LB-825

COLUMBATE DIELECTRICS

RADIO CORPORATION OF AMERICA

RCA LABORATORIES DIVISION

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Approved

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Introduction

Interest in the development of high K dielectric materials with thermal electrical properties better than the titanate dielectrics led to the investigation of a group of columbate compounds. Measurements were made of their d-c resistances, dielectric constants and dissipation factors as a function of temperature. From these tests sodium columbate and cadmium columbate were chosen as the most promising dielectric materials.

This bulletin describes the preparation and electrical characteristics of capacitors made from these compounds.

General Discussion

An ideal dielectric material for use in the manufacture of capacitors would be one having high dielectric constant, dielectric strength, d-c resistivity, and low dielectric losses. The K and power factor would be independent of frequency, temperature, applied voltage humidity and time. At present the most commonly used dielectrics are paper, mica, low K ceramic, and high K ceramic. Due to their poor operation as capacitors at high frequencies, paper condensers are confined to use as coupling and by-pass capacitors in low-frequency circuits. High cost and low K are limiting mica capacitors to transmitter applications. Where low capacity with good frequency stability is required, the low K ceramic units are excellent. However, for dimensional reasons and less stringent power factor and K requirements the high K ceramic capacitors are used extensively as coupling and by-pass condensers up to very high frequencies.

Ceramics are the most recent materials added to those used as condenser dielectrics, and most of these ceramics have been compounds of titanium dioxide (itself an excellent dielectric). These compounds are known as titanates. Magnesium titanate, for instance, is a compound formed by the combination of magnesium oxide and titanium dioxide. Various combinations of barium, calcium, magnesium, and strontium titanates are in extensive use today.

There are, however, applications where improved performance under extreme temperature conditions and space requirements would be desirable. These led to an investigation of more suitable dielectric materials. Molybdates, tantalates, tungstates, columbates, zirconates, and vanadates were made and tested. Of these materials the columbates of sodium and cadmium offered the most promising solution to the problem.

Processing

The general procedure giving the most satisfactory results is to dry mix thoroughly sodium carbonate (Na_2CO_3), cadmium oxide (CdO) and columbium oxide (Cb_2O_5) in the desired proportions. The mixture is lightly pressed, then calcined for one hour in air at 1900°F to 2200°F. The sintered mass is reground dry and passed through a 250-mesh screen. This powder can be pressed to final shape as is, or it can be mixed with any of the numerous temporary binders used in the ceramic industry such as methocel, carbowax, etc. Final firing is carried out in air or oxygen at 2300°F ± 100°F for ½ hour for pieces 50 mils or less thick. A longer firing schedule is required for thicker pieces. If the bodies are 15 mils or less thick and all moisture and temporary binder have been removed, a fine grain vitreous structure can be obtained by placing directly in an air atmosphere at 2400°F and held for 10 minutes before moving quickly to an 1800°F zone from which they can be cooled as quickly as 150°F per minute without danger of cracking. Bodies made in this manner have somewhat better breakdown characteristics than when the slower firing schedule is used.

During firing the dielectric units must be placed on a material with which they will not react or fuse. The best material for this purpose is barium zirconate. Very little reaction or leaching is evident even when the columbates are fired at temperatures near their melting points.

If the molding pressure is 30,000 p.s.i. the overall shrinkage will be 10 or 11 per cent.

Very little difficulty was encountered in being able to duplicate results. Various batches made from the same raw materials as well as from materials obtained at different times from the same source had substantially identical characteristics.

