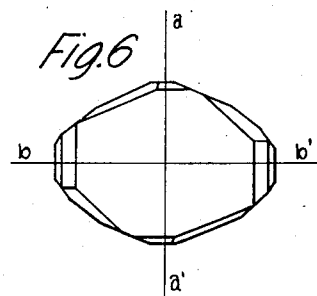
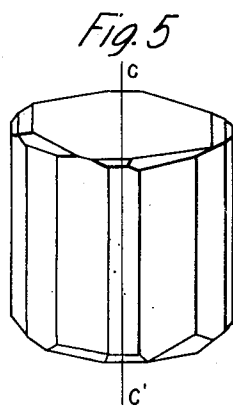
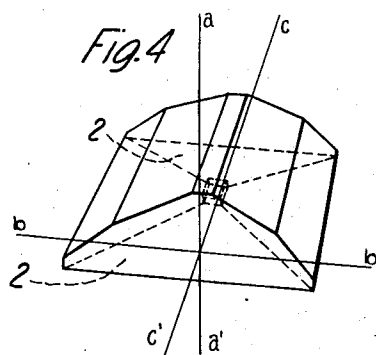
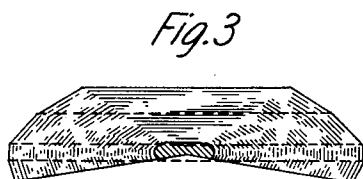
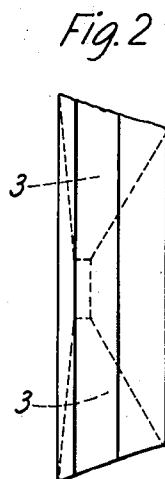
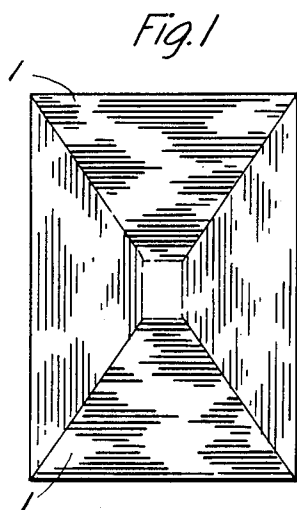


March 30, 1926.

1,578,677

A. M. NICOLSON
METHOD OF GROWING CRYSTALS
Filed Sept. 30, 1924



Inventor:
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UNITED STATES PATENT OFFICE.

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METHOD OF GROWING CRYSTALS.

Application filed September 30, 1924. Serial No. 740,747.

To all whom it may concern:

Be it known that I, ALEXANDER M. NICOLSON, a subject of the King of Great Britain, residing at New York, in the county of New York, State of New York, have invented certain new and useful Improvements in Methods of Growing Crystals, of which the following is a full, clear, concise, and exact description.

This invention relates to crystals of chemical compounds and to methods of producing the same.

It has for an object to improve methods of producing crystals and particularly, crystals possessing piezo-electric properties.

Another object is the provision of highly efficient methods of growing crystals and methods which will yield uniform products in any desired quantity.

The invention has particular reference broadly to crystals having the hour-glass structure and specifically to crystals of Rochelle salt.

An understanding of the "hour-glass" structure, as applied specifically to Rochelle salt crystals, will be evident from the detailed description given in connection with the drawings.

Fig. 1 of the drawings is an elevation showing the basal plane of a crystal of Rochelle salt having the hour-glass structure, and grown in accordance with the method comprised in this invention.

Fig. 2 is a sectional view in side elevation of the crystal shown in Fig. 1. This view is one through the "c," "a" plane of the crystal.

Fig. 3 is a sectional view in end elevation of the crystal shown in Fig. 1 and is a view through the "b," "a" plane.

Fig. 4 is a perspective view of such a crystal showing the several axes of the crystal.

Fig. 5 is an elevation of a complete crystal of Rochelle salt grown slowly and by suspension from a thread.

Fig. 6 is a top view of the crystal shown in Fig. 5.

