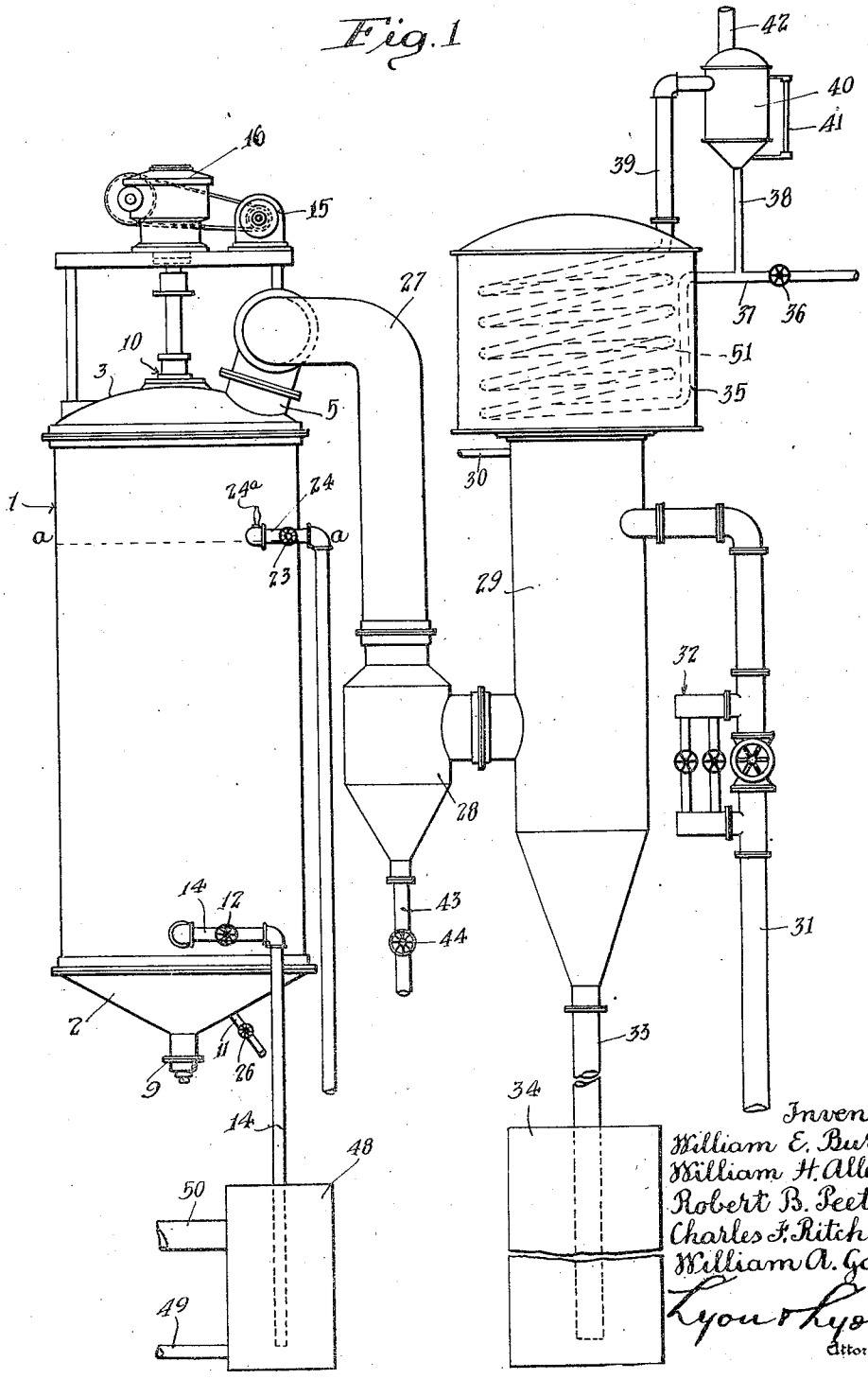
Sept. 13, 1938. W. E. BURKE ET AL 2,130,065

CRYSTALLIZATION METHOD

Filed March 7, 1930 3 Sheets-Sheet 1

Fig. 1



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CRYSTALLIZATION METHOD

Filed March 7, 1930 3 Sheets-Sheet 2

Fig. 2

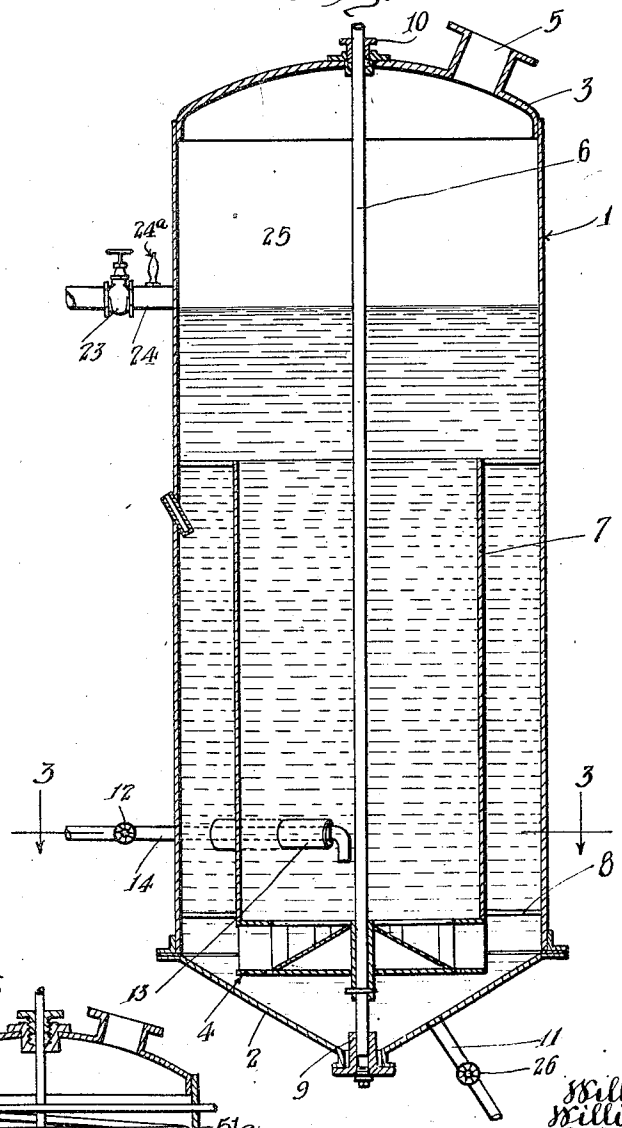
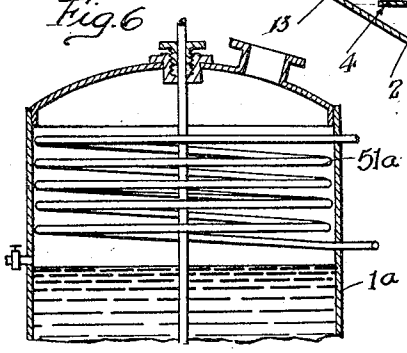


