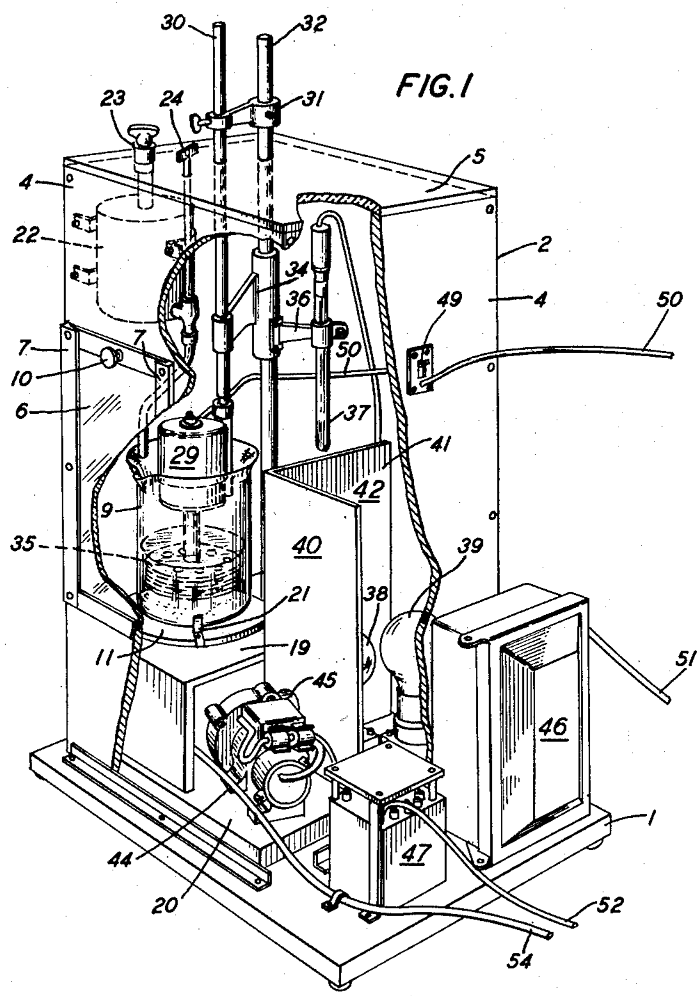
April 15, 1952 E. S. PENNELL 2,592,729

METHOD OF ETCHING ETHYLENE DIAMINE TARTRATE CRYSTALS

Filed May 25, 1949 2 SHEETS—SHEET 1

FIG. 1



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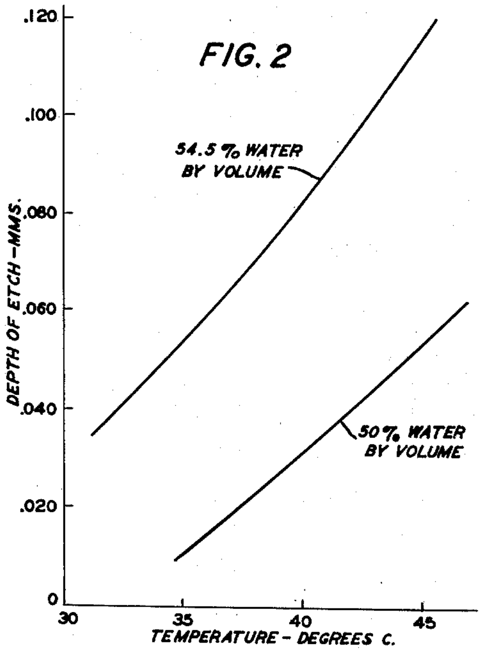

