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THIRD QUARTERLY REPORT

Ending

January 27, 1962

**PEM FOR PRODUCTION OF FLUORINATED BARIUM
TITANATE CAPACITORS FOR OPERATION TO 200°C**

**CONTRACT NO. DA-36-039-SC-85955
U. S. ARMY SIGNAL SUPPLY AGENCY
PHILADELPHIA, PENNSYLVANIA**

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**CORNELL-DUBILIER
ELECTRIC CORPORATION**

CERAMIC DIVISION · NEW BEDFORD, MASSACHUSETTS

62-2-5

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U. S. Army Signal Supply Agency
Philadelphia, Pennsylvania**

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By

CORNELL-DUBILIER ELECTRIC CORP.

Ceramic Division

New Bedford, Mass.



**Prepared by: L. E. Nordquist
Project Engineer**



**Approved by: R. L. Grove
Chief Ceramic
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TABLE OF CONTENTS

	Page
1. ABSTRACT	1-1
2. PURPOSE	2-1
3. NARRATIVE AND DATA	3-1
3.1 Review	3-1
3.2 Data Evaluation	3-1
3.3 Indicator Discs	3-3
3.4 Bulk Fluorination	3-3
3.5 Assembly and Encapsulation	3-3
4. CONCLUSION	4-1
5. PROGRAM FOR NEXT QUARTER	5-1
6. IDENTIFICATION OF PERSONNEL	6-1
7. DISTRIBUTION LIST	7-1

1. ABSTRACT

1.1 Binary and high K compositions are being life tested at 200°C and 500V in both the fluorinated and non-fluorinated condition. The marked improvement of the fluorinated dielectrics over those not fluorinated is reflected in life time, aging rates and insulation resistance. Improvement factors in some instances are so large as to be incalculable.

1.2 The use of indicator discs to monitor fluoride level within the kiln can be effective if a narrow fluoride range is required; however, careful selection of the composition to be fluorinated can provide a sufficiently broad fluorination range to make their use unnecessary.

1.3 Bulk fluorination of large quantities of capacitor discs has been only moderately successful. Improvements are being implemented to improve the technique.

1.4 Encapsulation and assembly problems present a major difficulty. It appears that the dielectric can be improved to withstand the rigors of 200°C operation, but the problems encountered in assembly and encapsulation might require a more involved solution.

2. PURPOSE

2.1 The purpose of this project is to establish the capability to fluorinate 16,000 capacitor discs per eight hour shift and to manufacture 4,000 capacitors each of four types in accordance with Signal Corps Technical Requirements SCS-37 dated 9 March, 1959 and amendment No. 1 dated 29 November, 1960. This requirement defines the quality and testing program for 200°C fluorinated ceramic capacitors as listed below.

2.1.1 CK63 barium titanate capacitors rated at 10,000 mmf. + -20%, 500 VDC at 85°C and 250 VDC at 200°C using barium titanate made with West German barium carbonate.

2.1.2 CK63 barium titanate capacitors rated at 10,000 mmf. + -20%, 500 VDC at 85°C and 250 VDC at 200°C using barium titanate made with domestic barium carbonate.

2.1.3 Barium titanate capacitors, maximum diameter 0.39 inches rated at 10,000 mmf. + -20%, 50 VDC at 85°C and 25 VDC at 200°C using barium titanate made with West German barium carbonate.

2.1.4 Barium titanate capacitors, maximum diameter 0.39 inches rated at 10,000 mmf. + -20%, 50 VDC at 85°C and 25 VDC at 200°C using barium titanate made with domestic barium carbonate.

3. NARRATIVE AND DATA

3.1 REVIEW

3.1.1 The fluorination of barium titanate type capacitors is performed by firing sintered capacitor discs in a fluoride atmosphere in a laboratory tunnel kiln. The fluoride level within the kiln is maintained during a firing run by introducing donor tablets on each setter along with the discs to be fluorinated. The capacitor discs tend toward a yellow color after fluorination and exhibit high insulation resistance values at elevated temperatures. It was also noted that the degree of fluorination required varies with the composition of the dielectric. The major improvement to the dielectric is in its life time at elevated temperatures, thereby permitting development of 200°C capacitors.

3.2 DATA EVALUATION

3.2.1 The fluorinated and non-fluorinated capacitor discs of Table I were assembled using a conductive epoxy cement to secure the wire leads, and a silicone bonded zirconium silicate dip to further protect the capacitor and prevent the leads from being loosened during handling. Unfortunately, the dip coating had an adverse effect on the insulation resistance values (I. R.) at elevated temperatures and values presented should be higher in most cases.