Fig. 6



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CRYSTALLIZATION METHOD

Filed March 7, 1930 3 Sheets-Sheet 3

Fig. 3

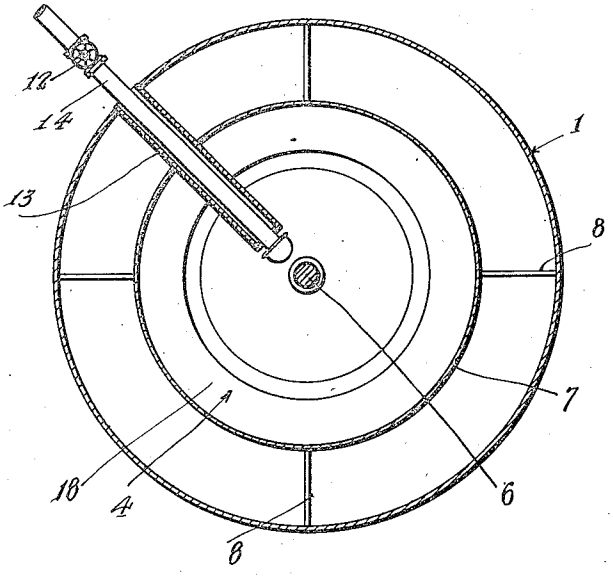


Fig. 4

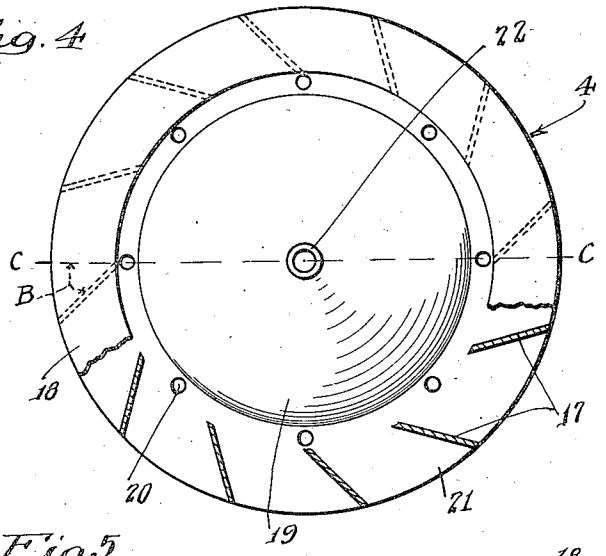
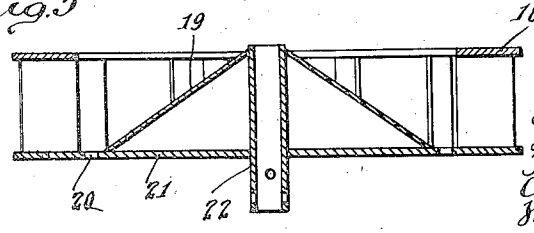


Fig. 5



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UNITED STATES PATENT OFFICE

2,130,065

CRYSTALLIZATION METHOD

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Application March 7, 1930, Serial No. 433,984

7 Claims. (Cl. 23—1)

This invention relates to methods and apparatus for forming satisfactory crystals of good size and habit from solutions by cooling. While the process and apparatus of this invention have been developed for and applied to the crystallization of perfect single crystals of borax of good size from hot aqueous solutions of the same, the present invention may be successfully applied to the crystallization of other solids from solutions thereof.

It is a comparatively simple matter to bring about the crystallization of borax from hot aqueous solutions by cooling. Extremely large crystals are easily prepared by allowing natural radiation of heat to cool saturated solutions over a long period of time. Rapid cooling in common types of equipment has been employed in the past for the production of finer crystals or the so-called granular borax. However, the borax so produced has, in the past, been of poor structure and of varying size.

It is one of the objects of this invention to provide methods and equipment by which granular borax crystals of good and uniform size and of good structure may be produced in a rapid and economical manner. By granular borax of good size, we refer to borax resembling common sugar crystals, and would offer a screen range of, say, from 50 mesh to 20 mesh as an example of size but we do not wish to limit our invention to these exact specifications since the process of this invention may be varied to a considerable extent to produce a larger or smaller size product, if desired. In fact, one of the advantages of the present invention lies in the ease of control of the present process.

Since the product of this invention comprises single, firm, well formed crystals, practically no disintegration or diminution of crystal size takes place in handling, drying, transportation, etc.

It has been found that dehydration of many hydrated crystals takes place more rapidly from broken or irregular crystal faces than from the perfect, well formed faces. The product of this invention, consisting of single, perfect crystals, is much less subject to dehydration than the agglomerate granular borax of the past.

When a concentrated solution of borax is cooled in cooling coils, a large deposit of that salt is formed upon the cooling coils. Such deposits require the use of means for removing the same, such as hot water, which must be reprocessed for the recovery of values therein contained. The adhering deposits seriously affect the crystal habit of the borax crystals subsequently produced therein, unless such deposits are always completely dissolved or otherwise removed prior to further crystallization of borax in such equipment. This is probably due to the excess or uncontrolled quantity of seed crystals thereby introduced which militate against the production of borax crystals of desired size and habit.