FIG. 2

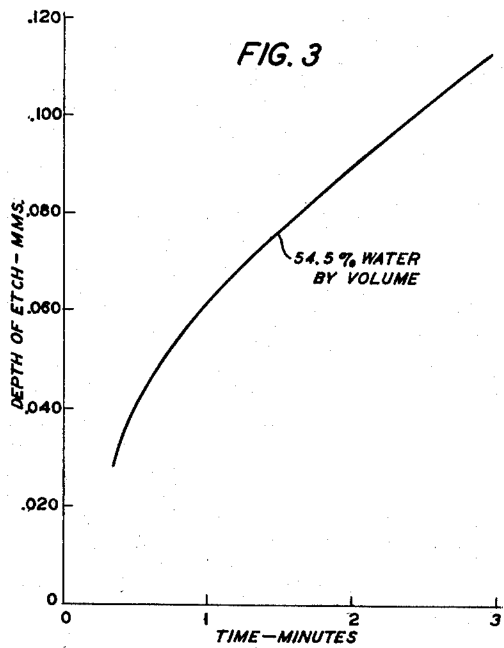

FIG. 3

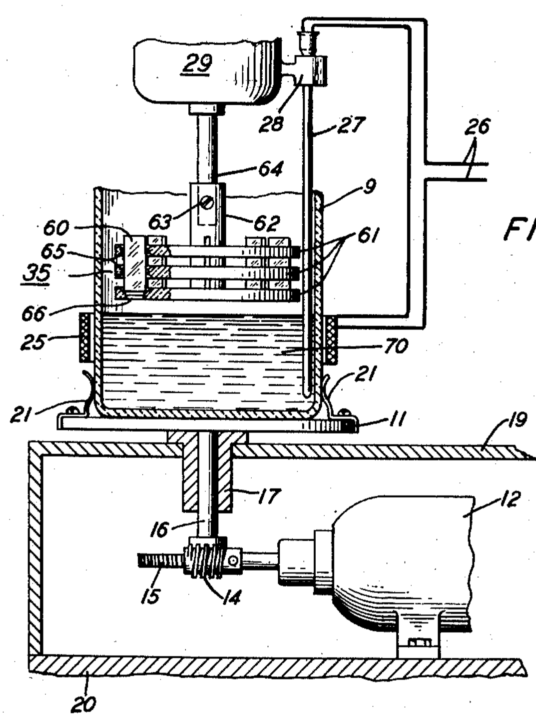

FIG. 4

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METHOD OF ETCHING ETHYLENE DIAMINE TARTRATE CRYSTALS

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2 Claims. (Cl. 41—42)

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This invention relates to the production of synthetic crystals, and particularly to an improved method of processing crystals of ethylene diamine tartrate.

The employment of synthetic piezoelectric crystals has expanded rapidly because of a great increase in the number of applications of piezoelectric phenomena, and the relatively short supply of natural quartz. Piezoelectric crystals have the ability to resonate very sharply, and possess a high degree of frequency stability. These and other characteristics make them extremely useful in the communication field, for example, for purposes such as the rigid frequency control of radio transmitters, and the separation of carrier channels in toll telephony, where sharp frequency discrimination is necessary.

Ethylene diamine tartrate, usually abbreviated as EDT, is one of the better known of the synthetic piezoelectric crystal materials. Large crystals are grown commercially from small seeds introduced into the mother liquor, which is a saturated solution of ethylene diamine tartrate. From the large crystals, blanks are cut approximately to size, with the proper orientations and of the proper shapes to provide the desired characteristics in the finished product. The blanks are then etched to eliminate surface irregularities and insure high stability of the frequency and other constants of the finished plate. The immersion etching brings the crystal closer to the proper frequency, but final frequency adjustments are commonly made following the plating of the etched surfaces with gold or a similar metal to serve as surfaces to which electrical connections may be made.

A substantial amount of wastage has been experienced in the preparation of EDT plates because of the presence of "bloom," which appears on the crystalline surface as whitish spots. Bloom interferes with the functioning of the crystal, and must be removed. In some cases the crystal may be then reprocessed for use at higher frequencies than were originally intended; in others, it must be discarded. Bloom has been identified as EDT·$1H_2O$, a previously unknown monohydrate form of EDT. It grows as a clear, crystalline material, but readily gives up its water of crystallization on exposure to dry air, leaving a finely divided anhydrous residue. It has been found that monohydrate formation, which is most troublesome in the etching stage, may be eliminated by the use of the method and apparatus described below. The etching must be carried out at an elevated temperature, and

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the crystals then dried substantially instantaneously in such a way that the temperature cannot drop below 41° C. at any point on the surface with which water may be in contact.

The crystals to be etched are mounted in a basket attached to the shaft of a high speed motor, and the motor and basket lowered until the crystals are submerged in the etching bath. The vessel holding the etching bath is mounted on a turntable, which is rotated slowly to agitate the etchant. The etchant may suitably be a mixture of propylene glycol and water. After the required depth of etch has been obtained, the basket is raised until the crystals are clear of the bath, and the high speed motor energized so that the crystal basket and crystals are rotated rapidly, subjecting them to a radial acceleration of about 600 G, to drive off the etchant. The motor, crystal basket, and etching bath with its turntable, are enclosed in a heat-insulated chamber, the temperature of which is kept above the 41° C. minimum by heating and air-circulating means controlled by a thermo-regulator.