3.2.2 Tables II and III represent an average of comparative electrical data of the fluorinated and non-fluorinated compositions of Table I. It will be noted that there is a marked improvement in the aging rates of the fluorinated discs.

This is especially noteworthy of the BaTiO_3 - CaTiO_3 binary where there is almost a tenfold reduction in the aging rate per decade. The increase in insulation resistance at 200°C attributed to fluorination treatment is again prominent. Figure I illustrates the I. R. vs. temperature of a fluorinated and non-fluorinated high K dielectric which shows promise of being suitable for 200°C capacitor use.

3.2.3 The life test results of these units portray the marked improvement of the dielectric after fluorination. Five samples of each composition were subjected to the life test conditions. This involves 36 groups or 180 capacitors from Table I compositions. These were further supplemented with additional high K compositions aimed towards development of a final mix for pre-production samples.

3.2.4 In most instances the dielectric constant is slightly increased by fluorination and the dissipation factor is usually lower than non-fluorinated units at temperatures above 125°C . Figure II illustrates the change in dielectric constant and P. F. vs. temperature for the fluorinated and non-fluorinated capacitors of Figure 1.

3.2.5 Life test data indicates that the barium titanate made with domestic barium carbonate is inferior to the barium titanate made with imported barium carbonate. This difference will be further examined and possible corrective measures will be investigated.

3.3 INDICATOR DISCS

3.3.1 The use of indicator discs to act as a visual aid in maintaining fluoride level within the kiln was further explored. Partial success was achieved in that compositions were developed having differing fluoride requirements and a color difference was observed in these discs when they were fluorinated simultaneously. Present fluorination technique has resulted in successful fluorination runs over an eight hour period with some high K compositions, suggesting that a broad fluorination range exists for these compositions and that indicator discs might not be necessary.

3.4 BULK FLUORINATION

3.4.1 The development of a bulk fluorination technique is necessary to permit fluorination of 16,000 capacitor discs per eight hour shift. Attempts at doing this by stacking the discs on edge, as in a roll of coins, were not successful in that the fluorides would not penetrate between the discs. Separating the discs with coarse granular ZrO_2 brought some improvement but not sufficient for satisfactory production. Further changes in fluoride material and stacking arrangement are being investigated which should improve bulk fluorination techniques.

3.5 ASSEMBLY AND ENCAPSULATION

3.5.1 The use of high temperatures and high temperature materials resulted in some new problems. The solder used in the assembly operation was

a eutectic alloy of 96 1/2 tin and 3 1/2 silver, with a melting point of 340°F. Capacitors were satisfactorily soldered, using these materials, but sustained operation at 200°C caused a severe alloying of the silver electrode into the solder, thereby destroying the bond. It was noted that certain silver paints were more resistant to this effect than others and possibly electrodes of other precious metals or other solders might prevent this. Evaluation of other materials is being conducted.

3.5.2 The encapsulation materials for this application are very limited and often require involved methods of application. Silicone materials investigated, withstood the 200°C temperature very nicely, but failed to provide sufficient protection during humidity testing. Epoxy materials have shown good temperature and moisture resistant characteristics, but have failed thermal shock tests. Zirconium silicate filled epoxy resins have shown good promise and further investigation is being conducted to develop methods of application other than casting or potting.

4. CONCLUSION

4.1 Present life test and aging data indicate that fluorinated dielectrics for 200°C operation are possible.

4.2 Fluoride level within a kiln is difficult to measure but can be maintained by regular additions of donor tablets and a measure of control can be achieved by using indicator discs.

4.3 Bulk fluorination of capacitor discs presents a problem in fluoride penetration throughout a closely packed setting of discs.

4.4 Assembly and encapsulation are apparent problem areas and new materials and methods are being investigated.

4.5 There is some evidence that the barium titanate made with domestic barium carbonate is inferior with respect to life time at 200°C and 500 VDC.

5. PROGRAM FOR NEXT QUARTER

5.1 The program for the next quarter will be as follows:

5.1.1 Selection of a high K composition, suitable for fluorination, and fabrication of pre-production samples.

5.1.2 Establishment of satisfactory assembly methods and materials.

5.1.3 Establishment of satisfactory encapsulation methods and materials.

5.1.4 Improvement of the bulk fluorination technique.

5.1.5 Further evaluation of barium titanate made with both domestic and imported barium carbonate.

6. IDENTIFICATION OF PERSONNEL

ROBERT L. GROVE 37 hours

Chief Engineer, Ceramic Division

LAWRENCE E. NORDQUIST 260 hours

Project Engineer

JAMES SOUZA 520 hours

Electrical Engineer

PAUL C. RICARD 520 hours

Chemist

I. S. LASSOW 23 hours

Clerk-Typist

CLAIRE MEDEIROS 3/4 hour

Clerk

CHARLES E. HODGKINS 12 hours

Chemical Engineer

Born April 26, 1932

Product Development Engineer, Ceramic Division,

Cornell-Dubilier Electric Corporation, 1956 to date

Development Laboratory, Cornell-Dubilier Electric

Corporation 1952 to 1954

New Bedford Institute of Technology, 1949 - 1951,

1954 - 1956 B. S. Chemistry, 1956

7. DISTRIBUTION LIST

7.1 The distribution list for this report will be identical with that submitted on the last quarterly report, with the following approved changes:

7.1.1 The following names are to be added to the previous list:

**Commanding General
U. S. Army Signal Supply Agency
ATTN: Chief, Quality Assurance Operations Division
225 South 18th Street
Philadelphia 3, Pennsylvania**

**Commanding Officer
Midwestern Regional Office, USASSA
ATTN: Chief, Quality Assurance Division
400 South Jefferson Street
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**Radio Corporation of America
Semiconductor Materials Division
Somerville, New Jersey
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TABLE I

COMPOSITIONS INVESTIGATED - WEIGHT PERCENT

	BaTiO ₃	CaTiO ₃	CaZrO ₃	SrTiO ₃	Fe ₂ O ₃	MgZrO ₃	Ce ₂ O ₃
228-A	95	5					
-B	90	10					
-C	80	20					
-D	70	30					
-E	60	40					
229-A	98		2				
-B	94		6				
-C	90		10				
-D	87		13				
-E	83		17				
230-A	90			10			
-B	80			20			
-C	70			30			
-D	60			40			
-E	50			50			
233-B	87		13		.1		
-C	87		12			1.0	
-D	87		13		.1		.2

TABLE II
Non-Fluorinated
Average Electrical Data of Capacitor Discs of Table II

Life Test Hours To Date 830

	Dielectric Constant	% P. F.	I. R. $\times 10^3$ Megohms @ 25°C	I. R. Megohms @ 200°C	% Age Per Decade	Lifetime Total Failed	Hrs. - 5 Min. - Hrs.	Units - Max. Hrs.
228 - A	921	1.2	140	30	1.2	5	-	<.1
-B	680	1.0	275	29	7.6	5	-	<.1
-C	600	.63	250	48	8.6	5	-	<.1
-D	538	.52	80	52	7.5	5	-	<.1
-E	429	.47	55	48	5.8	5	-	<.1
229 - A	1534	1.7	62	16	3.3	5	-	<.1
-B	1571	2.1	28	27	7.2	5	-	<.1
-C	2950	1.7	27	36	10.7	5	-	<.1
-D	7633	1.5	60	45	6.9	5	<.1	84
-E	2840	.50	115	83	1.3	5	100	187
230 - A	1406	1.7	30	3.5	1.6	5	-	<.1
-B	2158	2.5	17	4.2	4.1	5	-	<.1
-C	5188	.70	28	6.2	7.1	5	-	<.1
-D	1950	.50	40	20	3.2	5	<.1	1
-E	1020	.10	55	45	2.5	5	-	<.1
233 - B	6900	1.2	108	70	4.2	5	209	370
-C	5110	.84	155	140	4.6	5.	<.1	64
-D	7330	.85	115	310	4.3	0	-	-

TABLE III

Fluorinated

Average Electrical Data of Capacitor Discs of Table I

Life Test Hours To Date 830

	Dielectric Constant	% P. F.	I.R. $\times 10^3$ Megohms @ 25°C	I.R. $\times 10^3$ Megohms @ 200°C	% Age Per Decade	Lifetime Total Failed	Hrs. - 5 Units Min. - Max. Hrs. Hrs.
228 -A	928	2.0	80	60	0.4	0	-
-B	787	1.8	120	120	0.9	0	-
-C	665	1.8	275	190	0.8	1	410 -
-D	615	1.6	700	110	0.6	0	-
-E	503	1.4	900	200	0.5	0	-
229 -A	1890	2.5	25	80	3.5	0	-
-B	1950	3.9	15	185	4.5	0	-
-C	3336	4.4	20	7	5.7	2	< .1 698
-D	7503	2.0	135	25	2.0	1	410 -
-E	2865	.45	2500	60	0.9	0	-
230 -A	1789	3.0	30	27	1.1	0	-
-B	3018	3.9	30	2	1.8	1	312 -
-C	7128	.46	500	30	6.0	1	8 -
-D	1970	.90	500	12	1.2	0	-
-E	993	.40	500	18	1.6	0	-
233 -B	8824	1.7	150	300	1.5	0	-
-C	5640	.90	450	35	1.4	0	-
-D	7940	1.4	90	120	1.9	0	-



