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DRAFT

DEVELOPMENT OF NEW DIELECTRIC SYSTEMS TO PROVIDE A MINIMUM
VOLUMETRIC EFFICIENCY OF TEN JOULES PER CUBIC INCH

not present

QUARTERLY PROGRESS LETTER #2

Period: May 8, 1968 to August 8, 1968

To Sandia Corporation
Albuquerque, New Mexico

Contract No. 57-5750

Buyer: J. L. Miller, 4312

Requester: A. F. Hurford, 1432

SPRAGUE ELECTRIC COMPANY
North Adams, Massachusetts

September 9, 1968

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SUMMARY OF PROGRESS

The studies of polymer films loaded with barium titanate have been aimed at gathering needed information to cast loaded film on a production scale. The problems of getting fine dispersion have been fully solved and engineering studies for commercial scale casting have included variations of various lots of barium titanate powder, of solvent purification requirements, of optimum polymer concentrations for ball-milling dispersions, and of various lots of polycarbonate. Process improvements have been initiated to limit the brittle character of highly loaded films and the use of polymeric plasticizers has shown definite improvement but not enough for commercial processing at present.

The evaluation of unloaded polymer films was continued and during this quarter break-down voltages of 15 KV per mil were obtained with a chlorinated polyvinyl chloride film. These results compare very favorably with Mylar.

In studies of barium titanate powders dispersed in a glass matrix, we have found that we can decrease the glass content to as low as 15% (by volume) and these compositions have a dielectric constant of about 1000; dielectric strengths to date are relatively low.

Ceramic capacitor dielectrics of high density have been fabricated using barium tetratitanate of high purity. The resulting dielectrics had dielectric strength of as high as 1.3 KV per mil which is unusually high for ceramic materials.

POLYMER DIELECTRICS

H. Kachi

I. Dielectric Strength of Heat-Treated Chlorinated Polyvinylchloride

Films of Geon vinyl 101-EP (1/2 mil thick) were cast from 12 per cent solutions in tetrahydrofuran. In the following table sample no. 1 was heated at 55° for one hour; sample no. 2 was the identical sample further heated at 65° for one hour, etc. Therefore, each sample designation has received a cumulative heat treatment of all the samples above it.

Sample	Heating Temp.°C	Break-down Voltage, 25°C (KV/mil)
1	55	12.0 $\pm$ 1.3
2	65	13.7 $\pm$ 2.7
3	75	14.0 $\pm$ 2.9
4	85	14.2 $\pm$ 2.0
5	95	13.8 $\pm$ 1.6
6	105	15.1 $\pm$ 1.4
7	115	14.2 $\pm$ 1.7
8	125	14.4 $\pm$ 2.3
9	135	15.4 $\pm$ 0.9
10	145	16.8 $\pm$ 1.7

Dielectrics strengths achieved by the above thermal treatment are comparable to that of heat-treated Mylar, but the Geon chlorinated PVC softens at 110°C.

II. Heat Treatment of Mylar Film

Further experiments were run to determine the cause for the improvement of dielectric strength of 1/2-mil film.

Treatment	Density (25°C)	Amorphous Content by Density	D_{898}/D_{795}	V_{BD} , KV/0.5 mil
none	1.396	40.4%	0.714	5.7 ± 0.4
250°C for 1 minute	1.390	44.4%	1.23	8.1 ± 0.3

The ratio of infrared band intensities D_{898}/D_{795} is proportional to the amorphous content. According to the infrared measurements, the heated film should contain 1.72 times as much amorphous material as the untreated, but according to density measurements only 1.10 times as much. We suspect the density measurement is in error because of the presence of voids in the untreated Mylar which anneal out in the heat treatment.

Table 1
Summary of Film Electrical Properties

Volume Per Cent BaTiO ₃	Breakdown Voltage (KV/mil), V _{BD} *	Dielectric** Constant μ	Insulation Resistance (megohm- μ farad)	Energy Storage Factors at Breakdown	
				Volumetric $(V_{BD})^2 \times \epsilon$	Gravimetric $(V_{BD})^2 \times \frac{\epsilon}{\text{DENSITY}}$
9	6.2 $\pm$ 1.2	3.2		122	75
(20)	6.3 $\pm$ 1.0	7.3	235	292	135
31	5.0 $\pm$ 1.0	26.8	44	670	250
34	4.7 $\pm$ 0.6	35.2	110	780	276
0	16.5 $\pm$ 2.0	3.1		840	700

* Short-time method in silicone oil ("point" contacts) at room temperature.

