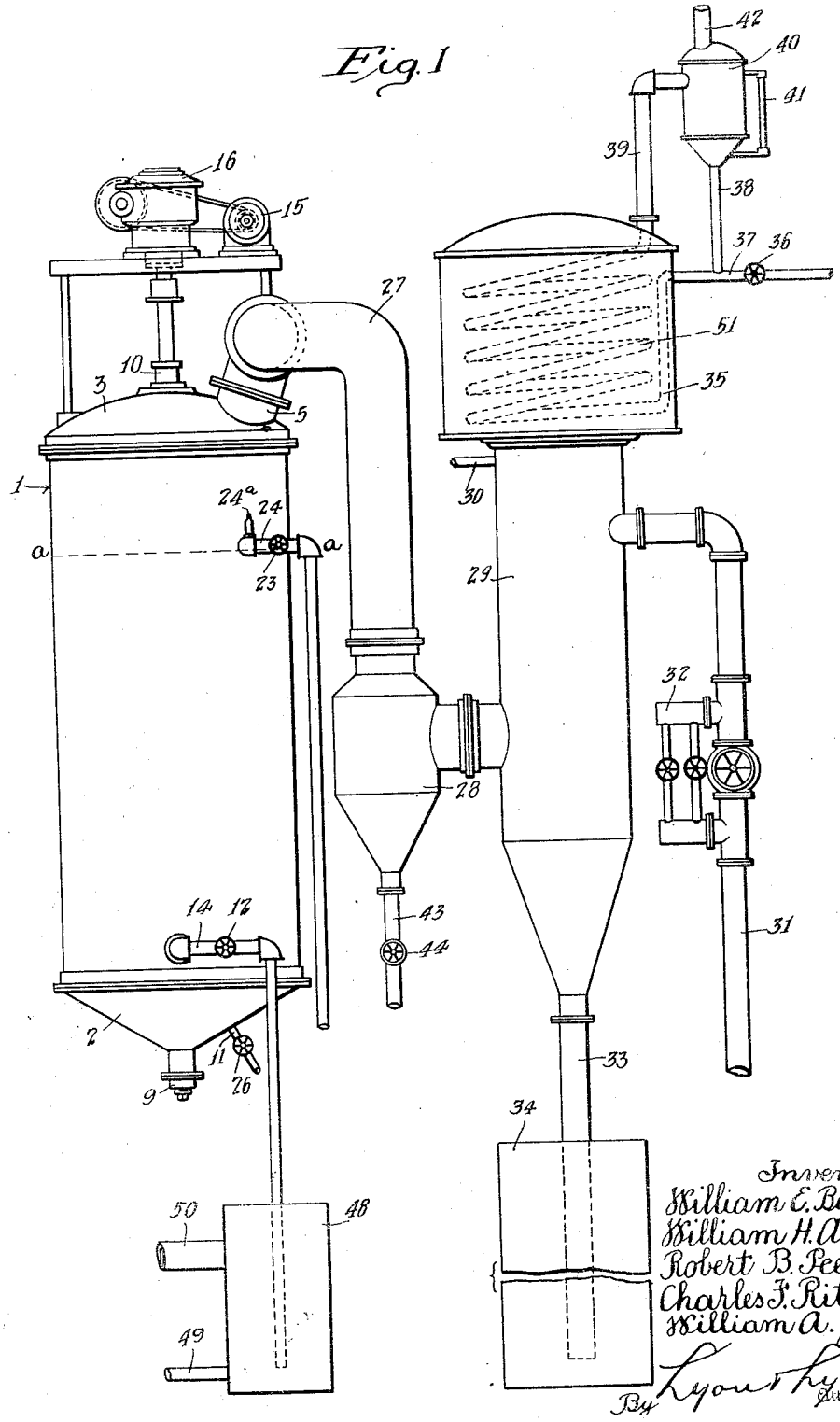
April 9, 1935. W. E. BURKE ET AL 1,997,277

CRYSTALLIZATION APPARATUS

Filed Sept. 6, 1932 5 Sheets-Sheet 1

Fig. 1



Inventors
William E. Burke
William H. Allen
Robert B. Peet
Charles F. Ritchie
William A. Gale

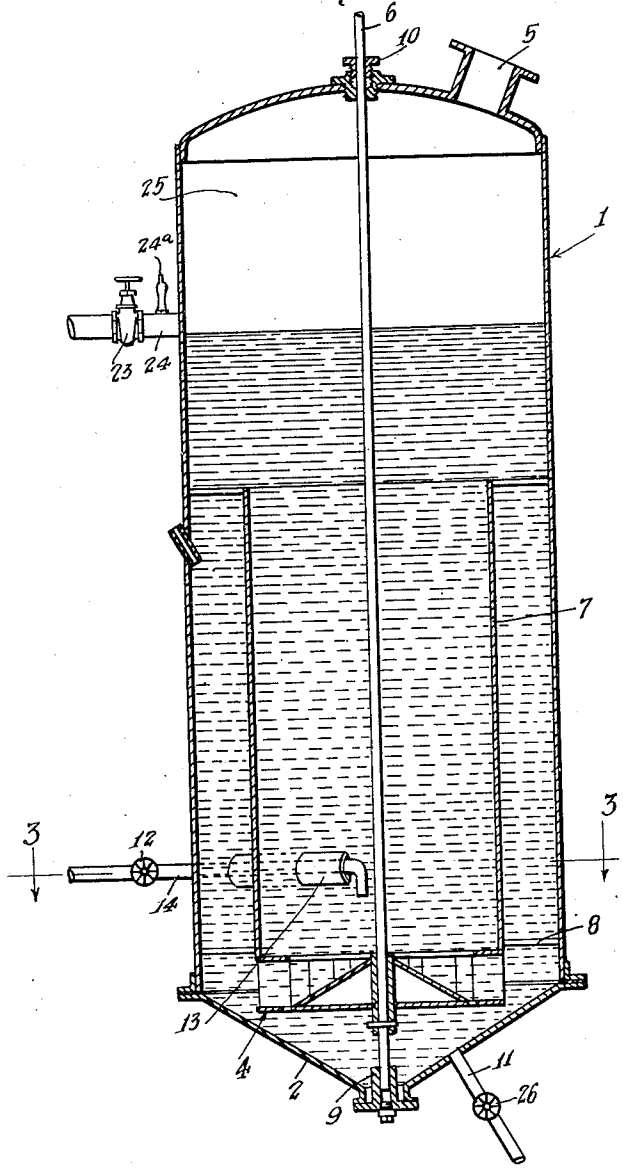
By Lyon & Lyon Attorneys

April 9, 1935. W. E. BURKE ET AL 1,997,277

CRYSTALLIZATION APPARATUS

Filed Sept. 6, 1932 5 Sheets-Sheet 2

Fig. 2



Inventors
William E. Burke
William H. Allen
Robert B. Peet
Charles F. Ritchie
William A. Gale