It is one of the objects of the present invention to provide means for cooling borax solutions for the production of crystals thereof, which means will eliminate the mechanical difficulties of cooling medium incrustation experienced in the older systems; which improved process may be operated continuously, if so desired.

We have found that cooling liquors by means of imposing a vacuum upon the hot liquors is an advantage over cooling the liquors in cooling coils, in that such vacuum cooling takes place at the surface of the boiling liquor and therefore, if such surface be maintained in constant agitation no incrustation can form upon the heat transfer medium. In vacuum cooling apparatus circulation and agitation is generally maintained by means of an outside circulation system including a pump. However, the use of a pump of the ordinary type has proven unsatisfactory in the production of borax crystals of good habit and size because the ordinary pump breaks up the crystals formed.

We have found that in crystallizing salts from solution through vacuum cooling that crystals of superior properties are produced by maintaining the contents of the cooling zone undergoing circulation down and around an internal well under the influence of the properly designed impeller type of pump.

Accordingly, the present invention includes the provision of a method and means for cooling liquors in a vacuum apparatus in which the liquor may be circulated in the vacuum evaporator without causing the crystals formed to be subject to abrasion and without producing what is known as "mechanical stimulus" within the system.

We have further found that in attempting to apply these principles to the production of large perfect single crystals of borax, it is necessary that a large degree of circulation be maintained in order to insure the requisite intimate mixing of crystals and liquor being cooled.

It is therefore an object of the present invention to provide a method and apparatus for cooling borax liquors which is adapted to permit a high degree of circulation of the liquor under-

going cooling while at the same time inhibiting mechanical stimulus and abrasion.

The present invention together with various objects and advantages thereof will best be understood from a description of a preferred form or example of a process and apparatus embodying the invention. For this purpose we have hereinafter described a preferred form and example of the invention, the description being given in reference to the accompanying drawings, in which

Figure 1 is an elevation.

Figure 2 is an elevation mainly in vertical section of the vacuum cooler.

Figure 3 is a section on the line 3—3 of Figure 2.

Figure 4 is a plan view partially in section of the impeller employed in the circulating system.

Figure 5 is an elevation of the impeller mainly in vertical section.

Figure 6 is a frgmentary elevation of the upper portion of the vacuum cooler shown in Figure 2 showing the addition of a cooling coil located within the crystallizer.

The apparatus forms the subject matter of our Patent 1,997,277, issued April 9, 1935.

Referring to the drawings, the vacuum cooler or crystallizer as best shown in Figure 2, comprises a right cylindrical shell 1 of steel or other suitable material which is provided with a bottom enclosure 2 which is preferably of shallow conical section. A semidome 3 is provided as an upper enclosure of the crystallizer which includes the vapor outlet 5. The crystallizer includes a circulation well 7 simulating a large section of pipe which is fixed concentrically in the shell 1 by suitable means. Preferably, such means comprises rectifying vanes 8 which extend vertically and are indicated as four in number. The rectifying vanes 8 serve the dual purpose of preventing swirling of the contents of the crystallizer and of holding the circulating well 7 in place. The crystallizer includes a concentric shaft 6 which at the lower end of the well 7 is provided with an impeller 4.

It is preferable that the space afforded between the lower extremity of the impeller 4 and the bottom enclosure, should be comparatively small since such constitutes a dead space. The diameter of the circulation well 7 should preferably be such that the cross sectional area of the well will be about one-half the total cross sectional area of the crystallization shell 1. In this way, there is no increase or decrease in the velocity of the liquor undergoing circulation. However, these proportions may be varied considerably without materially affecting the efficiency of the process or apparatus.

The impeller 4 should be a large diameter slow speed impeller. The impeller is approximately equal in diameter with that of the well 7. The shaft 6 to which the impeller is affixed enters the crystallizer through a suitable stuffing box 10 at the upper end and is prevented from swaying by a guide bearing 9 at the lower end of the crystallizer. If desired, the circulation well 7 may be mounted with the impeller and shaft thus eliminating any clearance between the well and the propeller. Suitable driving means such as the motor 15 and speed reduction gear box 16 of Fig. 1 are supplied for rotating the impeller 4 at a relatively low speed.

When a process and apparatus is to be operated continuously it is necessary to have a very large volume of circulation within the crystallizing zone in order to bring the said crystals into rapid and thorough contact with the liquor. This large volume of circulation must be attained by means which will not set up excessive mechanical stimulus within the system or have the effect of subjecting the crystals in the system to mechanical abrasion. By making the impeller 4 of large diameter it may be operated at a low speed while still imparting to the liquor a large centrifugal force sufficient to effect a large desired volume of circulation. Thus, the impeller of the present invention is made of a preferred diameter of approximately five feet and generally over three feet, as contrasted to the ordinary impellers for pumping liquids which rarely exceed a foot in diameter. The impeller is driven at a preferred speed of about 25 to 30 R. P. M., preferably below 100 R. P. M., which is to be contrasted with 400 or 500 R. P. M. which is generally considered a low speed fluid pump.

Preferably, the crystallizer is maintained in operation filled with liquor to the height of an overflow pipe 24 which is shown as provided with a suitable valve control means 23. The liquor in the crystallizer is admitted through a suitable line 14 shown fitted with a control valve 12. This line may terminate at the shell of the crystallizer where the crystallizer is to be operated in a batch manner, or it may extend within the shell through the circulation well 7, as indicated in the drawings, to the center of the crystallizer when the apparatus is to be operated continuously. In the latter case, it is preferable that a suitable jacket pipe 13 or similar device, be supplied in order to prevent undue cooling of the solution entering the crystallizer through the pipe 14. An outlet and control means such as 11 and 26 should be provided for emptying the contents of the crystallizer.

Figures 4 and 5 illustrate the details of the construction of the impeller 4 which has been employed with success in crystallizing single perfect crystals from borax. The impeller comprises impelling vanes 17 mounted vertically upon a base plate 21. The vanes 17 may be of the convolute contour accepted as good practice in centrifugal pump design, or they may comprise short straight pieces, as illustrated.

