Dec. 21, 1948. A. M. ROBINSON 2,456,995

PIEZOELECTRIC CRYSTAL WITH MOISTURE PROOF COATINGS

Filed April 18, 1946

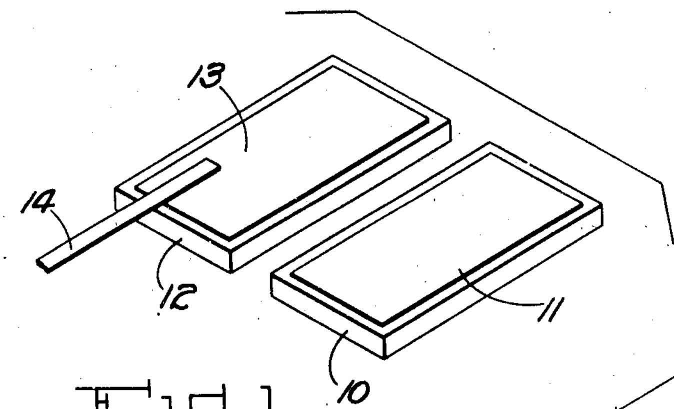

Fig. 1

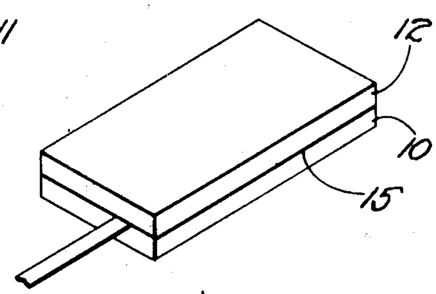

Fig. 2

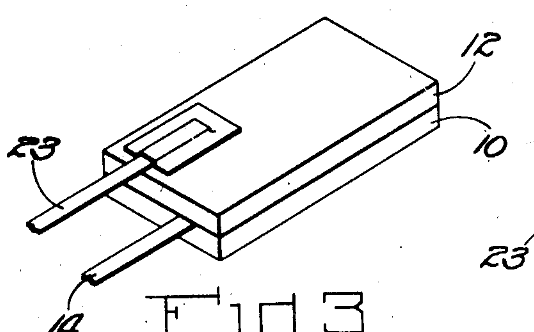

Fig. 3

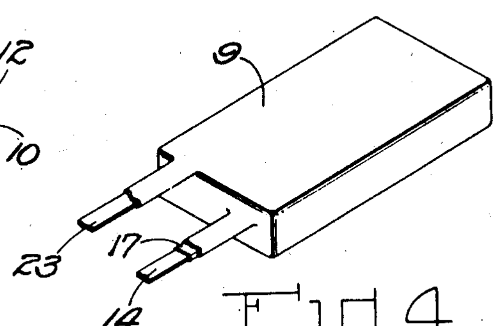

Fig. 4

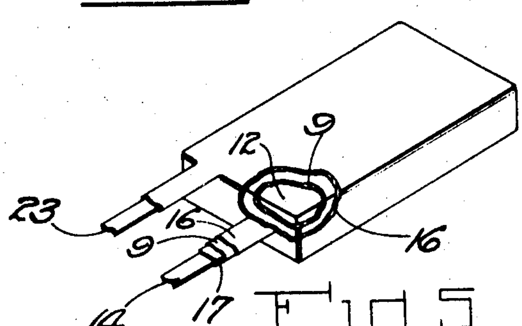

Fig. 5

INVENTOR:
ARTHUR M. ROBINSON
by Oike Calver & Porter
Attys.

Patented Dec. 21, 1948

2,456,995

UNITED STATES PATENT OFFICE

2,456,995

PIEZOELECTRIC CRYSTAL WITH MOISTUREPROOF COATINGS

Arthur M. Robinson, Boston, Mass., assignor, by mesne assignments, to The Brush Development Company, Cleveland, Ohio, a corporation of Ohio

Application April 18, 1946, Serial No. 663,239

8 Claims. (Cl. 171—327)

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The present invention relates to the protection of the surface of piezo-electric crystals and especially plates and assemblies of plates made from water-soluble piezo-electric crystals so that the surface between the electrodes and between adjacent plates sha'l remain in a permanently non-conductive condition even in the presence of moisture which would otherwise impair the performance of the crystal. Such plates have heretofore been generally provided with foil or other electrodes on their two major faces for establishing an electrostatic field in the plate, and face-to-face assemblies of such plates with electrodes secured thereto between their adjacent faces are widely used in microphones, phonograph pickups, etc. Such mu'tiple plate assemblies are described in the reissue patent to Charles B. Sawyer, No. 20,213, dated December 22, 1936, and No. 20,680, dated March 29, 1938, the patent to Alfred L. W. Williams, No. 2,106,143, dated January 18, 1938, and the patent to John H. Ream, No. 2,266,333, dated December 16, 1941. The performance of these devices may be seriously impaired when minute amounts of moisture exist on the edges of the plates or assemblies. The electrical leakage paths between electrodes are short and wide, conditions generally unfavorable for maintenance of high insulation resistance, and in the case of water so'uble salt crystals the leakage problem is unusually severe because any moisture present dissolves some of the salt to form a solution of a much higher electrical conductivity than that of water. In extreme cases, sufficient crystalline material may be dissolved, both on the edges and under the electrodes to destroy permanently the usefulness of the crystal. Piezo-e'ectric crystals of this type usually have a low melting point and often may be damaged when subjected to a temperature substantially lower than their melting temperature.