By Lyon & Lyon Attorneys

April 9, 1935. W. E. BURKE ET AL 1,997,277

CRYSTALLIZATION APPARATUS

Filed Sept. 6, 1932 5 Sheets-Sheet 3

Fig. 3

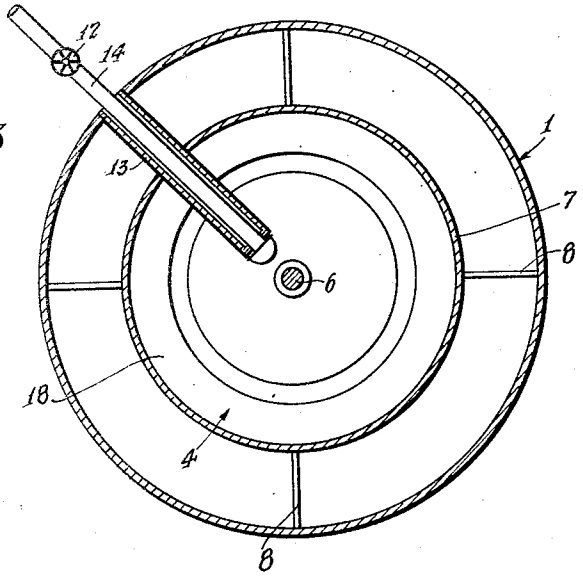


Fig. 4

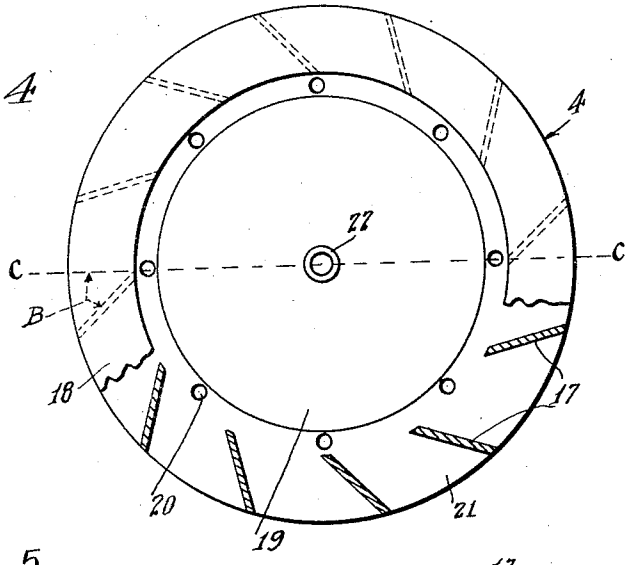
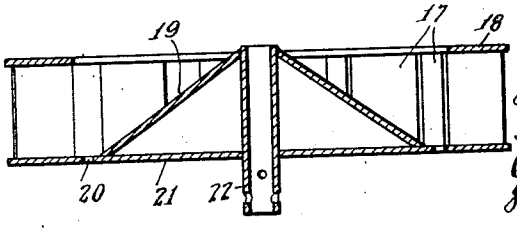


Fig. 5



Inventors
William E. Burke
William H. Allen
Robert B. Peet
Charles J. Ritchie
William A. Gale

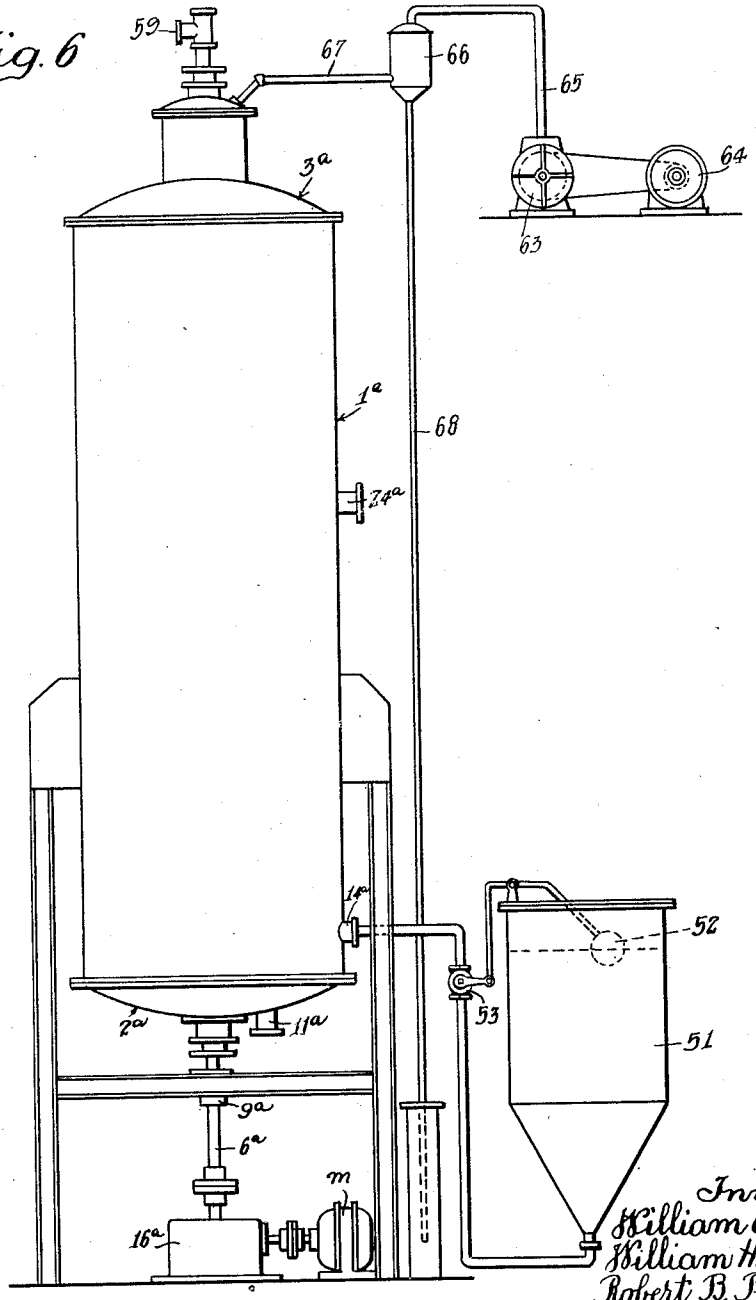
By Lyon & Lyon Attorneys

April 9, 1935. W. E. BURKE ET AL 1,997,277

CRYSTALLIZATION APPARATUS

Filed Sept. 6, 1932 5 Sheets-Sheet 4

Fig. 6



Inventors
William E. Burke
William H. Allen
Robert B. Peet
Charles F. Ritchie
William A. Gale