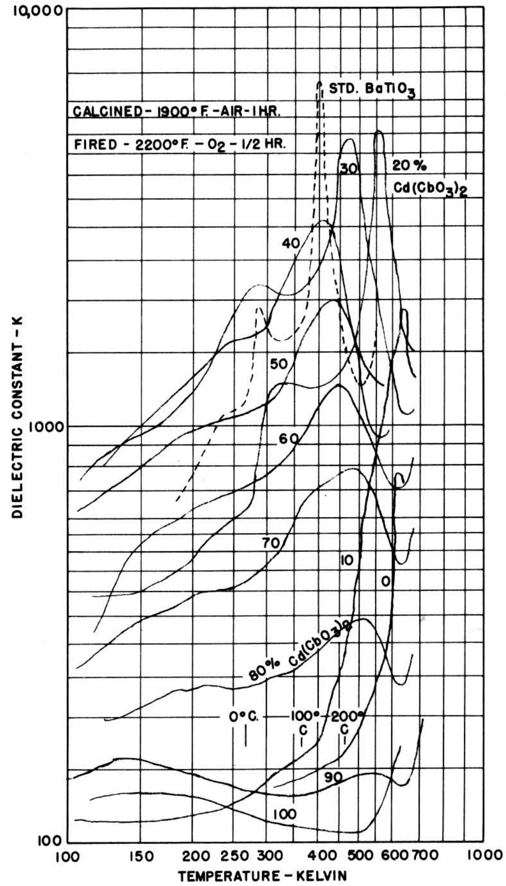

Fig. 1 – Sodium-cadmium-columbate series.

Composition

Fig. 1 shows the temperature dielectric constant characteristic of various mixtures of cadmium columbate and sodium columbate from 100 per cent to 0 per cent cadmium columbate. The dotted curve is the same characteristic for standard barium titanate. The increase in K shown at the extreme high temperature end is not a true increase in K; it is probably due to some sort of interfacial polarization which develops due to the high temperature. This polarization is accompanied by a sharp decrease in shunt resistance and a consequent increase in dissipation factor. From these curves a composition consisting of about 70 per cent sodium columbate and 30 per cent cadmium columbate by weight has not only the highest K but the K is substantially constant over the temperature range of 0°C to 100°C. This composition was chosen for further study.

To determine the optimum composition a standard mixture consisting of 2 parts by weight of Na_2CO_3 and 6.52 parts Cb_2O_5 was made. To this standard mixture various amounts of CdO were added and the temperature characteristics taken. These characteristics are shown in Fig. 2. No appreciable change in characteristics is evident after the CdO content is increased beyond 0.592 parts by weight. This is just sufficient CdO to completely satisfy the formula: 8 $NaCbO_3$ · 1 $Cd(CbO_3)_2$ and corresponds to the 100 per cent curve in Fig. 2. The chemical reactions involved probably are as follows:

$$Na_2CO_3 + Cb_2O_5 \rightarrow 2NaCbO_3 + CO_2\uparrow$$

and:

$$CdO + Cb_2O_5 \rightarrow Cd(CbO_3)_2$$

The quantities involved are such that the final product probably consists of 8 moles of $NaCbO_3$ to 1 mole of $Cd(CbO_3)_2$ with an excess of 4.5 per cent Cb_2O_5. Additional CdO combined with the Cb_2O_5, but the quantity of $Cd(CbO_3)_2$ thus formed is not sufficient to make an appreciabl

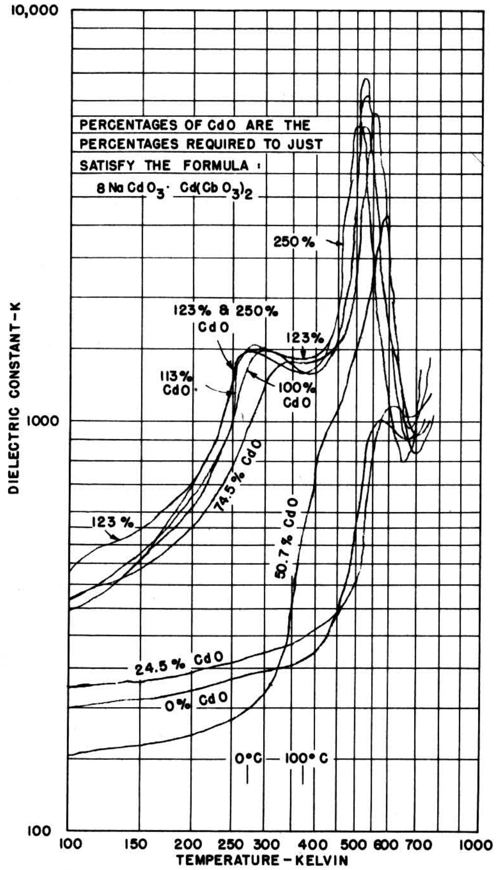

Fig. 2 – Effect of adding cadmium oxide to sodium-cadmium-columbate.

