AN INVESTIGATION OF SOME BARIUM TITANATE COMPOSITIONS FOR TRANSDUCER APPLICATIONS

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ABSTRACT

The most important factor limiting the use of barium titanate in high power electroacoustic transducer applications is the large dielectric loss in high exciting fields. It has been shown that the addition of cobalt to 5% calcium, 95% barium titanate compositions produces a large reduction in the loss in high fields without significantly affecting the piezoelectric constants of polarized ceramic.

I. INTRODUCTION

Barium titanate is a ferroelectric material exhibiting a large non-linear electrostrictive effect. For transducer applications barium titanate is manufactured as a ceramic and then polarized in a high d-c. electric field to "align" the spontaneous polarization of the individual crystallites in the direction of the applied field. On removal of the electric field, the remanent polarization is high and the ceramic element behaves as a quasi-piezoelectric crystal with the piezoelectric axis in the direction of the polarizing field. After such processing and within certain limits of mechanical and electric strain, the ceramic can be used as a linear electromechanical transducer element and is usually, though erroneously, said to be piezoelectric.

The properties of barium titanate can be profoundly affected by small percentages of additions, e.g. calcium and lead titanate. One effect of these additions is to change the transition temperatures. The transition in pure barium titanate at 10° C. is in the neighborhood of the ambient temperature and is therefore undesirable. The addition of 5% of either of the above additives shifts this transition point below 0° C.

It has been pointed out (Schofield and Brown 1957) that the major disadvantage of barium titanate as a transducer material is that the dielectric loss in high a-c. fields is large; although at low fields the loss tangent is only of the order of 0.01, as the field is increased the loss tangent rises sharply reaching about 0.1 in fields of 1 kv. r.m.s./cm. Although Baerwald and Berlincourt (1953) have shown that the high field dielectric loss can be substantially reduced by applying positive d-c. bias equal to the negative peak of the driving field, this technique in underwater transducers is not practical and materials requiring such treatment must be rejected as unsuitable for high power projectors. This led to a search for a material with piezoelectric constants similar to the presently available barium titanate compositions but with lower hysteretic losses.

It was reported in a recent U.K. Provisional Patent (1953) that the addition of small quantities of cobalt to barium–lead titanate compositions produces a large reduction in the high field losses. Other workers (Berlincourt 1955) have reported that the addition of small quantities of cobalt "had been used to

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  Contribution from the Naval Research Establishment, Dartmouth, N.S.

improve piezoelectric properties of marginal barium titanate lots", but with evidence of increased aging rates. The above work suggested that the effect of the addition of small quantities of cobalt to barium–calcium titanate should be investigated.

The following properties have been determined:

(i) magnitude and variation with temperature of the piezoelectric effects,

(ii) variation of characteristic constants after polarization,

(iii) dielectric or hysteretic losses in high a-c. exciting fields,

(iv) coercivity.

II. EXPERIMENTAL PROCEDURE

(a) Manufacturing Technique

The compositions investigated are listed in Table I. The materials are mixed in 2000 g. batches. The barium titanate (Tamco commercial piezoelectric grade), calcium titanate (Tamco commercial grade), and cobalt carbonate are mixed together with 400 cc. water, 70 cc. 10% ammonium hydroxide solution, 70 cc. of 1% tannic acid solution, 80 cc. 1% citric acid solution, and 4000 g. flint pebbles. After 1 hour of mixing the mill is emptied and the slurry converted into a wet filter cake. The wet filter cakes are then dried at 110° C., passed through a disintegrator, and the resulting powder stored in airtight containers. The powder is tempered as required with 6 cc. of a 10% solution of polyvinyl alcohol per 100 g. of mixture. Sufficient of the dampened mixture for a disk approximately $1\frac{1}{4}$ in. diam. by $\frac{1}{4}$ in. thick is then charged into a mold and pressed at 10,000 p.s.i.

The "green" elements are placed in a sagger in a gas-fired kiln and the temperature raised 350° C. per hour up to 1100° C. The temperature of the kiln is held at this level for 1 hour, then raised 100° C. per hour to 1400° C. After holding at this temperature for two hours, the gas is turned off and the kiln is allowed to cool. Steam is injected into the sagger at kiln temperatures above 600° C. and the humid atmosphere maintained until the gas is shut off.