By Lyon & Lyon

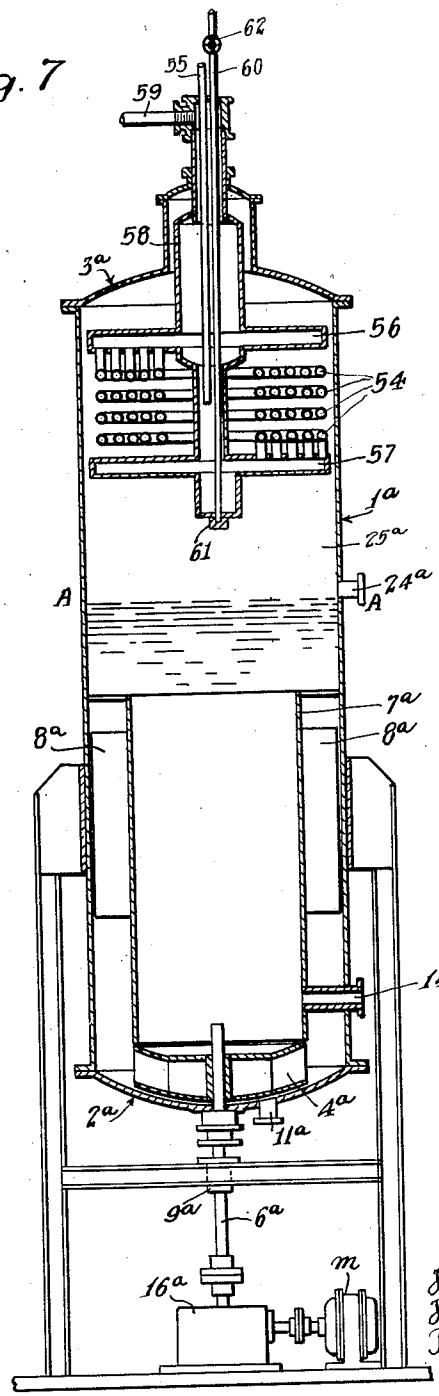
Attorneys

April 9, 1935. W. E. BURKE ET AL 1,997,277

CRYSTALLIZATION APPARATUS

Filed Sept. 6, 1932 5 Sheets-Sheet 5

Fig. 7



Inventors
William E. Burke
William H. Allen
Robert B. Peet
Charles F. Ritchie
William A. Gale

By Lyon & Lyon Attorneys

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UNITED STATES PATENT OFFICE

1,997,277

CRYSTALLIZATION APPARATUS

William E. Burke, William H. Allen, William A. Gale, and Charles F. Ritchie, Trona, Calif., and Robert B. Peet, Ithaca, N. Y., assignors to American Potash & Chemical Corporation, Trona, Calif., a corporation of Delaware

Application September 6, 1932, Serial No. 631,792

39 Claims. (Cl. 23—273)

This invention relates to an apparatus for forming crystals from a solution by evaporative cooling. This application is a division, in part, of our co-pending application, Serial No. 433,984, filed March 7, 1930.

One of the objects of the present invention is to provide an apparatus for forming satisfactory crystals of good size and shape from solutions by cooling. While the apparatus of this invention has been developed for and applied to crystallization of perfect single crystals of borax of good size from hot aqueous solutions of the same, the apparatus may be successfully applied to 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 an apparatus by which 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 apparatus.

There is a distinct advantage in the manufacture of perfect single crystal of a given size, as compared with a complex, stellated or aggregated crystal. In the early days of the borax industry, it was the universal custom to produce extremely large crystals by natural cooling over long periods of time. Such crystals were of exceedingly high purity and stood up under handling and transportation with a minimum of disintegration and dehydration. However, such methods of production were found to be costly and impracticable in the present day highly competitive markets.

Rapid crystallization methods were, therefore, substituted, resulting in the production of the so-called granular borax. However, the resulting product was of poor structure and was found to be subject to a great deal of mechanical disintegration and dehydration in commerce. The distaste of the trade for the granular borax so produced was a result of these factors and the psychology of the poor appearance of the same, rather than a result of a chemically inferior product.

The borax crystals produced by the apparatus of this invention comprise single or individual crystals, each an exact miniature of the larger crystals heretofore produced by the old time methods of very slow cooling. The individual faces of these crystals are clean; they are free of aggregations or parasitic growths and, taken collectively, constitute a free running, glistening product of most pleasing appearance.

Single crystals of uniform size are more easily separated from the adhering mother liquor than aggregated, twinned, or stellated crystals, thus assuring easier and more complete washing of the product. Likewise, since only a minimum of liquid may be retained upon the surface of the crystals produced by the process of this invention, the operation of drying is considerably facilitated as compared with the drying of granular borax produced by past practice.

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 re-processed 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 militates 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 apparatus 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 means for cooling the liquors in a vacuum evaporating 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.

Crystallization of a substance from its solute depends upon the mechanism of first bringing said solute to saturation with respect to the substance, then incurring supersaturation with respect to said substance. Supersaturation is the force by which crystallization processes take place, and the degree of said supersaturation constitutes a measure of the rate at which crystallization will proceed. The phenomenon of supersaturation varies widely with different substances and with various solutes. In some cases the supersaturation characteristics of a system may be so small as to approach zero as a limit; in others, especially in the case of hydrated salts, double salts and certain organic compounds, the supersaturation characteristics are very pronounced. It is to the latter type of substances that the process of the present invention is especially applicable.

Another principle of crystallization and supersaturation phenomenon upon which this invention is predicated resides in the ability of a solution to undergo supersaturation with respect to a solute to a rather definite extent or limit without precipitating therefrom spontaneously a crop of nuclei or fine seed crystals. This is known as the metastable limit of supersaturation. If a solution is caused to become supersaturated in excess of this metastable limit, then the driving force of crystallization, as it were, is exceeded and a quantity of seed crystals or nuclei are formed spontaneously. The exact values or constants describing in mathematical terms the limitations of these various phenomena are only known comparatively; but, whether the same are primarily evaluated or determined by trial and error for a particular system in question is of little consequence, for the final result is the same: the production of the desired crystals under controlled conditions. In order to produce a crop of single perfect borax crystals of a predetermined size from a given quantity of hot concentrated liquor, it is requisite that no more than a fixed number of seed crystals or nuclei be added or formed during the process of crystallization. The greatest cause of failure in past equipment arose from the inability to control the spontaneous formation of seed crystals in such equipment. It is easier to produce spontaneously an excess of seed crystals or nuclei than to prohibit such formation. Supersaturation values must be absorbed upon crystals already present in order to prevent the cooling process from establishing a degree of supersaturation in excess of the metastable limit. This means that the seed crystals must be maintained at all time in intimate admixture with the supersaturated liquor, and especially so at the point at which supersaturation is induced. We have found that the metastable limit especially in presence of seed crystals, is greatly reduced by any force producing an action of abrasion. Whether such reduction is caused by the mechanical production of small crystal fragments from the seed crystals already present or is due to some other cause, yet unexplained, we do not know.

