zone and means for withdrawing mature crystals from a lower part of the crystallizing vessel.

The accompanying drawings show diagrammatically three modifications of apparatus embodying principles of my invention and in which my novel process may be carried out. Figure 1 is a vertical section through a crystallizing vessel and shows a vacuum evaporator and other accessory equipment which may be used therewith; Figure 2 is a vertical section through a crystallizing vessel of different design and Figure 3 is a vertical section through three crystallizing vessels connected in series.

Referring to Figure 1, reference numeral 10

designates a crystallizing vessel. A barometric leg 11, attached to and communicating with vacuum evaporator 12, enters vessel 10 substantially vertically and extends to a location near the bottom of vessel 10, where it ends in tapered portion 13. Directing means 14 is disposed adjacent to the tapered end 13 of the barometric leg and in combination with the curved walls of vessel 10 is adapted to induce streamlined flow of liquid in the lower part of crystallizing vessel 10. A weir 15 is disposed in an upper part of vessel 10 and is adapted to regulate liquid level in the crystallizing vessel. A line 16 is attached to and communicates with that part of vessel 10 behind the weir 15, and is adapted to receive overflow liquid and to conduct the same to pump 17, from whence it may be pumped to evaporator 12 via line 18. Means for removing mature crystals, shown as air lift 19, is disposed in vessel 10 and is adapted to remove a slurry of mature crystals from the lower part of the vessel and to discharge the slurry through line 20. A movable sleeve 21 containing openings 22 is disposed to surround a portion of barometric leg 11 in an upper part of vessel 10 and is adapted to be moved to bring openings 22 into coincidence with corresponding openings 23 in barometric leg 11.

Vessel 10 may be circular in cross section or rectangular if of very large capacity. In the latter case the tapered end 13 of the barometric leg is drawn out in fishtail shape along the transverse axis of the vessel, while deflecting means 14 is correspondingly lengthened. Figure 2 shows an equivalent form of apparatus. In this embodiment of my invention a barometric leg 31 is constructed without openings in the upper part of crystallizing vessel 30. This leg 31 ends in a flared portion 32 adapted, in combination with the curved bottom of vessel 30 to induce streamlined flow in liquid in the lower portion of vessel 30. A plurality of curved pipes 33 are disposed with their lower ends adjacent to flared portion 32 and extend into an upper part of vessel 30. These pipes are adapted to conduct liquid from a location near the bottom of vessel 30 and adjacent to flared portion 32 to an upper part of vessel 30, and to prevent contact of such liquid with liquid and crystals in medial portions of vessel 30. Means 34 for removing mature crystals is disposed in vessel 30. Joint 35 is disposed in leg 31 adapted to be replaced with other joints of similar construction to regulate length of leg 31.

Figure 3 illustrates a multiple stage apparatus embodying principles of my invention. A plurality of crystallizing vessels 41, 42, 43 are arranged in a series characterized by diminishing size. Each crystallizing vessel is connected to and communicates with an adjacent vessel of the series via a line, as 75, 44. Means 46, 47 for transferring crystals from a smaller to the next larger crystallizing vessel of the series are singly disposed in lines 75, 44. A barometric leg 57 is disposed substantially vertically in the largest vessel 41 of the series with its lower end adjacent to line 75. A line 48 is attached to and communicates with barometric leg 57 and with lines 49, 50 singly disposed substantially vertically in each smaller vessel of the series, near one side of the smallest vessel 43 and adjacent to line 44 in intermediate vessel 42. Deflecting means 51, 52, 53 are disposed adjacent to the lower ends of barometric leg 57 and lines 49 and 50. Adjustable means 54, 55, 56 are disposed to support

deflecting means 51, 52, 53 at a selected distance and angle from the lower end of leg 47 and lines 49 and 50.

A means 58 is provided for transferring liquid and fine crystals from an upper part of the largest vessel 41 of the series to an upper part of the smallest vessel 43.

