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2,188,154

PIEZOELECTRIC SUBSTANCE AND PROCESS FOR PRODUCING IT

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FIG. 1

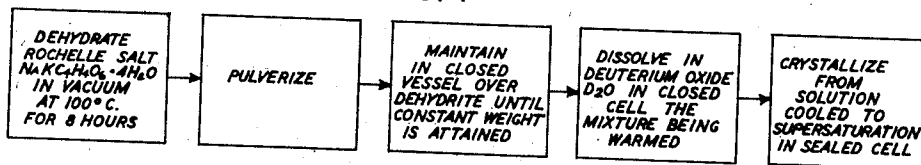


FIG. 2

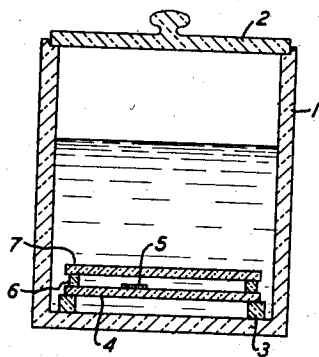


FIG. 5

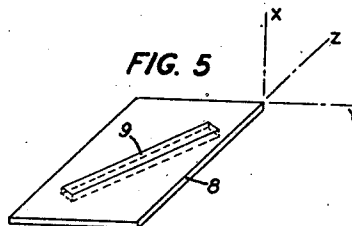


FIG. 6

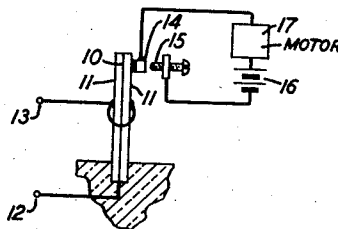
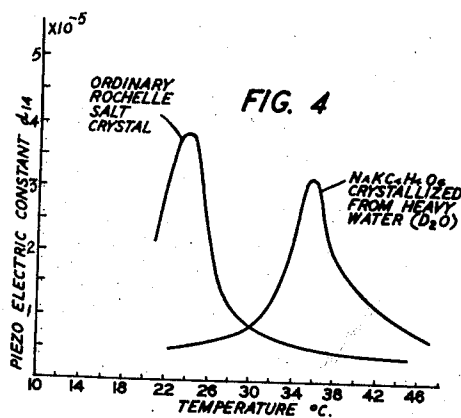
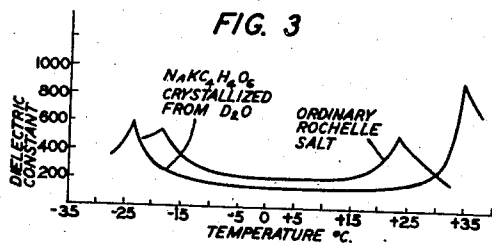
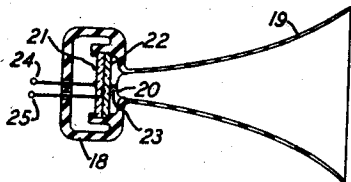


FIG. 7



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2,188,154

PIEZOELECTRIC SUBSTANCE AND
PROCESS FOR PRODUCING IT

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Application August 4, 1938, Serial No. 223,017

10 Claims. (Cl. 171—327)

This invention relates to piezoelectric substances and processes for producing them. More particularly, it relates to improvements in piezoelectric elements produced from Rochelle salt.

5 An object of the invention is to raise the upper Curie point of sodium potassium tartrate from its normal value of approximately 23° C. or 74° F. which corresponds approximately to normal room temperature to permit of the use of the material for piezoelectric elements up to temperatures of approximately 100° F.

10 Another object of the invention is to produce piezoelectric elements of high piezoelectric activity suitable for the actuating members of relays and loud-speaking telephones and capable of operating indefinitely at temperatures of the order of 100° F.