We have found that in order to produce a crop of single borax crystals of predetermined sizes from a given quantity of hot concentrated liquor, the vacuum cooling of the liquor must be regulated in order to both maintain the amount of supersaturation of the liquor with respect to borax below the metastable limit and also to maintain the quantity of said crystals present sufficiently low that all of the supersaturation of the liquor may be expended in growing these seeds to the desired size.

We have further found that mechanical stimulus must be avoided while circulation and agitation of the solution must take place to an extent sufficient to maintain the proper quantity of said crystals in intimate contact with the supersaturated liquor.

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 an apparatus for cooling borax or other liquors which is adapted to permit a high degree of circulation of the liquor undergoing cooling while at the same time inhibiting mechanical stimulus and abrasion.

Heretofore, vacuum or evaporative cooling has, as generally practiced, proceeded with a concentration of the solution due to the evaporation and removal of part of the water content of the solution in order to secure the desired cooling. Frequently, in a process of crystallizing the salt from solution it is undesirable to secure any concentration of the salt during the cooling operation, and this evaporative cooling can be used with such solutions only provided there is carefully and accurately supplied to the solution just the amount of water which the evaporative action will remove. In the past, this has been accomplished by prediluting the solution to be cooled. We have found, however, that by providing the evaporator with a cooling and condensing medium located within the shell of the evaporator itself, evaporative cooling may be carried on while the

vapors produced are condensed and returned to the liquid undergoing cooling, so that such cooling proceeds without any loss of liquid or concentration of the solution being cooled.

It is, therefore, an important object of the present invention to provide an apparatus for evaporative cooling of a solution in which means are provided for condensing vapors formed during the evaporative cooling operation and simultaneously returning these to the body of liquid undergoing cooling. Not only in this manner have we found that concentration of the liquid may be avoided, but we have further found that cooling to lower temperatures may be more readily attained in an evaporative cooler due to the fact that the condensate returned to the body of the liquid, is as a rule, of lower temperature than the remainder of the liquid, and thus the liquid undergoes additional cooling therefrom.

In the past extreme difficulty has been experienced in the operation of vacuum coolers when it is desired to cool a solution down to low temperatures, such as approach or are lower than atmospheric temperature. It is, therefore, one of the objects of the present invention to provide an apparatus for evaporative cooling of the liquid in which evaporative cooling may be carried out to lower temperatures than were heretofore readily attainable. For this purpose, it has been found that lower temperatures of cooling could be derived by supplying the evaporator with a refrigerating coil serviced with a primary refrigerant of the gaseous type, such as ammonia, sulphur dioxide, methyl chloride and the like. By the use of such refrigerating coils in the vapor space of the vacuum cooling apparatus, the vapors are cooled to a lower temperature than is attainable with the older barometric type condensers without the use of special condensing mediums therein, resulting in lower vapor pressures within the apparatus and a greater formation of vapors and cooling through a greater removal of heat of vaporization. By the use of the foregoing refrigerating coil in the vapor space of the evaporative cooler, we have been enabled to cool continuously large volumes of liquor to lower temperatures than we have found heretofore economically possible and with greater refrigeration efficiency.

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.

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. This is accomplished in the present invention by maintaining the contents of a cooling zone undergoing circulation down the inside of an internal well and up the outside thereof under the influence of a properly designed impeller type of pump.

We have found that in order to produce a crop of single borax crystals of predetermined size from a given quantity of hot concentrated liquor, the vacuum cooling of the liquor must be regulated in order to both maintain the amount of supersaturation of the liquor with respect to borax below the metastable limit, and also to maintain the quantity of said crystals present sufficiently low that all of the supersaturation of the liquor may be expended to growing these seeds to the desired size. To this end, it is an additional object of our invention that means be provided for controlling the degree of vacuum maintained within the crystallization chamber to effect these ends.

In many cases in the vacuum cooling of liquors for production of crystals, it is necessary to cool over an appreciable range of temperature so that the volume of water vapor created by the boiling of the liquor under the reduced pressure is very great, normally necessitating very large vapor lines leading to the evacuating apparatus. When a barometric condenser is used as the source of vacuum, this large volume of water vapor is not an especially serious factor other than necessitating the use of large vapor lines. When the cooling must be carried to a temperature lower than that available by the use of a barometric condenser with the condensing water available, it is often desirable to employ a vacuum pump in place of the barometric condenser. When a vacuum pump is so used the capacity must be so great, in order to take care of the large volume of vapor produced, as to make the vacuum pump method almost prohibitive. To this end, it is an additional object of our invention to provide means for so reducing the volume of water vapor passing to the vacuum pump that a pump of very small capacity may be used. This is accomplished, briefly, by including a suitable cooling coil in the outgoing vapor lines between the crystallization chamber and the vacuum pump, so that a large portion of the water vapor is condensed leaving only non-condensable gases to be drawn off by the vacuum pump.

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

Figure 1 is an elevation;

Figure 2 is an elevation, mainly in vertical section of the evaporative 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 embodied in the circular system;

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

Figure 6 is an elevation of a slightly modified form; and

Figure 7 is a similar elevation, mainly in vertical section, of the evaporator of Fig. 6.

Referring, first, to Figs. 1 to 5, inclusive, of the drawings, the vacuum cooler or crystalizer, as best shown in Fig. 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 semi-dome 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 of 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 stumulus 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 when 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 crystal 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 the 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 Fig. 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 non-condensable 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 Fig. 1. Such a level serves to cover the circulating well, which is quite important in the operation of the process of this invention. During the vacuum cooling and crystallization of borax from such solutions, a volume shrinkage of from 10–15% takes place if the condensate from the vapors produced is not returned. 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 is also 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 dissolved 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 the cooling operations 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 former 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 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 crystal-

lizer, 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 tri-sodium 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 per cent through 14 mesh and on 50 mesh. This represents a variation of from about 1.0 millimeter to about 0.35 millimeters 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 considerably less tendency toward dehydration in commerce than the crystals of prior art and, further, 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 pro-

duced 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 can not 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 per cent, 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 nearly 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 so-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 compressed ammonia, carbon dioxide, sulphur 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 especially 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 the case of continuous operation, where cooling is isothermal and where the water is hotter than desirable for total artificial cooling, it is necessary to conduct the cooling in two stages. In the first stage the liquor is cooled in a crystallizer as described to a temperature commensurate with the cooling water available, followed by vacuum cooling in a similar crystallizer actuated by means of a direct expansion surface condenser. These two (or more) stages must be carried out in independent pieces of equipment. In the case of batch operation, it is only necessary to employ two means of cooling. In the case of continuous operation, both the crystallizer vessels and the condensing means must be changed in passing from one stage of cooling to the other. The use of pumps for transferring sludge from the first stage crystallizer to the second is to be avoided, if possible. We prefer to rely upon differences of pressure and elevation for transferring the contents of the first crystallizer to the second. This is done in order to minimize mechanical abrasion in the system.