Each crystallizing vessel of the series has an overflow slot 60, 61, 62. Adjustable weirs 63, 64, 65 are disposed to cover the lower portion of slots 60, 61 and 62 and are adapted to control the liquid level in each vessel at progressively lower level from the largest vessel of the series to the smallest vessel.

A trough 66 is disposed adjacent to all crystallizing vessels of the series and is adapted to receive liquid and fine crystals overflowing from each through slots 60, 61, 62. A line 68 communicates with the interior of trough 66 and is adapted to withdraw liquid from the interior of the trough and to conduct it via pump 69 and line 70 to apparatus (not shown) for heating and supersaturating. A line 71 containing a regulating valve 72 branches off line 70 and is adapted to conduct a portion of liquid flowing through line 70 to a crystal trap 73 communicating with the interior of vessel 41 at a substantially central location in the bottom thereof. A line 74 is attached to and communicates with crystal trap 73 and is adapted to conduct a slurry of mature crystals to a filter, centrifuge or other means for separating crystals from liquid (not shown).

Operation

I prefer to begin operation, when apparatus comprising a single crystallizing vessel such as that shown in Fig. 1 is used, by introducing supersaturated solution through barometric leg 11 and introducing sufficient seed crystals, in any manner, to start crystallization.

The supersaturated solution is introduced at a controlled or predetermined velocity and rate of flow. Such solution enters from tapered end 13 as a jet. This jet is deflected by means 14 and the walls of vessel 10 to cause the liquid and crystals suspended therein to form two zones in vessel 10, namely, a lower zone wherein the liquid and crystals are maintained in substantially vertical streamlined rotation at a velocity of about 3 to 10 times that at which such crystals settle in such liquid, and an upper relatively quiescent zone. As crystals rotate with the solution in the lower zone fine particles are broken off by attrition. The shape of the walls of vessel 10 and deflecting means 14 are such as to maintain substantially streamlined flow in that part of the suspension which is rotating. It is, of course, impracticable to exclude all turbulence from such rotation but no excessive turbulence should be permitted as this would cause the formation of excessive numbers of fine crystal particles produced by attrition.

As the introduction of supersaturated solution continues there is continual transfer of liquid from the lower zone of rotation to the upper, relatively quiescent zone. This transfer of liquid carries the fine crystal particles produced by attrition into the relatively quiescent upper zone. Here additional supersaturated solution is added via openings 22 and 23 in sleeve 21 and leg 11. Rotation of sleeve 21 is employed to control the degree of supersaturation of the upper quiescent zone of liquid. The small crystal particles thus grow under controlled conditions until their size is sufficient to cause them to sink under the in-

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fluence of gravity until they are caught by the rotating liquid in the lower zone and quickly grown to mature crystals.

Excess liquid from the upper quiescent zone overflows weir 15 and is carried via line 16, pump 17 and line 18 to evaporator 12 where it is concentrated and reintroduced into vessel 10 via leg 11. A slurry of mature crystals is continuously withdrawn from vessel 10 via a conventional air lift 19 and is discharged via line 20.

A similar method of operation is used with the apparatus shown in Fig. 2. Here the flared end 32 and curved bottom of vessel 30 deflect the entering liquid to cause substantially vertical rotation of liquid in a lower zone overlaid with liquid in a relatively quiescent upper zone. The curved pipes 33 are adapted to receive a portion of the supersaturated liquid entering via leg 31 and to conduct the same to the upper quiescent zone of liquid. Control of the degree of supersaturation is achieved by varying the number, size and position of pipes 33. In this figure a lengthening joint 35 is shown inserted in leg 31 and illustrates one convenient means for controlling the velocity of the stream of supersaturated solution entering the vessel 30.

