

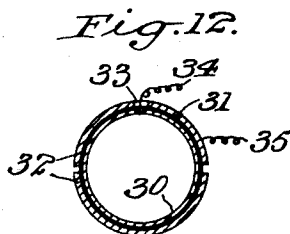
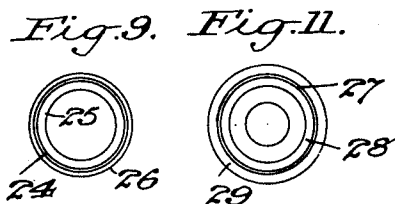
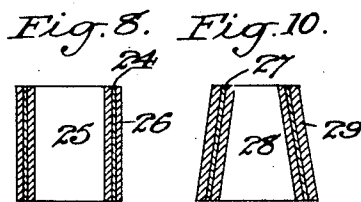
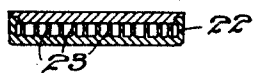
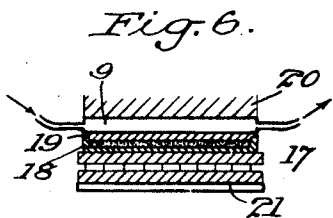
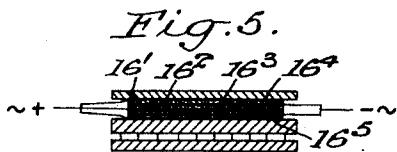
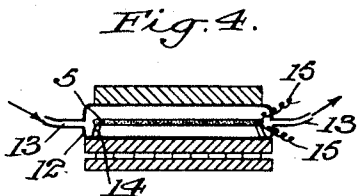
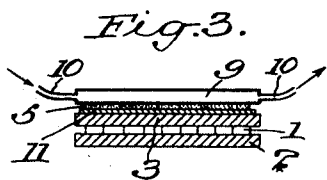
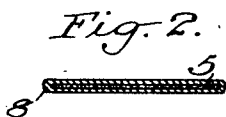
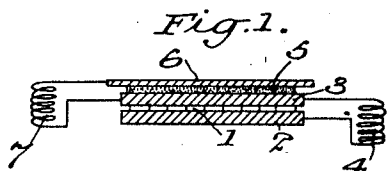
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PIEZOELECTRIC PLASTIC MATERIAL AND METHOD OF MAKING SAME

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PIEZOELECTRIC PLASTIC MATERIAL AND
METHOD OF MAKING SAME

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8 Claims. (Cl. 171—327)

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This invention relates to a piezoelectric plastic material and to the method of making such material.

An object of the invention is to provide a solidified plastic material having piezoelectric properties, with particular reference to the use of such material for the generation and reception of supersonic waves, as a substitute for and improvement over the piezoelectric quartz crystals heretofore used.

A further object is to provide a piezoelectric plastic material which can be formed in a wide variety of sizes and shapes, including large sheets or plates, for the reception and emission of supersonic waves, as well as smaller sizes for other electrical purposes and as substitutes for quartz or Rochelle salt crystals.

A further object consists in providing certain improvements in the form, construction and arrangement of the parts, and in the steps followed, whereby the above named and other objects may effectively be attained.

With the above objects in view it is proposed to incorporate in a suitable plastic material a quantity of piezoelectric substance in the form of fine particles evenly distributed in the plastic material, thus forming a composite mass which retains a certain degree of elasticity. In order that this product may, as a whole, exhibit useful piezoelectric characteristics, the crystals of the imbedded piezoelectric substance should be oriented in substantially the same direction with respect to their electrical axes, so that the compression and expansion of the composite material will cause the appearance on the faces of the crystal particles of uniformly oriented opposite electric charges. As a result the material will be electrically polarized in one or the other direction according to the sign of the compression and opposite electric charges will appear on opposite surfaces of a lamination in this material. For obtaining the most pronounced effect, the saturation of the plastic material with the uniformly oriented piezoelectric crystals should be substantially as dense as possible. The orientation of the crystal particles may be produced either in the course of the preparation of the material or after its otherwise complete fabrication, in accordance with the methods described below.