Obviously, in the case of a system which exists at a high temperature, but in which crystallization does not commence until a relatively low temperature is reached, it is advisable to precool by the most economic means, prior to delivering the liquor to the crystallizer serviced with direct expansion surface condenser cooling means. If no crystallization takes place during the first stage of cooling, the cooling and crystallizing equipment hereinbefore described is superfluous, and the primary stage of cooling is best conducted by passing the liquor through pipes over which the cooling water is passed. To this end, a suitable high head pump is placed to take suction from the hot liquor supply and to force said liquor through the preliminary cooling pipes and into the crystallizer in which the second stage of cooling and crystallization is brought about. Other means for carrying out the preliminary cooling, such as double tube coolers, tank coolers, etc., may be employed where conditions so warrant. The pre-cooled liquor may be delivered continuously to a crystallizer similar to that illustrated herein, and crystallization brought about by vacuum cooling accentuated by means of a direct expansion surface condenser.

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.

Now, referring more particularly to Figures 6 and 7, inclusive, of the drawings, a modified apparatus is therein illustrated in which the direct expansion surface condenser is assembled into the vapor space of the evaporator or crystallizer shell.

The modified form of apparatus includes the cylindrical evaporator shell 1^a, which is provided with a round bottom closure 2^a in place of the conical shape of the bottom 2 of the first form. A semi-dome 3^a is provided as an upper enclosure of the crystallizer. The crystallizer includes a circulation well 7^a similar to that of the previous form provided with rectifying vanes 8^a. There is provided a concentric stub shaft 6^a, which is connected in the lower end of the evaporator with the impeller 4^a. The impeller 4^a is identical in construction with the impeller 4 previously described, with the exception that its edge walls are curved slightly in order to conform with the curvature of the bottom wall 2^a. The curved bottom wall and curved edges of the impeller 4^a, together, aid in reducing any currents in the crystallizer and insuring a large circulation of liquid in operation without substantial mechanical shock. Furthermore, by curving the bottom wall 2^a and causing the impeller to closely conform in shape thereto it may be disposed close to the bottom wall and prohibit any salts from settling out under the impeller.

Stub shaft 6^a is provided with a bearing 9^a at the lower end and is driven through a suitable gear box 16^a by an electric motor *m*.

The evaporation shell 1^a is provided with an overflow pipe 24^a through which the liquid may be continuously withdrawn and with an inlet pipe 14^a leading to the center well. In this arrangement the inlet pipe 14^a is shown as leading only to the wall of the well 7^a though it may with advantage be led with insulation to the center of said well as described in connection with the inlet pipe 14 of Figure 2. The inlet pipe 14^a is connected preferably with a constant feed means comprising a chamber 51 having a float 52 controlling a valve 53 in the inlet. The contents of the bottom of the evaporator may be suitably withdrawn through a gate 11^a.

In the form of the invention shown in Figures 6 and 7 the vapors formed by the evaporative cooling conducted in the shell 1^a contact with a plurality of cooling coils 54, which are disposed within the shell 1^a and thereby cause the condensate of such vapors to fall back into the body of liquid within the shell 1^a which is being cooled. While various forms of cooling agents may be employed within the coils 54, in the present instance it is desired that said agents be of such a nature as will provide temperatures suitably low for the provision of high vacuum conditions within the crystallizer. To this end any refrigerant capable of producing the desired low temperature within the vapor steps of the cooling may be employed, but preferably such primary commercial refrigerants as ammonia, sulphur dioxide, methyl chloride, carbon dioxide, etc. are used. By a primary refrigerant is meant any refrigerant which has been produced by mechanical energy and which is used directly for the cooling of vapors rather than one which itself has been produced by absorption of heat by some other refrigerant. In the present case the refrigerant, such as liquid ammonia, is introduced

through a suitable inlet pipe 55 extending to a point approximately midway between the headers 56 and 57. The entering ammonia passes from the header 57 through the coils 54 to the header 56, from which it is discharged into a suitable separation chamber 58 which serves several purposes in the present apparatus: One purpose is the separation of the spent gaseous ammonia from the liquid ammonia, the latter dropping back to the bottom header 57, while the former passes off through an outlet pipe 59 surrounding the inlet pipe 55. A suitable oil drain is provided by tube 60 extending into a depression 61 at the bottom of the surface condenser. The oil carried in with the ammonia is suitably removed by opening release valve 62 in line 60 to allow the pressure within the condenser to discharge the oil. If the oil tends to congeal, the oil drainage may be suitably arranged by the use of a gravity line from depression 61.

When a surface condenser is employed, as shown in Figures 6 and 7 ,within the vapor space of the evaporator 1^a, a material advantage ensues, in that a large part of the water vapor evaporated from the surface of the liquid being cooled during the cooling operation is condensed by said surface condenser and falls back to the surface of the liquid.

Even with this reduction in the volume of gases necessary to be removed in the process of maintaining the vacuum, said volume is still so great that unsatisfactorily large vacuum pump equipment would normally be necessary for this removal. This is particularly true when high vacuum is desired in the cooler or crystallizer shell 1^a. In accordance with another feature of the present invention, however, we have made the separating chamber 58 in the ammonia return line of such size that it almost fills the vapor outlet 4^a of the crystallizer. With such an arrangement the outgoing vapors comprising generally water vapor with small amounts of non-condensible gases are brought into close contact with the surface condenser and an appreciable reduction in water vapor ensues due to condensation of a portion thereof. The remaining water vapor, together with a small volume of non-condensible gases present, can be handled by a vacuum pump of suitably small capacity. The increase in non-condensible gas concentration in the outgoing vapors possible by use of this feature of the invention can be readily appreciated by the following example:

When the crystallizer is being operated so that the condensing temperature of the water in the vapor space 25^a is 63° F., the temperature within the chamber 58 is approximately 50° F. The absolute pressure of the water vapor at 63° F. is 14.52 mm. of mercury, while at 50° F. it is 9.21 mm. of mercury. The non-condensible gas pressure within the vapor space 25^a is of a very low order of magnitude and can be neglected for the purpose of this calculation. A difference of 14.52 minus 9.21 or 5.31 mm. of mercury, is therefore possible by bringing the outgoing gases into close contact with the chamber 58. This value of 5.31 mm. represents the reduction in the water vapor pressure and must be balanced by a corresponding increase in the non-condensible gas pressure since the total pressure in the vapor space is constant. It is, therefore, possible to remove vapors containing approximately

$$\frac{5.31}{14.52}$$

or 36.5% of non-condensible gases, in accordance with this feature of the invention, whereas formerly the non-condensible gas concentration was extremely low and probably less than 1%.