The rough disks are lapped to ensure that the plane surfaces are parallel and also perpendicular to the axis of the disk. The grinding process is followed by a stringent solvent (trichloroethylene) and alkaline (hot sodium meta-silicate) degreasing. The surfaces to be electroded are sprayed with a thin coat of Dupont conducting silver No. 4756 and the disks are then fired in an electric furnace at 700° C. The silver forms a very strongly adhering electrode approximately 0.0005 in. thick.

(b) Polarization

Two techniques of polarization are available: firstly, a high d-c. field may be applied across the electrodes at room temperature and, secondly, the ceramic may be cooled through the Curie point with a high d-c. field applied. It has been shown that the second technique is more satisfactory and the investigations described in this paper have been carried out on ceramic hot polarized in a field of 10 kv./cm. with the specimen immersed in a silicone oil bath.

(c) Dielectric Constant

The measurements of capacity were made on a Schering bridge (GR-716C capacity bridge) at a frequency of 1 kc., the dielectric constant being calculated from the expression for a parallel plate condenser:

$$(1) \qquad\qquad\qquad K = xC/0.0884A,$$

where x = thickness in cm.,

$\qquad C$ = capacity in $\mu\mu f.$,

$\qquad A$ = area in cm.^{2}

(d) Piezoelectric Measurements

The coupling coefficient is probably the most important figure of merit of any transducer material. For a given mode of vibration, it is defined as the square root of the ratio of energy stored in mechanical form to the total input electrical energy. In terms of the physical constants of a piezoelectric material, the longitudinal mode coupling factor may be expressed in m.k.s. units as:

$$(2) \qquad\qquad\qquad k_{31} = d_{31}/(K\epsilon_0/Y)^{\frac{1}{2}},$$

where d_{31} = transverse piezoelectric constant in coulombs/newton,

$\qquad K$ = relative dielectric constant = ϵ/ϵ_0,

$\qquad \epsilon_0$ = permittivity of free space,

$\qquad Y$ = Young's modulus at constant field.

Mason (1950) has shown that for simple modes of vibration, the coupling factor can be expressed in terms of the resonant and antiresonant frequencies. For a radially resonant disk polarized along the axis, the relation is:

$$(3) \qquad\qquad k_r = (2.51\Delta f/f_R)^{\frac{1}{2}}/(1+2.51\Delta f/f_R)^{\frac{1}{2}},$$

where k_r = radial coupling coefficient,

$\qquad \Delta f = f_A - f_R$,

$\qquad f_R$ = resonant frequency,

$\qquad f_A$ = antiresonant frequency.

In order to calculate the other piezoelectric quantities of interest the following expressions were used:

$$(4) \qquad\qquad\qquad Y = (2\pi a f_R/2.03)^2 \rho(1-\sigma^2),$$

where a = radius of disk in meters,

$\qquad \rho$ = density in kg./m.^{3},

$\qquad \sigma$ = Poisson's ratio, assumed to be 0.3;

$$(5) \qquad\qquad\qquad d_{31} = k_r[(1-\sigma)K\epsilon_0/2Y]^{\frac{1}{2}},$$

$$(6) \qquad\qquad\qquad d_{31} = K\epsilon_0 g_{31}.$$

The piezoelectric constants can therefore be evaluated from measurements of the coupling factor, capacity, density, and dimensions of the specimens.

The coupling coefficient was determined by the resonance–antiresonance method using a circuit similar to that described by Mason.

(e) Coercivity

The "static" coercivity was determined as the negative d-c. field which reduced the coupling coefficient to zero.

(f) Dielectric Loss

The losses in a vibrating polarized barium titanate element excited by an a-c. electric field have both dielectric and elastic components, although at frequencies well removed from the resonance of the specimen, the losses are almost entirely hysteretic or dielectric in origin. The electrical behavior can be represented by a series resistance R and electrostatic capacity C; the electrical dissipation factor can then be expressed as $\tan \delta = \omega C R$.

It has been shown by Baerwald and Berlincourt (1953) that, although the low field electrical losses follow a relaxation-type frequency dependence, at high fields the losses are of a hysteretic type and independent of frequency. The mechanical loss component is insignificant at frequencies well removed from the resonance of the sample; the measurements were therefore made at a suitable single frequency, 12 kc.