As illustrated, the vanes 17 are near the periphery of the impeller where vanes of the convolute contour would be practically straight. The impeller includes a sleeve 22 which is drilled and keyed to fit the shaft 6 and a base plate 21 is fixed to the sleeve 22. In order to prevent undue liquor slippage, an annular cover plate 18 is mounted over the top of the vanes 17. This cover plate has the additional property of strengthening the vane assembly.

The vanes 17 are short and the angle B between the foot of the vane and diameter C—C of the impeller is approximately 45°. The impeller also includes a false cone 19 which additionally strengthens its assembly. There is also preferably drilled a number of small holes 20 in the base plate 21, their purpose being to admit a small amount of circulating fluid into the dead space between the assembled impeller and the bottom section 2 in the crystallizer in order to prevent undue settling of crystals in this space.

Consistent with proper evaporator design, a sufficient vapor space 25 is provided above the normal liquid level within the crystallizer in order to prevent undue splashing of the liquor into the vapor lines during cooling operation.

The vapor lines and other accessories of the

crystallizer should be built sufficient in size to accommodate the maximum amount of vapor to be taken from the surface of the boiling liquid.

Now referring more particularly to Figure 1, the vapor passes from the crystallizer 1 through the vapor outlet 5 and vapor line 27 to a barometric condenser 29 or other suitable means for condensing vapors from the crystallizer. Preferably, the vapor line 27 includes a suitable mist separator or splash pot 28 in order to trap any liquor splashed or carried over. The liquor trapped may be returned to the crystallizer or to any other convenient point by means of line 43 and valve 44. A pipe 30 is connected to the shell of the barometric condenser 29 for the purpose of removing noncondensible gases. Said pipe 30 may be connected with a suitable vacuum pump or jet exhauster, not shown.

Water is admitted to the barometric condenser 29 through a suitable line 31 controlled by valves of the regulating manifold 32. Heated condenser water is returned by means of line 33 to a suitable hot well 34 from which it may be conducted to operate cooling towers or for other suitable purposes. The hot well 34 serves as a barometric seal for the condenser 29.

Having thus described the principles of construction of the equipment of this invention, we will now show how it is applied to the problem of crystallizing a substance, (first as applied to batch operation and later to continuous operation) specifically borax, from its solution. The hot concentrated borax liquor employed by us contained about 16 per cent of anhydrous borax ($Na_2B_4O_7$), together with fractional percentages of other neutral and basic salts, such as sodium chloride, sodium phosphate, etc. This liquor was found to be saturated with respect to borax at 60° C., but was delivered to the crystallizer at 75° C. or higher, in order to facilitate handling.

A crystallizer, essentially like that described in the foregoing drawings, being eight feet in diameter, was filled with 5500 gallons of hot concentrated borax liquor, which volume brought the liquid level up to a point corresponding to the line, *a—a*, of Figure 1. Such a level serves to cover the circulating well, which is quite important in the operation of the process of this invention. During vacuum cooling and crystallization of borax from such solutions, a volume shrinkage of from 10–15% takes place. It is requisite that such shrinkage should not decrease the liquor level below the point where adequate circulation may be maintained through the well supplied for this purpose.

In addition to the height of liquor requisite at the outset to compensate said shrinkage, it is also preferable that an excess equal at least to the effective pumping head or lift of the impeller should be provided, in order that the rate of circulation may in no way be diminished. In the equipment depicted, about 3 to 4 feet of liquor is provided to cover the upper rim of the circulation well. If the liquor level is allowed to drop below the top of the well during operation, circulation will cease, resulting in; (*a*) poor and uneven cooling with attendant flashing or bumping; (*b*) improper suspension of crystals, resulting in the production of fine and poorly formed ones; (*c*) and mechanical abrasion of any good crystals already formed, due to the same settling in the bottom of the equipment. This latter effect is not only deleterious to the desired crystal growth, but also is likely to cause mechanical difficulties with the impeller. Excessive heads of liquor above the top of the circulation well are not recommended, for such are likely to prevent the circulating liquor from being positively forced to the cooling surface.

After filling the crystallizer with hot liquor and properly setting various valves, it is best practice to start the impeller to circulating if this has not already been done. The impeller employed by us is essentially a low speed pump. In the case of example cited, it is about 5 feet and 4 inches in diameter and is caused to revolve at the rate of 27 revolutions per minute, resulting in an average velocity of upward flow of liquor between the shell and the circulation well of approximately 3 feet per second. This is equivalent to a flow of from 30,000 to 35,000 gallons per minute of liquor. The impeller causes the liquor and suspended crystals to stream upward in a positive fashion, the circulation well and the vanes directing the flow thereof. Liquor and crystals return to the pump or impeller by moving downward through the circulation well, hence short circuiting or eddying in excess of that allowed by certain known holes and clearances is prevented. The foregoing volume of liquor is caused to circulate with an expenditure of approximately 5 horsepower. If such volumes were to be handled through common centrifugal pumps, power greatly exceeding this value would be required, and exceedingly large and expensive pipe lines would be required. However, the greatest advantage of the present system lies in the utilization of a large diameter impeller which rotates at an exceedingly slow speed. This insures a minimum of mechanical abrasion of the crystals within the equipment. If the equipment is so constructed that the circulation well and the impeller rotate with respect to each other, a safe clearance between the same may be provided, sufficient to allow free passage of the largest crystals formed within the equipment, preventing mechanical abrasion from this source.

To our knowledge there is no standard pump on the market which embodies a sufficiently large diameter runner and sufficient freedom from close clearances to assure the requisite freedom from mechanical abrasion as is provided by this equipment of our invention. Furthermore, the assemblage of said impeller and circulating well within the crystallizer shell itself dispenses with the necessity for large pipe lines, valves, etc., which are costly and inconvenient to maintain and operate.