We have found that the use of this feature of the invention, causing a reduction in the volume of outgoing vapors, not only makes possible the use of suitably small vacuum pump equipment but also materially increases the ease and efficiency with which the non-condensible gases are removed from the vapor space of the crystallizer. Without the use of a surface condenser in the outgoing vapor line, we have found that the non-condensible gases tend to collect adjacent the surface of the coils rather than to pass out with the outgoing vapors. When the outgoing vapors are passed over a surface condenser however, to reduce the water vapor content thereof, the movement of the water vapor created a marked sweeping action, causing the non-condensible gases to move away from the surfaces of the coil and out through the vapor outlet. This advantage we consider to be a very important one in the operation of high vacuum equipment.

These advantages may also be obtained by placing a small auxiliary condenser in the outgoing vapor line, and this form may be used with advantage in conjunction with the combination of a vacuum cooler and a barometric condenser, as in Figures 1 and 2.

Vacuum is maintained in the crystallizer by means of a vacuum pump 63 driven by motor 64, which draws a vacuum on line 65 connected through a separator 66 and line 67 to the dome of the crystallizer. The separator 66 is provided with a barometric tail pipe 68.

The apparatus shown in the modification of Figures 6 and 7 may be employed in various processes of crystallizing borax or other solids from solution. For example, hot concentrated borax containing liquor containing approximately 16% anhydrous borax together with fractional percentages of other neutral and basic salts, such as sodium chloride, sodium sulphate, etc., is fed into the apparatus. This liquor is found to be saturated with borax at a temperature of 60° C., but is usually delivered to the crystallizer at 75° C. or higher in order to facilitate handling. Sufficient liquor is placed in the crystallizer to bring the liquor level up to a point corresponding to the line A—A, such level surface being employed to cover the circulating well. During the vacuum cooling and crystallization of borax from such a solution, the volume shrinkage shall not decrease the liquor level below the point where adequate circulation may be maintained through the well 7^a supplied for that purpose. In addition to the height of the liquor at the outset sufficient to compensate for such shrinkage, an excess equal at least to the effective pumping head or lift of the impeller should be provided to prevent decrease of the rate of circulation.

In some instances, it may be preferable to carry off the condensate from the surface condenser. In such cases, an inverted cone louver may be suitably provided to separate the condensate and the body of the liquor in the cooler. Vapors from the surface of the liquor pass through the openings of the louver and are condensed on the surface of the condenser. The condensate drops back to the upper surface of the louver and flows to the bottom adjacent the walls of the cooler. A condensate outlet is conveniently placed in the wall of the cooler near the bottom of the louver.

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 was allowed to drop below the top of the well during operation, circulation would cease, resulting in: (*a*) Poor and uneven cooling with attendant flashing or bumping; (*b*) improper suspension of crystals resulting in production of fine and poorly formed crystals; (*c*) mechanical abrasion of any crystals already formed, due to the same settling to 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 circulation liquor from being positively forced to the cooling surface.

As previously pointed out, circulation necessary for efficient crystallization must be such as to bring all of the liquor into the rapid and thorough contact with the crystals and into rapid and thorough contact with the surface exposed to the cooling source. It is thus an object to provide not merely mixing of the liquors and crystals, but rather a more or less straight line of movement of the entire body of liquor so that all of it comes into intimate contact with the cooling surface over a very short period of time. This is particularly true in the operation of high vacuum equipment, and the reasons therefor will be evident from the following explanation. When a vacuum crystallizer is being operated at a fairly high temperature, a small difference between the temperature of the medium and the temperature to be attained in the crystallizer may easily occasion boiling from a considerable depth due to the steepness of the vapor pressure-temperature curve at higher temperatures. At lower temperatures on the other hand, a smaller difference in temperature will cause boiling practically only at the surface of the liquor as the vapor pressure-temperature curve flattens out appreciably at lower temperatures. Thus when operating at high temperatures the effect of the vacuum itself will cause considerable circulation of liquor whereas at low temperatures substantially only surface circulation occurs as a result of the vacuum itself. This latter, or low temperature condition, exists in the operation of vacuum crystallizers under high vacuum, and in each cases it is necessary to provide means for circulating the liquor which will cause all of the same to come into intimate contact with the surface where the cooling takes place in a very short period of time. For example, in the operation of high vacuum crystallizers as described herein for the production of borax, we have found it preferable to provide a circulation rate which is such that any given unit of the liquor makes a complete circuit from the surface and back to it in approximately ten seconds. Such a circulation is provided by the combination of impeller and internal circulating well as set forth herein, in accordance with our invention.

An important feature of the modified form of apparatus shown in Figures 6 and 7 is that it permits the use of lower cooling temperatures than could be economically maintained with the old style of coolers. We have successfully and economically cooled borax liquors at 25° C. in the apparatus shown in Figures 6 and 7, whereas in previous practice cooling only to about 30° C., or higher, could be economically realized.

Furthermore, the apparatus of the modified form, shown in Figures 6 and 7, may be more easily controlled as to cooling temperature and enables, therefore, a better control over the size and shape of the crystals precipitated in the evaporator.

While the particular form of the apparatus herein described is well adapted to carry out the objects of this invention, it is to be understood that various modifications and changes may be made without departing from the principles of the invention, and the invention includes all such modifications and changes as come within the scope of the appended claims.

We claim:

1. An apparatus for forming single nuclei crystals from a liquor which comprises, a vacuum cooling chamber having a circulating means, a barometric condenser connected with said vacuum cooling chamber, and a surface condenser also connected with said vacuum cooling chamber for condensation of vapors from the liquid being crystallized.

2. In an apparatus for crystallizing liquors, the combination of a cooling chamber comprising a portion for holding the liquors to be crystallized and a vapor space thereabove, means for applying a vacuum to said chamber and means for removing non-condensible gases from said chamber, an outlet for passage of non-condensible gases from said vapor space to said evacuating means, and means for reducing the temperature of said gases below the vapor temperature within said chamber, said means being disposed substantially adjacent to the point of exit of the gases from said vapor space.

3. In combination in an apparatus for crystallizing salts from solution, a cooling chamber having an outlet for non-condensible gases, a vacuum pump for removing said gases through said outlet, and a surface condenser disposed within said outlet, so as to bring said gases into intimate contact with said condenser.