15 Rochelle salt or sodium potassium tartrate represented by the formula $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ exhibits within a small range of ordinary temperatures an extremely high electric susceptibility and piezoelectric effect along certain crystal axes. The material is, accordingly, very useful in devices in which electrical displacements are to be converted into mechanical displacements or vice versa. The use of Rochelle salt as a piezoelectric material is, however, limited by the fact that the upper boundary of the temperature range of its high activity, known as the Curie point, occurs at about 23° C. that is, at about ordinary room temperature. Above that temperature an abrupt decline in the magnitude of its piezoelectric activity occurs and this characteristic has limited Rochelle salt as a piezoelectric element to applications in which such a decrease in piezoelectric activity can be tolerated or compensated. A further object of the invention is, therefore, to increase the piezoelectric activity of Rochelle salt in the temperature region above 23° C.

20 This invention is based on the discovery that Rochelle salt crystallized from a solution in deuterium oxide or heavy water, D_2O , has properties which differ materially from those of ordinary Rochelle salt crystals. Of particular interest is the fact that the upper Curie point or temperature at which the highest piezoelectric activity occurs and beyond which it rapidly declines is raised to about 34° C. thus extending the temperature range of high piezoelectric activity by approximately 11° C. This increase in range includes the normal variations in atmospheric temperature.

25 Various other features and aspects of the invention will be apparent from consideration of

the detailed specification in connection with the accompanying drawing in which:

Fig. 1 is an operational diagram of one form of the method employed for producing piezoelectric elements in accordance with this invention;

Fig. 2 illustrates apparatus for growing piezoelectric crystals;

Fig. 3 illustrates the graphs of the dielectric constant plotted against temperature of piezoelectric elements of ordinary Rochelle salt and of sodium potassium tartrate crystallized from deuterium oxide solution;

Fig. 4 shows graphs of the piezoelectric constant of the same types of elements plotted against temperature;

Fig. 5 illustrates the preferred orientation of piezoelectric elements constructed in accordance with the invention;

Fig. 6 illustrates diagrammatically piezoelectric relay apparatus involving the novel piezoelectric element, and

Fig. 7 shows a loud-speaker utilizing the piezoelectric structure of this invention.

One method of producing piezoelectric elements in accordance with this invention is outlined in five steps in Fig. 1. Ordinary commercial Rochelle salt crystals may be dehydrated in some suitable manner. In one example, the Rochelle salt material which had been originally crystallized from an N/10 solution of sodium hydroxide and distilled water was dehydrated at 100° C. for eight hours in vacuo. It was then pulverized and placed in a glass vessel over dehydrite until it attained a constant weight. The resulting anhydrous sodium potassium tartrate was dissolved in 99.5% deuterium oxide D_2O by warming the mixture in a glass cell. In this process the mass of the anhydrous Rochelle salt employed amounted to about 65% of that of the deuterium oxide so that the resulting solution was somewhat super-saturated at ordinary temperatures. The piezoelectric elements were produced one at a time by crystallizing in a sealed cell from the solution cooled to the point of super-saturation. After each completed crystal had been removed and before the introduction of a new seed there was added to the solution and dissolved by warming a quantity of dehydrated pulverized Rochelle salt of a mass of about three-quarters that of the crystal which had been removed.

The apparatus for crystallizing the piezoelectric crystal from the super-saturated solution is illustrated diagrammatically in Fig. 2 in which a container 1 is closed by the tightly fitting cover

2, sealed with stop-cock grease. Within the container 1 resting on small glass blocks 3 is the glass plate 4 upon which a small seed crystal 5 of Rochelle salt may be placed. Supported on plate 4 and suitably spaced therefrom by glass spacers 6 is a second glass plate 7. As the solution is cooled, for example, by placing the container 1 in tap water, the solution becomes super-saturated and a single crystalline plate grows outward from the seed crystal 5 between the spaced glass plates 4 and 7. Such plates of an area of one to three square inches and 100 mils thick may be grown over periods varying from one to three days depending upon a number of factors including the area of the desired crystal, the ambient temperature and the orientation of the seed crystal. When a plate of the crystallized material is removed from the solution an additional amount of anhydrous tartrate of the order of three-quarters of the weight of the removed crystal may be dissolved in the solution before introduction of the new seed crystal.

