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PROPERTIES OF PIEZOELECTRIC TITANATES AND ZIRCONATES INCLUDING A DISCUSSION OF THEIR CONTROL AND EVALUATION

by

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PROPERTIES OF PIEZOELECTRIC TITANATES AND ZIRCONATES INCLUDING A DISCUSSION OF THEIR CONTROL AND EVALUATION

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Note: This paper is in two parts. The first part, by T. G. Kinsley, reports on the program pursued by Sandia Corporation in a planned effort toward obtaining more uniform and efficient piezoelectric ceramics. The second part, by R. D. Wehrle, discusses specifications and tests used by Sandia to insure procurement of satisfactory piezoelectric elements.

PART I

For approximately four years Sandia Corporation has been working on a program to insure better, more uniform piezoelectric ceramics. The first approach to this problem was to investigate the raw material source and the uniformity of the material supplied to the fabricators. This approach was drastically changed as a result of the Titanium Alloy Company's "Round Robin Test" sponsored by their Wm. Baldwin. He supplied a group of fabricators with a quantity of identical raw material and asked each to report on the performance of test specimens produced by them from this material. Their reported results varied so widely that it was clear that the responsibility for the variations in the cured product lay with the fabricators rather than with the raw material. Although the fabricators who participated in this program were primarily interested in dielectric materials the physical requirements for dielectric specimens are close enough to piezoelectric elements to validate the results.

Because of this experience, we have concentrated on cooperative efforts with the suppliers who make our piezoelectric elements. Our interests are primarily in voltage and energy-producing devices. Uniformity of performance of the ceramic is of more importance to us than its high average efficiency as a voltage or energy generator. Naturally we would prefer both high efficiency and uniformity if obtainable.

From the first, we were encouraged to use a composition which was by weight 4 per cent lead titanate and 96 per cent barium titanate. This material was recommended by Dr. W. P. Mason of the Bell Telephone Laboratories. The effect of adding lead to the composition was to move the Curie point up the temperature scale and the second transition point down. The result is a wider and smoother operating characteristic, without much loss in efficiency. These bodies were also able to take more abuse electrically and mechanically without becoming deactivated than can the barium titanate compositions. As a result of these recommendations and our findings we are still using this composition.

More recently we have been interested in wider temperature ranges of operation, especially at higher temperatures. This demand for performance in the higher temperature range is responsible for our interest in the lead zirconate-lead titanate compositions as well as in the lead metaniobate. Both of these materials demonstrate much higher Curie points than does the 4 per cent lead titanate-barium titanate composition described. These lead zirconate-lead titanate compositions have been designated PZT by the Clevite Research Center. First information on this material came to us from the development work done on these bodies at the Bureau of Standards. The 385 C Curie point and a higher piezoelectric constant make this material interesting in spite of its lower dielectric. We are now having trouble with volume resistance in the upper temperature