4. In combination in a crystallization apparatus, a cooling chamber for holding the solution to be crystallized, said chamber having a vapor space above the liquor level and an outlet for gases, evacuating means for removing gases and vapors from said outlet, and a condenser disposed within said outlet, the outlying gases coming into intimate contact with said condenser.

5. In combination in a crystallization apparatus, a cooling chamber for holding the solution to be crystallized, said chamber having a vapor space near the top, and an outlet for gases and vapors from said space, a surface condenser arranged within said vapor space, one portion of said condenser being arranged within said outlet and evacuating means for removing gases and vapors from said outlet.

6. In an apparatus for crystallizing salts from solution, the combination of a crystallizing chamber, having a liquor containing portion and a vapor space thereabove, means for applying a vacuum to said vapor space, and a surface condenser arranged within said vapor space.

7. An apparatus for cooling a liquid while precipitating solids therefrom, which comprises a crystallizing chamber, a surface condenser within such chamber but located above the normal liquid level for condensing vapors rising from the liquid, and returning the condensate thereto, and evacuating means for removing non-condensable gases from said chamber, whereby to maintain the liquid therein undergoing evaporative cooling.

8. An apparatus for cooling a liquid while precipitating solids therefrom, which comprises a crystallizing chamber, a surface condenser within such chamber, but located above the normal liquid level for condensing vapors rising from the liquid, and returning the condensate thereto, and evacuating means for removing non-condensable gases from such chamber, whereby to maintain the liquid therein undergoing evaporative cooling, and means for supplying a primary refrigerant to said surface condenser, said surface condenser being provided with means for expansion of the refrigerant during cooling operations.

9. In combination in a crystallization apparatus, a cooling chamber for holding the solution to be crystallized, said chamber having a vapor space near the top, and an outlet for gases and vapors from said space, a surface condenser disposed within said vapor space, said condenser comprising a plurality of conduits for circulation of a gaseous refrigerant and a separation chamber for separation of spent gaseous refrigerant and liquid refrigerant, said chamber being arranged within said outlet to substantially fill the same and thereby restrict the passage of vapors therethrough.

10. In combination in a crystallization apparatus, a cooling chamber for holding the solution to be crystallized, said chamber having a vapor space near the top, a condenser disposed within said vapor space for circulation of a suitable refrigerant, one portion of said condenser being disposed within said outlet to substantially fill the same and thereby restrict the passage of vapors therethrough.

11. In an apparatus for crystallizing liquors, the combination of a cooling chamber comprising a portion for holding the liquors to be crystallized and a vapor space thereabove, means for evacuating said chamber, a circulating well in the liquor-holding portion of said chamber having a cross-sectional area substantially equivalent to one-half the area of said chamber, and an impeller disposed at one end of said well and adapted to draw liquor and sludge down through said well and pass the same up along the outside of said well.

12. In an apparatus for maintaining a liquor in circulation, the combination with a chamber for holding the liquor, of a circulating well arranged vertically within said chamber, a centrifugal impeller mounted to rotate in a horizontal plane below the lower end of said well, the intake and discharge ports of said impeller being arranged to cause circulation of the liquor up the outside of the well and down within said well, and means for rotating said centrifugal impeller.

13. In an apparatus for crystallizing liquors, the combination of a cooling chamber comprising a portion for holding the liquors to be crystallized and a vapor space thereabove, means for evacuating said chamber, an outlet for passage of gases and vapors from said vapor space to said evacuating means, a circulating well arranged vertically within the liquor-holding portion of said chamber, a centrifugal impeller rotatably mounted to rotate in a horizontal plane near the lower end of said well, the intake and discharge ports of said impeller being arranged to cause circulation of the sludge up the outside of the well and down within said well, and means for rotating said centrifugal impeller.

14. In an apparatus for maintaining circulation of a liquor, the combination with a chamber for holding the liquor, of a circulating well having a cross-sectional area substantially equivalent to one-half the area of said chamber, and a centrifugal impeller disposed below said well and adapted to draw the liquor and sludge down through said well and pass the same up along the outside of said well.

15. In an apparatus for crystallizing liquors, the combination of a cooling chamber comprising a portion for holding the liquors to be crystallized and a vapor space thereabove, means for evacuating said chamber, an outlet for the passage of gases and vapors from said vapor space to said evacuating means, a circulating well having a cross-sectional area substantially equivalent to one-half of the area of said chamber disposed within the liquor-holding portion of said chamber, and a centrifugal impeller disposed at the lower end of said well and adapted to draw liquor and sludge down through said well and pass the same up along the outside of said well.

16. In combination in a crystallizer, a chamber for holding the solution to be crystallized, means for cooling said solution, a circulating well having a cross-sectional area substantially equivalent to one-half the area of said chamber, and a centrifugal impeller disposed adjacent one end of said well and adapted to draw the liquor and sludge down through said well and pass the same up along the outside of said well.

17. An agitator for crystal sludges which comprises the combination with a chamber for holding the sludge, of a vertical circulating well, an impeller mounted to rotate in a horizontal plane below said well, said impeller comprising a plurality of vertical impeller vanes spaced peripherally around a central intake opening.

18. An apparatus for crystallizing salts from solution comprising a crystallizing chamber, a well for dividing said chamber into an upward and a downward path for circulation of the solution to be crystallized, a centrifugal impeller mounted near the lower end of said well, the cross-sectional area of the discharge ports of said impeller being approximately equal to the area of said well.

19. In an apparatus for effecting circulation of sludges, the combination with a chamber for holding the sludge, of a circulating well having a cross-sectional area substantially equivalent to one-half the area of said chamber, and a centrifugal impeller disposed at the lower end of said well and adapted to draw liquor and sludge down through the said well and pass the same up alongside of said well, the total cross-sectional area of the discharge ports of said centrifugal impeller being substantially equivalent to the cross-sectional area of said well.

20. An apparatus for crystallizing salts from liquors through vacuum evaporative cooling comprising a cooling chamber including a portion for holding the liquors to be crystallized and a vapor space thereabove, means for evacuating said chamber, a circulating well having a cross-sectional area substantially equivalent to one-half the area of said chamber and located within the liquor-holding portion of said chamber, a centrifugal impeller disposed at the lower end of said well and adapted to draw liquor and sludge down through said well and pass the same up along the outside of said well, the total cross-sectional area of the discharge ports of said centrifugal impeller being approximately equal to the cross-sectional area of said well.

21. An agitator for crystal sludges comprising a chamber for holding the sludge, a vertical cir-

culating well within said chamber, and a centrifugal impeller mounted in a horizontal plane adjacent the bottom of said well, said impeller including a lower plate, an annular upper plate and a plurality of vertical vanes disposed between said plates to impart substantially radial movement to the liquor entering said impeller.