The piezoelectric and dielectric properties of sodium potassium tartrate elements crystallized from a deuterium oxide solution differ markedly from those of Rochelle salt elements crystallized from a water solution. The dielectric constants as measured with 1000 cycle alternating current, of the two types of elements with changing temperatures are plotted in Fig. 3 in which the upper graph relates to ordinary Rochelle salt and the lower to sodium potassium tartrate crystallized from a solution in deuterium oxide. The dielectric constant varies with size, cut of specimen, field strength and frequency of measuring current. The values given apply for a given crystal under given test conditions. It will be seen that the dielectric constant for ordinary Rochelle salt has two maxima, one at about -18°C . and one at about $+23.6^{\circ}\text{C}$. The corresponding maxima for the material crystallized from deuterium oxide occur at about -24°C . and about $+34.5^{\circ}\text{C}$. The presence of deuterium in the crystal has decreased the lower Curie temperature by approximately 5°C . and raised the upper maximum approximately 11°C . The temperature range of high activity has thus been extended to include the normal variations occurring in atmospheric temperature thus greatly enhancing the utility of the material for piezoelectric purposes in industrial applications.

In addition to the change in the location of the Curie point the magnitude of the dielectric constant experiences a change, the magnitude of the constant for the crystal from the deuterium oxide solution being approximately 25% less than that of the ordinary Rochelle salt crystal. The dielectric constant of the new crystal as measured at a frequency of 1000 cycles per second is somewhat less than 200 throughout the range of -10°C . to about $+25^{\circ}\text{C}$.

The dynamic piezoelectric constant d_{14} of specimens of ordinary Rochelle salt and of sodium potassium tartrate crystallized from heavy water is shown in Fig. 4. In both instances the graphs represent the "short circuit constants" that is, the constants which would be measured by a very low impedance instrument. The piezoelectric constant of the new material reaches its maximum at a considerably higher temperature than does that of Rochelle salt. In general, it is somewhat lower in value than the piezoelectric constant of Rochelle salt but from a practical standpoint that is not particularly serious and

it is greatly outweighed by the superior performance of the new material in the higher temperature range.

The underlying principles which govern the change in the properties of the material have not been definitely determined. The facts at hand indicate that the piezoelectric properties of Rochelle salt are related in some manner to its water of crystallization. There appears to be some basis for the theory that molecular mobility is closely associated with piezoelectric properties. Consequently the upper Curie point at which the piezoelectric activity of the material begins to fall off rapidly might be expected to occur when the material attains such a temperature that nearly all of the molecules of the water of crystallization are rotating. Deuterium oxide has a heavier molecule than water and is slightly more polar. Consequently, if deuterium oxide molecules be associated with Rochelle salt as its water of crystallization it might be expected that it would require a higher temperature to impart sufficient energy to the deuterium oxide molecules to give them the degree of mobility at which the piezoelectric effect begins to diminish. It is, of course, possible that in the process described in connection with Fig. 1 in addition to driving off the ordinary water of crystallization and replacing it by deuterium oxide certain exchange reactions may occur in which oxygen-bound hydrogen atoms of the material are replaced by deuterium. Irrespective, however, of the theory, the piezoelectric and dielectric properties of the novel substance are very readily ascertainable and are such as to constitute the production of this material an important advance in the piezoelectric art.

Fig. 5 illustrates the preferred orientation for piezoelectric elements consisting of the material embodying this invention. The slab 8 which consists of sodium potassium tartrate crystallized from a solution in deuterium oxide is of the type which may be ground between the glass plates 4 and 7 of Fig. 2, if the seed crystal be properly oriented with its X or a axis in the direction of the spacing between the plates and its Y or b and Z or c axes in a plane parallel to the surface of the plates. The element 9 which is to be cut from the slab 8 is so oriented that its thickness is in the direction of the X axis and its longitudinal axis lies at an angle of 45° to the Y and Z axes. The element 9 when cut, as indicated, and subjected to an electric field in its thickness direction, that is, in the direction of the X axis, will, accordingly, extend or contract in length depending upon the polarity or direction of the electric field.