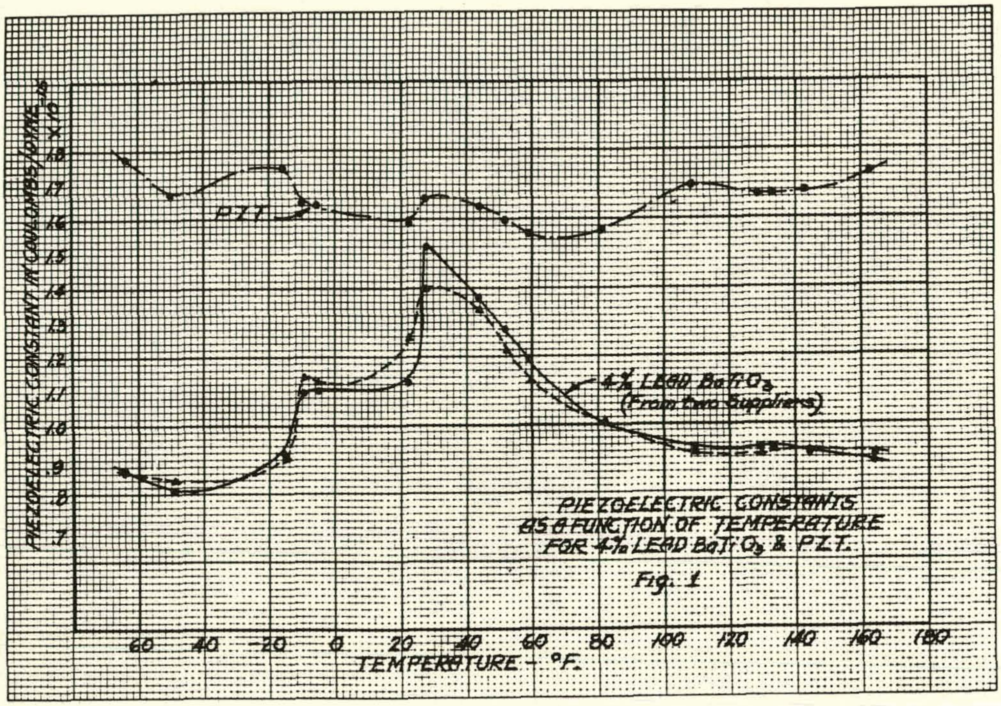


Fig. 1

range, but are optimistic that these problems will be overcome. If they are overcome, we should have satisfactory characteristics up to approximately 370 C (almost 700 F).

It is claimed that lead metaniobate compositions, primarily a General Electric product, will operate at temperatures considerably above 370 C. We have not had any test samples as yet, but the available test data supports this claim. Additional data, such as aging characteristics, resistance to electrical and mechanical abuse, and electrical leakage characteristics, are needed, however, to establish the superiority of the metaniobates at high temperature. As with PZT, the electrical conductivity is the chief problem with metaniobate.

Those engaged in this work have been encouraged by the success recently reported from hot pressings, where ceramic molds have been used to retain the forces at curing temperature.

Figure 1 shows the piezoelectric constant (d_{33}) measurements on 4 per cent lead titanate-barium titanate bodies compared with the lead zirconate-lead titanate bodies over the temperature range from -65 to +165 F. Although this graph does not show the highest values we have checked nor the smoothest characteristic, the comparison is outstanding.

Figure 2 graphically depicts the expected open-circuit voltage per mil-inch thickness of specimen per psi, when stressed in compression. This may be an unusual plot, but it is practical for our applications. To calculate an expected voltage it is only necessary to pick the ordinate figure from the graph corresponding to the temperature of interest, and multiply this by the thickness of the specimen between electrodes in mil-inches, times compressional stress in psi. The efficiency of PZT as a voltage generator is definitely emphasized.

Figure 3 shows the expected energy in joules per cubic inch from a specimen of PZT per psi of axial stress in compression. To calculate expected energy one takes the ordinate figure at the point of interest and multiplies this by the cubical content of the specimen, in cubic inches, times the square of the compressional stress in psi. The last two graphs (Figs. 2 & 3) are based on Fig. 1 which showed piezoelectric constant values (d_{33}) over a temperature range. These values were established on a group of test specimens by the use of a remotely operating testing unit, which, after stabilizing period, recorded these (d_{33}) values directly. The elements were stressed to approximately 200 psi to obtain these values.

To use these graphs for calculating voltage or energy, one must assume the charge developed is linear with stress over the range