It has heretofore been known that crystals of the required size and structure for piezo-electric appliances could be grown from seed crystals by the application of a temperature gradient to a saturated solution of the salt. This method, under conditions of rapid cooling, such as a temperature drop in the

mother liquor of from 35-38° C. to 20° C. over a period from 10 to 20 hours, for example, has been found to produce large crystals having the desired "hour-glass" structure. Crystals of Rochelle salt may be grown in the mother liquid by suspension from a thread, by flotation on mercury or by being laid on a glass plate, but it has been found that for piezo-electric appliances it is usually desirable to employ but half the complete crystal, shown in Figs. 5 and 6, and for this reason the crystal is usually grown by laying a seedling upon a glass plate or upon mercury.

Referring to Figs. 1, 2, 3 and 4 of the drawings, which indicate the general appearance of crystals grown in accordance with this invention, the crystal surfaces may be classified into two systems of surfaces, or zones, which are normal to each other. One system of zones is parallel to the principal or crystallographic axis "c," and therefore engirdles the crystal. The other system of zones comprises the two basal planes parallel with the "a" and "b" axes. In this classification of the crystal surfaces, the three axes, "a," "b" and "c," are all perpendicular to each other.

In accordance with this invention the hour-glass structure is produced by growing the crystals with the "c" and "b" axes in a horizontal position, in which position a crystal is represented in Fig. 4 of the drawings. This growth forms a particular habit, becoming dominant along the "c" and "b" axes, while development along the "a" axis upwards is suppressed on account of the supersaturation and consequent gradation in density of the liquor. This upward development along the "a" axis may be further suppressed by methods and for reasons pointed out in my prior Patent 1,438,965, dated December 19, 1922.

The crystals are grown from perfect nuclei, possessing definite form and having "a," "b" and "c" axes corresponding to the "a," "b" and "c" axes shown in Figs. 4, 5 and 6. In obtaining seed crystals, generally from a previous cropping, those seeds are selected in which growth along the "b" axis is fully developed (which happens when the seed nucleus grows with its "c" and "b" axes horizontal). These seeds are square, or nearly so, which signifies that the growth

along the "b" axis is about as great as or greater than that along the "c" axis. The thickness of the selected seed crystal along its "a" axis is generally 4/10 of that along its "b" axis. This dimension is a function of the density and head of the mother liquor.

It has been noted that the crystal usually grows to the desired size, to such a size for instance, that it weighs about 100 grams, during a period of from 5 to 10 hours and may be taken from the mother liquor when it has attained such size, although growth may be continued for days, during the condition of saturation, by allowing the crystal to remain in the mother liquor. It appears probable that rapid growth due to this rapid cooling of the mother liquor, causes the crystal to develop internal stresses producing strain regions symmetrical with the principal axis "c." One cause of these stresses may be the contraction which results when the temperature of the mother liquor falls. In this respect, it has also been noted that as Rochelle salt crystallizes, heat is given off and it is believed that this heat may momentarily arrest crystallization until the temperature again falls, when crystallization with the consequent evolution of heat, and the arrest of crystallization again results. Working upon this theory, the crystal should be developed in definite layers corresponding to the periods during which crystallization takes place; it has been noted in this connection that the crystal is built up in such a manner of definite layers of Rochelle salt. It is believed, further, that this continued cycle of events throughout the crystallization period may cause the stress which results in the hour-glass structure. This composite or hour-glass structure, which results from this stress, is closely related to the surface zones defined above and to the electric poles which will now be described in relation to the composite structure.

At each end of the seed nucleus in the crystal and along its "c" axis there appears a pyramid, the base of which forms a polar terminal. These pyramids are not always pronounced in the seed nucleus but are more evident in the grown crystal after the latter has been dessicated, as described in my prior Patents 1,414,370, dated May 2, 1922 and 1,438,965, dated December 19, 1922. These pyramids in the crystal are indicated at 1 in Fig. 1, at 3 in Fig. 2, and at 2 in Fig. 3. They consist of stratifications parallel to the "b" axis and normal to the "c" axis and the remainder of the crystal structure, the stratifications of which are parallel to the "c" axis. The electrical performance of the crystal suggests that the crystal molecules throughout

the pyramidal regions are subject during growth to forces which turn them, in planes containing the principal axis, through a right angle. This is indicated by the fact that the crystal, after the treatment, mentioned above, which tends to render more pronounced these pyramidal terminals, develops its electrical poles (plus or minus corresponding to the conventional analogous and antilogenous poles) in accordance with the system of zones referred to above. The poles are accordingly orthogonal, that is, at right angles to each other. This signifies that the bases of the pyramids, which occupy almost the entire area of the basal planes of the crystal, are electrically plus when the remainder of the crystal structure is minus and vice versa.