Fig. 3 illustrates apparatus for multiple stage operation. Supersaturated solution is introduced through barometric leg 57 and lines 48, 49 and 50 into vessels 41, 42 and 43. Adjustable means 54, 55 and 56 are suitably operated to bring deflecting means 51, 52 and 53 to the distance from the lower end of leg 57 and lines 49 and 50 required to impart sufficient velocity to liquid entering each evaporating vessel of the series to maintain rotation of the major portion of the liquid at a velocity of about 3 to 10 times that with which crystals settle in such liquid. After crystallization begins fine crystals produced by attrition move with upflow of liquid into an upper relatively quiescent zone in each vessel. From the upper zone of the largest vessel 41 liquid containing these fine crystals is transferred to the smallest vessel 43 and there the crystals grow in liquid of controlled degree of supersaturation. When these grow to sufficient size they sink into line 44 and are transferred by means 47, contra to fluid flow, into vessel 42. Here the crystals circulate in contact with liquid of a controlled degree of supersaturation and increase in size. When of a size determined by the velocity of rotation in vessel 42 and the velocity of flow from vessel 41 to 42 via line 75 the crystals sink into line 75 and are transferred as seed crystals to vessel 41 by means 46. The seed crystals then circulate in vessel 41 until mature. Mature crystals sink into salt trap 73 and are withdrawn as a slurry via line 74.

From the upper quiescent zone in each vessel liquid overflows weirs 63, 64 and 65 into trough 66 and is withdrawn therefrom via line 68, pump 69 and line 70 to an evaporator (not shown) or any other equipment desired. A portion of the liquid flowing through line 70 is withdrawn via line 71 containing a regulating valve 72 and is introduced into salt trap 73 thus causing an upward flow of liquid in trap 73 and furnishing a further means of controlling the size of mature crystals.

In order to maintain in a crystallizing vessel two zones of the characteristics described, it is necessary that the velocity of the incoming solution be controlled or predetermined so that the stream imparts kinetic energy to the contents of the vessel at a rate not less than that at which potential energy is lost when such introduction

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of liquid is suddenly stopped. The minimum energy input will vary with the size and shape of crystals produced, the difference in density of crystals and solution, the viscosity of the solution and other smaller effects. The minimum requirements may be approximated from experimental measurements of the density of suspension for a given rate of flow through the suspension as is shown by the following example.

Example I

Using ammonium nitrate granules of 8- to 10-mesh screen size (Tyler standard) at room temperature (20°-25° C.), it was found that 30 pounds of crystals per cubic foot could be suspended in a current of saturated solution flowing at the rate of 0.06 cubic feet per second per square foot cross sectional area. This weight of crystals per cubic foot of suspension became less as the rate of circulation increased or as the particle size decreased, but the value specified above serves as a typical example.

The apparent density of the crystals was 100 pounds per cubic foot. The void space between the crystals was therefore

$$\frac{100-30}{100}=0.7 \text{ cubic foot}$$

The density of crystals in a static bed was found to be 60 pounds per cubic foot. By a calculation similar to that above the void space was therefore found to be 0.4 cubic foot. In going from the dynamic state—in which 30 pounds per cubic foot of crystals are held in suspension—to the static state, 0.3 cubic foot of solution must therefore diffuse from a given mass of crystals.

In a suspension, crystals under the influence of gravity tend to settle downward causing the solution to diffuse upward. After a sudden interruption of the flow of solution to a suspension, transition of crystals from the dynamic to the static condition will start at the bottom, causing solution to diffuse out of the lowermost masses of crystals. This diffusing solution keeps the crystals above temporarily in suspension, and the transfer from the dynamic to the static state is therefore restricted to the lower zone of the dynamic part of the suspension. Experimental observation indicates that conditions in the upper part of the suspension remain essentially constant down to the zone in which crystals transfer from the dynamic to the static state. In the given example crystals will therefore settle out at such a rate that the supply of solution resulting from diffusion will produce an upward flow of 0.06 cubic foot per second per square foot of area. Since 0.3 cubic foot diffuses from 1 cubic foot of suspension, the rate at which the suspension settles out per square foot area is

