

UNITED STATES PATENT OFFICE

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METHOD OF GROWING PIEZOELECTRIC CRYSTALS

Marie Bruzau, Paris, France, assignor to International Standard Electric Corporation, New York, N. Y., a corporation of Delaware

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The present invention relates to piezoelectric systems, and more particularly to the production of artificial piezoelectric crystals.

It is of prior knowledge through various writings that numerous salts possess piezoelectric properties, but they generally occur in the form of crystals of too small a size to be serviceable for industrial uses; such as, in the art of telecommunications.

One of the objects of this invention is to produce crystals of piezoelectric substances of sufficient size and purity to be employable for the above-mentioned and other purposes.

According to features of the invention, the formation of crystals of compact form and sufficient size is effected by crystallization of a saturated solution that contains certain additional products.

Research work has been carried out with various substances and particularly with monopotassic phosphate ($\text{PO}_4\text{H}_2\text{K}$) which has piezoelectric properties, as pointed out by S. B. Elings and P. Torptra in "Zeitschrift für Krystallographie," page 282, vol. 67 of 1928.

However, this salt crystallizes in the form of fine needles that are unserviceable for the uses under consideration. It has already been disclosed that in alkaline solutions it crystallizes into prisms of more compact form (L. Standenmaier, "Zeitschrift für anorganische Chemie," 1894, vol. 5, page 385). But neither are the crystals thus obtained satisfactory for the purposes mentioned.

Various processes have been investigated that would produce larger size crystals by crystallization, particularly by the addition of foreign substances to a saturated solution that is made to crystallize on a germ by reduction of the temperature or by evaporation.

To facilitate a fuller and more complete understanding of the matter of this invention and how the invented process can advantageously be practiced, a specific embodiment thereof, namely the preparation of crystalline potassium dihydrogen phosphate will now be described, but it is clearly to be understood that this example is provided by way of illustration and not by way of limitation, since conceivably the various aspects and modifications of the specific embodiment will become readily apparent to one skilled in the art.

According to the present invention, potassium borate is added to a saturated solution of potassium phosphate. In one embodiment, the applicant has used with success a solution com-

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prising approximately 1500 grams of water, 500 grams of potassium phosphate ($\text{PO}_4\text{H}_2\text{K}$) and 27 grams of potassium borate. A seed crystal of potassium dihydrogen phosphate was suspended in this saturated solution at about 50 to 70° C., the crystal being supported by one or more hairs and being preferably directed so as to have one point face downward.

The temperature of the solution is progressively diminished at a controlled rate of about $\frac{1}{10}^\circ$ per diem. After a period of about six and one half months or thereabouts, it is found that a large crystal growth is formed upon the seed crystal and this crystal growth is structurally uniform crystalline potassium dihydrogen phosphate. This crystal is removed from the bath in the usual manner, dried and then can be subdivided as suited for specific applications in optical and piezoelectric devices.

The seed crystal used is potassium phosphate ($\text{PO}_4\text{H}_2\text{K}$). The crystals resulting from the crystallization process have been found to be free of the borate except for possible spectroscopic traces which may be present by occlusion.

It is fundamental to the process that the crystallization stimulating substance and the salt used must have an ion in common. The role of the potassium borate may be said to be twofold:

(1) The ions BO_3^- and K^+ introduced have an action favorable to the production of large crystals. Experimentation has proven that the presence in the solution of an excess of ions K^+ is favorable to the production of crystals which possess characteristics favorable for piezoelectric applications.

(2) It produces a variation of the hydrogen ion concentration pH of the bath. It has been found, pursuant to this invention, that the formation of the desired large crystals is favored by maintaining the hydrogen ion concentration of the solution at about pH 5. If the solution in which the crystal is grown has a lower hydrogen ion of concentration than pH 5, i. e., is more acidic, the desired large crystals will not form, but instead the material will crystallize as extremely fine needles unsuited for piezoelectric applications.

What is claimed is:

1. Process for manufacturing abnormally large crystals suitable for optical and piezoelectric uses, that comprises regulating growth of said crystals from a germ crystal of potassium phosphate in a super saturated solution of the acid salt of

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potassium phosphate, also containing in a dissolved state, the borate of the same metal.

2. Process for manufacturing abnormally large crystals suitable for optical and piezoelectric uses, that comprises the steps of suspending a germ crystal of potassium phosphate in a heated and supersaturated solution of the acid salt of potassium phosphate, also containing in a dissolved state, the borate of the same metal and gradually lowering the temperature of said solution over an extended period of time.

3. Process for manufacturing abnormally large crystals, suitable for optical and piezoelectric uses, of potassium phosphate, that comprises slowly growing the crystals in the aqueous bath supersaturated with the dissolved acid salt of potassium phosphate and also containing, in dis-

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solved state, the borate of the same metal, the potassium borate being present in the proportion of about 5.5 per cent, based on weight of dissolved potassium phosphate, the hydrogen ion concentration of said bath being about pH 5.

MARIE BRUZAU.

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The following references are of record in the file of this patent:

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