In the production of crystals having this hour-glass structure, by methods heretofore employed, it has been found that not only could successive growths not be guaranteed from a specifically prepared liquor, but variations in the quality of the growth often proved unavoidable in spite of extreme care as regards uniformity of the crystallization operations. These variations refer principally to the size and clarity of resulting growths and to the degree of spontaneous precipitations. It was noticed for example, in practising methods described above, that the crystal of Rochelle salt was often undersized, or that a large number of nuclei were present which resulted in the production of a quantity of small crystals, instead of a single large crystal, as was desired.

In this respect, applicant has discovered that the crystal structure, as finally produced, is determined to a large extent not only by the conditions under which it is actually grown but also by the manner of preparing and handling the solution which is to be used for growing crystals.

One cause of the presence of a quantity of small crystals along with one larger Rochelle salt crystal, which grew from the seedling inserted, was thought to be the presence of impurities in the raw material from which the mother liquor was produced. The raw material usually employed to form the saturated solution of Rochelle salt was commercial Rochelle salt and it was believed that this material possibly contained, other than pure Rochelle salt, also some uncombined sodium and potassium tartrates.

It has been pointed out by van Leeuwen in "Zeitschrift für Physik. Chemie" 1897—23—33, that in cooling a Rochelle salt solution from above 40° C. to below 40° C. crystals of both Rochelle salt and sodium tartrate were formed and that in cooling from above 55° C. to below 55° C. these crystals and, in addition, potassium tartrate crystals were formed. This suggests a reason for the

possible presence of varying amounts of sodium and potassium tartrate in commercial Rochelle salt.

Although the control of the solution up to and during the period of crystal growth has such a determining effect as noted above upon the crystal structure, it is practically immaterial, according to the method of the invention, what the previous history of the raw material has been or whether sodium or potassium tartrate are present in relatively large amounts. The process according to the invention can therefore use commercial Rochelle salt as the raw material and this fact alone makes for economical production since it is a convenient and cheap form of raw material.

According to the features of the invention, an improved method of growing crystals comprises the solution of sodium potassium tartrate to form a nearly saturated solution of Rochelle salt having a history regulated as regards temperature; then, always regulating the temperature, growing crystals from a solution as thus prepared by starting the hour-glass structure with rapid cooling and employing thereafter any temperature gradient which will insure the maintaining of a super saturated mother liquor. Such a process as practiced under the invention consists of substantially three stages, namely:

1. The process of aging.
2. The production of a stock solution.
3. The crystallization process.

Steps (1) and (2) can be combined into one more or less continuous process if desired, but are given herein as two steps for clearness.

The aging process consists substantially in allowing commercial Rochelle salt to remain in contact with water until an equilibrium between the sodium tartrate, potassium tartrate, sodium-potassium tartrate and water is reached, at all times keeping the temperature below 40° C. It has been found that such an equilibrium is reached when the density has become constant with constant temperature. In allowing commercial Rochelle salt to dissolve in this manner in water, it appears that the uncombined sodium and potassium tartrates which are believed to be present re-combine to form pure Rochelle salt, and in this manner the percentage of uncombined sodium and potassium tartrates in the mother liquor is materially reduced. In accordance with the invention, the aging process might be carried out in two steps, the first of which might consist in allowing commercial Rochelle salt to dissolve in water, while the second might consist in stirring this solution in contact with Rochelle salt until the density has become constant, maintaining the temperature of the solution, throughout the process, by

means of a thermostat at between 38 to 40° C.

While the use of two steps in the aging process has been suggested herein, it will be appreciated that it is not intended to place any restriction upon the process other than those set forth in the claims, but that the process may be carried out in any desired manner such as, for example, simply stirring water in contact with Rochelle salt until a constant density is reached.