** Sputtered 3/4" copper electrodes

Excellent agreement was found between this method and one employing a 3-inch square copper plate and a 1/4-inch diameter copper rod as electrodes.

CERAMIC-LOADED POLYMER DIELECTRICS

D. Kelley and H. Kachi

The studies of polymer films loaded with barium titanate have been aimed at gathering needed information to cast loaded film on a production scale. The problems of getting fine dispersion have been fully solved and engineering studies for commercial scale casting have included variations of various lots of barium titanate powder, of solvent purification requirements, of optimum polymer concentrations for ball-milling dispersions, and of various lots of polycarbonate.

Comparisons of loaded films were made with BaTiO_3 powders which had been calcined by a rotary drum technique versus powders calcined by a fluid bed technique. No significant differences were observed in dielectric breakdown strengths of comparably loaded films.

The use of unpurified dioxane is suitable for milling BaTiO_3 powder. Fairly good dielectric strength is found in films made using this type dispersion plus polycarbonate solution made using purified dioxane. However, concentrated polycarbonate solutions (15%) made using unpurified dioxane are cloudy and gel much more rapidly than when dried and distilled solvent is used.

The powder can also be milled in concentrated (15%) polymer solution to give predominantly sub-micron particle size. However, for a given milling time a higher concentration of large aggregates is present than when a dilute suspension is milled.

Our current laboratory procedure in preparing loaded films is as follows:

Barium titanate powder was milled in dilute polycarbonate-dioxane solution to reduce aggregate size. After settling the supernatant was decanted to give a dispersion containing 40-45 weight per cent BaTiO_3 . Casting solutions were prepared by mixing various ratios of the above dispersion and a 15 weight per cent solution of polycarbonate (Marlon M-60) in dioxane. The mixtures were cast on a glass plate using a 0.003 inch applicator; the films were allowed to dry to about 1/2 mil thickness at room temperature and then were baked 24 hours at 110°C.

Typical properties of polycarbonate films loaded with various amounts of barium titanate are summarized in Table 1 and Figure 1.

Films became more brittle with increasing BaTiO_3 level. Break-down voltage values given in the table were obtained with films which contain ca. 1% residual solvent. More complete drying yields lower values of V_{BD} , due to increased brittleness and probably the formation of microscopic defects

during handling. Moisture content is also an important factor. After the standard 24 hour bake, a film stored in a desiccator with Drierite had a V_{BD} value 20 per cent higher than one stored under room conditions.

Films containing 20 volume per cent $BaTiO_3$ were made less brittle by incorporating 5% (based on polycarbonate) of either Ganex V-804 or V-904, polyvinylpyrrolidone-based dispersants. However, a 20% reduction in break-down voltage occurs. In addition, 20% Ganex level failed to render flexible heavily filled films (ca. 40% BT). (The milky appearance of films containing no $BaTiO_3$ indicates the Ganex polymers are not completely compatible with polycarbonate.) A similar decrease of 20% in V_{BD} accompanied the incorporation of 5% Hycar CTBN (liquid rubber) in films containing 27 and 35 volume per cent $BaTiO_3$. The films were not noticeably less brittle due to the Hycar.

The voltage coefficient of capacitance was measured for a 1/2-mil $BaTiO_3$ filled polycarbonate film having a break-down voltage of 6.1 ± 0.6 KV/mil. The dielectric constant at zero applied D.C. bias was $\epsilon = 8.3$. The observed per cent decrease in capacitance was 1.9% and 5.2% for 500 and 1000 volts/mil bias respectively.

Two other polymers were examined as possible binders for $BaTiO_3$. The Geon PVC-type material shows good dielectric strength but softens near $110^\circ C$. The loaded Geon was quite flexible despite heavy loading.

Polymer	Vol.% $BaTiO_3$	Breakdown Voltage (KV/mil)	Dielectric Constant
Geon 101-EP	0	12.0 ± 2.3	
Geon 101-EP	(36)	4.0 ± 0.3	
Vitel PE-200	(28)	2.7 ± 0.6	26

CERAMIC-LOADED GLASS DIELECTRICS

I. Burn

Investigation of the influence of glass composition on the dielectric properties of barium titanate-in-glass composites has continued. For the most part this has consisted of examining the effect of additions of CdO , ZnO or BaTiO_3 to a lead-bismuth-borate glass that had given promising results earlier.

