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2,836,501

ELECTROSTRICTIVE CERAMIC MATERIALS

Joseph W. Crownover, Sherman Oaks, Calif., assignor to Electric Machinery Mfg. Company, Minneapolis, Minn., a corporation of Minnesota

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This invention relates to improved ceramic electrostrictive materials and more particularly the invention relates to such materials in which compounds of titania as the predominating constituent are used in combination with certain other compounds as additives whereby the desired characteristics of the materials are achieved. A principal one of the additives and one which is quite critical as to the electrostrictivity is calcium stannate.

This application is a continuation-in-part of an earlier filed application, Serial No. 498,473, filed April 1, 1955. The earlier application discloses an invention which seeks to utilize the electrostrictive properties of high dielectric ceramic materials and to provide ceramic materials having enhanced electrostrictive properties. The invention of this application provides improved electrostrictive ceramic materials and compositions in which the desired characteristics are otherwise improved and stabilized and in which the reproducibility of the materials is improved.

In the improved compositions of this invention, the electrostrictive property of the material has been enhanced and stabilized and the piezoelectric property has been rendered insignificant or negligible. The electrostrictive composition of this invention is adapted for use in various types of transducers, such as switches, relays, motors, loud speakers, etc., and makes possible the practical design and application of many new types of transducers wherein electrical impulses are transduced into mechanical motion which was otherwise not possible. The ceramic materials of this invention are materials which retain only a negligible or insignificant polarization charge, and the significance of this is that if polarization of the ceramic may be retained and increased, it may also be decreased with the result that the ceramic as an actuator or transducer is unstable and is not practical for use in many types of transducers, such as relays. In the compositions of this invention in which the electrostrictive property is utilized, the lack of stability resulting from reliance on polarization charge of the material is eliminated.

Electrostriction in the broadest sense of dielectrics pertains to an interrelationship between the electric field and the deformation of the dielectric in that field. Although this includes the piezoelectric phenomenon, most authorities, in order to avoid confusion, reserve the term "electrostrictive" for the effect wherein the deformation of the dielectric material subjected to an electrostatic field is proportional to the square of the impressed electric field, thereby being independent of the applied field's polarity. The distinction is explained in the volume by Cady Piezoelectricity (McGraw-Hill Book Co., 1946). Where the polarization charge is not being depended on for the deforming and actuating effect, the device operates effectively in one mechanical direction for either polarity of applied potential.

The compositions of this invention, which are essentially barium titanate ceramics, provide a very large dimensional change when subjected to electrostatic fields,

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and this dimensional change results from the electrostrictive properties of the materials.

In accordance with the foregoing, it is an object of the invention to provide improved compositions having pronounced electrostrictive properties and which do not retain any significant polarization charge, comprising barium titanate composition including other compositions as additives.

Another object of the invention is to provide improved electrostrictive ceramics comprising barium titanate as a predominating constituent and including as an additive calcium stannate.

Another object of the invention is to provide improved electrostrictive ceramics comprising barium titanate as a predominating constituent and including as additives, aluminum oxide, calcium oxide, copper oxide, iron oxide, magnesium oxide, lead oxide, silicon dioxide, strontium oxide, zirconium dioxide, titanium dioxide, and calcium stannate.

Another object of the invention is to provide improved electrostrictive ceramics comprising barium titanate as a predominating constituent and having as a constituent in a minor percentage calcium stannate and titanium dioxide and having trace additives in a range of percentages of aluminum oxide, calcium oxide, copper oxide, iron oxide, magnesium oxide, lead oxide, silicon dioxide, strontium oxide and zirconium dioxide.

In general, the novel compositions of the present invention comprise fired mixtures of barium titanate and calcium stannate, and in minor percentages additives of the compositions indicated in the table which follows. The general classes of compositions covered by the invention are indicated in the table. As appears in the table, the calcium stannate content of the material will be in the range of from 2% to 8%. For most of the samples the titanium dioxide additive is .9%. As to the other additives, that is, the aluminum oxide, calcium oxide, copper oxide, iron oxide, magnesium oxide, lead oxide, silicon dioxide, strontium oxide and zirconium dioxide, these additives will be in the percentage ranges as indicated in the table, these ranges and the ranges for barium titanate being percentages of the composition without the added titanium dioxide and calcium stannate.