A stock solution is then prepared by slightly under-saturating the saturated solution of the previous step by the addition of water whose temperature is not above 40° C. and filtering, after which the under-saturating process is continued to the desired degree. It has been found desirable to maintain a container of water in the same thermostat used in the aging process so that water, having the same temperature as the saturated solution, may be used; in this manner, the temperature of the mother liquor during preparation may be more accurately controlled. The use of a slightly under-saturated solution in place of the usual saturated solution has been found desirable as the temperature of such a solution may be lowered several degrees below 38° C., depending upon the degree of under-saturation, before saturation with its resultant spontaneous precipitation results. It has been found desirable to eliminate spontaneous precipitations as those solid particles which are thereby formed have been found to act as individual nuclei in the crystallization stage, and owing to their presence, a number of small crystals are formed instead of one large crystal as is desired. The possibility of allowing a reduction in the temperature before spontaneous precipitation results is desirable in that such reductions in temperature become unavoidable during the transfer of the mother liquor from one stage to another, such as in the filtering step, or in the transfer of the liquor to crystallizing dishes, for example. A stock solution as prepared above is suitable for use as a mother liquor for growing crystals at any desired time and may be maintained in good condition so long as the temperature is always maintained between 38 and 40° C.

The final, or crystallization, stage consists in inserting a seed crystal, of the type described above, in a quantity of this stock solution in a crystallizing dish or other suitable container, and carrying the temperature from 38-40° C. down to approximately 20° C. over a period of from 10 to 12 hours, causing rapid cooling at the start in order to induce growth of the hour-glass structure. This desired temperature gradient may be satisfactorily produced by enclosing the crystallizing dish within a booth for example, the booth temperature being con-

stant at about 20° C. By enclosing the liquor within such a booth, the cooling action of air currents is substantially eliminated and the temperature drop of the mother liquor is therefore gradual. The employment of a booth temperature of about 20° C. insures rapid cooling at the start as the mother liquor, when introduced into the booth, is at a temperature of about 38° C.; after this rapid cooling, however, the mother liquor temperature gradually approaches the booth temperature. In this manner rapid cooling results at the start, while thereafter, the temperature decreases more slowly and the ratio of the temperature drop to the time becomes smaller as the time increases. These conditions of temperature history have been found to produce very satisfactory results.

While rapid cooling has been found to be desirable in order to insure growth of the hour-glass structure, the cooling should not be too rapid, as it has been found that sudden drops in temperature may often result in spontaneous precipitations, as pointed out above.

Applicant has found, in practising methods of growing Rochelle salt crystals, that satisfactory and uniform results were not obtained if, at any time during the history of the solution, the temperature had been raised above 40° C. Heretofore, it has been common practice to warm the mother liquor, during preparation, in order to facilitate solution of the Rochelle salt. In such practice, applicant has found that if the temperature has at any time during preparation of the solution been above 40° C., variations in the crystals formed resulted; these variations refer principally to the number and uniformity of crystals formed in the crystallization stage. In accordance with the features of this invention, therefore, the mother liquor should possess a well regulated temperature history so that the temperature has never been above 40° C. and preferably has always been at 38° C.

In a method of crystal production which applicant has found satisfactory, Rochelle salt is allowed to stand in contact with water for a period of several months, the temperature always being maintained below 40° C. This solution is then stirred at 37.5 to 39.5° C. in contact with Rochelle salt until the density has become constant at a value approximately 1.39 (38° C./50° C.). Water, whose temperature has likewise been controlled at approximately 38° C., is added, with stirring, to the constant density solution until its density reaches a value between 1.37 (38° C./50° C.) and 1.38 (38° C./59° C.). This solution is then filtered and after being filtered is maintained at a temperature of 38-40° C. until it is desired for use as mother liquor. At such a time it is poured without allowing appreciable chilling to take place,

into crystallizing dishes, which in turn, are placed in a booth, such as described above, and a seedling inserted, as likewise pointed out above. Crystals grown in this manner have been found to possess the properties and characteristics desired for piezo-electric appliances, and further, the results obtained have given indications of great uniformity.