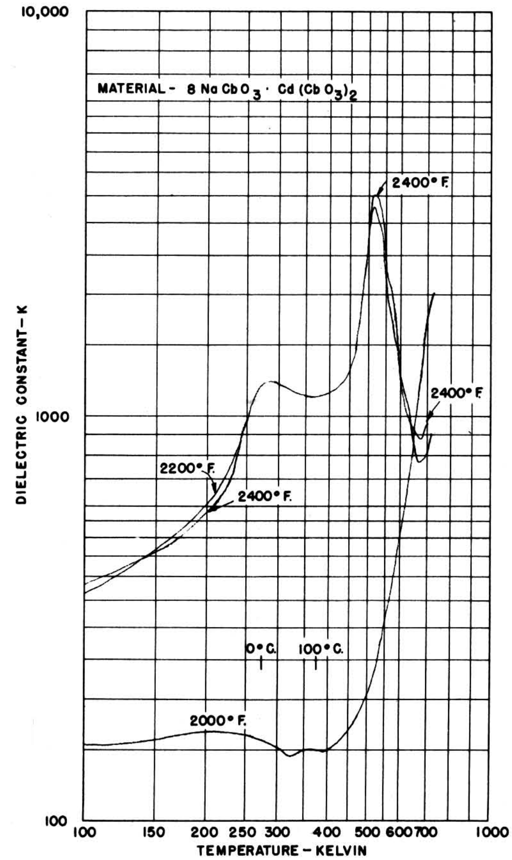

Fig. 3 – Effect of firing temperature.

difference in the temperature characteristic except at the low temperature end. CdO decomposes at 165^{0}F and Cd boils at 1418^{0}F; therefore, any unreacted CdO would be expected to decompose, then the Cd would boil off. This accounts for the independence of the temperature characteristic from CdO content above the amount required to completely react the Cb_2O_5.

Referring again to Fig. 2 the constant K portion of the temperature characteristic is somewhat extended at the low-temperature end when the CdO content is increased to 123 per cent of the amount required to satisfy 8 $NaCbO_3$ · 1 $Cd(CbO_3)_2$. From this the final composition was chosen to be 1 part CdO, 2.74 parts Na_2CO_3, and 8.94 parts Cb_2O_5.

Results

This mix was tested for the effect of calcining temperature, firing temperature, firing atmosphere, method of mixing, and different batches of raw materials. Calcining below 1900^{0}F produces a material which does not grind easily, and it forms a fluffy powder with very poor molding characteristics. A very hard material is formed if the calcining temperature is above 2400^{0}F. The calcining time is not critical. Best results are obtained with calcining temperatures between 1900^{0}F and 2100^{0}F, and Fig. 3 shows the effect of firing temperature on this material when calcined at 1900^{0}F for one hour and then fired at the indicated temperatures for ½ hour in oxygen. As long as the firing temperature is above 2100^{0}F but not higher than 2400^{0}F, essentially the same temperature characteristic is obtained regardless of the firing time. However, long firing times encourage the formation of a coarse crystalline structure which materially lowers the electrical breakdown characteristics of the dielectric. On pieces 360 mils in diameter and 24 mils thick best results are obtained by completely burning out any binder at some low temperature such as 1500^{0}F, then immediately placing the bodies in air at 2400^{0}F and holding for 10 minutes before removal to an 1800°F zone where they are allowed to cool at a rate slow enough to prevent fracture due to thermal shock. Most of the firing was done in oxygen until a test showed that about 20 per cent lower power factors are obtained if air instead of oxygen is used for the firing atmosphere. No noticeable differences are found in the temperature dielectric constant characteristic. Mixing can be done wet or dry without appreciably affecting the characteristics.