The rate of upward flow of liquor should be several times as great as the settling rate of the largest crystals produced within the crystallizer, and equipment of our invention is designed to this end. The rate previously quoted is quite sufficient to maintain crystals of 10 mesh size (about 2 millimeters of side or diameter) in suspension and to prevent undue concentration of crystals in the lower extremity of the vessel. We realize that smaller crystals would require a lesser rate of liquor circulation, and so design such equipment accordingly. In order to reduce mechanical abrasion to a minimum throughout the period of crystallization, the speed reducing means, 13, of Figure 1, may be variable, and so manipulated as to supply the desired circulation rate throughout the operation of producing a batch of crystals.

After filling the crystallizer and starting the rotation of the impeller, it is advantageous to maintain the liquor in circulation for a short time in order that any small residues may be dis-

solved from the crystallizer parts. One of the inherent characteristics and advantages of a properly designed and operated vacuum crystallizer resides in the fact that crystal deposits are reduced to a minimum. We find that only a slight deposit is formed upon the walls, from the original liquor level down to the final liquor level, during a batch operation; but no appreciable deposit is formed upon any of the submerged parts. A slight residue, of course, is likely to remain in the lower portions after removing the completely cooled batch from the crystallizer. The hot liquor introduced, being unsaturated by several degrees, easily dissolves these slight deposits each time, thereby insuring a sterile or nucleus-free system. This fact constitutes a great operating advantage, as no time is lost in pumping water to the cooler and no wash liquors are produced which have to be reprocessed.

Following the preceding preliminary manipulations, cooling operations may be commenced. The first phase of which comprises rapidly removing the heat in excess of the saturation temperature, i. e., in the example cited, cooling from 75° C. to about 60° C. or slightly below. The only factors limiting this preliminary rate of cooling are those of design of vapor space, vapor lines, condensing equipment, etc. Said preliminary cooling is carried to the temperature of saturation with respect to borax or slightly below, thereby incurring a small but comparatively stable degree of supersaturation. For example, liquor saturated with respect to borax at 60° C. may be cooled to 57° C. or 58° C. in this preliminary step. Cooling is abruptly stopped at this point which may be accomplished in one of several manners, the most simple of which consists of admitting air to the crystallizer through a suitable vacuum release valve 24a which may be fitted to the outlet 24 of Figure 1, for example. The impeller is allowed to rotate, circulating the liquor at all times.

In forming large single nuclei crystals of borax at temperatures below approximately 60° C. it should be appreciated that the borax crystals precipitate as the dekahydrate. At temperatures above approximately 60° C. borax precipitates as the pentahydrate. If large, single nuclei crystals of the dekahydrate are to be produced it is important to prevent any formation of pentahydrate crystals of borax in cooling the liquor down to the transition temperature. If crystals of the pentahydrate of borax are formed in this cooling operation or are otherwise introduced into the liquor, when the liquor passes through the transition temperature in the cooling operation, these crystals break up forming a large number of nuclei which have the effect of bringing down the borax dekahydrate in small crystals, thus preventing the desired production of large crystals.

Thus, in case the liquor processed when cooling to the transition temperature, is materially supersaturated with respect to the pentahydrate, it must be carefully cooled and maintained supersaturated.

We term this period of time between the point of cessation of preliminary cooling and the point when relatively slow, controlled cooling is again inaugurated, the "induction period". It is during this induction period that the nuclei or seed crystals are formed. This latter process may be brought about spontaneously, or it may be aided by inoculating the batch with borax crystals.

Referring to the first alternative, it is only necessary to allow the batch of liquor, which has been slightly supersaturated, to continue circulating for a period of 15–30 minutes, during which time spontaneous seed crystal formation ensues. Although this procedure requires the least effort on the part of the operator, it presupposes an intimate knowledge of the composition of the borax liquor. If, due to errors in the supposed liquor concentration, too great a degree of supersaturation is induced in the primary step of cooling, an excessively large number of seed crystals or nuclei are likely to be formed. On the other hand, if insufficient supersaturation is induced during the primary cooling stage, then no seed crystals will be spontaneously produced in a reasonable length of time and the succeeding steps of the process will be unfavorably affected thereby.

We have found it advisable, especially when inexperienced operators and varying liquor concentrations are involved, to inoculate the batch of liquor, at the start of the induction period, with borax crystals. To this end borax crystals, preferably of relatively small size, may be introduced. This may be accomplished by suspending the crystals in a small quantity of water or borax liquor and pouring the same, or sucking the same by means of the vacuum within the crystallizer, into the batch of liquor. While the actual number of seeds thus introduced should not exceed the number expected from the finished batch, it is not necessary that the maximum number be supplied for such added crystals act as inoculation means by which the discharge of supersaturation for the production of additional nuclei may be brought about under the controlled conditions of this process of our invention. This latter method of operation possesses the further advantage in that the induction period is greatly shortened. The primary cooling step is stopped at or just below the point of saturation, seed crystals are introduced and the controlled cooling commenced, as described below:

Following the induction period, the cooling period proper takes place. During this period, in which the liquor is cooled to the desired low temperature for the crystallization of borax, the cooling is conducted in a controlled and predetermined manner; slowly at first, then with increasing rapidity as the size of the crystals within the crystallizer are increased, and offer an ever increasing surface area of borax. Crystallization mechanism depends upon the production of supersaturation and the orderly deposition of said supersaturation upon the surface of other crystals. Hence, there are two rates involved in such a mechanism, the one being determined by the rate of cooling and the other depending upon surface area at hand for deposition of said supersaturation and the availability of said area. The positive circulation provided by the apparatus of this invention insures the desired availability factor at the point of production of supersaturation. However, if the surface area of crystals present is insufficient and the metastable limit of supersaturation is exceeded as a result of too rapid cooling, then additional nuclei or seed crystals will be formed. For these reasons, cooling is conducted slowly at the start of the cooling period and may be increased as crystal growth proceeds.

We do not wish to infer that the process of this invention is theoretically perfect and that the precepts herein set forth are carried out to

their ultimate perfection, but we do avow that large single crystals of fairly uniform size and good habit or structure are produced by the process of this invention. The crystal size of the final product will be influenced to a considerable extent by the rate of cooling. Since time is the essence of most commercial processes, it is desirable to maintain a rate of cooling which, at all times, will approach the maximum allowable for the production of the desired crystals, and it is largely to this end that the practice of increasing the rate of cooling as crystallization proceeds is carried out.