The normal commercially available capacity bridges and Q-meters are not designed for measurements at high a-c. voltages and it was found necessary to construct the substitution resonance bridge shown in Fig. 1. The bridge is
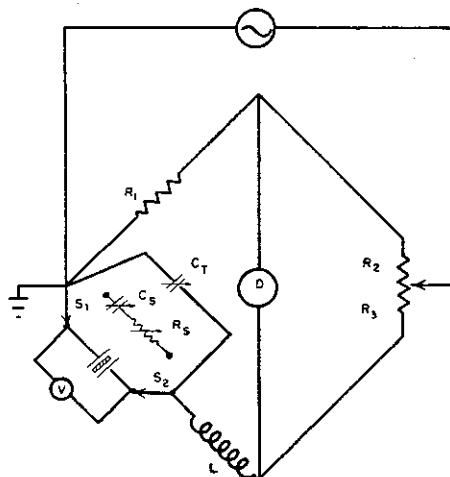

FIG. 1. Substitution bridge.

essentially a Wheatstone network in which three arms are resistive and the fourth contains the sample under test. A fixed inductance L approximately tunes out the capacity of the ceramic specimen while the variable condenser C_T allows fine tuning. The bridge is thus balanced by adjusting C_T for maximum voltage across the specimen and setting the ratio R_2/R_3 for minimum detector response. The barium titanate specimen is then replaced by the

substitution components, which are adjusted to rebalance the bridge using a small signal voltage. To reduce the effect of surface and absorbed moisture, the measurements were made with thoroughly dried samples in a desiccated atmosphere.

Confirmation that the mechanical component of tan δ was small was obtained from hysteresis loops using a circuit similar to that described by Sawyer and Tower (1930). The values of tan δ calculated from hysteresis loops at 60 c.p.s. and 10 kc. were in good agreement with the results obtained by the direct electrical measurements.

III. EXPERIMENTAL RESULTS

It is known that the electromechanical properties of barium titanate can be critically dependent on the composition and firing conditions, and that samples of apparently identical manufacture can exhibit considerable variation in characteristics. A complete investigation of the properties of these materials would, therefore, have to include a statistical examination of large numbers of specimens of separate mixes and firings. Because sufficient effort was not available for such an exhaustive program, the properties of compositions No. 2, 3, 4, and 5 were determined from 30 disks which had been prepared in three separate batches, A, B, and M, of 10 disks each; only 20 disks of the remaining three compositions were manufactured in two separate batches, B and M, of 10 disks each (Table I). Batches A and M were manu-

TABLE I

COMPOSITION OF DMTS* CERAMICS

Series No.	No. of disks	Barium titanate "lot" No.	Wt. % of added cobalt carbonate	Wt. % of cobalt carbonate after firing
B1	10	47	0	0
M1	10	61	0	0
A2	10	47	0.25	0.23
B2	10	47	0.25	0.23
M2	10	61	0.25	0.23
A3	10	47	0.50	0.43
B3	10	47	0.50	0.37
M3	10	61	0.50	0.37
A4	10	47	0.75	0.58
B4	10	47	0.75	0.62
M4	10	61	0.75	0.53
A5	10	47	1.0	0.62
B5	10	47	1.0	0.74
M5	10	61	1.0	0.67
B6	10	47	1.25	0.86
M6	10	61	1.25	0.91
B7	10	47	1.5	1.09
M7	10	61	1.5	1.05

*Department of Mines and Technical Surveys.

factured from the same lot, No. 47 of barium titanate, the final series being prepared from a new lot, No. 61, of basic material. Each mix was prepared and fired separately.

At the sintering temperature of the ceramic, cobalt is volatile, and the amount remaining after firing may be expected to vary. The last column of Table I lists the average percentage of additive expressed as cobalt carbonate present after firing.* Taking into account the volatility of cobalt the differences in the percentage additive found in samples of the same composition from different batches are surprisingly small.