Fig. 2

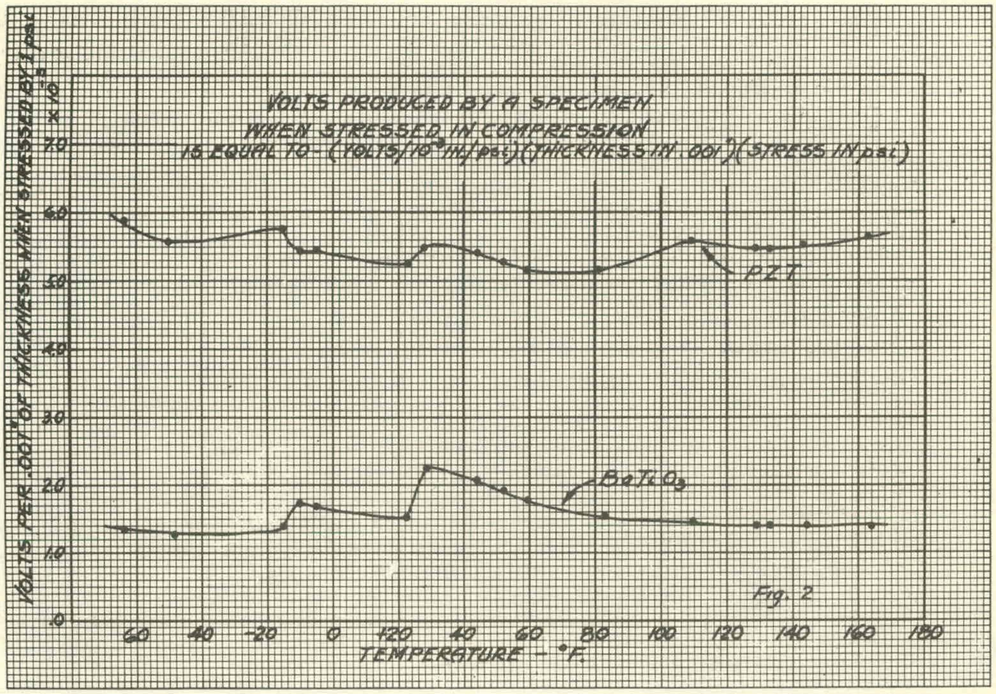
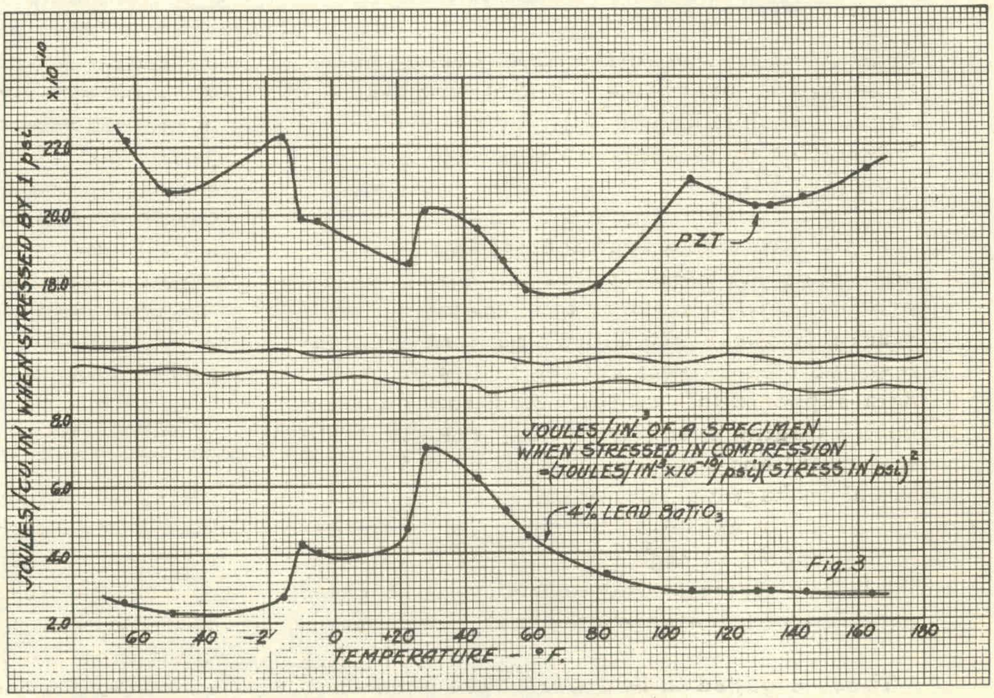


Fig. 3



of interest. It is common knowledge that the charge developed by barium titanate is not linear with stress at the higher values, when these stresses are applied statically. The degree of stress at which the nonlinearity begins varies with different compositions and is not the same in like compositions produced by different fabricators. In most compositions this point of nonlinearity, at which the composition's ability to produce further charge is exhausted, occurs at about 20,000 psi. The few specimens of PZT that have been checked over a wide stress range have shown an amost linear characteristic up to their crushing point. Furthermore the PZT specimens which have been stressed statically to nearly the crushing point have not depoled, whereas barium titanate after being highly stressed statically is almost always nearly void of poling. Whether this depoling takes place in barium titanate when it is stressed dynamically for very brief periods (for milliseconds or perhaps microseconds) is a controversial point. Some say it does not depole if the stress remains for only such a brief period; others claim that it will depole in such brief periods if the charge is taken off deliberately, or if there is an electrical breakdown. It is not possible to make a statement on the point as we have not yet run satisfactory checks on this phenomenon.