We have varied the controlled cooling period from one hour to five hours, with resulting increase of crystal size as the time is increased; but we will describe a particular instance of practical operation in which the final or main cooling is done in 90 minutes—cooling from about 58° C. to 35° C., or from 136° F. to 95° F., as these particular data were recorded. Taking the end of the induction period or the beginning of the cooling period as zero time, we cool the liquor at a smooth and continuously increasing rate; the temperature of the liquor at the end of each of the six succeeding fifteen minute periods being 135.0, 131.5, 126.0, 118.0, 108.0, and 95.0° F., respectively, making a total of 41° F. of cooling accomplished in one and one-half hours.

The maximum rate at which the controlled cooling of any liquor may be executed depends upon a large variety of factors. In order to grow large crystals, it is requisite that excessive spontaneous seed formation be prevented. Rate of cooling may be calculated and set to correspond to a given or known rate of crystallization, at the same time taking into account the surface area afforded by the seed crystal within the crystallizer, if these constants are known. If not known, it is a simple matter to examine the product within the crystallizer as crystallization proceeds, and to note whether appreciable formation of new nuclei has taken place between given intervals of time. If such is found to be the case, then it is known empirically that the particular rate of cooling employed during said intervals was excessive, and the cooling rate may be decreased to prevent further recurrence of the undesirable phenomena. Since factors effecting crystallization are not, at this time, well evaluated and since various constants are known to change considerably over a wide cooling range, this empirical method is recommended for establishing control of any given crystallization process. With the improved mechanical equipment of this invention, many undesirable and uncontrollable factors of prior equipment are eliminated and it becomes a simple matter for a competent chemist or chemical engineer to determine the few empirical factors requisite to the production of crystals of the desired habit and size.

One point of marked improvement in the process and equipment of the present invention is the ease with which the cooling may be controlled. With properly designed equipment, extremely slow rate of cooling as well as extremely rapid rates may be obtained with ease and the change from one to the other is easily and quickly accomplished. While a surface condenser may be employed as the cooling means, the above described test was conducted, using a barometric condenser in which type the hot vapors mix directly with the condensing medium—water.

Cooling control may be established by regulating a valve placed on the vapor outlet 5 of Figure 1, or by other means; but, we have found that very satisfactory cooling control is maintained by regulating the quantity of water passing to the barometric condenser. For regulating very low rates of cooling, small valves are necessary, while larger flows may be adjusted by means of proportionately larger valves. Hence, we prefer to construct a parallel manifold of different size pipes and valves varying from, say, one inch to, say, eight inches as shown by 32 of Figure 1 to serve the barometric condenser. This allows of the use of the smaller valves when regulation of slow cooling is desired, and the larger ones when more rapid cooling is indicated. The inherent nature of this equipment dispenses with the lag and change of rate of heat transfer common to the equipment of prior art, and the desired adjustment of rate of cooling depends entirely upon the intelligence and skill of the operator. Mechanically controlled cooling may be substituted to replace or assist the operator; said mechanical control being usually accomplished by means of a predetermined pressure-time or temperature-time template, regulating (usually through electrical means) the cooling control means; for example, the flow of water sent to the condenser.

Upon reaching the desired low temperature, which in the foregoing example was determined by the temperature of the condenser water available rather than chemical considerations, the vacuum release valve is opened and the contents of the crystallizer allowed to flow out through a bottom outlet 11 and control valve 26, passing to a suitable storage tank, in turn serving means for separating the mother liquor from borax crystals, such as a centrifugal or a filter. The crystals are given a slight wash with water to displace adhering mother liquor and then dried. A yield of about 6 tons of crystal borax, or a yield in excess of two pounds per gallon of hot liquor fed to the crystallizer was obtained.

The resulting product is found to consist mainly of well formed transparent single crystals, free from twinning or parasitic overgrowths. The habit of the crystals, that is in this case, their general shape, is usually tabular when produced from pure solutions or those containing only neutral salts as impurities. If the solution contains appreciable quantities of basic salts as impurities, such as sodium carbonate, sodium metaborate or trisodium phosphate, a crystal of more cubic habit will be formed. As stated, the crystals produced in the foregoing example were quite perfect in structure, constituting a glistening, free running product when dried for the removal of free moisture, and when screened to size showed approximately all through 14 mesh, 15% retained on 20 mesh, 25% retained on 30 mesh, 30% retained on 40 mesh, and 25% retained on 50 mesh, making a total of about 95 percent through 14 mesh and on 50 mesh. This represents a variation of from about 1.0 millimeter to about 0.35 millimeter in the diameter or mean length of side for the greater part of the product. We have found that this product is much more easily separated from the mother liquor and subsequently more easily dried than the product of prior art produced in indirect coolers. The appearance of the product was infinitely improved as compared with the former grade of granular borax. We have found that these crystals show considerable less tendency toward dehydration in commerce than the crystals of prior art and, fur-

ther, that practically no disintegration takes place, even under severe handling conditions.

The foregoing exposition has set forth a specific example of crystallization of borax from hot concentrated solutions thereof, relating to the utilization of the equipment of our invention in a batch or discontinuous manner. This equipment may likewise be operated continuously, and we have in practice made minor changes in the arrangement of said equipment to allow of this method of operation. For continuous operation, it is preferable that the inlet pipe 14 of Figures 1 and 2 should be extended to the central portion of the crystallizer. This assures complete and thorough mixing of the hot incoming liquor with the main body of circulating liquor. Other minor changes may also be made. The greatest single advantage of continuous operation, of course, resides in the saving of time which is lost in filling and emptying the batch equipment, and also the saving of time and labor required by the primary cooling and induction period steps, including the formation or addition of seed crystals. The process, as operated continuously, is a simple operation and requires far less skill and labor on the part of the operator than the batch process. On the other hand, it has been found that the crystal size and the uniformity of the product may be somewhat decreased as compared with batch operation material, produced at the same rate of (final or controlled) cooling. This reduction, however, is only slight in certain instances and has been found to be a function of the purity of the borax liquor. If said liquor be essentially free from impurities, especially salts of weak acids, the borax crystals produced by continuous operation are nearly as satisfactory as those produced from similar liquor by batch methods. If impurities are high, considerable reduction of crystal size is likely to result from continuous operation. Details of continuous operation are, like those of batch operation, to a great degree dependent upon the characteristics of the system involved and said characteristics must be determined in each case. However, it may be said that when employing borax liquor simulating that described hereinbefore, results quite similar to those previously noted were obtained upon continuous operation.