(a) Dielectric Loss

The loss tangent of representative samples of the seven DMTS materials is plotted against a-c. exciting field in Fig. 2. It appears that the dielectric
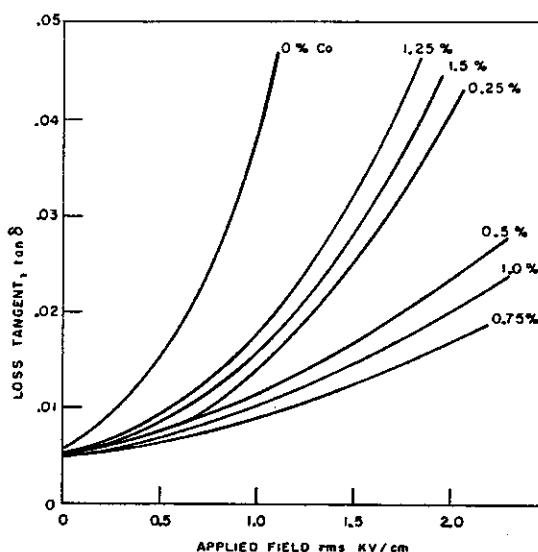

FIG. 2.   Dielectric loss vs. exciting field.

losses are dependent on the amount of cobalt additive, and that there is an optimum amount of added cobalt carbonate, about 0.75%, which will produce minimum high field losses; however, the dielectric loss is not a critical function of the percentage of added cobalt.

(b) Temperature Dependence of Characteristics

At a phase transition the characteristics of a material usually change abruptly; in barium titanate at each of the three phase transition temperatures, the dielectric constant exhibits a maximum. In Fig. 3 the dielectric constant is plotted as a function of temperature over the range 0° C. to

*The chemical analysis of the A series of compositions was carried out by Mr. D. G. Gage of the Physical Chemistry Section of N.R.E.; analysis of the later series was carried out at the laboratories of the Department of Mines and Technical Surveys.
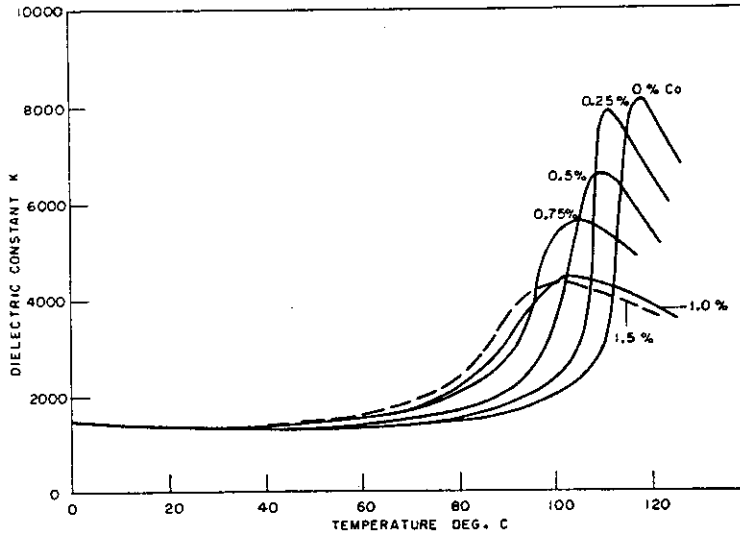
FIG. 3.   Temperature dependence of dielectric constant.

130° C. (1.25% Co has been omitted for clarity). It can be clearly seen that there are no phase transitions between 0° C. and the Curie point; also, as the percentage of cobalt additive increases the Curie temperature decreases. Although the dielectric constant at the Curie temperature is reduced by the addition of cobalt, there is little effect on the dielectric constant at room temperature.

The variations of coupling coefficient and radial mode frequency constant over the possible range of temperatures encountered in the sea, 0° C. to 30° C., are shown in Figs. 4 and 5. An inspection of Table II, which presents a summary of the variation of the characteristics over the temperature range
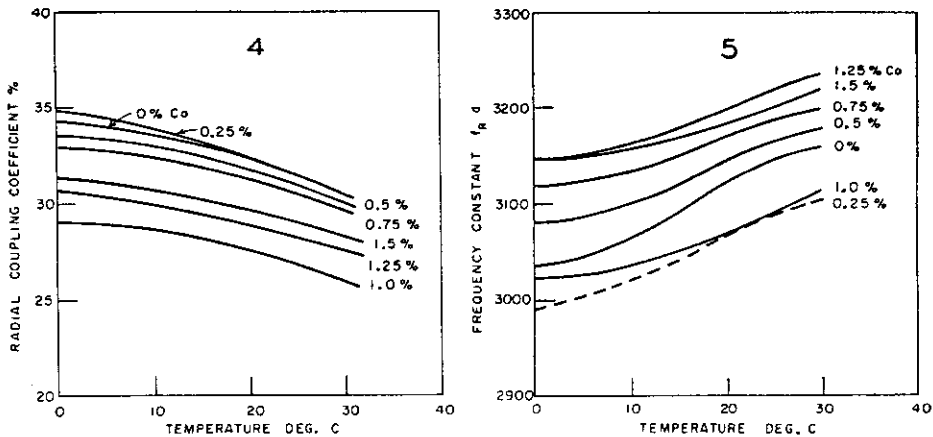

