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FERROELECTRIC CRYSTAL UNIT
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2,857,532

FIG. 1

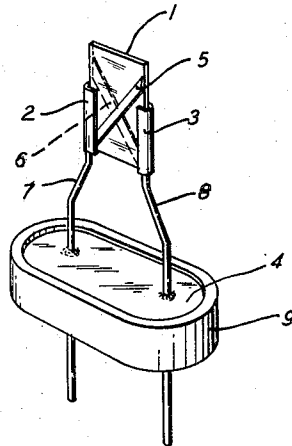


FIG. 2

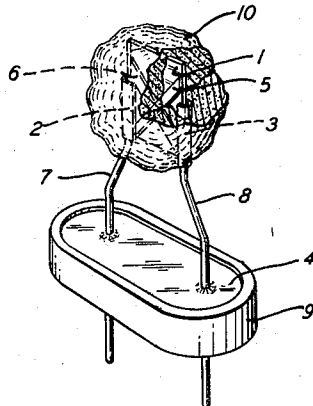
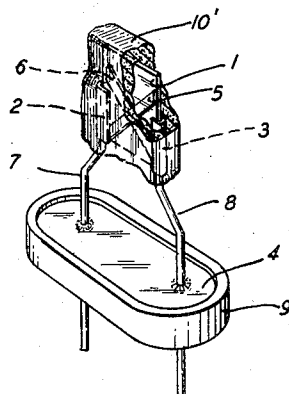


FIG. 3



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FERROELECTRIC CRYSTAL UNIT

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4 Claims. (Cl. 310—8.9)

This invention relates to ferroelectric storage devices, and more particularly to such of those devices as comprise active elements including ferroelectric single crystals. Its principal object is to preserve the valuable properties of such devices against degradation.

Several types of electronic memory circuits now under development employ active elements comprising single crystals of ferroelectric material such as, for example, barium titanate. Included in this category are shift-register circuits which are widely used in telephony and related communication systems to store large numbers of information bits in accessible form. In circuit arrangements suitable for this purpose, the active elements may comprise single crystals of barium titanate which serve as matrices on which large numbers of parallel electrode strips are extended in respectively different directions on the upper and lower surfaces, thereby forming patterns containing large numbers of crossover points, each of which points serves as a separate storage unit.

Operation of storage circuits of the type mentioned is based on an electrostatic characteristic exhibited by ferroelectric crystals, which is similar to the well-known magnetic hysteresis. For example, when an electrical field is applied in the direction of the electrical axis of a ferroelectric crystal, a charge is produced in the crystal element which remains, at least in part, after the removal of the applied field. This residual charge is termed the "remanent polarization" of the crystal. In shift-register circuits of the type described, comprising matrix elements consisting of ferroelectric single crystals, it is obviously desirable for storage purposes to have this "remanent polarization" retained in the storage crystal substantially undiminished for long periods of time, so that when a sensing pulse is later applied, the stored record is intact. The term "single crystal" as used in this specification and the claims hereinafter, refers to a crystal structure in which the electrical domains are substantially aligned in a single direction.

However, it has been found that barium titanate single crystals suitable in other respects for use in various types of storage and shift-register circuits often exhibit, under operating conditions, substantial losses in remanent polarization which impose serious limitations on their usefulness in these applications. These losses are believed to be due, at least in part, to loss of oxygen ions from the crystal lattice leaving a residual charge on the crystal surface which opposes the remanent polarization thereby causing decay. Other factors, which are also believed to contribute to decay are reduction in the effective electrode surface, disintegration in the surface portions of the crystal lattice, and adsorption of impurities on the surfaces of the crystal and the electrodes. Moreover, the aforesaid factors, in combination with the delicate construction of these units, tend to render them mechanically and electrically unstable.

Accordingly, a major object of the present invention is to substantially reduce decay in ferroelectric crystal units; and more particularly, to reduce decay in barium

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titanate single crystals which serve as components of switching and storage devices; such as, for example, shift-registers.