In the preparation of the compositions of the invention, the ingredients as indicated in the table are in the form of comminuted ceramics. The ceramic bodies may be prepared in a manner conventional with barium titanate electrical ceramics or ceramic films, the desired amounts of titanium dioxide and calcium stannate in comminuted form being mixed in a resin binder and the body then formed into a film and fired using conventional techniques. Such conventional techniques are illustrated in such patents as Lies No. 2,539,446, Howatt No. 2,486,410 and Kulcsar No. 2,735,024. Or, the preparation of the compositions may be essentially in accordance with the method of my earlier filed application, Serial No. 425,664, filed April 26, 1954. In accordance with that method, the materials in the proportions as given in the table are mixed with a liquid thermoplastic resin and a suitable plasticizer in proportions to form a thick liquid adapted to flow on to a moving flat surface in a uniform layer. In other words, the basic materials are formed in very thin sheets of uniform thickness by a slip casting process with the ceramic particles dispersed uniformly through a body of polymerized thermoplastic resin. As an example of the composition of the liquid mix, it may comprise the comminuted ceramic materials, a low molecular weight liquid polyvinyl chloride resin and a suitable plasticizer. The relative weights of the various components, as an example, are within the proportions. 10 to 12 pounds of comminuted ceramic, 1 to 3 pounds of liquid polyvinyl chloride and 1 to 3 pounds of the

plasticizer, with exact proportions depending upon the thickness of the slip desired.

These ingredients are mixed to form a liquid having a viscosity similar to that of a heavy paint. The liquid is then deposited upon a pre-heated moving surface in such a way that the thickness of the thin layer, or slip, is uniform within very small tolerance limits. Before the slip is deposited on the surface, a thin layer of parting agent, such as mineral oil, is sprayed thereon in order to prevent coagulation of portions of the thin layer, or slip, after deposition thereof upon the moving surface, and also to aid in the removal of the product therefrom after subsequent heat treatment.

The moving surface, which may comprise a thin metallic member, is preheated to a temperature somewhat above the polymerization temperature of the resin used and when the thin layer of slip is deposited on the surface, those portions of the layer adjacent to the heated surface will be momentarily heated to the polymerization temperature of the resin, resulting in the formation of an adherent film of liquid on the surface. The fact that polymerization is induced in that portion of the resin in intimate contact with the surface is sufficient to aid materially in the production of a uniformly thin layer, or film, of slip material.

The thin slip layer is next subjected to an elevated temperature for a length of time sufficient to complete the curing of the resin to produce a tough, flexible sheet or ware within which the ceramic particles are surrounded and bonded together by the polymerized resin. For rapid polymerization of the polyvinyl chloride, the temperature should be maintained between 350° and 375° F. It is understood that lower temperatures may be utilized in conjunction with a longer time duration of heat treatment of the slip.

BaTiO ₃ , percent	Al ₂ O ₃ , percent	CaO, percent	CuO, percent	Fe ₂ O ₃ , percent	MgO, percent	PbO, percent	SiO ₂ , percent	SrO, percent	ZrO ₂ , percent	TiO ₂ , percent	CaSnO ₃ , percent	Strain Factor	Sample
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	.9	2.0	4.6	A
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	.9	6.0	6.9	B
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	.9	6.5	5.5	C
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	.9	7.0	4.8	D
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	.9	7.5	6.2	E
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	.9	8.0	4.8	F
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	1.25	7.5	7.4	G
98.91-95.61	0.45-0.75	0.020-0.30	.002-.006	.005-0.1	.01-.50	.01-.24	.30-1.50	.3-.90	.005-.20	1.5	7.5	5.8	H

Removal of the ware from the metallic surface is effected by means of a knife or blade set at a slight angle to the surface and in contact therewith to separate the ware without deforming or injuring it. The ware is then cut to size and baked at the sintering temperature of the ceramic to bring about burning out of the polymerized resin and to induce combination and uniting together of the ceramic particles. The oven temperatures for sintering are critical and should lie within the range 2430° to 2460° F. For example, sintering of a sample of ware at 2440° for one hour gives very favorable results.