When the crystals and basket have been centrifuged dry, the chamber is opened and the crystals removed. They must thereafter be protected from water from any source, including perspiration, breath moisture, or excessive humidity, during subsequent steps in production. When the etching is carried out as described above, it has been found that the loss from bloom formation may be reduced to a negligible amount.

The invention may be better understood by reference to the drawings in which:

Fig. 1 is a perspective view of a preferred embodiment of the apparatus of the invention, partially broken away to shown the details of the construction more clearly;

Fig. 2 is a graph showing the depth of etching as a function of temperature for a given time of immersion;

Fig. 3 is a graph showing the depth of etching as a function of time; and

Fig. 4 is a fragmentary view, partially in section, showing details of the construction of the etching bath, the basket, and the turntable drive.

It is to be understood that the embodiments shown are illustrative only of the principles of the invention, and that it is intended to include within the scope of the appended claims all variations in the form and arrangements of the elements, and all substitutions of materials, which may occur to those skilled in the art.

In Fig. 1 of the drawings there is shown a simplified embodiment of the equipment for practicing the invention. Base 1 supports a closed, controlled-temperature chamber 2, the walls 4 of which are made of suitable heat-insulating material. The top 5 of the chamber 2 is made of a transparent material such as that known under the trade name of "Lucite," a thermoplastic methyl methacrylate resin, in order that the attendant may inspect the operations within the chamber. An observation panel 6 of similar material is slidably disposed in guides 7 in one of the chamber walls 4, adjacent to the etching bath vessel 9. Panel 6 may be raised by means of a knob 10 to afford access to the vessel 9 when the etchant is to be renewed, or when the etched crystals are to be replaced by a new batch for treatment.

The etching bath vessel 9 is mounted on a turntable 11, which is rotated at a very slow speed, usually about one revolution per minute, by means such as those shown in detail in Fig. 4. An electric motor 12, acting through a worm gear 14 and a pinion gear 15 provides for this rotation. The direct connection between pinion gear 15 and turntable 11 is made through a shaft 16 extending through a journal bearing 17 fixed in a bearing support frame 19. The bearing support frame 19 is secured to a subbase 20, which in turn rests on base 1. Subbase 20 acts also as an inner positioning guide for the walls 4 of chamber.

Spring clips 21 are provided on the turntable 11 and arranged to receive the vessel 9 and hold it centered on turntable 11. Vessel 9 is preferably transparent, easily cleaned, and chemically inert with respect to the etchant. A glass beaker, of the type commonly used in chemical laboratories, and of suitable size, is satisfactory for this purpose.

The etchant, which is preferably a mixture of propylene glycol and water, is stored prior to use in a closed tank 22, mounted within chamber 2 and fillable through a port 23, until it has warmed up to the ambient temperature, which is held at 45° C. or above. It is then transferred by gravity feed to the vessel 9 through operation of an externally controllable valve 24. It is necessary to retain the etchant in the closed tank 22 until it has reached equilibrium with the temperature of chamber 2, and transfer it to vessel 9 only just before etching, because evaporation from the surface of the etchant, once it has been delivered to the vessel 9, will cool it rapidly. A drop of several degrees below the chamber temperature will occur, mostly in the first fifteen minutes of exposure, and more slowly thereafter, so that the time during which surface evaporation may occur should be minimized. Fresh supplies of etchant must be introduced through port 23 to maintain proper strength.

In some cases it may be desirable to use the embodiment shown in Fig. 4, in which the temperature of the etchant in the vessel 9 is separately controlled and the tank 22 may be omitted. A heating coil 25 is disposed around vessel 9, but spaced therefrom sufficiently to allow the vessel to be readily inserted or removed. Heating current is supplied to coil 25 from a conventional source, not shown, through leads 26 under the control of a thermo-regulator 27, so mounted, as by a bracket 28 secured to the centrifuge motor 29, that it is suspended in the liquid during the etching. With this construction, the temperature of the etchant may be held within narrow limits than with that shown in Fig. 1.

In either embodiment, centrifuge motor 29 is fixed to a rigid support rod 30. Rod 30 extends slidably through the chamber top 5 and is secured by a clamp 31 which may be loosened to permit adjustment of the vertical position of the motor from the outside of chamber 2. Clamp 31 is secured to a relatively heavy main support arm 32 extending upwardly from the subbase 20. Main support arm 32 carries also an alinement bracket 34 through which the support rod 30 is slidably journaled within chamber 2. Bracket 34 serves to maintain the axial position of motor 29 properly fixed, particularly during the centrifuging. Bracket 34 must be high enough, however, to allow motor 29 to be raised for removal of vessel 9 without injury to the crystal basket 35, which is fixed to the motor shaft, and is described in detail below. Bracket arm 36 fixed to bracket 34 carries a thermo-regulator 37 which controls the chamber temperature, and which, like regulator 27 shown in Fig. 4, is of a conventional type.