The use of the figures "38° C./50° C." herein in connection with density readings is intended to define the density of a substance at a temperature of 38° C. as given by a hydrometer which is calibrated for use at 50° C. In other words, it specifies the relation in weight between equal volumes of a particular substance and water, the temperature of the substance being 38° C. and that of the water 50° C.

The amount of water added to under-saturate the mother liquor and therefore, also, the density of the mother liquor will depend primarily upon the degree of under-saturation which is desired. This degree of under-saturation will, of course, depend upon the amount of cooling which it is estimated the liquor must undergo before actual crystallization is desired. The density of the unsaturated mother liquor may be varied, for example, between 1.36 and 1.39 (38° C./50° C.) This variation in the degree of under-saturation employed makes this method applicable over a wide range of conditions to which previous methods were not applicable.

In selecting raw material to produce a mother liquor for use in the method of the invention it has been found that commercial Rochelle salt regardless of its degree of dehydration or decomposition, may be used, as long as it is free of other impurities. It is desirable, however, to pulverize the raw material employed in order to hasten solution, as it has been noted that an especially long period of time is required to form a saturated solution of Rochelle salt from dehydrated crystals of Rochelle salt.

It has also been found desirable in many instances to cover the surface of the liquor during the crystallization stage in some suitable manner, so that the surface will not be cooled appreciably more rapidly than the remainder of the liquor. A porous covering stretched across the top of the crystallization dish, for instance, would retard such cooling. Another method of retarding this surface cooling action might be to cover the surface of the liquor with a warm metallic plate.

In the elimination of spontaneous precipitations, it has been found desirable not only to prevent chilling, as noted above, but also to prevent the subjection of the mother liquor to vibrations during the crystallization stage, as it has been noted that spontaneous precipitations are often caused by vi-

brations. It has further been noted in this respect that the mother liquor should not be contaminated by any small particles of foreign matter as such particles act, in many instances, similar to spontaneous precipitations, as nuclei for crystal growth.

Instead of using a small crystal as a nucleus from which to grow a crystal, a fragment of a full grown crystal having the desired characteristics may be used as a nucleus to start crystallization. This avoids having to select a seedling crystal of the proper characteristics according to the procedure pointed out above, and gives a greater assurance of obtaining a crystal having the desired characteristics.

What is claimed is:

1. The method of preparing a mother liquor from which to grow hour-glass crystals of Rochelle salt, comprising dissolving Rochelle salt in water to secure complete equilibrium between the solvent and the solute, maintaining the solution at all times at a temperature not exceeding 40° C. and adjusting its density to a value between 1.37 and 1.38 (38° C./50° C.).

2. The method of producing Rochelle salt crystals comprising dissolving Rochelle salt in water, aging the resulting solution at a temperature at least as low as 40° C., undersaturating said solution by adjusting the density to a value between 1.36 and 1.39, and growing the crystals from said solution by applying rapid cooling.

3. The method of producing Rochelle salt crystals comprising forming a solution of Rochelle salt in water, maintaining said solution in contact with Rochelle salt between

temperatures of 37.5° to 39.5° C. until practically complete equilibrium is obtained between solvent and solute, slightly undersaturating said solution still maintaining the temperature within the mentioned region, and growing crystals from said solution by starting rapid cooling from said temperature region.

4. In the art of growing Rochelle salt crystals from a solution of the salt in water, the method comprising maintaining the solution from which the crystals are grown at a temperature at least as low as 40° C. from and during the time the solution is made until the crystal is grown.

5. The method of producing crystals of Rochelle salt which comprises producing a mother liquor and growing crystals from said liquor, at all times maintaining the temperature of said liquor below 40° C.

6. The method of producing crystals of Rochelle salt having the hour-glass structure which comprises producing a nearly saturated solution of Rochelle salt, placing a nucleus composed of Rochelle salt in contact with said solution, controllably regulating the temperature of said solution so that its temperature has never been above 40° C., and lowering the temperature of said solution after insertion of said nucleus, at a rate adapted to cause a degree of supersaturation favorable for growth of the hour-glass structure.

In witness whereof, I hereunto subscribe my name this 29th day of September A. D., 1924.

ALEXANDER M. NICOLSON.