22. In an apparatus for crystallizing salts from solution, the combination of a crystallizing chamber, a circulating well mounted in said chamber and a closed, single suction, centrifugal impeller mounted for rotation adjacent to the lower end of said well, the cross-sectional area of the intake ports of said impeller being substantially equivalent to the cross-sectional area of the discharge ports thereof.

23. An apparatus for circulating crystal sludges, comprising a chamber having a vertical circulating well, and a single suction, closed, centrifugal impeller mounted horizontally near the lower end of said well, said impeller comprising a bottom plate, an annular top plate, and a plurality of short vertical vanes mounted between said plates around a central opening and connecting the inner and outer edges of said plates, the diameter of said impeller being substantially equivalent to that of said well.

24. An apparatus for crystallizing salts from solution, comprising a crystallizing chamber having a circulating well and an annular return chamber, rectifying vanes in said annular return chamber, the annular space of said return chamber being substantially unobstructed except for said rectifying vanes, and a centrifugal impeller at the lower end of said circulating well for drawing liquor through the circulating well and pumping it back around the annular return chamber.

25. In combination, in an apparatus for crystallizing salts from solution, a cooler including a chamber for holding the solution to be crystallized and a vapor space thereabove, means for evacuating said chamber, a vertical circulating well in said chamber, an inlet for introducing solution into said chamber at a point below the level of the liquor at which said solution will boil, an impeller for drawing liquor down said well and returning the same around the outside thereof and an outlet above the top of said well.

26. In an apparatus for crystallizing salts from solution, the combination with a crystallizing chamber comprising a liquor-holding portion and a vapor space thereabove, means for applying a vacuum to said vapor space to cause vaporization of the solution to be crystallized, of a circulating well supported vertically beneath the liquor level in said portion, an impeller causing circulation of said solution down and around said well, and means for introducing liquor into said well at a point below the level at which ebullition of said incoming liquor will occur.

27. In combination, in an apparatus for crystallizing salts from solutions, a crystallizing chamber, means for applying a vacuum to said chamber, an internal circulating well dividing said chamber into up and down passages, impelling means for causing the liquor to be crystallized to flow through said passages and an inlet for introducing said liquor to be crystallized into the said downward passage.

28. A crystallizing apparatus which comprises a crystallizing chamber, means for applying a vacuum to said chamber, an internal circulation well within said chamber, impelling means for causing movement of the liquor to be crystallized down the interior of said well and up the outside thereof and an inlet for introducing liquor to be crystallized into the interior of said well at a point below the level of ebullition of said liquor, the height of said well being sufficient to permit a thorough distribution of the fresh liquor with the cooling liquor below the ebullition level within said chamber.

29. An apparatus for crystallizing salts from solution comprising a cooling chamber having a portion for holding liquor to be crystallized and a vapor space thereabove, means for removing non-condensible gases from said vapor space, and surface condensing means for condensing water vapor from the gases and vapors rising from the liquor being cooled whereby a vacuum is established and said liquor is cooled through vaporization of water therefrom.

30. A vacuum evaporative cooling apparatus, comprising a vacuum cooling chamber including a portion for holding liquors and a vapor space thereabove, means for evacuating said chamber, an outlet for gases or vapors from said vapor space to said evacuating means, and a surface condenser for condensing water vapor from the gases and vapors going to said evacuating means, and means for servicing said surface condenser with a primary refrigerant.

31. A vacuum evaporative cooling apparatus, comprising the combination of a vacuum cooling chamber having a liquor containing portion and a vapor space thereabove, means for applying a vacuum to said vapor space, a surface condenser arranged within said vapor space, and means for servicing said surface condenser with a primary refrigerant.

32. An apparatus for cooling a liquid while precipitating solids therefrom, which comprises a crystallizing chamber, a primary refrigerant serviced surface condenser located within such chamber above the normal liquid level therein, for condensing vapors rising from the liquid, an evacuating means for removing non-condensible gases from said chamber, whereby to maintain the liquid therein undergoing evaporative cooling.

33. An apparatus for crystallizing salts from solution, comprising a cooling chamber having an outlet for non-condensible gases, said cooling chamber having a surface condensing means disposed within the vapor space of said chamber for condensing and refluxing the vapors in said chamber, a vacuum pump for removing non-condensible gases from said chamber, and surface condensing means disposed at the outlet of non-condensible gases from said chamber and arranged to bring said non-condensible gases into intimate contact therewith.

34. In vacuum evaporative apparatus, the combination with a chamber for holding the liquor to be vaporized and containing a vapor space, means for removing non-condensible gases from said space, means for condensing vapors from said solution and means arranged between said condensing means and said evacuating means for further cooling said vapors.

35. An apparatus for circulating sludges, comprising a chamber for holding the liquor to be circulated, a vertical circulating well having a cross-sectional area substantially equivalent to one-half the area of said chamber, and a single suction, closed, centrifugal impeller disposed horizontally below the well, said impeller comprising a bottom plate, a narrow annular top plate, and a plurality of short vertical vanes

mounted between said plates around a central opening and connecting the inner end and outer edges of said plates, the diameter of said impeller being at least as great as that of said well and the cross-sectional area of the intake ports of said impeller being substantially equivalent to the cross-sectional area of the discharge ports thereof.

36. In a vacuum crystallizer, the combination of a chamber for holding the solution to be crystallized and having a vapor space, a vacuum pump for evacuating said space, means for condensing vapors rising from said solution as a result of the application of a vacuum thereto, and means disposed between said condensing means and said vacuum pump for further cooling the gases going to the vacuum pump.

37. In an apparatus for crystallizing salts from solution, the combination of a crystallizing chamber having a liquor containing portion, a vapor space thereabove, and a non-condensible gas outlet, means for removing non-condensible gases from and applying a vacuum to said vapor space, a surface condenser arranged within said vapor space, and means for further cooling the gases leaving said vapor space.

38. In vacuum evaporative apparatus, the combination with a chamber for holding the liquor to be vaporized and having a vapor space, means for removing non-condensible gases from said space, means for condensing vapors from said solution and surface condensing means arranged between said non-condensible gas removal and said condensing means, the gases and vapors passing toward said gas removal means coming into intimate contact with said surface condensing means.

39. In combination in a crystallization apparatus, a cooling chamber for holding the solution to be crystallized, said chamber having a vapor space and an outlet for gases, evacuating means for removing gases and vapors from said outlet and applying a vacuum within said chamber and a condenser disposed within said vapor space, the outgoing gases coming into intimate contact with said condenser.

ROBERT B. PEET.
WILLIAM E. BURKE.
WILLIAM H. ALLEN.
WILLIAM A. GALE.
CHARLES F. RITCHIE.