The temperature is maintained substantially uniform throughout chamber 2 by provision for rapid forced circulation of the air under the control of thermo-regulator 37, which may be adjusted as indicated by experience to maintain the temperature in all parts of chamber 2 above the desired minimum.

It has been found advantageous to use a pair of incandescent bulbs as the heating elements, and to enclose them in a tunnel which protects the vessel 9 from direct radiation. As seen in Fig. 1, incandescent lamp bulbs 38 and 39 are conventionally mounted in a corner of chamber 2, preferably diagonally opposite vessel 9, to secure a relatively even temperature gradient throughout the chamber. Lamps 38 and 39 are energized from any convenient power source, not shown; lamp 38 is fed directly from that source, while the connection to lamp 39 is completed through thermo-regulator 37. The size of the lamps is so chosen that the steady heat from lamp 38 will almost balance the heat loss from chamber 2 after it has been brought up to a temperature of about 45° C. The additional heat necessary to keep the chamber from falling below that temperature is then supplied by lamp 39 under control of the thermo-regulator 36. Tunnel walls 40 and 41 of heat-insulating material are disposed on subbase 20, cooperating with adjacent chamber walls 4 and subbase 20 to form a tunnel 42 open at the upper end only. A small high-speed centrifugal blower unit 44 is mounted on subbase 20 and arranged to maintain continuous rapid circulation throughout the chamber 2 by drawing air therefrom and forcing it into the lower part of tunnel 42 through a port 45 formed in tunnel wall 40. The air flows around the lamps 38 and 39, is heated, and is discharged back into the chamber from the open upper end of tunnel 42.

Certain additional equipment is disposed on base 1 outside the chamber 2. This includes a switch box 46, in which are mounted the relays, not visible in the drawings, actuated by thermo-regulator 37, and also by thermo-regulator 27 in the embodiment of Fig. 4. These relays control directly the supply of current to the lamp 39 and to the heating coil 25. A transformer 47 is provided to convert any conventional alternating-current power supply to meet the needs of the blower 44, which is conveniently a compact type designed for low voltage operation. A manual switch 49 is provided to control the operation of centrifuge motor 29, supplied with power through lead 50 from a conventional source, not shown. Similarly not shown are the conventional power sources supplying lamp current to switch box 46 through lead 51, blower motor current to transformer 47 through lead 52, and turntable motor 12 current through lead 54. It will be obvious that a control panel could be provided if desired, on which control switches for all elements utilizing electric current could be brought together. Such a showing, as well as the wiring detail, has been omitted here for the sake of clarity, as it is well within the ability of anyone skilled in the art to provide such connections.

Returning to the construction of the crystal basket 35, it consists, as seen in Fig. 4, of three axially spaced discs 61 of Lucite fixed on a hub 62 secured by a set screw 63 to the shaft 64 of centrifuge motor 29. A plurality of evenly spaced axially aligned bores 65 is formed in the discs 61, with the ends of each bore carefully chamfered. The bores 66 in the lowermost of discs 61 are of slightly smaller diameter than those in the other discs. This permits a crystal to be dropped into each group of aligned bores with its longitudinal axis parallel to the shaft of motor 29, and supported vertically by the lowermost of discs 61 without interference with the free circulation of the etchant about the crystal. During etching, with relatively slow movement of the etchant relative to the crystals the alinement of the crystals in the bores is immaterial. During centrifuging the greater magnitude of the centrifugal forces constrains the crystals to assume positions in their bores substantially normal to radii of the discs 61 drawn through the crystal centers. The smooth bores 65 and 66 with chamfered edges offer negligible resistance to this change of position; with proper spacing of discs 61, adequate support for the crystals during centrifuging is provided, and no breakage results. Obviously, the size of the discs and bores, and the number of discs and bores used, may be changed to accommodate differing sizes of crystals.

When a batch of crystals is to be etched, chamber 2 is brought to a temperature of about 45° C., and fresh etchant in the closed tank 22 is allowed to reach equilibrium with the chamber temperature. Vertical support rod 30 is lifted to raise the crystal basket 35 above vessel 9, observation panel 6 is opened, and crystals 60 are inserted in the basket. Panel 6 is quickly closed, and after a short wait for temperature equilibrium to be reestablished in the chamber, the proper quantity of etchant is transferred, under control of valve 24, from the storage tank 22 to the vessel 9, to constitute the etching bath 70. Rod 30 is then lowered until all the crystals are submerged in the etchant, and the turntable motor 12 is started. This position of the crystal basket is seen in Fig. 1.