The crystallizer is first filled to the overflow level, *a*—*a* of Figure 1, the impeller started and allowed to operate continuously, and a batch of crystals produced. When the contents of the crystallizer has been cooled to the desired low temperature, a constant flow of liquor is admitted through line 14 of Figures 1 and 2, and a constant flow of crystals and mother liquor, termed "sludge", continuously withdrawn from the crystallizer. The level of the liquor in the crystallizer is maintained at some point approximately between the afore described liquor level *a*—*a* and not lower than about a foot above the upper extremity of the circulation well, for the principles applying to circulation rate and boiling conditions are as equally true in the case of continuous operation as in batch operation. A suitable gauge glass may advantageously be affixed to the crystallizer to enable determination of the liquor level.

However, automatic regulation may be secured by placing below the crystallizer, at a distance equal to the barometric column of liquor involved, a constant level tank 48 of Figure 1. This tank is so arranged as to be always filled with hot borax liquor by means of inlet line 49 and overflow line 50. Its distance from the line *a*—*a* of Figure 1 is such that liquor cannot be drawn into the crystallizer above this height. Since a constant temperature of discharge, hence a constant vacuum is maintained within the crystallizer during continuous operation, this device serves as an automatic liquor feed means. It is then only necessary to regulate the speed of the outflowing sludge, in order to fix the rate of liquor flow to the crystallizer.

The herein described crystallizer may easily handle 60 gallons per minute of hot unsaturated borax liquor, or at a rate approximately equal to the volume rate at which liquor was cooled during the main cooling period of the batch operation. Stated in other terms 5,400 gallons of hot liquor are cooled every 90 minutes by this continuous process, while about 5,500 gallons of similar liquor were cooled during the final cooling period, in the foregoing example of batch operation. Hence, in this particular comparison which has been chosen from actual operating data because of points of similarity, time required to fill, empty and bring the batch to the point of final or controlled cooling is saved by the continuous process. This may represent a saving of as much as 50 percent, which constitutes a marked advantage in favor of the continuous process. When employing the previously described liquor, the product resulting from this continuous operation of the equipment of our invention was found to be merely equal to the product of batch operation. Said product comprised, when dry, glistening, well formed single crystals of good structure and habit; the screen analysis of which was only slightly inferior to the one above quoted.

One of the drawbacks of a vacuum cooling system as compared with cooling by direct means lies in the fact that cooling water of a given temperature is a less effective cooling medium in the former case than in the latter. This phenomenon is the result of the co-called boiling point rise or decrease of vapor pressure of the liquor being cooled due to the presence of dissolved salts. The loss of cooling power of water when employed as a direct condensing medium is approximately equal to the so-called boiling point rise of the liquor being cooled. In addition to this effect, it is also impossible in many instances to obtain a cooling water from the usual sources which is sufficiently cold to serve the desired purpose. In the case of crystallizing relatively pure borax liquor whose boiling point rise is comparatively slight, the latter effect is a more serious drawback in practice than the former. It is possible to overcome this defect by refrigerating artificially the condensing water. However, this may require that common salt or calcium chloride be added to the water in the usual manner of refrigerating systems to prevent freezing in said system. The inherent dilution due to direct condensation of vapors in such cold brine results in an increase of volume thereof, necessitating continued disposal and further additions of calcium chloride or salt to the remaining brine. In order to overcome this defect and, at the same time to increase the efficiency of refrigerating systems as applied to the process of our invention, we have devised improved means for bringing about low temperature crystallization in vacuum coolers.

To this end, we employ a surface condenser, serviced directly with a suitable primary refrigerant. By primary refrigerant, we mean com-

pressed ammonia, carbon dioxide, sulfur dioxide, methyl chloride or any of the other substances commonly employed in commercial refrigerating systems. In Figure 1, we have shown an elevation of one adaptation of this feature of our invention, in which 35 represents a tight shell containing pipes for bringing about heat transfer between the hot vapors and the refrigerant, which shall be referred to as liquid ammonia since this is the refrigerant employed by ourselves.

Such heat exchanger may comprise the conventional high pressure tubing employed in the brine tanks of ice plants, the liquid ammonia being within the pipes and the hot vapors without. Liquid ammonia is admitted (from the compressors and condensers) through a reducing valve 36 and line 37, to the heat transfer pipes or coils 51 within the shell 35. In such coils the ammonia is boiled and vaporized, the gas passing out through a suitable line 39 through a separator 40 and thence back to the compressors through line 42. The separator 40 is one type commonly employed in the operation of flooded ammonia systems, for separating entrained liquid ammonia from the gas before conducting the latter to the compressors. Liquid ammonia so separated is returned to the coils by a line 38. A gauge glass 41, may be employed to prevent flooding of the separator. Other conventional systems for handling such refrigerants may be employed, including automatic control means. The details of design of the surface condenser in which the refrigerant is directly vaporized embrace standard engineering practice and are not herewith described minutely.

Figure 1 shows the direct-expansion ammonia surface condenser as directly superimposed over the barometric condenser. Such an arrangement is suited to a two-stage cooling system for the batch crystallization of hot borax liquor cooling, for example, from 75° C. to 15° C.