According to this invention, it is possible to use small and inexpensive pieces of crystal material which need not be worked to any particular shape. It is also possible to use crystals having very pronounced piezoelectric prop-

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erties (large modulus of piezoelectricity) which would otherwise be difficult to handle and fragile or brittle in the form of large individual crystals. For instance, Rochelle salt has a relatively low durability, but when used in the form of minute particles, disseminated in a plastic composition forming a matrix and enclosure for each particle, the valuable properties of this salt are retained and composite piezoelectric masses of otherwise impossible sizes and shapes may readily be formed. When plastic compositions, such as polystyrenes, which do not absorb water, are used the crystals will be hermetically sealed against the effects of moisture. The piezoelectric modulus of certain substances, such as Rochelle salt, is several scores of times greater than that of quartz, so that a composite material including such substances may still have a large piezoelectric effect notwithstanding the presence of non-piezoelectric spaces in the material, depending on the concentration of the crystal particles. A limit of such concentration may be considered reached when the plastic material becomes merely a filler for unavoidable spaces between the crystal particles and acts as a medium for assuring the passage of waves and the transmission of pressure or displacement.

Certain piezoelectric crystals, such as quartz and Rochelle salt, when submitted to pressure which is equal from all sides, do not produce any electric polarization because of the effect of compensation. Certain other crystals, such as tourmaline, do produce such polarization. These two types of crystals will be referred to respectively as "type A" and "type B," and it will be understood that the characteristics just referred to must be given due recognition in carrying out the steps of manufacturing a composite piezoelectric plastic material.

In one specific method, the finely divided crystals are mixed with a plastic composition while the latter is in a liquid phase, before or during its polymerization. The plastic should be selected such that it will remain liquid or semi-liquid at temperatures sufficiently low for the crystals to retain their piezoelectric properties (which condition can easily be met in the case of quartz and tourmaline). During the progressive solidification of the plastic and at the moment when it acquires a sufficient degree of viscosity, the material is subjected simultaneously to mechanical vibration of a very high frequency and to an alternating electric field of the same high frequency; with or without the superimposition of static fields of pressure and direct electric po-

tential. (If only static mechanical pressure or only a static electric field is superimposed the ratio of frequencies must be 1:2 or 2:1.) Certain phase difference between the electric and mechanical oscillations may be employed according to the crystals used and according to the difference in densities of the crystals and plastic material.

If the plastic material is sufficiently viscous it will have a tendency to move in opposition to the imposed mechanical oscillations, like a solid body, this effect being more marked with higher mechanical frequencies. The lateral compensation of the piezoelectric effect will therefore not take place or will be incomplete, even for the type A crystals, and piezoelectric charges will appear, because there will not be sufficient time for compensation to be established at the sides of the crystal to cause disappearance of the electric charges. It is sufficient if the lateral pressure is different from the longitudinal pressure. With type A crystals it is thus necessary to use a phase in which the plastic material begins to acquire sufficient viscosity so as to prevent compensation, while being at the same time sufficiently fluid to permit orientation of the crystals. If necessary, the frequency may be increased or the process may be started at a less viscous phase. The process of orientation of the crystals will be continued with or without interruption until the material is solidified, at least to such an extent that the orientation of the crystals will be retained.

In the case of type B crystals, the electric charges will appear even if the liquid is not viscous, and the effect of orientation may be obtained merely by the combination of static pressure and a static electric field. In practice, alternating mechanical and electric fields are preferably used, but very high frequencies or viscosities are not necessary. The mechanism of orientation is the same in the case of either type of crystal.

The alternating mechanical compression will produce on the crystals suspended in the viscous plastic material piezoelectric charges of opposite signs, alternating with the frequency of the applied mechanical compression. At the same time alternating electric fields of the same frequency are applied synchronously to the material and the crystals, tending to dispose the crystals with their charge in the direction of the electric fields, that is, in the direction of the propagation of mechanical oscillations, since the direction of the electric fields is arranged to coincide with the direction of propagation of the mechanical oscillations. The material will be subjected to this treatment for a suitable period of time, preferably as short as possible for the solidification of the material. Uniformity of the crystals as to form and size is desirable.

It will be understood that, with crystals which have a low melting point or which rapidly lose their piezoelectric properties at higher temperatures, the plastic should be of a type which can be polymerized or solidified at a low temperature (as by the action of light or other radiation) or which may be made fluid or semi-fluid at relatively low temperatures, such plastic materials including, for instance, Celluloid and cellulose acetate. It is sufficient that the thermoplastic material, charged with crystals, should pass in cooling through a short phase of sufficient viscosity at a temperature below the temperature at which the physical and electrical properties of

the crystals are affected. Thus, for example, Rochelle salt melts in its water of crystallization at 70° to 80° C. and loses its piezoelectric properties at about 40° C. The emulsion of the liquid plastic material with the crystals of Rochelle salt can be subjected to the action of a temperature higher than the melting point of the salt, being then transformed into an emulsion of melted particles of salt, so long as the process includes a final phase in which the plastic material is still liquid or semi-liquid at a temperature below 40° C. In this phase the salt will be recrystallized and will assume the desired orientation upon treatment as described above. It is also possible for the crystallization and orientation to be carried on progressively in cases where the plastic material solidifies first on the surface while its core is still liquid.