The ceramic materials having compositions as in the foregoing were formed into thin sheets and for purposes of examining their electrostrictive properties, the sheets were cut into strips of suitable width and length. Electrodes were applied to opposite faces of the strips and a preferred way of doing this is by painting the opposite faces with silver paint or other electrically conductive material. Such a strip may be mounted in the manner of an actuator, for example, it may be mounted as a cantilever member or it may be mounted at both ends. The application of voltage between the electrodes will result in an expansion of the material in the direction between the electrodes and a constriction or contraction in the other dimensions. The effect is quadratic, as has been explained in the parent application referred to above. That is, the deformation of the material is in the same sense irrespective of the polarity of the applied voltage.

In examining the compositions as listed in the table to determine their degree of electrostrictivity, the materials were tested to determine the magnitude of the response, that is, the deformation of the material under test conditions relative to the applied voltage. The magnitude of the response, that is, the deformation, is indicated in the table by the figure appearing under the heading identified as strain factor. This factor is representative of the electrostrictive response of the material to applied voltage. In these compositions, the amount of the trace additives in each composition was in the percentage range indicated in the table. The compositions in the table are arranged in the order first of increasing percentage of calcium stannate and then increasing percentage of titanium dioxide. While there is variation in the strain factor, it is shown by the table that the strain factor is substantial for all of the compositions shown within the range of 2% to 8% of calcium stannate.

The peculiar advantages of the compositions shown in the table for various applications may be seen from the indication of the strain factor in the table. The materials are electrostrictive as distinguished from piezoelectric and respond to the application of voltage in the same sense irrespective of its polarity, that is, they are not charged either before or during their use in various types of transducers.

With further reference to the hereinafter set forth table, it will be noted that with barium titanate of 95.61% purity, i. e. containing 4.39% by weight of trace additives and with the minimum percentages of titanium dioxide (0.9) and calcium stannate (2.0), the pure barium titanate and trace additives will constitute 97.1% by weight of the electrostrictive material. Thus, with this degree of purity of the barium titanate, the trace additives will constitute 4.26% by weight of the material.

I claim:

1. A fired ceramic electrostrictive material composed of barium titanate having not more than 4.39% by weight of trace additives and containing 2% to 8% by weight of calcium stannate and 0.9% to 1.5% by weight of titanium dioxide.
2. A fired ceramic electrostrictive material composed of barium titanate having not more than 4.39% by weight of trace additives including traces of metal oxides and containing 2% to 8% by weight of calcium stannate and 0.9% to 1.5% by weight of titanium dioxide.
3. A fired ceramic electrostrictive material composed of barium titanate having not more than 4.39% by weight of trace additives including traces of aluminum oxide, calcium oxide, copper oxide, iron oxide, magnesium oxide, lead oxide, silicon dioxide, strontium oxide and zirconium dioxide, and containing 2% to 8% by weight of calcium stannate and 0.9% to 1.5% by weight of titanium dioxide.
4. A barium titanate electrostrictive material composed of a composition expressed as BaO, TiO₂, SnO₂ and CaO such that the CaO and SnO₂ are combined to give a calcium stannate content of 2% to 8% by weight and there is sufficient TiO₂ to combine with all of the BaO to leave an excess of TiO₂ of 0.9% to 1.5% by weight.
5. A barium titanate electrostrictive material composed of a composition expressed as BaO, TiO₂, SnO₂

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and CaO and including traces of metal oxides of not more than 4.26% by weight, the CaO and SnO₂ being combined to give a calcium stannate content of 2% to 8% and there being sufficient TiO₂ to combine with all of the BaO to leave an excess of TiO₂ of 0.9% to 1.5% 5 by weight.

6. A barium titanate electrostrictive material composed of a composition expressed as BaO, TiO₂, SnO₂ and CaO and including traces of Al₂O₃, CuO, Fe₂O₃, MgO, PbO, SiO₂, SrO and ZrO₂ totalling not more than 10 4.26% by weight, the CaO and SnO₂ being combined to give a calcium stannate content of 2% to 8%; and there

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being sufficient TiO₂ to combine with all of the BaO to leave an excess of TiO₂ of 0.9% to 1.5% by weight.

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