In order to conserve artificial refrigeration, we prefer to cool as low as possible by means of the water available. To this end cooling to say, 35° C. is accomplished as hereinbefore described by means of water, the latter being employed in this instance in the barometric condenser 29. Upon reaching the economic cooling limit of said water, the valves of manifold 32 are tightly closed, liquid ammonia is then admitted to the direct-expansion surface condenser 35 and cooling completed by this means. Condensate from the surface condenser is disposed of through the tail pipe 33 in the example cited.

In case abstraction of water from the liquor being cooled is undesirable, the direct expansion surface condenser may be so placed that the condensate therefrom will return to the crystallizing vessel instead of passing down the tail pipe 33, as illustrated in Figure 1. By building the direct expansion surface condenser as an assembly into the vapor space of the crystallizer shell 1, the aforementioned desired result is fulfilled and vapor lines, etc. are eliminated. Under high vacuum conditions, this elimination of vapor lines is of considerable advantage.

While on the face of it, this system of vacuum crystallization, accomplished by means of a direct expansion surface condenser, is simply a means to an end, the system possesses many points of advantages in the consideration of economy, as compared with means or combinations of means employed by prior art.

While the process of this invention is effective in producing crystals from solution, as hereinbefore described, and specifically for producing single borax crystals of good size and habit from hot concentrated borax solutions, it has been found that the addition of minute quantities of a suitable hydrophilic colloid, as described in co-pending application of Robert B. Peet, Serial No. 355,664, is of material value in preventing aggregation of the single crystals. This process of the co-pending application may be advantageously employed in connection with the process and apparatus of this invention.

While the particular method and apparatus herein described is only one of the many embodiments this invention may take, and is well adapted to carry out the objects of the present invention, it is to be understood that various modifications and changes may be made without departing from the invention, and the invention is of the scope set forth in the appended claims.

We claim:

1. A process of crystallizing a salt from solution, which process comprises passing a solution of said salt into a crystallizing zone in which a body of said solution is maintained under a pressure below atmospheric sufficient to evaporate said body of said solution and cool the surface of the body of said solution at which said evaporation is taking place through removal of heat of vaporization while continuously subjecting the body of solution within said zone together with crystals present to a circulation to and from the evaporating surface of said liquid at the rate substantially in excess of the settling rate of the crystals present.

2. A process of crystallizing a salt from solution, which process comprises passing a solution of said salt into a crystallizing zone in which a body of said solution is maintained under a pressure below atmospheric sufficient to evaporate said body of said solution and cool the surface of the body of said solution at which said evaporation is taking place through removal of heat of vaporization while continuously subjecting the body of solution within said zone together with crystals present to a circulation to and from the evaporating surface of said liquid at a rate substantially in excess of the settling rate of the crystals present, while condensing the vapors evaporated from said body and returning them to the evaporating surface of said body.

3. A process of crystallizing borax from solution, which process comprises passing a solution of borax containing insufficient borate to crystallize the pentahydrate upon cooling but sufficient to crystallize the decahydrate into a crystallizing zone in which a body of said solution is maintained under a pressure below atmospheric sufficient to evaporate said body of solution and cool the surface of the body of said solution at which said evaporation is taking place through removal of heat of vaporization, while circulating the solution in said zone to and from the evaporating surface of said solution at a rate substantially greater than the settling rate of the crystals being formed so as to carry the crystals in said zone substantially to said evaporating surface.

4. A process of crystallizing borax from solution, which process comprises passing a solution of borax containing insufficient borate to crystallize the pentahydrate upon cooling but sufficient to crystallize the decahydrate into a crystallizing zone in which a body of said solution is maintained under a pressure below atmospheric sufficient to evaporate said body of solution and cool the sur-

face of the body of said solution at which said evaporation is taking place through removal of heat of vaporization, while circulating the solution in said zone to and from the evaporating surface of said solution at a rate substantially greater than the settling rate of the crystals being formed so as to carry the crystals in said zone substantially to said evaporating surface, while condensing the vapors from said evaporating zone and causing the same to be returned to the evaporating surface of the liquid in said zone.

5. A process of crystallizing borax from solution, which process comprises passing the solution of borax containing insufficient borate to crystallize the pentahydrate upon cooling but sufficient to crystallize the decahydrate into a crystallizing zone in which a body of said solution is maintained under a pressure below atmospheric sufficient to evaporate said solution and cool the surface of the body of said solution at which said evaporation is taking place through the removal of heat of vaporization, the entering solution of borax having a concentration of borax not substantially above the saturation value at 60° C. and containing sufficient borax to exceed saturation at the temperature to which this solution is cooled, circulating the solution within said crystallizing zone at a sufficient rate to substantially prevent settling of crystals of borax formed and in direction to cause said solution and admixed crystals to be brought repeatedly to and from the evaporating surface of the body of solution in said crystallizing zone.

6. A process of crystallizing borax from solution, which comprises passing a solution of borax, which solution of borax containing insufficient borate to crystallize the pentahydrate upon cooling but sufficient to crystallize the decahydrate is insufficiently concentrated to crystallize the pentahydrate on cooling, into an evaporating zone where the solution is maintained under a pressure below atmospheric sufficient to evaporate said solution and cool the surface of the body of said solution at which said evaporation is taking place through removal of heat of vaporization to a temperature at which said solution will crystallize the decahydrate, while maintaining the solution undergoing circulation at a rate substantially in excess of the settling rate of crystals of decahydrate being formed and causing the solution and admixed crystals to pass to and from the evaporating surface in said crystallizing zone.

7. A process of crystallizing borax from solution, which process comprises passing the solution of borax into a crystallizing zone, the solution of borate containing insufficient borate to reach saturation at temperatures at which the pentahydrate precipitates from solution but containing borate in excess of saturation value at the temperature at which the solution is to be cooled, in said crystallizing zone maintaining a body of said solution under pressure below atmospheric sufficient to evaporate said solution and cool the surface of the solution at which evaporation is taking place through removal of heat of vaporization, and circulating the body of solution at a sufficient rate above the settling rate of the crystals being formed to maintain a substantially homogeneous mixture of crystals and solution, the direction of circulation being to and from the evaporating surface of the body of solution, and maintaining the rate of cooling of the body of solution so that the body of solution is held in a metastable supersaturated state.

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