Dr. Hans Jaffee and his group at Clevite Research Center have shown that because of this linear vs nonlinear condition PZT should produce nearly 50 times as much energy at a stress of about 55,000 psi as does barium titanate. Since such high stresses are difficult to control, very abusive to any specimen, and beyond our present requirements, we see little need to dwell further on these very high stresses at this time. It is extremely interesting, however, to observe that this chart (Fig. 3) indicates energy ratios strongly in favor of PZT, between the temperatures of -65 and +165 F, even though the stress applied was only about 200 psi.

The remotely operated testing unit shown in Fig. 4 is designed to accommodate 24 specimens of different sizes. The unit is driven by a Geneva motion operated by a flexible cable, which allows the motor to be outside the temperature chamber. This unit is designed to operate from some very low temperature, perhaps -100 F up to +600 F. With this tester we hope to check the performance of the PZT bodies over this wide range. No oil lubrication can be used on the moving parts, consequently special dry lubricants must be used.

We are using X-ray techniques instead of the slow laborious chemical analyses to check our materials and bodies for content and impurity percent, which we then correlate with electrical performance. These X-ray techniques have been found quite satisfactory for checking grain size, crystal structure, and impurity and ingredient content, between fabricating operations and after firing, for verification with electrical performance. By using the latest in Scalers and taking much longer counts, we appear to be getting greater accuracy than has been obtained heretofore.

Figure 5 shows counts per second on lead titanate-barium titanate compositions obtained on our X-ray fluorescence equipment, plotted against per cent lead over the per cent range shown on the abscissa. The compositions plotted on the abscissa were samples of raw powder, lightly compressed in the specimen holder. The linearity of this graph with per cent lead is graphical proof of the accuracy and usefulness of this process. Further evidence of the accuracy of this method was established when we were able to check the difference between 6.00 and 6.01 per cent of lead in a composition. After we have a family of graphs made on the elements of interest in a certain composition carefully prepared from prechecked raw ingredients, we should be able to evaluate our cured material by direct comparison. Thus we should have a check on the

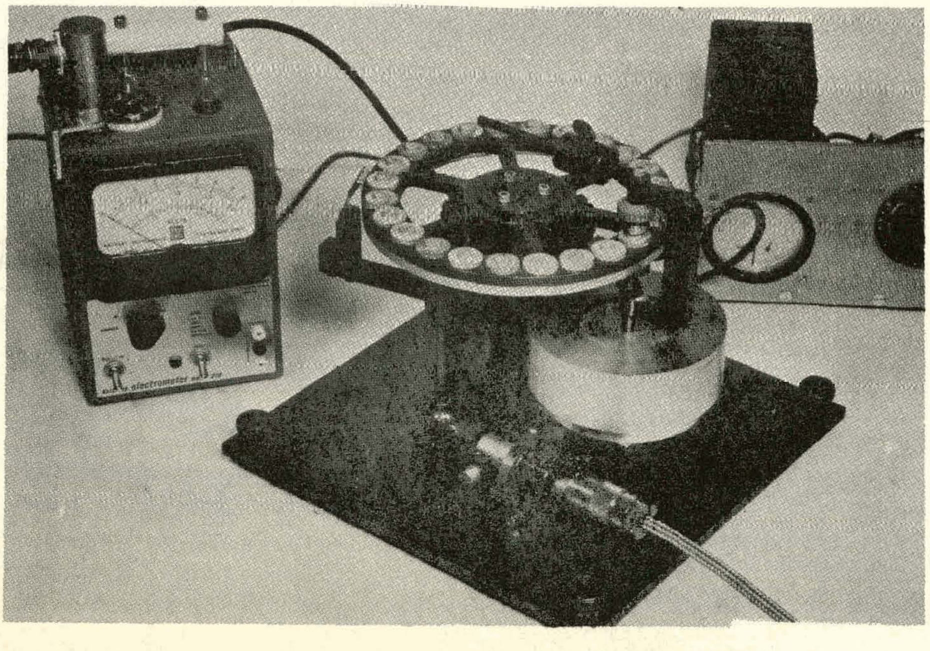


Fig. 4--Remotely operated wide temperature range piezoelectric constant measuring equipment.

loss of certain elements by vaporization as well as other slight losses due to conversions during curing.