These and other objects are realized in accordance with the present invention by coating the entire assemblage of a barium titanate single crystal element, including the electrodes thereof, with a wax petroleum distillation product prepared in the manner described in detail in C. R. Burch et al. Patent 1,955,321, April 17, 1934, which will be designated hereinafter as "petroleum wax." The substantial reduction in decay which has been achieved by this coating technique is believed to be due, at least in part, to the function served by the coating in preventing loss of oxygen by the crystal. Moreover, such a coating also serves to protect the electrodes and the surfaces of the crystal lattice and electrodes from disintegration and from the adsorption of impurities on the surfaces of the crystal and its electrode which might cause unfavorable chemical reactions to occur. The aforesaid characteristics, together with the physical rigidity provided by such a coating, are effective in providing a mechanically and electrically stable storage unit whereby said device is preserved against electrical and mechanical degradation arising respectively from ion migration and mechanical shock.

The technique of the present invention involves applying to the crystal a small piece of petrolatum wax, a product formed by the vacuum distillation of petrolatum in the manner described in Patent 1,955,321, dated April 17, 1934, which is mentioned above. One manner of applying petrolatum wax involves suspending the barium titanate single crystal unit, which is to be coated, from a suitable support, placing small pieces of the wax on the upper and lower surfaces of the crystal, including the electrodes, and placing the entire assemblage in an oven maintained at 90 degrees centigrade for about 30 minutes. The upper and lower portions of wax then run together, forming a globule which envelops the whole assemblage, including the electrodes. This coating hardens at room temperature.

In accordance with an alternative method, the crystal units are coated with petrolatum wax which has been first dissolved in an excess of benzine until it forms with the solvent a viscous fluid which just flows. After the unit is dipped into this solution, the excess benzine is evaporated off, leaving a thin substantially uniform coating of petrolatum wax covering the entire crystal assemblage.

The invention will be described more specifically hereinafter with reference to the attached drawings in which;

Fig. 1 shows a typical barium titanate crystal unit including mounting elements and attached electrodes prior to coating;

Fig. 2 shows a barium titanate crystal unit such as indicated in Fig. 1, after coating with petrolatum wax in molten form; and

Fig. 3 shows a barium titanate crystal unit similar to that shown in Fig. 1 which has been coated by dipping into a solution of petrolatum wax in benzine.

As pointed out previously, ferroelectric crystals are utilized as active elements in certain types of electrical storage circuits because of their property of retaining a limited polarization charge after removal of the field which initially generates the charge. For optimum operation of such circuits it is obvious that the polarization charge retained by each of the storage elements should remain substantially stable over a considerable time interval under the environmental conditions which obtain during operation of the circuit. Loss of a portion of its remanent polarization charge by a ferroelectric crystal is termed "decay." The effect of decay in the ferroelectric crystal components of a storage circuit is manifested by inability of an applied electric field to switch the polarity of the

individual ferroelectric units (domains) with the desired accuracy and rapidity. The decay factor therefore constitutes a serious limitation on the use of ferroelectric crystals in computing and switching devices.

In accordance with theory based on experimental observation, decay in barium titanate crystals (the most commonly used ferroelectric material) appears to result to at least some extent from the loss of oxygen by the crystal lattice in an electrolytic reaction, wherein oxygen ions in the crystal lattice are more readily converted to free oxygen molecules on the surface of the crystal and its electrodes, than vice versa. This produces a loss of oxygen ions which leaves an excess of positively charged barium ions in the crystal lattice, which is believed to account, in large measure, for the decay of the remanent polarization charge stored in the crystal. It is probable that further loss of oxygen by the crystal lattice is prevented by the eventual formation of a layer of Ti_2O_3 , or some such compound, on the surface of the crystals. The rate at which the reaction between the oxygen ions and oxygen atoms takes place is a function of many factors, including the form and extent of the electrodes, and the rate and symmetry of the applied pulses.

