NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
FIRST QUARTERLY REPORT
Ending
July 27, 1961

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

XX X UNCLASSIFIED XX X

CORNELL-DUBILIER ELECTRIC CORPORATION
CERAMIC DIVISION - NEW BEDFORD, MASSACHUSETTS
FIRST QUARTERLY REPORT

Ending

July 27, 1961

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

Unclassified

By

CORNELL-DUBILIER ELECTRIC CORP.
Ceramic Division
New Bedford, Mass.

Prepared by: L. E. Nordquist
Project Engineer

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

1. ABSTRACT 1-1
2. PURPOSE 2-1
3. NARRATIVE AND DATA 3-1
   3.1 Introduction 3-1
   3.2 Special Test Facilities 3-2
   3.3 Fluorination Technique 3-2
4. CONCLUSION 4-1
5. PROGRAM FOR NEXT QUARTER 5-1
   5.1 Introduction 5-1
   5.2 Composition 5-1
   5.3 Assembly 5-2
6. IDENTIFICATION OF PERSONNEL 6-1
7. DISTRIBUTION LIST 7-1
1. ABSTRACT

1.1 The manufacture of ceramic capacitors suitable for operation to 200°C represents a new area of interest. The problems associated with this type of capacitor require specialized equipment, assembly techniques and materials. Specialized equipment has been and is being constructed to provide rapid testing and evaluation of fluorinated capacitors. Life test equipment permitting external monitoring of capacitors during test is close to completion. In addition, a high temperature chamber has been constructed for rapid evaluation of dielectric constant, dissipation factor and insulation resistance over a wide temperature range.

1.2 A study was made of the reports on degradation and fluorination of ceramic dielectrics as reported by Linden Laboratories, Inc. A sound approach to the problem of manufacture of fluorinated ceramic capacitors which would permit maximum use of present production facilities was established. A two fire approach is planned, the first representing a binder burn off and partial sintering to be followed by a fluorination-maturing firing. It is believed that this would provide maximum control of the fluorination treatment. A temporary tunnel kiln has been assembled. A pusher mechanism has also been constructed to provide accurate soaking periods from 30 minutes to two hours. The fluoride atmosphere will be provided by introduction of volatile fluorides on a regular schedule.
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 4000 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 INTRODUCTION

The problems involved in the manufacture of fluorinated ceramic capacitors suitable for operation to \(200^\circ\text{C}\) require an intensive evaluation of many factors. Some of the more pertinent items are as follows:

3.1.1 Dielectric composition best suited for maximum fluorination benefit.

3.1.2 Reproducible and controlled method of fluorination.

3.1.3 Assembly and encapsulation materials suitable for operation at \(200^\circ\text{C}\).

3.2 SPECIAL TEST FACILITIES

3.2.1 The work accomplished in this first quarter can be best described as construction and preparation for solution of the first two items. The test equipment and facilities will serve as tools for quality control and experimental investigations. In view of this approach, the life test oven and associated fixtures have been so designed as to permit external monitoring of each capacitor on test. It is believed that this will allow maximum flexibility and speed for evaluating a large variety of compositions and fluorination trials simultaneously.

3.2.2 The most notable change in the ceramic dielectric after fluorination appears to be its increased insulation resistance at elevated temperatures. This phenomena plus the change in dielectric
constant, dissipation factor and color should provide a good means of evaluating control of the fluorination firing. A special high temperature test chamber has been constructed for this purpose.

3.3 FLUORINATION TECHNIQUE

The techniques of fluorination and the resultant improvement to the dielectric has been extensively investigated by Linden Laboratories. An examination of the reports on this matter and discussions with the personnel involved in this work have helped formulate the approach to be followed.