$$\frac{0.06}{0.3}=0.2 \text{ cubic foot per second}$$

The density of saturated ammonium nitrate solution at 20°-25° C. is 82 pounds per cubic foot or 18 pounds less than that of crystals. Therefore, the apparent weight of 30 pounds of crystals in suspension is

$$\frac{30}{100} \times 18 = 5.4 \text{ pounds}$$

The total potential energy of a given suspension may then be calculated by taking the product of the apparent weight per cubic foot of suspension times the volume of the suspension times the difference in the position of the center of gravity of the crystals in suspension and after they have

been allowed to settle out. Assuming a suspension 10 feet deep, the center of gravity would be 5 feet above the bottom in the dynamic state and 2.5 feet above the bottom with the crystals settled into a static bed giving a difference of 2.5 feet. The potential energy per square foot would therefore be $2.5 \times 10 \times 5.4 = 135$ foot-pounds.

If the rate of collapse is 0.2 cubic foot per second, the total time of collapse is 50 seconds and the rate of decrease in potential energy, which must be balanced by an equal rate of kinetic energy input, is

$$\frac{135}{50} = 2.7 \text{ foot-pounds per second}$$

This amount of power incorporated in 0.06 cubic foot of solution per second (5 pounds) requires a difference in pressure of

$$\frac{2.7}{5} = 0.54 \text{ foot head}$$

or an initial velocity of about 6 feet per second ($6^2 = 2 \times 0.54 \times g$). The peripheral velocity of the rotating suspension will be considerably less than this depending on wall friction and other retarding influences. A velocity of about 1 to 3 feet per second was observed in an experimental demonstration unit, whereas the relative velocity between crystals and solution is of the order of 0.1 to 0.3 foot per second.

I have found that a principal factor affecting the strength and smoothness of the crystals produced is the per cent rate of growth, which is defined for this disclosure and claims as

per cent of rate of growth =

$$\frac{\text{hourly production rate, lb./hr.}}{\text{total effective suspension, lb.}} \times 100$$

I have found that ammonium nitrate crystals grown at a 10 to 12 per cent rate of growth were dense, strong and had a smooth surface, whereas those grown at a 15 per cent rate of growth were of poor quality. In the present process the rate of growth may be controlled by varying either the amount of crystals in suspension or the production rate.

With the apparatus and conditions shown and described herein an adequate supply of seed crystals averaging about 0.1 cubic millimeter in size is produced by attrition. I have found that the use of seed crystals produced by attrition is another major factor leading to the formation of dense, strong smooth crystals. The production capacity of apparatus for crystallizing ammonium nitrate is about 2 to 4 pounds per hour per cubic foot of suspension.

Factors affecting the production rate are the degree of supersaturation of the solution, the density of the crystal suspension and the volume of the effective zone of growth. By operating according to the method described above it is possible to use a much higher degree of supersaturation than has been feasible heretofore. In the present type of operation ammonium nitrate solutions of from 0.003 to 0.10 pound per gallon supersaturation may be used. Rotation of a zone of growing crystals distributes the supersaturated liquid throughout a large volume and dense suspensions of growing crystals may be used.

The temperature of crystallization is not critical from the standpoint of operation; however, since ammonium nitrate forms one type of crystal at temperatures between -0.4° and 90.1° F. and another type between 90.1 and 183.6° F., I prefer to

crystallize this material at about room temperature. For best operation the temperature of crystallization and room temperature should be approximately the same in order to minimize uncontrollable heat transfer between the room and apparatus, but operation has been carried on using an insulated crystallization vessel which gave excellent results when the difference between crystallizer temperature and that of the room was 20 to 30° F.