Etching is continued for the time, which may be determined by means discussed hereafter. Rod 30 is then raised until the crystals 60 are clear of the bath 70, as shown in Fig. 4, and switch 49 thrown immediately to energize the centrifuge motor 29. The excess solution driven off the crystals and basket is caught by the wall of vessel 9 and returned to the bath 70. The 3600 R. P. M. motor used subjects the crystals to a centripetal acceleration of about 600 G., which is adequate to remove all surplus moisture from the crystals and basket substantially instantaneously. Rod 30 is then raised until the basket 35 clears vessel 9, turntable motor 12 is stopped, panel 6 opened, and the crystals 60 removed from the basket. In some cases it may be desirable to remove basket 35 as a unit to prevent cooling chamber 2 unduly. The crystals must be kept dry during subsequent manufacturing stages.

Vessel 9 is then removed to discard the used etchant, and replaced in the chamber 2. If the embodiment of Fig. 4 is being used, a fresh supply of etchant is added before the vessel 9 is replaced; in the embodiment of Fig. 1, it is added from tank 22 after replacement of the vessel in the chamber. With a new group of crystals inserted, the cycle is ready to be repeated.

The length of submersion in the etching bath is determined by several factors, among which are the etchant used, its temperature and concentration, and the depth of etch required. It is preferred to use a mixture of water and propylene-glycol, as the etchant, with about 50 per cent water by volume.

Propylene glycol-water is more satisfactory for this purpose than other commonly used mixtures, such as methyl alcohol and water, since less temperature shock results in drying from chamber temperature, and since the glycol evaporates more slowly from the mixture than does the water, so that changes due to evaporation into the heated chamber atmosphere result in a less active etchant. This is desirable to prevent excessive etching, and marking of the etched faces during drying. That it is important to control the concentration of water carefully may be seen by inspection of the graph shown in Fig. 2. The curves there shown represent the depth of etch in millimeters for a two-minute immersion period as a function of temperature, in the range between 35° C. and 45° C. It will be observed that, at the chamber temperature of 45°, an increase of only 9 per cent in water content, from 50.0 per cent to 54.5 per cent of the mixture by volume, increases the depth of etch from .053 millimeter to .117 millimeter, or more than doubles the rate of etching.

The relation between the depth of etch and time of immersion for a 54.5 per cent water mixture is shown in Fig. 3. The required depth of etch to obtain approximately the proper crystal size for a given frequency may be readily obtained by micrometer measurements of the unetched blanks, and the necessary etching time quickly obtained by the use of Fig. 3, or an equivalent graph for etchants of differing strengths. Final precision adjustment requires electrical measurement of the natural frequency of oscillation of the crystal, in many cases with the appropriate crystal faces plated with a metal coating. This final adjustment is commonly made by grinding, by the addition of metal plating, or by local etching and drying carried out in accordance wtih the teachings of this invention, at a temperature of about 41° C. The adjusting to frequency is well understood by those skilled in the art, but the present invention affords the assurance that the final etching steps will not result in the destruction of the crystal through monohydrate formation.

It will be seen by inspection of the curves of Figs. 2 and 3 that as with proper control of temperature of etchant strength, the depth of etch is related to immersion time in a simple manner. Hence the operations performed manually as described above may be easily accomplished by automatic equipment making the etching process readily adapted to large scale production.

In summary, the method and apparatus described above make it possible to etch EDT crystals without allowing the formation of the monohydrate, which has constituted a serious threat to the continued production of synthetic crystals of this type.

What is claimed is:

1. The method of etching ethylene diamine tartrate crystals which comprises immersing said crystals in a mixture of water and propylene-glycol in controlled proportions for a desired time, lifting said crystals from said mixture, and instantaneously drying the surface of said crystals, while maintaining said crystal, and said water, and propylene-glycol mixture at a temperature of at least 41° C.

2. In the processing of ethylene diamine tartrate crystal plates, the method of reducing said plates to size by immersion in an etchant bath of water and material selected from the group including propylene-glycol and methyl alcohol, which comprises heating said bath and plates to a temperature in excess of 41° C., preventing the temperature from falling below 41° C. at any point on said plates during immersion, and drying said plates instantaneously on removal from said bath.

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