It has been found in accordance with the present invention that decay is substantially reduced in units comprising single crystals consisting essentially of barium titanate by coating the entire assemblage of such units including the electrodes with an organic wax, to be known more specifically hereinafter as "petrolatum wax," which is formed from the distillation of petrolatum in a manner set forth in detail in Patent 1,955,321 to C. R. Burch et al., April 17, 1934, specifically page 6, lines 78 through 95.

As taught in the aforesaid patent, petrolatum wax is obtained by distilling petrolatum at a pressure of about 0.001 millimeter of mercury at a temperature between 100 and 320 degrees centigrade. In accordance with a preferred method disclosed in the aforesaid patent, the distillate is condensed on a surface that is spaced from the surface of the distilland by less than the mean-free path of a molecule of the distillate vapor. A residue paste which remains after removal of about 10 percent of the condensate distilled at the lower temperatures, is then pressed through a filter. The wax so obtained is characterized by a vapor-pressure of less than 10^{-6} millimeters of mercury at 70 degrees centigrade. A product of the type described is manufactured commercially by the James G. Biddle Company of Philadelphia, Pennsylvania, and may be obtained under the trade name of "Apiezon wax." The grade particularly suitable for the uses of the present invention is known as "W-hard."

As previously stated, the beneficial effect of petrolatum wax treatment on ferroelectric single crystal units is believed to be due, at least in part, to the fact that the wax forms a relatively thick coating making intimate contact with the crystal surfaces and the electrodes, which coating is impervious to the diffusion of gases, and accordingly acts to reduce the loss of oxygen from the crystal structure and its electrodes. Such a coating also prevents water vapor and other gases which might have deleterious effects, from coming in contact with the electrodes and crystal surfaces. This characteristic, together with the coating's protective action in preventing the disintegration of the electrodes and the lattice structure on the crystal surfaces, serves to provide an electrical storage unit having a high degree of electrical and mechanical stability.

The use of petrolatum wax coating on ferroelectric crystal units in accordance with the present invention will be illustrated by specific reference to a ferroelectric memory element, such as shown in Fig. 1, which includes a single crystal consisting essentially of barium titanate.

Barium titanate single crystals suitable for use in memory units treated in accordance with the present invention are prepared, for example, in the manner described in detail in J. P. Remeika, application Serial No. 344,373, 75

filed March 24, 1953, by dissolving stoichiometric quantities of barium carbonate and titanium dioxide in potassium fluoride flux, and heating the composite up to a temperature within the range 1150–1225 degrees centigrade. The composite is maintained at this temperature for about 10 hours, and is gradually cooled to 855 degrees centigrade, at which point the flux is poured off. The crystals which form out of the composite are then cooled quickly to room temperature. From thin triangular plates grown in this manner, which are characterized by a "c" or electric axis in the thickness direction, are cut crystal elements of dimensions suitable for various types of memory circuits including shift-registers. The crystal element in the present illustrative embodiment is 75 mils square and 2 mils thick.

The crystal 1 is mounted in a holder, comprising a pair of flat, slotted members 2 and 3, of silver, for example, one pair of whose ends are respectively soldered to leads 7 and 8, which are rigidly mounted in an insulating glass bead 4 enclosed in a metal collar 9.

A pair of silver electrode strips 5 and 6, for example, about 75 mils long and 4 mils wide, and having a thickness of about 200 angstroms, is evaporated along opposite diagonals on upper and lower surfaces of the rectangular crystal element 1, so that they cross above and below a portion at about the center of the crystal element 1.