Operation according to the proposed invention can be briefly summarized as follows. The major portion of the suspension is caused to rotate at an average velocity of about 1 to 3 feet per second, the velocity being least at the center of rotation and increasing progressively as the distance from the center becomes greater. The shape of the container is so designed as to allow the free rotation of the suspension. Since the maximum velocity at which crystals settle out under the force of gravity is less than 0.3 feet per second, this rotational velocity is sufficiently in excess of the settling rate to sweep crystals along with it. The rotation is maintained at the proposed velocity by introducing a stream of solution tangentially into the rotating body at an approximate calculated jet velocity of 6 to 10 feet per second. This jet is distributed uniformly over the bottom of the crystallizer container in one or more steps to sweep along any crystals which tend to settle from the suspension. Since the solution and crystals rotate concurrently, the relative velocity between the two remains small and permits the maintenance of a relatively dense suspension. Efficient utilization of the entire suspension is enhanced by a relatively high rate of rotation, while the maximum density of suspension is obtained at low rates of rotation. In actual practice a compromise between these two factors is involved, giving a speed of rotation at which a maximum production rate is obtained. This corresponds approximately to the conditions given above.

Example II

Ammonium nitrate was crystallized without use of the rapidly rotating zone of crystal growth described above. A tilted plate similar to deflecting means 51 in Fig. 3 was then installed and crystallization was continued with the growing zone of crystal growth rotating substantially vertically in substantially streamlined flow at an average velocity of from 1 to 3 feet per second and overlaid by liquid in an upper quiescent zone.

The following comparable results were obtained:

	Without rotation	Rotating zone
Duration of test	48 hr.	48 hr.
Crystallization temperature, $^\circ$ F.	80-82	78-81
Rate of recirculation of solution, gal./min.	90-110	90.
Initial supersaturation, lb./gal.	.007	.007.
Average rate of production of crystals, lb./hr.	44	40-20.
Weight of crystals in suspension, lb.	500-120	500-150.
Screen analysis of product, per cent:		
+8 mesh	19	45.
-8 to +12 mesh	37	39.
-12 to +20 mesh	27	12.
-20 to +35 mesh	13	4.
-35 mesh	4	0.
Quality of product crystals	Rough, weak, and friable.	Dense, smooth, and strong.

Steady state operation was not obtained in either case. In each case the weight of crystals in suspension continually decreased as operation progressed, from 500 pounds to 120 pounds and

150 pounds, respectively. The principal advantage gained was in the improved quality and size of crystals produced in the rotating zone.

Example III

Operation was continued as described in Example II with a rotating zone of crystal growth but with the addition of supersaturated solution at a controlled rate of about 10 gallons per minute to the upper quiescent zone. Fine crystal particles produced by attrition and present in this upper zone were thus grown at controlled rate until large enough to sink under the influence of gravity until caught by the rotating suspension of crystals in the lower zone. Steady state operation and high production rate were obtained without sacrifice of crystal size and quality.

Introduction of supersaturated solution into the upper quiescent zone was discontinued. Operation with a rotating zone was continued as a check on the effect of introducing supersaturated solution into the upper quiescent zone. The following comparable results were obtained:

	With introduction of supersaturated solution	Without introduction of supersaturated solution
Duration of test, hr.	24	8
Temperature of crystallization, °F.	97	97
Weight of crystals in suspension, lb.	400-550	500-220
Recirculation of solution, gal./min.	105	100
Initial supersaturation, lb./gal.	0.008	0.009
Average production rate, lb./hr.	52	52
Screen analysis of product, per cent:		
+8 mesh	10	2
-8 to +12 mesh	64	8
-12 to +20 mesh	26	52
-20 to +35 mesh	0	20
-35 mesh	0	18

When the introduction of supersaturated solution into the upper quiescent zone was discontinued the product contained an excessive proportion of fine crystals and the weight of crystals in suspension decreased so rapidly as to indicate that a high production rate could not be maintained.

It will be obvious to those skilled in the art of crystallization that many modifications may be made in the apparatus and process shown and described without departing from the spirit and scope of this invention, which is limited only by the subtended claims.