Fig. 6 illustrates diagrammatically a piezoelectric relay of the general type disclosed in the copending application of W. P. Mason, Serial No. 131,160 filed February 23, 1937. The relay comprises two thin long plates of sodium potassium tartrate similar to element 9 of Fig. 5 produced by crystallization from a solution in deuterium oxide. The plates are glued together and clamped at one end as described in the Mason application to which reference has been made. Their inner electrodes 10 and their outer electrodes 11 consisting of metal foil or of other conductive material such as finely powdered or colloidal graphite are connected respectively to the input terminals 12 and 13 of the relay. The two piezoelectric elements are so cut and their juxtaposed faces so selected that an electromotive force acting between the center electrode 10

and the outside electrodes 11 will cause one plate to extend in length and the other to contract, thus compelling the assemblage to flex laterally and to move the insulated contact 14 carried thereby with respect to the adjustable stationary contact 15. An electromotive force of reverse polarity will cause flexure in the opposite direction. Accordingly, if the input terminals 12 and 13 be connected in a circuit including the source of electromotive force and a circuit closer in series it is possible to control the local circuit of the source 16 and the motor 17 connected to electrodes 14 and 15 from a remote point.

Fig. 7 discloses an embodiment of the invention in a piezoelectric loud-speaker 18 which may be of the general type disclosed in Reissue Patent 20,213 granted December 22, 1936, to C. B. Sawyer or of that disclosed at Fig. 3, page 1401 of an article by Ballantine published in the Proceedings of the Institute of Radio Engineers, vol. 21, No. 10, October 1933. The device 18 comprises a horn 19 provided with a diaphragm 20 positioned adjacent its throat and driven by an assemblage of piezoelectric plates 21 and 22 consisting of sodium potassium tartrate crystallized from a solution of deuterium oxide in accordance with this invention which are so cut and mounted that under the influence of an applied electromotive force the plates warp in such manner as to drive the diaphragm 20 through the mechanical connecting element 23 by which the diaphragm is connected to a center portion of the plates. Accordingly, the loudspeaker 18 operates effectively in response to audio frequency electromotive forces applied to its input terminals 24 and 25 to produce corresponding audio frequency sound waves. Inasmuch as the piezoelectric elements possess ability to function effectively at temperatures considerably in excess of that of ordinary room temperatures such a loud-speaker may operate effectively for an indefinite period at temperatures of the order of 100° F. at which the usual Rochelle salt loud-speaker is comparatively useless.

The high Curie point property of the novel material makes this material suitable for all sorts of piezoelectric devices at elevated temperatures in which Rochelle salt is to be employed as, for example, for high quality microphones for sound pick-up, for devices for measurement of stresses, and for indication of vibrations in machines and of shocks and tremors occurring in the earth. It is, therefore, to be understood that the invention is in no way to

be limited to the specific applications illustrated but only by the scope of the appended claims.

What is claimed is:

1. The method of increasing the upper Curie point of Rochelle salt which comprises crystallizing sodium potassium tartrate from a solution in deuterium oxide.

2. A piezoelectric material comprising a crystalline element of sodium potassium tartrate crystallized from a deuterium oxide solution.

3. A piezoelectric material comprising crystalline sodium potassium tartrate, the water of crystallization of which consists of deuterium oxide.

4. The method which comprises dehydrating sodium potassium tartrate, pulverizing the dehydrated material, dissolving it in deuterium oxide and crystallizing the dissolved material from the solution.

5. The method of increasing the upper limit of the temperature region of high piezoelectric activity of sodium potassium tartrate from about 75° F. to about 100° F. which comprises growing crystals from a solution of sodium potassium tartrate in deuterium oxide.

6. A piezoelectric crystal having a dielectric constant of less than 200 at 1000 cycles throughout the range of 0 to 20° C. comprising sodium potassium tartrate in which the water of crystallization is substantially entirely deuterium oxide.

7. A crystal of sodium potassium tartrate in which a portion of the hydrogen content has been replaced by deuterium.

8. The method of improving the piezoelectric properties of sodium potassium tartrate which comprises replacing a portion of its hydrogen content by deuterium.

9. A piezoelectric structure adapted to operate effectively in the region of 70° F. to 100° F. comprising a crystalline member of sodium potassium tartrate, a portion of the hydrogen of which has been replaced by deuterium.

10. A piezoelectric instrument comprising a mechanical member having mass which is mounted to permit movement of the member, a piezoelectric element physically connected to the member to impart motion thereto, the element consisting of sodium potassium tartrate crystallized from a solution in deuterium oxide whereby the piezoelectric element is highly effective to impel the mass of the member at temperatures ranging from 70° F. to 100° F.

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