It must be understood that absorption effects from one element in the composition will have a bearing on the counts per second obtained on the other elements. Therefore, if we expect small percentages of certain elements which are known to have high absorption characteristics, such as the lead, to be driven off in the firing procedures a family of graphs on raw material specimens would be in order, to establish accuracy in such measurements made on fired material. As this X-ray work continues, we hope to verify our findings from time to time by chemical analyses. To date we have not been completely successful in getting the cured material into a solution satisfactory for precise analyses.

Figure 6 is a similar graph showing zirconium content in accurately prepared mixtures of lead zirconate-lead titanate compositions. This again is just one of the graphs of a family of standards we will need to evaluate our product at various points, during and after the fabricating process. The accuracy of these quickly made X-ray fluorescence analyses must be verified. Despite the limitations of chemical analyses, at this time, we have to rely upon that method for this verification.

PART II

We, at Sandia Corporation, are also attempting to obtain more uniform quality of piezoelectric bodies by rather rigid and comprehensive specifications. Since the manufacturer's processes are considered proprietary, we can only specify the properties desired in the end product and the nominal mixtures of the principle ingredients to be used. For these reasons, we specify as completely as possible, and with relatively close tolerances, the piezoelectric coefficient (d_{33}), the Curie temperature, compressive strength, dielectric constant, depoling characteristics, and physical dimensions. Physical dimension includes such things as parallelism and flatness of the electrode faces and perpendicularity of the faces with the axis of the specimen. Specifications of this sort have enabled us to establish a higher quality of product, but at increased cost for the item.

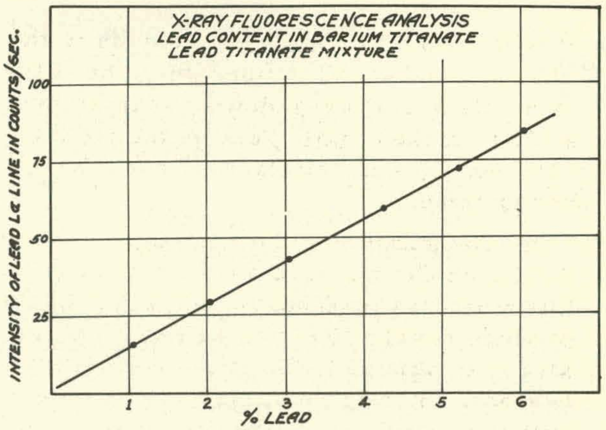


Fig. 5

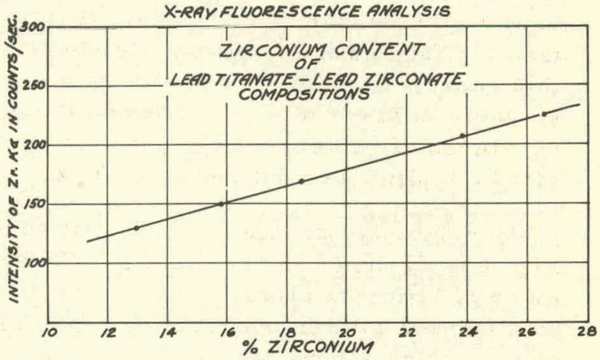


Fig. 6

We also describe the types of acceptance tests to be performed on the piezoelectric materials, the ambient conditions under which tests are to be made, and the equipment to be used. These steps were taken because the methods used by fabricators to measure the piezoelectric properties vary, making it difficult to correlate the test results. We are primarily interested in the d_{33} coefficient and there are at least two ways of determining the value of this parameter. One is the resonance-anti-resonance method which has been used by many and is a valuable tool for determining such things as coupling. However, the determination of d_{33} by this method involves considerable calculation, requires evaluation of other properties of the material, and is limited to certain geometric shapes. The second method is quite simple. It consists of measuring the charge developed by the piezoelectric body when it is axially stressed to a given value. The calculations involved are very simple as shown by the equation:

$$d_{33} = \frac{CV}{F},$$

in which d_{33} has the units of coulombs per dyne,

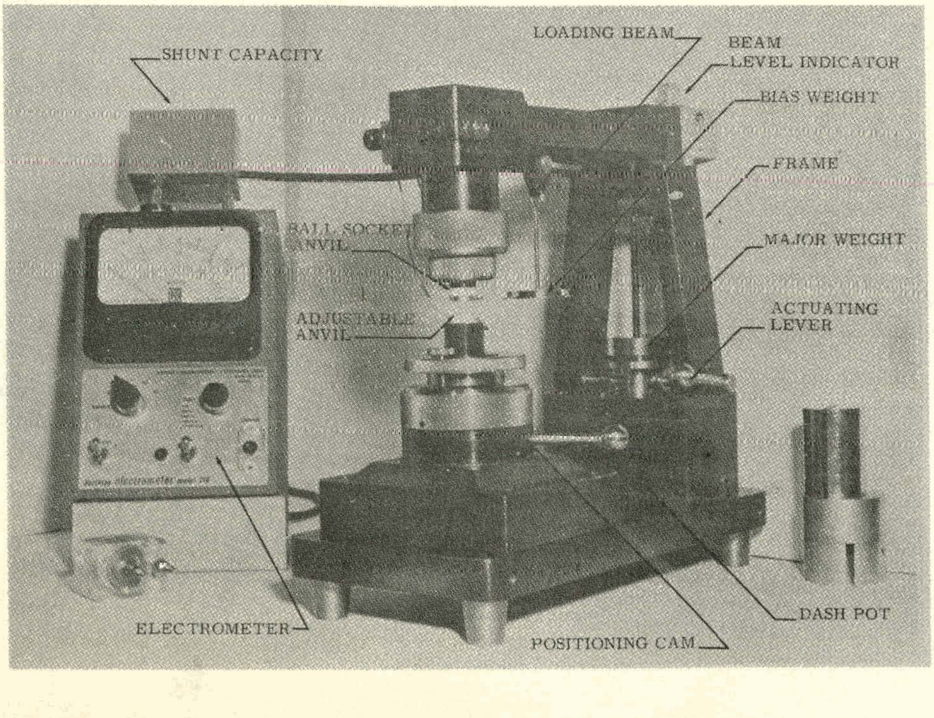
C = the total capacity of the test equipment in Farads, including the test specimen,
V = measured voltage, and
F = stressing force in dynes.

The accuracy of this method is dependent upon the accuracy of the test fixture and instrumentation and also upon the parallelism and flatness of the electrode surfaces of the piezoelectric body, all of which can be controlled quite closely. The simplicity, speed and accuracy of this method of measurement have persuaded us that, at least for our purpose, it is the better of the two methods mentioned.

A direct-measuring device used for determining d_{33} over a temperature range was shown in Figure 4 and referred to in Part 1 of this paper. Figure 7 shows test equipment designed and built for precision measurements of the d_{33} at room temperature. It consists of a stressing mechanism, a shunt capacity, and an electrometer. This machine has a simple lever-loading beam on which various weights can be placed to produce the desired force on the test specimen. Two weights are used, a bias weight to maintain good electrical contact and a major weight to provide a differential force for producing the charge to be measured. A dash pot has been built into the frame of the mechanism to allow the major weight to be applied slowly and smoothly. The base anvil can be adjusted to permit crystals of various lengths to be measured. A built-in ball socket joint in the top anvil makes it possible to compensate for small amounts of unparallelism of the test specimen. The thrust rod is guided by a linear ball bearing and the pivot point of the beam is supported by ball bearings to reduce friction to a minimum. The faces of the anvils are electrically connected to a high impedance electrometer which is shunted by a high quality capacitor to reduce the voltage amplitude to a value which will utilize the most accurate portion of the electrometer scale.

To operate this mechanism, a specimen is placed between the anvils. Proper load weights are placed in position and the base anvil adjusted until the beam level indicator lamp shows the beam to be level. The actuating lever is moved to apply the major load. The meter is then zeroed and the actuating lever is moved again to remove the major load. The resulting voltage can then be used in the equation previously mentioned and the d_{33} determined. Proper selection of the major weight and shunt capacitor will produce a factor of 1 in the equation--d_{33} can then be read directly from the meter.

Fig. 7--Piezoelectric constant measuring equipment.