FIG. 4.   Temperature dependence of coupling coefficient.
FIG. 5.   Temperature dependence of frequency constant.

TABLE II

PERCENTAGE VARIATION OF CHARACTERISTICS FROM
0° TO 30° C.

% Cobalt in composition	Coupling coefficient	Dielectric constant	Frequency constant
0	14	14	4
0.25	14	14	4
0.5	11	8	3
0.75	11	5	3
1.0	10	3	3
1.25	11	2	3
1.5	10	3	3

0° C. to 30° C., shows that the addition of cobalt has produced a reduction in the temperature coefficients over this range.

(c) Dependence of Coupling Factor on Polarizing Field

At temperatures below the Curie point the induced polarization in a ferroelectric ceramic is a function of the magnitude and duration of the application of the polarizing field. However, if the ceramic is cooled through the Curie point with the polarizing field applied, the remanent polarization seems to be time independent. Furthermore, the hot polarizing technique results in a higher maximum remanent coupling factor for a given polarizing field for field strengths below 20 kv./cm.

The time dependence of coupling factor for polarizing fields up to 20 kv./cm. at room temperature is shown in Fig. 6 for DMTS 1% cobalt composition.
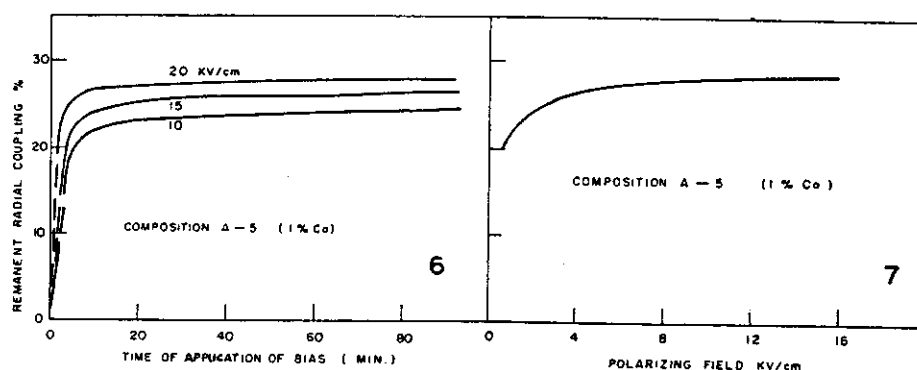

FIG. 6. Time dependence of coupling at room temperature.
FIG. 7. Field dependence of coupling (hot polarization).

The field dependence of coupling factor for the same disk hot polarized is presented in Fig. 7. It can be seen that the saturation coupling of 0.28 can be produced either by hot polarizing in a field of 10 kv./cm. or by room temperature polarizing in a field of 20 kv./cm. applied for about 30 minutes. All the compositions behaved in a similar manner and could be satisfactorily polarized in the above fields.

(d) *Aging of Characteristics*

Several previous investigations (Berlincourt 1955; Moseley 1955; Gray and Herbert 1956) have shown that the aging of the electromechanical characteristics of barium titanate appears to obey a logarithmic law with time. Accordingly, the room temperature dielectric constant, coupling coefficient, and frequency constant were measured over a period of time and the values, corrected to 20° C., are plotted on a linear scale against logarithm of time in Figs. 8, 9, and 10. It is readily apparent that the aging at room temperature does follow a logarithmic law, at least over the period from 1 to 100 days after polarization.

Since the decay curves are logarithmic, the characteristics can be fitted to an equation of the type

$$y = A \log t + B,$$

where B = the initial value 1 day after polarization,

  A = a decay constant,

  t = time in days.