In accordance with the present invention, in one aspect, a crystal assemblage, such as described with reference to Fig. 1, is coated by the following simple process. A couple of strips of aluminum foil are attached to the crystal holder elements 2 and 3, with globs of silver paste, the other ends of these strips being attached to a suitable support. Slightly softened pieces of petrolatum wax, of a grade which is characterized by being quite fluid at 150 degrees centigrade, are attached to the upper and lower surfaces of the crystal 1, suspended in the manner described, or by some other means. This assembly is then placed in an oven for about 25 minutes at a temperature of about 90 degrees centigrade, so that the wax on the two sides fuses together into a single enveloping ball, such as indicated in Fig. 2 of the drawings, in which the petrolatum wax coating 10 is shown with a portion broken away, the other elements of the crystal assemblage corresponding, as indicated by like designation numbers, to those indicated in Fig. 1.

In accordance with an alternative method, the petrolatum wax is dissolved in benzine to facilitate coating.

This method is carried out by allowing a piece of petrolatum wax to stand in an excess of benzine for about a day, thereby forming a viscous liquid which just flows.

The process of dissolving the wax may be accelerated by placing the solvent and the solute in an oven at between 70 and 90 degrees centigrade.

When the solution has reached the right consistency, a crystal unit, such as illustrated, for example, in Fig. 1, is dipped into the solution forming a coating 10', as shown, with a portion thereof broken away, in Fig. 3. The excess benzine is evaporated off by placing the coated units in a slightly evacuated chamber at a pressure of about 370 millimeters of mercury.

The effectiveness of the petrolatum wax coating treatment in reducing decay is indicated by aging experiments made on units which comprise single crystals consisting essentially of barium titanate prepared in the manner described in the above-mentioned J. P. Remeika application Serial No. 344,373, in which 2 percent of the titanium ions in the lattice structure are replaced by iron ions. All of the tested units included silver electrodes of 16 square mil area evaporated on opposite surfaces thereof.

Eight of these units, designated 1 through 8 in Table I, hereinafter, were coated with petrolatum wax in the manner indicated in Fig. 2. The remaining nine units, designated A to I, respectively, in Table II, were left uncoated, thereby constituting a control group. All of the

crystals in both groups were grown in the same crystal melt.

TABLE I

Crystal No.	Values Representing Twice Polarization Charge		
	After 113 Hrs., ± 20 v. R. M. S., 60 C. P. S.	After Total of 120 Hours Square Wave	Total Percentage Change in Twice Charge
1.....	56.0×10^{-10} Coulombs..	56.5×10^{-10} Coulombs..	+ .9
2.....	55.0×10^{-10} Coulombs..	54.00×10^{-10} Coulombs..	-1.8
3.....	55.0×10^{-10} Coulombs..	55.5×10^{-10} Coulombs..	+ .9
4.....	56.0×10^{-10} Coulombs..	56.00×10^{-10} Coulombs..	0
5.....	54.0×10^{-10} Coulombs..	54.00×10^{-10} Coulombs..	0
6.....	44.0×10^{-10} Coulombs..	43.00×10^{-10} Coulombs..	-2.3
7.....	50.0×10^{-10} Coulombs..	50.00×10^{-10} Coulombs..	0
8.....	57.5×10^{-10} Coulombs..	57.5×10^{-10} Coulombs..	0

TABLE II

Crystal No.	Values Representing Twice Polarization Charge		
	After 113 Hrs., ± 20 v. R. M. S., 60 C. P. S.	After Total of 120 Hours Square Wave	Total Percentage Change in Twice Charge
A.....	56×10^{-10} Coulombs.....	52.5×10^{-10} Coulombs.....	-6.2
B.....	55×10^{-10} Coulombs.....	10×10^{-10} Coulombs.....	-81.8
C.....	53×10^{-10} Coulombs.....	39×10^{-10} Coulombs.....	-26.4
D.....	27×10^{-10} Coulombs.....	5.4×10^{-10} Coulombs.....	-80.0
E.....	59×10^{-10} Coulombs.....	58×10^{-10} Coulombs.....	-1.7
F.....	10×10^{-10} Coulombs.....	7.0×10^{-10} Coulombs.....	-30.0
G.....	54×10^{-10} Coulombs.....	45.0×10^{-10} Coulombs.....	-16.6
H.....	54×10^{-10} Coulombs.....	37.0×10^{-10} Coulombs.....	-31.5
I.....	58×10^{-10} Coulombs.....	27.0×10^{-10} Coulombs.....	-53.4