The present invention relates to moisture proofing piezo-electric crystals which tend to absorb moisture and cause electrical failure of the crystal. Piezo-electric crystals of this type usually have a !ow melting point and often may be damaged when subjected to a temperature substantially lower than their melting temperature. An illustrative example of this type of crystal is a Rochelle salt crystal having a melting point between 70° and 80° C., but which may be damaged and rendered unsuitable as a piezo-electric crystal if subjected to a temperature as great as about 55° C. For various reasons we'l known to the art, the film thickness of the protective coating should not exceed 0.005 inch. This makes it very difficult

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to coat the crystal with a material which will prevent the transfer of moisture vapor.

Prior to the present invention, a certain degree of moisture protection has been achieved in commercial practice by wrapping the crystal in metal foil and then coating with asphalt or similar material. From a production point of view, this method is time-consuming, expensive and requires special skill for the satisfactory application of the metal foil.

In accordance with the present invention, I envelope the crystal with a metal film by electro-deposition. The metal film cannot be deposited directly upon the crystal by electro-deposition because the crystal would be damaged by immersion in the electroplating solution. However, I have discovered that the crystal can be coated first with a thin adherent layer of a non-conductive moisture-resistance organic film-forming material, such as shellac, nitrocellulose, ethyl cellulose, etc. This affords the crystal sufficient protection against moisture so that it can be immersed in an electroplating bath and coated with a metal film by electroplating.

To assist in a further understanding of the invention, a piezo-electric crystal embodying my invention is shown in the accompanying drawings, in which:

Fig. 1 shows two plates with applied electrodes;

Fig. 2 shows the plates superimposed on each other and cemented together;

Fig. 3 shows the assembly after the application of an outer electrode;

Fig. 4 shows the assembly after the application of the non-conductive coating, and

Fig. 5 shows the assembly after metal plating.

Referring to the drawings, at 10 and 12, Fig. 1, are shown two crystal plates whose edges are preferab'y slightly rounded. To these are cemented electrodes 11 and 13, a conductive lead being secured to one of them at 14. At 15 the plates are then cemented together as illustrated in Fig. 2, and an outer conductive lead 23 (see Fig. 3) is secured to the plate 12. The crystal is then coated with a solution of the organic film-forming material in a solvent which is not a solvent for the crystal and then the solvent is dried out. The surface of the non-conductive coating indicated at 9 (Fig. 4) then is sensitized by treatment with a so'ution of a stannous salt, preferably, in the presence of hydrogen ions. This is followed by depositing a film of silver upon the sensitized surface by treatment with a solution of a silver salt and a reducing agent. The crystal then is coated with a metal film 16, see Fig. 5, such as copper, by electro-deposition. If the nature of the electroded crystal is such that a potential difference is to be developed or applied between different portions of electrode means adjacent the surface of the crystal, the crystal should be insulated from the copper film to prevent short-circuiting of the electrode means. This may be done by coating with the non-conductive organic film-forming material. Preferably, the solution of the organic film-forming material used for forming the inner moisture resistant coating contains a finely divided filler to assure a coating of sufficient thickness at the corners and edges of the crystal. The finely divided filler may be either electrically conductive or non-conductive depending upon the type of crystal being prepared. Thus, if the piezo-electric crystal being prepared consists of a single crystal between two electrodes or if it consists of a plurality of series connected plates, an electrically non-conductive filler, such as powdered mica, may be used. If the piezo-electric element is of the type known as a parallel assembly, having for example two crystals cemented together with an electrode between them and two external electrodes connected together, an electrically conductive filler, such as graphite, may be used. While a resinous coating affords the crystal sufficient temporary protection so that it can be coated with a metal film by electroplating, it is not an adequate protection against moisture since in time it permits the transfer of enough moisture to ruin the crystal.

The practice of the invention is illustrated by the methods for coating Rochelle salt crystals described in the following examples.

EXAMPLE I

A Rochelle salt piezo-electric element consisting of a single slab cut along the proper axis and having two electrodes cemented to the flat surfaces of the slab was dipped twice in the following solution and the solvent dried out. This operation was repeated to provide a coating of adequate thickness around the crystal and the portions of the electrodes adjacent the surface of the crystal.