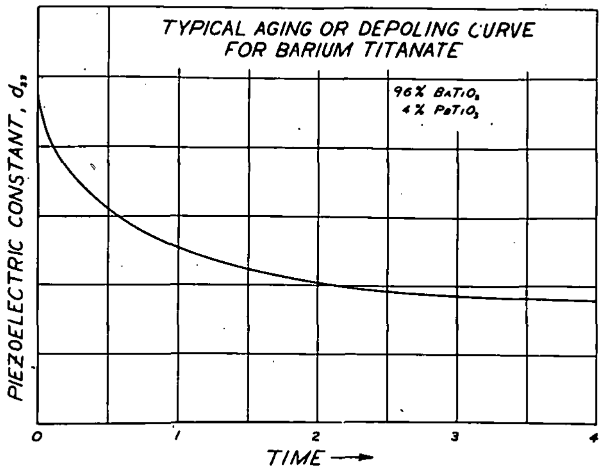


Fig. 8

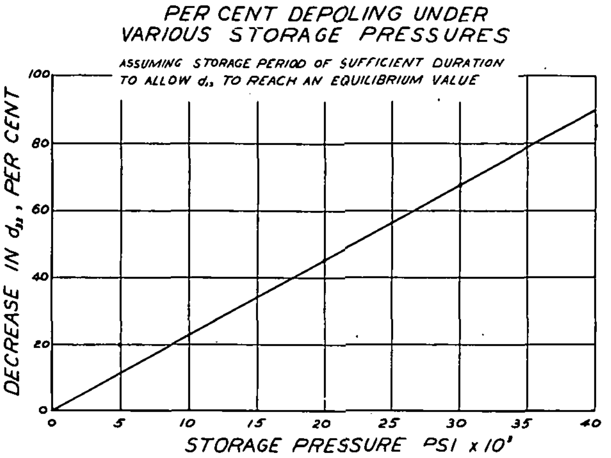


Fig. 9

For best accuracy, the test specimen must be reasonably flat and parallel. Capacity of the specimen and all shunt capacity of the test equipment must be carefully measured and the force applied to the specimen must be accurately determined. Leakage resistance of the entire electrical circuit must be in the order of 10^{14} ohms. The bodies to be measured should be stabilized at the temperature of the test fixture and should be handled only with thermally insulated tongs. Since the load can be removed from the specimen more uniformly than it can be applied, all readings should be made during removal of the major weight. Relative humidity in the immediate area of the test equipment should be low enough that the charge produced will not leak off rapidly enough to affect the accuracy of the reading. If these conditions are complied with, the accuracy of the d_{33} value will be well within ±5 per cent.

Another problem which has been troublesome with barium titanate ceramics is that of losing piezoelectric efficiency under various conditions of use. Natural aging is a factor because these ceramics have a continuous decay of d_{33} as shown by Fig. 8. This decay is a function of time. The most rapid aging occurs immediately after fabrication and appears to follow the logarithmic curve shown where the abscissa is in days. Rate of decay appears to be approximately 3 per cent per decade, but varies somewhat with batches of material and also with temperature.

A second type of depolarization is caused by stress. Figure 9 shows the effect of stress on depoling as being linear. The time function is, however, absent and the rate of depoling is again a logarithmic function. The most rapid rate occurs initially, and then diminishes as indicated in the previous figure in which hours are plotted as the units of the abscissa.

In an attempt to develop an accelerated aging test for piezoelectric bodies, we are investigating the effects of a coercive electrical field applied to the ceramics. A d-c field of about 10 to 15 volts per mil-inch of thickness is applied to the specimen with the polarity opposite to the original polarizing voltage and maintained for a specified period of time. We have found that the curves thus obtained have the general shape of the previous aging curve of Fig. 8 and we are now attempting to correlate this rapid depoling technique to actual room temperature aging. At the present time we do not have sufficient data to prove this theory, but hope that in the future we will be able to predict aging characteristics of piezoelectric ceramics in this manner.

Acknowledgement

The writers wish to acknowledge the helpful consultation rendered by Dr. W. P. Mason of Bell Telephone Laboratories and Dr. Hans Jaffe of Clevite Research Center. We also wish to express our appreciation to the members of Sandia Corporation who were so helpful in compiling this information, especially to Messrs. W. K. Dolen and M. M. Karnowski and their supervisors who made the information presented on X-ray analyses available.

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