To the crystals in each batch, twenty volt, 60 cycle per second, alternating current voltage was applied across the electrode terminals for a total of 113 hours. The results of this test are indicated in the second column from the left, in Table I, which refers to the coated group, and in the corresponding column of Table II which refers to the uncoated control group.

Although most of the units in both groups retained about the same remanent polarization charge after the 113-hour 60 cycle aging period, several individual elements in the control group showed marked decay. Note particularly units D and F.

In addition to this 60 cycle aging test, a more conclusive test was carried out by applying to the crystals of both groups, a 1,000 cycle per second square wave, of 40 volts peak.

The results of this test, after a total of 120 hours, are indicated by the third columns from the left in Tables I and II. The right-hand column in each table shows the percent change in polarization charge sustained in each case after the 120 hour square wave test as compared to the polarization retained after the 60 cycle alternating current test. It is quite apparent from the results of these tests that the petrolatum wax coating is effective in substantially reducing decay in ferroelectric single crystal storage units.

It will be apparent to those skilled in the art that the present invention is not restricted to the specific embodiments shown herein, which merely serve as illustrations.

What is claimed is:

1. An electrical storage unit comprising in combination

a ferroelectric crystal, electrical conducting means applied to opposite surfaces of said crystal, and a coating covering the exposed surfaces of said ferroelectric crystal and said electrical conducting means, said coating comprising an organic wax which is derived from a process wherein petrolatum is subjected to thermal decomposition comprising vaporization of said petrolatum at a pressure of about 0.001 millimeter of mercury and at a temperature between 100 and 300 degrees centigrade, and the residual paste comprising about 90 percent of the condensate of said vaporization at the higher temperatures in said range is pressed through a filter.

2. An electrical storage unit comprising in combination a single crystal consisting essentially of barium titanate, electrical conducting means applied to opposite surfaces of said crystal, and a coating applied to the exposed surfaces of said crystals and said electrical conducting means, said coating comprising an organic wax which is derived from a process whereby petrolatum is subjected to thermal decomposition comprising vaporization of said petrolatum at a pressure of about 0.001 millimeter of mercury at a temperature between 100 and 300 degrees centigrade, and the residual paste comprising about 90 percent of the condensate of said vaporization at the higher temperatures in said range is pressed through a filter.

3. An electrical storage unit comprising in combination a ferroelectric single crystal, electrical conducting means coupled to opposite surfaces of said crystal and a coating covering said conducting means and at least a portion of the surfaces of said crystal, said coating comprising an organic wax which is derived from a process whereby petrolatum is subjected to thermal decomposition comprising vaporization of said petrolatum at a pressure of about 0.001 millimeter of mercury at a temperature between 100 and 300 degrees centigrade, and the residual paste comprising about 90 percent of the condensate of said vaporization at the higher temperature of said range is pressed through a filter.

4. An electrical storage unit comprising a single crystal consisting essentially of barium titanate, electrical conducting means applied to opposite surfaces of said crystal, and a coating applied to the exposed surfaces of said single crystal and said electrical conducting means, said coating comprising an organic wax which is derived from a process whereby petrolatum is subjected to thermal decomposition comprising vaporization of said petrolatum at a pressure of about 0.001 millimeter of mercury at a temperature between 100 and 300 degrees centigrade, condensation of the distillate derived from said vaporization upon a surface that is situated at a distance from the surface of the distilland less than the mean-free path of a molecule of the distillate vapor, and filter-pressing the residual paste comprising about 90 percent of the condensate of said vaporization at the higher temperature of said range.

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