From the foregoing it will be seen that a modified method of making the composite material, including the orientation of crystals having a low melting point, as in the case of Rochelle salt, may include the mixing of a warm emulsion of liquid plastic and melted piezoelectric material, the latter being suspended as fine droplets within the former. This mixture is then solidified in any suitable manner as by polymerization, drying, refrigeration, etc., preferably in the form of sheets of the order of .5 mm. thickness. The temperature at which the material solidifies should not exceed 200° C. (with provision for operation at increased pressure if necessary) since Rochelle salt loses its water of crystallization at a temperature of 215° C.

A mixture such as just described may also be formed by the suspension of a large number of small crystals of Rochelle salt in a plastic material which is liquid down to temperatures below 70° C. and which may be solidified at lower temperatures, or the Rochelle salt in the form of a crystalline powder may be mixed with powdered plastic material which is thereafter formed, by known methods, into a homogeneous solid mass. In each case the result should be a solid composite plastic material heavily charged with finely distributed crystals of Rochelle salt.

Since the crystals, in the cases last described, are not oriented, such orientation must be made to take place within a solid plastic material. This is effected by heating the material to a temperature sufficient to melt the crystals in their water of crystallization (approximately 80° C.) the crystals being oriented during the phase of recrystallization of the salt. In this orientation during recrystallization, the crystals must be oriented particularly during the initial phase while the crystal is still small in relation to the drop of liquid salt in which it floats and while it is still movable within this drop. (It will be understood that the physical shape of each crystal, spherical or otherwise, has no effect on the orientation of the crystal with respect to its piezoelectric properties.)

In this case the prepared sheets of composite plastic and crystal material are heated above 80° C. and are then subjected to an intense and rapid cooling together with synchronized mechanical and electric oscillations. Reformation of the crystals from their melted condition will commence or will continue in the presence of electro-mechanical orienting forces acting on the crystals during their growth. A slight difference in density between the crystal and the melted salt in which it is suspended is sufficient to prevent the initial adhesion of the crystal to the

wall of plastic material surrounding it, in the presence of mechanical oscillations. On the other hand, the use of high electric frequencies will assure the penetration of the electric fields throughout the composite material in spite of the low conductivity of the molten salt and the inertia of positive ions. The application of a constant strong mechanical pressure may also aid in carrying out the process.

As a modification, the composite sheet may be cooled quickly to obtain a state of super-melting at a temperature below 40° C., after which mechanical and electrical oscillations of high frequency are applied to cause rapid crystallization and orientation.

It is also desirable to provide at the end of the process a mechanical compression of the sheet at a slightly raised temperature (below 70° C.) causing the plastic material to flow in order to eliminate any spaces or cracks around the crystals and to assure the material and mechanical continuity of the whole composition.

Practical embodiments of the invention are shown in the drawings in which

Figs. 1, 3, 4, 5 and 6 show, in vertical section, apparatus for carrying out the process of manufacture described above.

Fig. 2 shows a detailed modification of a part of the apparatus applicable, for instance, to Figs. 1 and 3.

Fig. 7 shows a detailed modification of a part of the apparatus applicable particularly to Fig. 6.

Fig. 8 represents a vertical section through a cylindrical assembly including the piezoelectric plastic material.

Fig. 9 represents a top plan view of the cylinder shown in section in Fig. 8.

Figs. 10 and 11 represent corresponding sectional and top plan views of a frusto-conical assembly.

Fig. 12 represents a section through a spherical assembly.

As shown in Fig. 1, a mosaic of quartz 1 is mounted (as by gluing) between lower and upper steel plates 2 and 3 having a thickness of $L/2$, in order to form a sandwich type generator of high frequency mechanical oscillations, the plates 2 and 3 being connected respectively to the electrodes of a source 4 of high frequency alternating current. A layer of liquid or semi-liquid plastic material 5 charged with small piezoelectric crystals is shown between the plate 3 and a plate or electrode 6; the plates 3 and 6 being connected to a source 7 of high frequency electric current adapted to set up an electric field between said plates. The plate 6 may be made thicker and may be applied under pressure, if desired. The liquid or semi-liquid material 5 may also be replaced by a solid sheet containing the piezoelectric crystals, in accordance with alternative methods described above. The plastic and crystal material 5 may also be encased in an envelope 8 of solid plastic material as shown in Fig. 2.