However, the rate of aging is more readily appreciated by expressing the decay as a percentage change per time decade. An inspection of the values listed in Table III indicates that the cobalt additive produces a slight increase

TABLE III

AGING OF CHARACTERISTICS
(Percentage change per time decade)

% Cobalt in composition	(1) Coupling factor	(2) Dielectric constant	(3) Frequency constant
0	1.5	0.4	0.3
0.25	1.8	0.8	0.4
0.5	1.6	1.1	0.4
0.75	1.9	1.3	0.4
1.0	2.8	1.7	0.5
1.25	3.1	1.7	0.6
1.5	3.1	1.7	0.5

in the rate of aging of coupling factor and dielectric constant; aging of the frequency constant is not significantly altered.

Although the rate of aging at room temperature is small, at elevated temperatures in the neighborhood of the Curie point, the decay may be considerably accelerated. Specimens of the compositions were therefore stored at 60° C., 70° C., 80° C., 90° C., and 100° C. and the electromechanical constants periodically measured at room temperature. As examples of the effect of temperature on aging, the decay of coupling factor as a function of time is plotted in Figs. 11 and 12 for storage at 60° C. and 90° C. respectively. It is readily apparent that the initial rate of decay increases rapidly with temperature until at 90° C. compositions of 0.75% to 1.5% Co are substantially depolarized after only a few minutes at this temperature. The dielectric constant is affected in a similar but less spectacular manner; the decay of the frequency constant remains relatively unchanged.
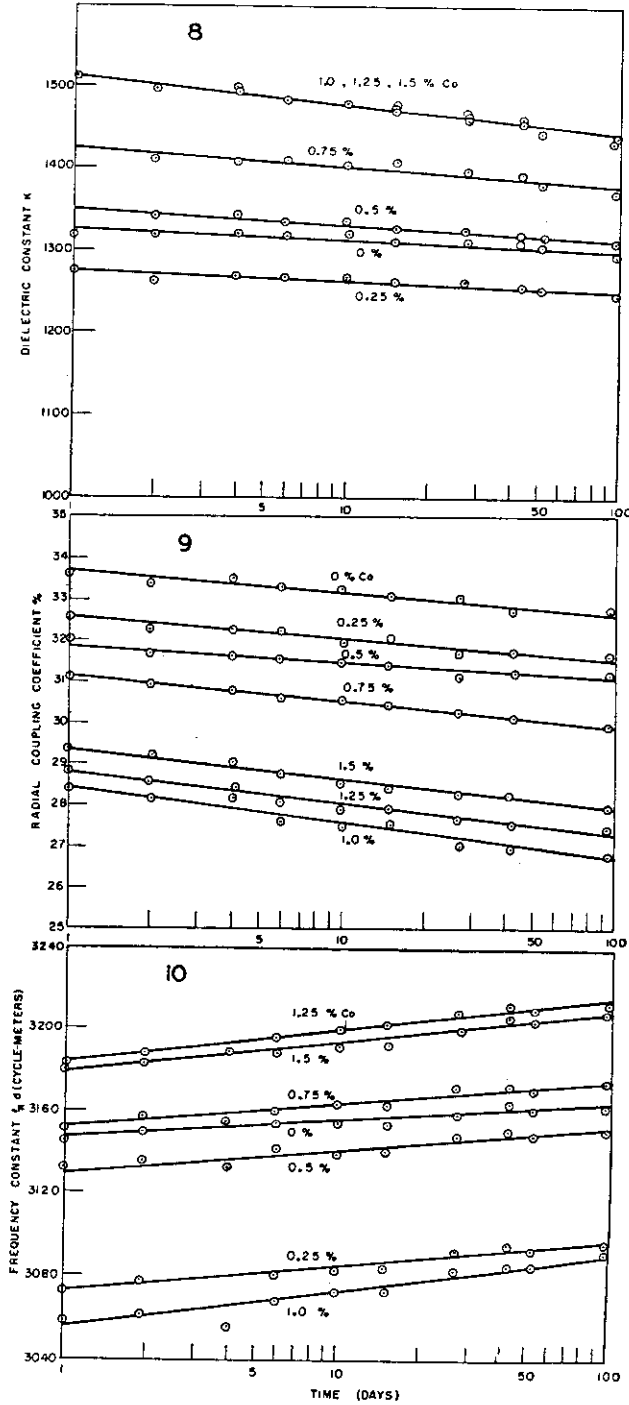
FIG. 8.   Aging of dielectric constant.
FIG. 9.   Aging of coupling coefficient.
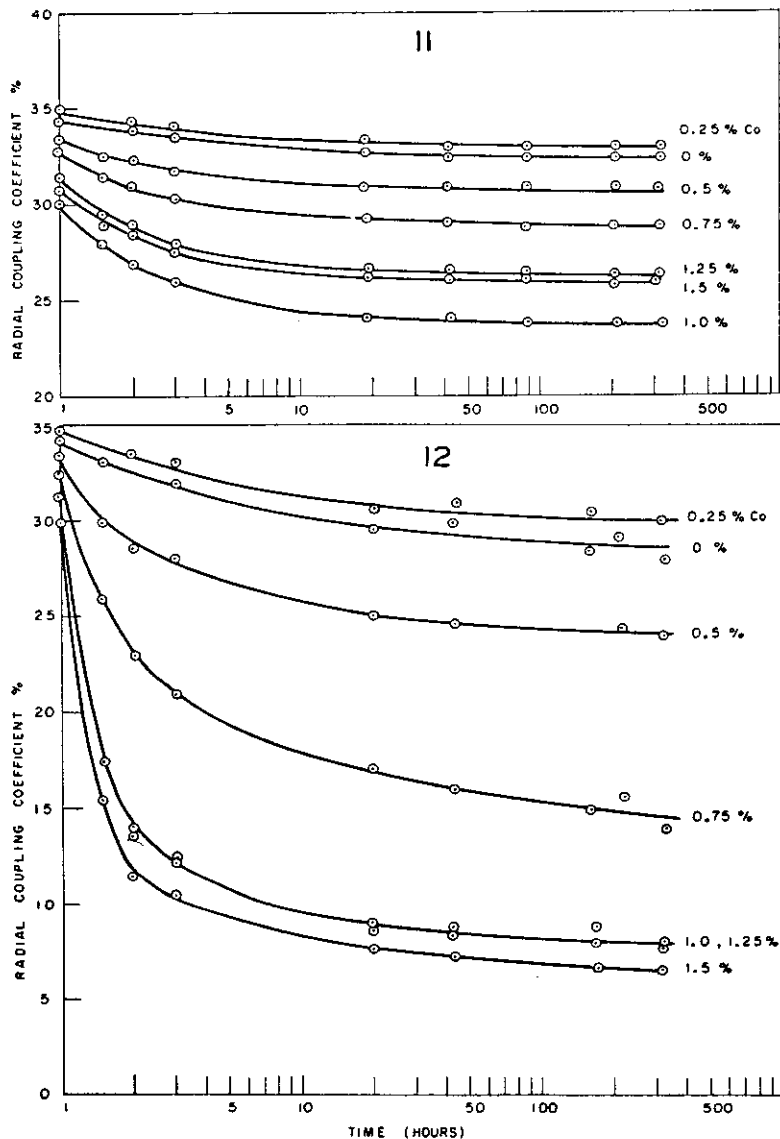FIG. 10.   Aging of frequency constant.