3.3.1 A two fire operation was decided upon. The unfired capacitor discs would be fired in standard production kilns. This eliminates the problem of fire out of organic binders in the fluorination firing. The degree of firing would be determined by the results of the fluorination treatment. The other advantages of using prefired discs are smaller size, greater flexibility of loading and that fluorination equipment can be simplified and more easily controlled. The second firing or fluorination treatment will be performed in a continuous pusher type tunnel kiln. An experimental kiln for this purpose, along with a mechanical pusher, has been constructed. The kiln has a 20 inch hot zone, 3 inches wide and 1 1/8 inches high. The over-all length of the tunnel is approximately 56 inches. The heating elements are isolated
from the work zone by nitride bonded silicon carbide plates 1/2 inch thick. The mechanical pusher has a 4 speed range giving soaking periods from 30 minutes to 2 hours. This kiln will be used for experimental firings leading to the construction of the final kiln.

3.3.2 The fluoride atmosphere will be provided by additions of volatile fluorides on a regular schedule. This method of fluoride additions has been successfully tried.
4. CONCLUSION

Based on the results of fluorination treatment by Linden Laboratories, Inc., an ambitious program of dielectric improvement has been sponsored by the U. S. Signal Corps. The fulfillment of this contract will result in ceramic capacitors capable of extended life at 200°C. To this end, a program which would permit a thorough investigation of compositions and fluoride treatment has been planned. Special equipment and kilns have been constructed for this purpose.
5. PROGRAM FOR NEXT QUARTER

5.1 INTRODUCTION

The establishment of a reproducible fluorination cycle with barium titanate will establish the firing and charging period of the fluorination kiln. This data can be correlated with that obtained by Linden Laboratories. When satisfactory operation of the fluorination kiln is completed, all effort will be directed towards development of an optimum composition.

5.2 COMPOSITION

As was noted by Linden Laboratories, all compositions are not equally improved by fluorination and considerable work is required to arrive at a composition that will give maximum reliability at 200°C. A series of binary compositions with barium titanate will be evaluated to broaden knowledge of fluorination and also will serve as an aid in selecting the best capacitor formulation. The final compositions should have the following properties after fluorination:

5.2.1 Dielectric constant of approximately 5000

5.2.2 Aging rate not to exceed 1.6% per decade

5.2.3 Withstand a voltage stress of 30 volts per mill for 2000 hours at 200°C

5.2.4 Exhibit high insulation resistance throughout temperature involved.

5.2.5 Withstand assembly and encapsulation techniques required.
5.3 ASSEMBLY

In keeping with the need for a high temperature capacitor, conventional assembly techniques using high temperature materials will be evaluated. The continued improvement of organic resins indicate that this approach might be satisfactory. If this approach does not provide a high quality capacitor capable of meeting all test requirements, the use of silver wire leads and glass encapsulation will be investigated.
6. IDENTIFICATION OF PERSONNEL

ROBERT L. GROVE 40 hrs.
Chief Engineer, Ceramic Division
Born April 2, 1920
Chief Engineer, Ceramic Division, Cornell-Dubilier Electric Corporation 1949 to present
Ceramic Engineer, Globe Union, Inc. 1943 to 1949
Ceramic Engineer, Westinghouse Electric Corp. 1942 to 1943
University of Illinois, 1942, B. S. Ceramic Engineering

LAWRENCE E. NORDQUIST 416 hrs.
Project Engineer
Born April 11, 1930
Ceramic Research Development Engineer, Cornell-Dubilier Electric Corporation 1955 to present
Engaged in titanate research, development and production since 1954
USAF, 1st Lt., Airborne Electronics, 1951 to 1954
University of Illinois, 1951, B. S. Ceramic Engineering

JAMES SOUZA 200 hrs.
Electric Engineer
Born February 7, 1935
Measurements and development, Ceramic Division, Cornell-Dubilier Electric Corporation.
New Bedford Institute of Technology, 1961, B. S. Electrical Engineering
7. DISTRIBUTION LIST

Merck & Company
Rahway, New Jersey
Attn: H. Lazalear

Bell Telephone Laboratories
Murray Hill, New Jersey
Attn: Dr. M. Rigterink

Micamold Div.
General Instrument Corporation
65 Gouverneur Street
Newark, New Jersey
Attn: Mr. Wm. Contardi

Aerovox Corporation
Olean, New York
Attn: Dr. A. Rudriquez

Muter Company
1255 S. Michigan Avenue
Chicago, Illinois

Globe Union, Inc.
Div. Centralab Corp.
900 E. Keefe Avenue
Milwaukee 1, Wisconsin
Attn: Mr. R. Roup

Aerovox Corp.
New Bedford, Mass.
Attn: Mr. H. Pickett

Sprague Electric Co.
Attn: Mr. J. Fabricius

Radio Materials Corp.
3325 N. California Ave.
Chicago 18, Ill.