Having described my invention and explained its operation, I claim:

1. A process for crystallizing a material characterized by rapid rate of crystal growth which comprises withdrawing solution of such material from the top of such solution contained in a crystallizing vessel; circulating the withdrawn solution through an evaporator; therein concentrating the solution to a selected degree of supersaturation; continuously introducing a stream of the resulting supersaturated solution into a lower part of said crystallizing vessel containing a suspension of crystals of said material in supersaturated solution thereof; directing said stream and controlling its velocity to maintain two zones in the resulting rising suspension of crystals, namely, a lower zone of crystal growth wherein a suspension of relatively coarser growing crystals is maintained in continuous rapid, substantially vertical streamlined rotation by kinetic energy imparted by said stream, and an upper, relatively quiescent zone containing a suspension of finer crystals; transferring fine crystals from said lower zone to said

upper zone by upward flow of solution; continuously introducing a controlled stream of supersaturated solution of said material into said upper zone; therein contacting said fine crystals with resulting supersaturated solution of said material of a controlled degree of supersaturation until their size is substantially increased; introducing the resulting crystals of increased size into said lower zone as seed crystals; and withdrawing strong mature crystals from a lower portion of said lower zone.

2. A process for crystallizing a material characterized by rapid rate of crystal growth which comprises withdrawing solution of such material from the top of such solution contained in a crystallizing vessel; circulating the withdrawn solution through an evaporator; therein concentrating the solution to a selected degree of supersaturation; continuously introducing a stream of the resulting supersaturated solution into a lower part of said crystallizing vessel containing a suspension of crystals of said material in supersaturated solution thereof; directing said stream and controlling its velocity to maintain two zones in the resulting rising suspension of crystals, namely, a lower zone of crystal growth wherein a suspension of relatively coarser growing crystals is maintained in continuous rapid, substantially vertical streamlined rotation by kinetic energy imparted by said stream, and an upper, relatively quiescent zone containing a suspension of finer crystals; transferring fine crystals from said lower zone to said upper zone by upward flow of solution; withdrawing said fine crystals and introducing them into a secondary crystallization zone; therein contacting said fine crystals with supersaturated solution of said material of a controlled degree of supersaturation until their size is substantially increased; introducing the resulting crystals of increased size into said lower zone as seed crystals; and withdrawing strong mature crystals from a lower portion of said lower zone.

3. A process for crystallizing a material characterized by rapid rate of crystal growth which comprises withdrawing solution of such material from the top of such solution contained in a crystallizing vessel; circulating the withdrawn solution through an evaporator; therein concentrating the solution to a selected degree of supersaturation; continuously introducing a stream of the resulting supersaturated solution into a lower part of said crystallizing vessel containing a suspension of crystals of said material in supersaturated solution thereof; directing said stream and controlling its velocity to maintain two zones in the resulting rising suspension of crystals, namely, a lower zone of crystal growth wherein a suspension of relatively coarser growing crystals is maintained in continuous rapid, substantially vertical streamlined rotation by kinetic energy imparted by said stream, and an upper, relatively quiescent zone containing a suspension of finer crystals; transferring fine crystals from said lower zone to said upper zone by upward flow of solution; withdrawing said fine crystals from said upper zone; introducing the withdrawn fine crystals into the first of a series of secondary crystallizing vessels; therein contacting said fine crystals with supersaturated solution of said material of a controlled degree of supersaturation until their size is substantially increased; withdrawing the resulting crystals of increased size and introducing them in turn into each of the subsequent secondary crys-

tallizing vessels in the series; contacting the resulting crystals of increasing size with supersaturated solution in each of the secondary crystallizing vessels in turn; withdrawing the resulting crystals of increased size from each of said vessels in turn; introducing the resulting crystals of increased size withdrawn from the last of said vessels in series into said lower zone as seed crystals; and withdrawing strong mature crystals from a lower portion of said lower zone.