FIG. 11.   Aging of coupling coefficient at 60° C.
FIG. 12.   Aging of coupling coefficient at 90° C.
Specimens placed in oven at time = 1 hour.

(e) *Electromechanical Characteristics*

Table IV is a summary of the physical, electromechanical, and piezoelectric properties. The figures listed are the values of the characteristic constants of average specimens corrected to 20° C. 1 day after polarization.

(f) *Reproducibility*

The reproducibility of the properties among the three batches can be appreciated from Table V, which summarizes the values of coupling factor,

TABLE IV

PROPERTIES OF BaTiO$_3$ CERAMICS WITH COBALT ADDITIVES
(Representative values at 20° C., 1 day after polarization)

	Symbol	Multiply by	B-1	B-2	B-3	B-4	B-5	B-6	B-7
					Wt. % cobalt added:				
			0	0.25	0.5	0.75	1.0	1.25	1.5
Density (g./cm.³)	ρ	1	5.74	5.61	5.64	5.69	5.73	5.70	5.71
Dielectric constant at 1 kc.	K	1	1320	1270	1340	1420	1500	1500	1500
Frequency constant (cycle-m.)	$f_R d$	1	3150	3070	3130	3150	3060	3180	3180
Radial coupling coefficient	k_r	1	0.34	0.33	0.32	0.31	0.28	0.29	0.29
Piezoelectric d constant (coulombs/newton)	d_{31}	10^{-12}	61	60	59	59	56	55	59
Piezoelectric g constant (m.²/newton)	g_{31}	10^{-3}	5.2	5.3	5.0	4.7	4.3	4.1	4.4
Elastic modulus (newtons/m.²)	Y_{31}	10^{11}	1.24	1.16	1.22	1.24	1.18	1.29	1.16
Curie temperature (° C.)	T_c	1	118°	111°	110°	105°	104°	100°	100°
Coercive field (kv./cm.)	E_c	1	6.3	6.8	7.9	8.5	7.6	7.5	7.1
Dielectric loss at 2 kv. r.m.s./cm.	tan δ	1	>0.1	0.041	0.023	0.017	0.020	0.055	0.046

TABLE V

REPRODUCIBILITY OF BATCHES

(Summary of values for 10 samples of the 0.75% cobalt composition
of each batch, 1 day after polarization)

		A-4	B-4	M-4
Coupling factor (%)	High	26.8	31.6	31.2
	Average	26.6	31.2	30.4
	Low	26.4	30.7	29.6
Dielectric constant	High	1116	1420	1379
	Average	1100	1404	1366
	Low	1091	1385	1345
Frequency constant	High	3241	3156	3153
	Average	3223	3149	3144
	Low	3201	3136	3137

dielectric constant, and frequency constant obtained from the 10 samples of each of the three batches of the 0.75% cobalt composition. The agreement between batches B and M is excellent; the somewhat lower values of coupling factor and dielectric constant for batch A are probably due to the lower densities of the disks in this batch. Although the data are not presented here, the other cobalt compositions are equally reproducible.

It should be noted that the preliminary results (Schofield and Brown 1957) were obtained from A batches in which the coupling factor and dielectric constant are lower than the other two batches.

IV. DISCUSSION

For projector applications the major defect of most barium titanate compositions is the large dielectric loss under high a-c. exciting fields. The rise in temperature of the ceramic produced by the dielectric or hysteretic loss increases the loss tangent at that particular field and the effect is cumulative until a temperature equilibrium is attained. We have shown that if the temperature of the ceramic approaches the Curie point, partial or total loss of electromechanical activity may result. The dielectric loss thus imposes a limit on the power handling capacity of a barium titanate composition and must be treated as a factor of prime importance in the selection of a material for use in high power projectors.

An examination of the results presented in Table IV shows that the introduction of cobalt into the 5% calcium composition has produced a large reduction in the high field loss tangent together with a small decrease in coupling factor and piezoelectric constants. The addition of cobalt has, therefore, significantly increased the power handling capacity of the 5% calcium composition ceramic without an appreciable loss in electromechanical activity.

The mechanism whereby the addition of cobalt to calcium–barium titanate compositions decreases the high field dielectric loss is not fully understood. The dielectric loss in ferroelectric materials may be calculated from the area of the minor hysteresis loops through which the sample is cycled when an a-c. field is applied. An examination of the change in area of the minor polariza-

tion-field loops with increasing field from a low value shows that the elliptical shape of the loop remains unchanged until in the neighborhood of the knee of the major hysteresis loop a bulge develops on the ellipse and much larger increases in area occur. This is in accord with the direct electrical determinations of tan δ. No plausible mechanism to explain the effect of the addition of cobalt on the shape of the minor hysteresis loops can yet be given.

Further evidence that the addition of cobalt has some basic effect on the structure of the ceramic lies in the variation of dielectric constant with temperature. Not only is the Curie temperature decreased but the Curie peak is considerably broadened. It appears that the introduction of cobalt has caused the phase transition from tetragonal to cubic to be less clearly defined and to take place over a wider temperature range.

Summarizing, we have shown that the addition of cobalt to 5% calcium, 95% barium titanate produces a large reduction in hysteretic loss in high electric fields without a significant reduction in piezoelectric characteristics. It should be noted that the addition of cobalt to lead–barium titanate has a similar effect. The percentage addition of cobalt to the calcium composition is not critical and it should not be difficult to manufacture reproducible ceramic on a mass production scale.

ACKNOWLEDGMENTS

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