	Per cent by weight
Spar varnish	57.1
Toluol	7.9
Powdered mica (200 mesh)	29.7
Powdered mica (160 mesh)	5.3

The spar varnish used is an oil-modified Glyptal type varnish.

After the coated crystal has been dried, an electrode, such as a strip of metal foil, was secured to the surface of the coating for connecting the crystal to the source of electric current during the subsequent copper plating operation. The crystal thus prepared was immersed in the following solution for 5 minutes.

	Per cent by weight
Stannous chloride	25.0
Distilled water	71.0
Concentrated hydrochloric acid	5.0

The sensitized or "tinned" crystal then was immersed in distilled water for 5 minutes and then silvered by immersing in the following solution for 5 minutes or for a time necessary to deposit a suitable film of silver upon the sensitized crystal.

SILVERING SOLUTION

	Parts
Solution A	1
Solution B	9

Solution A

Sugar	gms.	90
Water	cc.	250
Nitric acid (concentrated)	do.	4
Ethyl alcohol	do.	175
Water to make	do.	1000

Solution B

Silver nitrate	gms.	5
Water	cc.	400

Ammonium hydroxide (28–29% NH_3) until precipitate is nearly redissolved.

Then add

Potassium hydroxide	gms.	3.6
Water	cc.	100

Then add

Ammonium hydroxide until precipitate is nearly redissolved

Then filter

After immersion in the silvering solution the crystal was rinsed in distilled water and a layer of copper applied electrolytically. This may be applied directly to the moist crystal but it is preferred to dry the crystal before plating. The following plating solution was used.

COPPER PLATING BATH

Copper sulfate	gms.	210
Sulfuric acid (concentrated)	cc.	26
Water	do.	1000

Current 10 amperes per square foot at 70° C.

EXAMPLE II

A Rochelle salt piezoelectric element similar to the elements described in Sawyer Reissue Patent 20,213 consisting essentially of two slabs cut along a proper axis and cemented together with an electrode between them having a lead extending out from the assembly, and having an external electrode, with a lead extension, covering the outside surface was dipped twice as described in Example I in a mixture of 20 parts by weight of graphite and 80 parts by weight of the following lacquer. This makes the coating electrically conductive so that the external electrode of the crystal may be used as the electrode in the subsequent copper plating.

LACQUER

½ sec. nitrocellulose (30% alcohol)	50
"Superbeckacide #1003" (pure phenoldehyde resin)	18
"Beckosol #1224" (an alkyd resin solution)	10
Solvent	325

SOLVENT

Ethyl acetate	15
Butyl acetate	20
Amyl acetate	10
Butyl alcohol	10
"Cellosolve"	10
Toluol	35

The graphite in the coating renders the coating electrically conductive so that the external electrode of the crystal may be used for connecting the crystal to the source of electric current during the subsequent copper plating operation.

The thus coated crystal was sensitized, silvered and then coated with an electrically deposited film of copper in the manner described in Example I, except the external electrode of the crystal was connected via its lead extension to the source of electric current during the copper plating operation.

Crystals coated with a metal film as described have withstood immersion in water at 100° F., for over 4 months without failing. For the purpose of test, when the electrical resistance, measured between electrodes, of the crystal has dropped to 1 megohm the crystal is considered to have failed. Asphalted foil wrapped crystals, tested in the same manner, failed in from 38 to 95 hours.

The method of the invention is especially useful for coating plates and multiplate assemblies of piezo-electric crystals of Rochelle salt but it is useful also for coating whole crystals, and sections and assemblies of other than plate shape, and is useful with other piezo-electric crystals, such as ammonium dihydrogen phosphate and lithium sulfate.

I claim:

1. A piezo-electric salt crystal having a moisture-proof continuous coating comprising a waterproof inner layer and outer layer of metal plating.

2. A piezo-electric salt crystal having a moisture-proof continuous coating comprising an inner layer of a non-conductive, organic film forming material deposited from a non-aqueous solution and an outer layer of metal plating.

3. A piezo-electric Rochelle salt crystal having a moisture-proof coating comprising an inner layer which is essentially a water proof, non-conductive organic film forming material and an outer metallic layer.

4. A piezo-electric crystal having a moisture proof coating comprising an inner layer which is essentially a water proof non-conductive organic film forming material, and an outer metallic layer, said inner layer including a filler.

5. A composition in accordance with claim 4 in which the filler is non-conductive.

6. A crystal in accordance with claim 4 in which the filler is powdered mica.

7. A crystal in which the filler is conductive.

8. A crystal in accordance with claim 4 in which the filler is graphite.

ARTHUR M. ROBINSON.

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