4. A process for crystallizing ammonium nitrate which comprises withdrawing an aqueous solution thereof from the top of such solution contained in a crystallizing vessel; circulating the withdrawn solution through an evaporator; therein concentrating the solution to a selected degree of supersaturation; continuously introducing a stream of the resulting supersaturated solution into a lower part of said crystallizing vessel containing a suspension of ammonium nitrate crystals in supersaturated aqueous solution; directing said stream and controlling its velocity to maintain two zones in the resulting rising suspension of crystals, namely, a lower zone of crystal growth wherein a suspension containing relatively coarser growing crystals is maintained in substantially vertical streamlined rotation by kinetic energy imparted by said stream and at a speed of from about 3 to about 10 times that with which such crystals sink in such solution, and an upper, relatively quiescent zone containing a suspension of finer crystals; transferring fine crystals from said lower zone to said upper zone by upward flow of solution; continuously introducing a controlled stream of supersaturated aqueous solution of ammonium nitrate into said upper zone; therein contacting said fine crystals with resulting supersaturated aqueous solution of ammonium nitrate of a controlled degree of supersaturation until their size is substantially increased; introducing the resulting crystals of increased size into said lower zone as seed crystals; and withdrawing strong, dense, mature crystals of ammonium nitrate from a lower portion of said lower zone.

5. A process for crystallizing ammonium nitrate which comprises withdrawing an aqueous solution thereof from the top of such solution contained in a crystallizing vessel; circulating the withdrawn solution through an evaporator; therein concentrating the solution to a selected degree of supersaturation; continuously introducing a stream of the resulting supersaturated solution, containing from 0.003 to 0.1 pound per gallon of ammonium nitrate in excess of the quantity required to saturate said solution, into a lower part of said crystallizing vessel containing a suspension of ammonium nitrate crystals in supersaturated aqueous solution; directing said stream and controlling its velocity to maintain two zones in the resulting rising suspension of crystals, namely, a lower zone of crystal growth wherein a suspension containing relatively coarser growing crystals is maintained in substantially vertical streamlined rotation by kinetic energy imparted by said stream and at a speed of from about 3 to about 10 times that with which such crystals sink in such solution, and an upper, relatively quiescent zone contain-

ing a suspension of finer crystals; transferring fine crystals from said lower zone to said upper zone by upward flow of solution; withdrawing said fine crystals from said upper zone; introducing the withdrawn fine crystals into the first of a series of secondary crystallizing vessels; therein contacting said fine crystals with supersaturated aqueous solution of ammonium nitrate of a controlled degree of supersaturation until their size is substantially increased; withdrawing the resulting crystals of increased size and introducing them in turn into each of the subsequent secondary crystallizing vessels; contacting the resulting crystals of increasing size with supersaturated solution in each of the secondary crystallizing vessels in turn; withdrawing the resulting crystals of increased size from each of said vessels in turn; introducing the resulting crystals of increased size withdrawn from the last of said vessel in series into said lower zone as seed crystals; and withdrawing strong, dense, mature crystals of ammonium nitrate from a lower portion of said lower zone.

6. A process for crystallizing ammonium nitrate which comprises withdrawing an aqueous solution thereof from the top of such solution contained in a crystallizing vessel; circulating the withdrawn solution through an evaporator; therein concentrating the solution to a selected degree of supersaturation; continuously introducing a stream of the resulting supersaturated solution into a lower part of said crystallizing vessel containing a suspension of ammonium nitrate crystals in supersaturated aqueous solution; directing said stream and controlling its velocity to maintain two zones in the resulting rising suspension of crystals, namely, a lower zone of crystal growth wherein a suspension containing relatively coarser growing crystals is maintained in substantially vertical streamlined rotation by kinetic energy imparted by said stream and at a speed of from about 3 to about 10 times that with which such crystals sink in such solution, and an upper, relatively quiescent zone containing a suspension of finer crystals; transferring fine crystals from said lower zone to said upper zone by upward flow of solution; withdrawing said fine crystals and introducing them into a secondary crystallizing zone; therein contacting said fine crystals with supersaturated aqueous solution of ammonium nitrate of a controlled degree of supersaturation until their size is substantially increased; introducing the resulting crystals of increased size into said lower zone as seed crystals; and withdrawing strong, dense, mature crystals of ammonium nitrate from a lower portion of said lower zone.

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