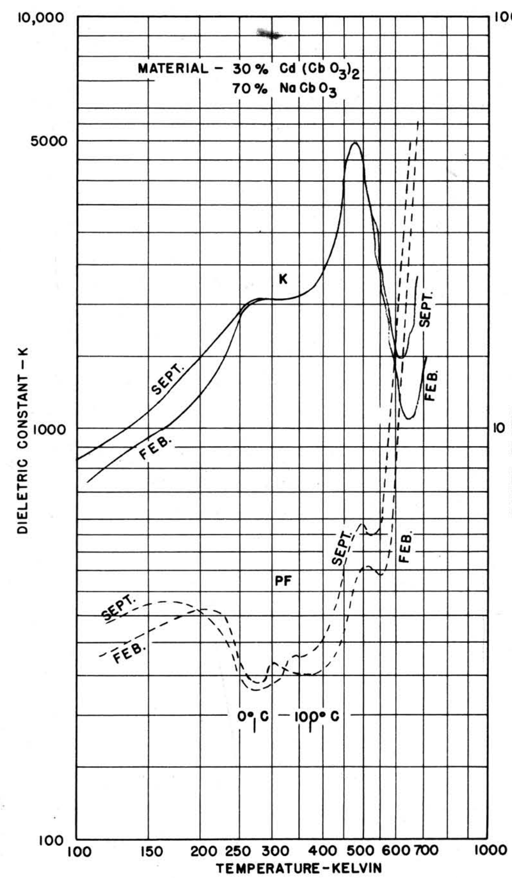

Fig. 4 - Effect of aging.

The effect of aging over a 7-month period is shown in Fig. 4. From -10°C up, no appreciable change in dielectric constant takes place; however, the power factor shows increases up to 30 per cent. Over the normal operating range the increase in power factor does not exceed 15 per cent. Below -10°C the dielectric constant shows increases up to 20 per cent, and the power factor changes from -10 per cent to +15 per cent of its original value.

The voltage breakdown characteristics of the columbates up to 50 mils thick are very similar to those of the titanates - about 100 volts/mil. For thicker units flash breakdowns of the two materials are comparable but the life of the columbates under continued stress is much shorter than the titanates. For this reason the competitive value of the columbates is in the thin units.

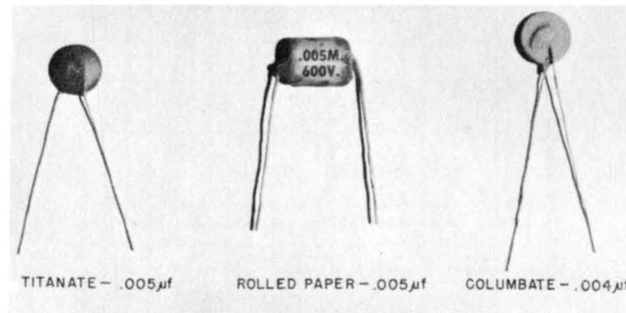

Fig. 5 - The units tested for comparison.

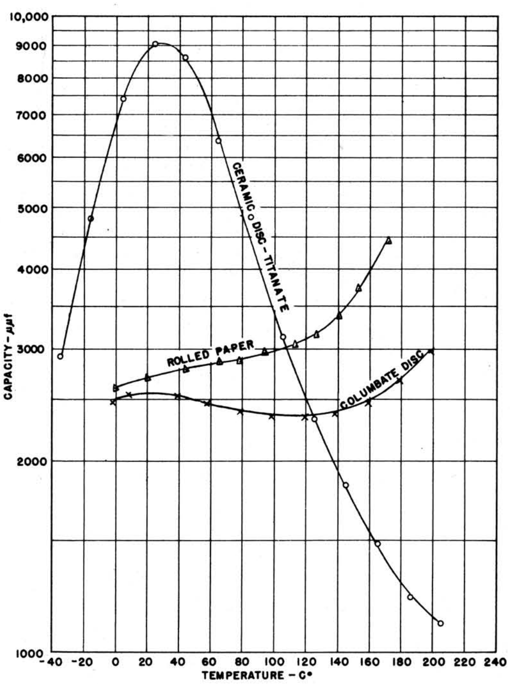

Fig. 6 - Comparison of temperature-capacity characteristics.

Columbate disc capacitors were made and compared with a titanate disc capacitor and a roll paper capacitor. The units tested are shown in Fig. 5. The temperature-capacity curves of the three condensers are shown in Fig. 6. The columbate capacitor has the most desirable temperature characteristic of the three. The power factor temperature curves shown in Fig. 7 show the columbate unit to have the highest power factor, but it is the least variable with temperature. As shown in

Fig. 8 the d-c leakage resistance of the columbate condenser is only one tenth that of the titanate, but it is twice as high as the rolled paper. These ratios are nearly constant over the entire operating range of temperatures.