In Fig. 3 the plate or electrode above the material being treated is replaced by a hollow member 9 arranged with inlet and outlet ports 10 for the circulation of a cooling or refrigerating medium; and the exchange of heat between the composite material 5 and the plate 3 may be prevented by the provision of a thermo-insulating layer 11, as shown. In this and succeeding figures the electrical connections of the plates 2 and 3 are omitted, it being understood that they are the same as shown at 4 in Fig. 1. In the present case the plate 3 and the member 9 are

understood to be connected to a source of high frequency electric current such as shown at 7 in Fig. 1.

In Fig. 4 the composite material 5 to be treated is immersed in a non-conducting heating or cooling liquid which is circulated through a hollow member 12 by means of ports 13, the material being supported in the liquid on the supports 14. The material is provided with upper and lower conducting surfaces having electric connections 15 in order that an alternating electric field may be set up in the material between said surfaces.

In each of the foregoing cases it is assumed that the composite plastic material has a thickness no greater than half of the wave length of the mechanical vibration applied to said material. If the thickness exceeds $L/2$ the electric field in synchronism with the mechanical oscillations at the same frequency will act on the crystals in different layers in such a way as to impart opposite polarization and orientation to said crystals. For thicker sheets and for a sufficiently large wave length of mechanical oscillations, the thickness may be equal to a multiple of $L/2$, such a thick sheet being split after construction in a direction perpendicular to the direction of propagation of mechanical vibrations, and in planes such that each layer will have a thickness equal to $L/2$; each such layer containing crystals oriented in the same direction. In practice it is preferable to separate the layers by thin electrodes such as metal foil (if the material is in solid form) or thin metal plates (if the material is liquid or semi-liquid). A stack of such sheets can be treated simultaneously by connecting the interposed electrodes alternately to the opposite electrodes of the source of alternating electric current. Such an arrangement is shown in Fig. 5, wherein four layers of material are associated with five thin metallic electrodes 16¹, 16², 16³, 16⁴, 16⁵, the electrodes 16¹, 16³ and 16⁵ being connected, for instance, to the positive electrode of the alternating current source, and the electrodes 16² and 16⁴ being connected to the negative electrode of said source. The several electrodes 16¹⁻⁵ form a condenser and the direction of the electric field in adjoining layers of the material is reversed so that the mechanical vibration of said layers in opposite phases will result in orientation of the crystal particles in the same direction in all the layers.

In some cases it may be preferable to form relatively large or extensive masses of piezoelectric material unmixed with a plastic matrix. This can be done conveniently by filling a mold cavity with melted piezoelectric material (such as Rochelle salt melted in its water of crystallization), recrystallizing the material, and subjecting it during recrystallization to the electrical and mechanical oscillations described herein, for effecting the proper electrical orientation of the recrystallized material. This procedure may be facilitated by subjecting the material to strong pressure in a closed container. Apparatus for carrying out this modified procedure is shown in Fig. 6, wherein the melted piezoelectric material 17 is placed in a tray 18 having a tight cover 19. A hollow member 9 for the circulation of a heating or cooling medium extends over said cover and mechanical pressure may be provided by a press member 20 exerting a downward force on the assembled parts which are supported on an air cushion 21, adapted to reflect mechanical vibrations. In Fig. 7 is shown a tray 22 divided into compartments by the inner walls 23, each

compartment being adapted to contain a quantity of melted piezoelectric material which will thus be formed in the shape of blocks.

The new piezoelectric plastic material disclosed herein may be used for the stabilization of high frequency electric current, in which case a thin layer of the material is used in place of the quartz plate as the middle part of a piezoelectric sandwich. For obtaining the most constant results it is desirable to form the outer vibrating plates of a material such as Invar steel, having a thermal coefficient of expansion approaching zero, while the plastic material should be in the form of a very thin layer containing extremely fine crystals from emulsions or a fine powder of a piezoelectric substance. Such a sandwich may be made in the form of a hollow cylinder or frustum of a cone, as shown in Figs. 8 to 11.

In Figs. 8 and 9 a thin layer of piezoelectric plastic material 24 is closely held between inner and outer cylinders 25, 26 of Invar steel, the layer 24 being compressed between the cylinders or cemented thereto in order to insure complete mechanical continuity in an axial direction. In Figs. 10 and 11 the plastic layer 27 and the steel layers 28, 29 are frustoconical in shape, in order to facilitate assembly and to insure the necessary mechanical continuity.

If it is desired to have the sandwich responsive to a band of wave lengths, as in a wave band filter, the thickness of the metal, whether cylindrical or conical, may be varied progressively from one end to the other, so that each section of the system transverse to its axis will have a mechanical resonance frequency progressively varying within the desired limits.