Erie Technical Ceramics
State College, Pa.
Attn: Mr. L. Koppell

Linden Labs. (2 copies)
Boalsburg, Pa.
Attn: Mr. P. Marshall, Jr.

Gulton Industries, Inc.
212 Durham Ave.
Metuchen, New Jersey
Attn: Mr. G. Howatt

Astron Corporation
255 Grant Ave.
E. Newark, N. J.
Attn: Mr. R. Black

Gudeman Company
340 Huron St.
Chicago 10, Ill.
Attn: Mr. L. Grimm

Good-All Electric Mfg. Co.
112 W. First St.
Olgallala, Nebraska
Attn: Mr. L. Kolste

John E. Fast Co.
3580 Elston Ave.
Chicago 41, Ill.
Attn: Mr. Wm. Franklin

General Electric Co.
Hudson Falls, New York

Titanium Alloy Mfg. Co.
111 Broadway
New York 6, N. Y.
Attn: Mr. D. Wheeler

Titanium Alloy Mfg. Co.
Niagara Falls, New York
Attn: Dr. S. Urban

B. F. Drakenfeld Co.
Washington, Pa.

Saxonburg Ceramics Co.
Saxonburg, Pa.
Attn: Mr. Pabst

Scintilla Div.
Bendix Aviation Corp.
Sidney, New York
Attn: Mr. T. Tognola
Ceramics For Industry
Cottage Place
Mineola, L. I., New York
Attn: Mr. R. Duran

Mr. A. Gunzenhauser
69 - 113th St.
Forest Hills 75, L. I., New York

General Electric Company
Research Labs., The Knolls
Schenectady, New York
Attn: Dr. A. J. Pincus

U. S. Stoneware Company
Akron 9, Ohio
Attn: Mr. H. Frahme

American Lava Corp.
Chattanooga, Tennessee
Attn: Mr. M. Mayfield

Stupakoff Div. Carborundum Corp.
Latrobe, Pa.

Coors Porcelain Co.
Golden, Colorado
Attn: Mr. L. Ferreira

Minnesota Mining & Mfg. Co.
Central Research Labs.
2301 Hudson Road
St. Paul 19, Minn.
Attn: Mr. H. Thurnauer

Gladding, McBean & Co.
2901 Los Feliz Blvd.
Los Angeles 39, California

Western Gold & Platinum Co.
525 Harbor Blvd.
Belmont, California
Attn: Mr. W. Hack

Sandia Corporation
Albuquerque, New Mexico
Attn: Dr. T. Kinsley

Dupont Company
Inorganic Chemicals Division
Wilmington, Delaware

Rutgers University
School of Ceramics
New Brunswick, New Jersey
Attn: Dr. J. Koenig

Mr. A. Cunha
Metuchen, New Jersey

Naval Research Labs., Anacostia
Washington, D. C.
Attn: J. Murray

Commander
Wright-Patterson Air Force Base,
Ohio
Attn: Mr. L. Conlon, ASRCTC,

Western Electric Company
North Andover, Mass.
Attn: Mr. R. Campaigne

Alfred University
School of Ceramics
Alfred, New York

University of Illinois
School of Ceramics
Urbana, Ill.

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Mass.
Attn: Mr. Wm. Westphal

Raytheon Mfg. Co.
Chapel St.
Newton, Mass.
Attn: Mr. F. Fallon

Temperature-Pressure Lab.
State College, Pa.
Attn: Dr. R. Roy

American Cyanamid & Chemical Corp.
Rockefeller Center
New York, N. Y.