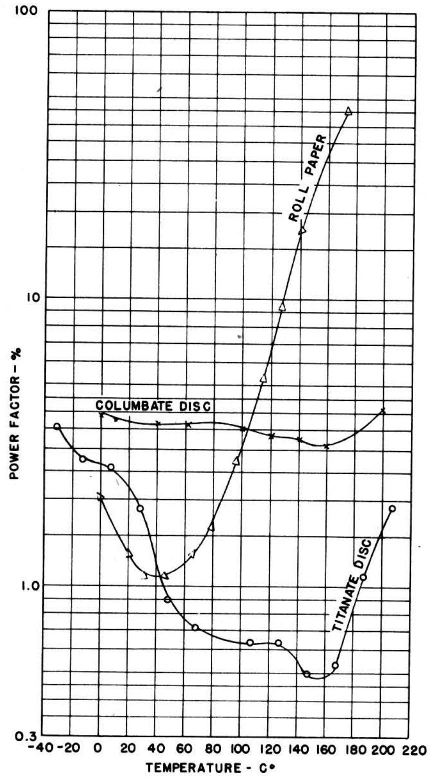

Fig. 7 - Comparison of temperature-power factor characteristics.

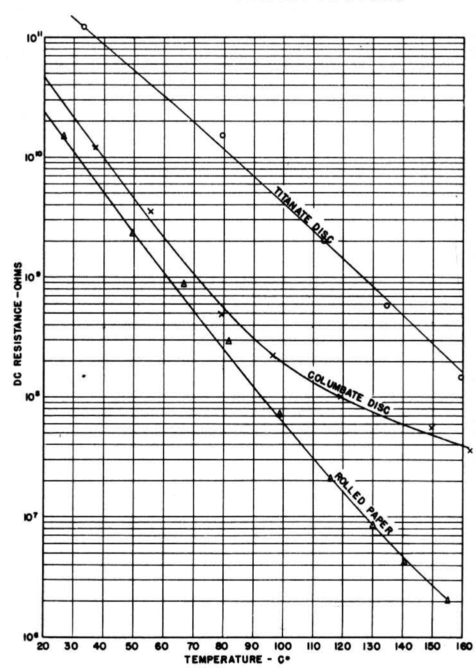

Fig. 8 - Comparison of temperature - DC leakage resistance characteristics.

Most ceramic dielectrics of the high K type change dielectric constant with d-c gradient. This characteristic for the three condensers under consideration is shown in Fig. 9. The rolled paper unit, of course, shows no change of K with electric stress. The titanate unit, however, decreases in capacity to 0.58 times its original value with a field of 30 volts/mil. Under the same stress the columbate decreases to only 0.85 times its original value.

Just as with the titanates the columbates must be carefully sealed against humidity.

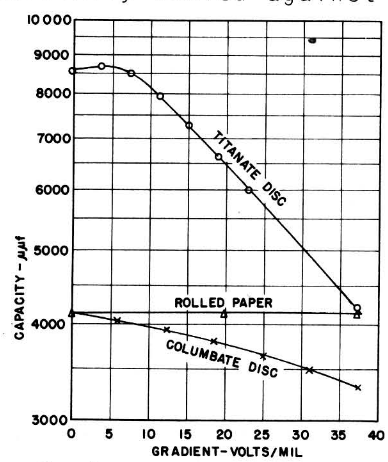

Fig. 9 - Comparison of capacity - DC gradient characteristics.

Conclusion

The columbate dielectrics have desirable characteristics for use where physical size and freedom from the effects of temperature are important factors and where low power factor and high voltage breakdown are of less importance. Specifically, columbate condensers could be used for by-pass condensers in r-f, i-f and a-f amplifiers and as coupling condensers in a-f and video amplifiers. They could be used in the resonant circuits of the horizontal and vertical oscillators in television sets. The roll paper capacitor-resistor integrating network used to separate the vertical pulses in a television receiver might be a printed circuit on a slab of columbate material. The columbates may meet the need for small-size by-pass condensers capable of operating at 250°C for use in compact military equipment such as the proximity fuse and airborne apparatus.

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