In Fig. 12 the device is shown in the form of concentric spheres, an inner sphere 30 of steel being surrounded by a very thin layer 31 of piezoelectric plastic material, which in turn is closely surrounded by two hemispheres 32 of steel, an opening 33 being provided to permit one electrical connection 34 to be made with the interior of the sphere 30, and the other electrical connection 35 being made with the outer surface of the hemispheres 32. Wave band response in this form can be secured as described above by progressive variations in the thickness of the spheres 30 and/or 32.

In the forms shown in Figs. 8 to 12, the proportions of the device should be so selected as to avoid mechanical resonance with radial oscillations which form a fundamental frequency of the system. Adjustment to a desired frequency may be effected by the electrical deposition of a metal on the outer or inner metallic surface, while controlling the resonance frequency of mechanical oscillations. Automatic regulation of the amount of metal deposited may be effected by providing a relay which will automatically open the electrolytic circuit when the proper frequency of mechanical oscillations has been attained.

While certain piezoelectric materials have been mentioned as suitable for inclusion in the plastic composition it may be noted that other materials such as saccharose, tartaric acid, etc., could also be used. It will be obvious from the description of the methods of manufacture that the plastics most readily adaptable to use in carrying out this invention are those which are thermoplastic in character or those which may be polymerized at temperatures below the critical temperature of the crystals which are being used. In the case of thermosetting plastics the proper orientation of the crystals may be effected by the melting

and recrystallization procedure described as a modified form of the method. The plastic should also have suitable electrical properties, and such materials as chlorinated rubber, the majority of phenol-formaldehyde base plastics and phenol-furfural compounds, acrylates and metacrilates can be used either in powder form or as liquids.

While it is convenient to refer to the crystal material as being in the ideal condition of complete orientation, with the electrical axes of the crystals oriented in substantially uniform directions, it is intended that such substantial uniformity should include the situation in which a sufficient proportion of the crystals have on the average a predominant orientation of their axes so that a useful piezoelectric effect will be observed.

It will be understood that various changes may be made in the construction, form and arrangement of the several parts without departing from the spirit and scope of my invention and hence I do not intend to be limited to the particular embodiment herein shown and described, but what I claim is:

1. The method of making a composite piezoelectric plastic material comprising, placing a quantity of finely divided piezoelectric crystals within a fluid body of plastic material, distributing said crystals substantially uniformly throughout said plastic, solidifying said plastic, melting said crystals, recrystallizing and orienting said crystals in situ so that at least an effective proportion thereof will have their electrical axes oriented in substantially uniform directions.

2. The method of making a sheet of composite piezoelectric plastic material according to claim 1 in which the crystal material is oriented in the sheet in a direction substantially perpendicular to the surfaces of said sheet.

3. The method of making a composite piezoelectric plastic material according to claim 1 in which the crystals are melted by heating the composite material, are recrystallized by cooling, and are oriented in situ during the recrystallization.

4. The method of orienting piezoelectric crystal material which comprises, providing a quantity of finely divided piezoelectric crystal material, supporting said material in condition for free rotation and orientation and subjecting said material simultaneously to mechanical oscillations and electrical oscillations of the same frequency.

5. The method of orienting piezoelectric crystal material which comprises, providing a quantity of finely divided piezoelectric crystal material, supporting said material in condition for free rotation and orientation, and subjecting said material simultaneously to high frequency mechanical oscillations and high frequency electrical oscillations of the same frequency.

6. The method according to claim 5 in which the crystal material is in solid form and is suspended in a fluid or semi-fluid body of plastic.

7. The method according to claim 5 in which the crystal material is in solid form and is suspended in a fluid or semi-fluid body of plastic, and in which the mechanical and electrical oscillations are applied to the suspension of crystals in plastic during at least a part of the process of solidification of said plastic.

8. The method according to claim 5 in which the crystal material is in the form of melted globules contained within a solid body of plastic

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and in which the orientation of the crystals is effected during recrystallization thereof.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date	Number
1,886,234	Meissner	Nov. 1, 1932	476,506

Number
1,900,038
1,969,379
1,830,328
2,229,172
2,138,036

10

Name	Date
Bower	Mar. 7, 1933
Meissner	Aug. 7, 1934
Nicholson	Nov. 3, 1931
Hawk	Jan. 2, 1941
Kunze	Nov. 29, 1938

FOREIGN PATENTS

Country	Date
Great Britain	May 9, 1929
Germany	May 22, 1929