It has been found that the formation of extraneous phases during sintering is a major cause of reduced permittivity of composites of this type. Silicate or borate phases readily form if the softening temperature of the glass is high (above about 900°C), and new titanate phases are usually produced when fluxing agents (PbO , Bi_2O_3) are added to the glass. Glasses containing BaO , some with additions of BaF_2 , are presently being tried in an attempt to suppress the formation of secondary phases. With 45 vol.% glass, the dielectric constant of the composites is commonly 250-300 when the lead-bismuth-borate glasses are used, with or without additions of 10 wt% CdO , ZnO or BaTiO_3 . Higher dielectric constants, up to about 400, can be obtained with composites in which (semiconducting) CdO is precipitated from the glass during firing, but the dielectric strength is reduced in this case.

Densification has been found to occur with smaller amounts of glass than was earlier thought possible. This is because the barium titanate is usually soluble to some extent in the glasses used, and sintering can take place by the solution and precipitation process. Composites containing only 15 vol% glass have been prepared with a dielectric constant above 1000 but the dielectric strengths are relatively poor. The range between 15 vol% and 45 vol% has yet to be explored.

The dielectric strengths of composites containing 45 vol.% glass generally range from approximately 350 to 1000 volts per mil. Addition of CdO to lead-bismuth-borate glass, whilst not influencing the dielectric constant of the composites appreciably, appears to improve the dielectric strength. The measured strengths, however, are very sensitive to fabrication faults (porosity, non-uniform thickness, etc.) and this often masks the intrinsic strength of the material. Efforts are therefore being made to sinter the composite to as near theoretical density as possible so as to realize the optimum strengths of the materials.

It is intended to begin discharge tests on some of the materials prepared so far. Thick film units are being made and will be tested as soon as the assembling of the necessary equipment is completed.

CERAMIC DIELECTRICS

R. P. Auty

One of the limitations of normal ceramic capacitors is the low dielectric strength in comparison to other dielectric materials, and, therefore, these have not been used for energy storage. Improvement is worth investigation if the breakdown field is limited by porosity or charge carriers accumulated by diffusion on the outside of the grains.

Our program is to investigate the electrical properties of high density, non-ferroelectric polycrystalline ceramic bodies. Barium tetratitanate was chosen as a low dielectric constant material which is made in high purity and sinters easily to high density. The nonferroelectric material was chosen to avoid field-dependence of capacity and the mechanical shock of rapid capacitor discharge.

Table 2 shows the results of breakdown testing of barium tetratitanate sintered in air with a density $98 \pm 0.5\%$ of x-ray density. Electrodes were applied immediately after firing. Although the results were promising, the hypothesis was made (and confirmed in Table 2) that the control of the oxygen partial pressure during firing would also affect the electrical characteristics. Consequently, annealing studies were carried out in an attempt to approach equilibrium conditions. Not only were the high voltage test results improved but large improvements were noted in temperature coefficient of capacitance and in the ac losses at 130°C (Table 3). It should be noted that the ac losses for all units were too small at room temperature to be measured on our bridge.

Table 2

Barium Tetratitanate
Breakdown Testing
Sputtered Electrodes

	No Anneal			Annealed 1 mm air 1/2 hr 1000°C		
	1	2	3	4	5	6
DC Voltage (KV)	26	26	30	30	30	30
Thickness (mils)	23.0	25.5	23.0	24.0	25.0	24.0
Field (KV/mil)	1.1	1.0	1.3	1.3	1.2	1.3
Comments	Fail	Fail	Fail after 50 secs.	No failure after 1 min.		

Table 3

Barium Tetratitanate

Anneal
Conditions

Temp°C	1225°C	1225	1225	1225	1225	1000	1200	1180
Press mm	760	100	20	5	1	5	5	5
Atm	air	air	air	air	air	O ₂	air	air
Time hr	1	1	1	1	1	1/2	1	1
K 25°C, 1 KHz	39.8	39.9	38.9	39.9	39.9	45.2	38.6	34.1
K 130°C, 1 KHz	47.7	46.6	43.9	42.5	46.6	45.7	33.4	39.8
D 130°C, 1 KHz	.3874	.2107	.2482	.1695	.1730	.1312	.1526	.0284
Temp Coeff ppm (25°-130°C)	+1890	+1599	+1224	+620	+1599	+105	-1283	+1592
% X-ray Density	98.5	98.4	98.7	98.4	98.4	94.9	98.6	98.5