SECOND QUARTERLY REPORT

Ending

October 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

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CORNELL-DUBILIER
ELECTRIC CORPORATION

CERAMIC DIVISION · NEW BEDFORD, MASSACHUSETTS

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By

CORNELL-DUBILIER ELECTRIC CORP.

Ceramic Division

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Project Engineer

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1. ABSTRACT

1.1 The improvement of titanate dielectrics by high temperature fluorination presents a problem in composition and treatment involving narrow working limits. For many compositions the fluorination treatment is critical and one can easily over or under fluorinate.

1.2 Capacitor discs of high K composition were fluorinated by pushing setters containing the discs through a tunnel kiln treated with a single charge of volatile fluorides. This resulted in a complete range of fluorination treatment during the run.

1.3 Continuous fluorination runs were made by placing a smaller amount of volatile fluorides on each setter during the run. This resulted in a continuous output of discs having the improved properties attributed to fluorination.

1.4 Insulation resistance measurements of the well fluorinated discs at elevated temperatures showed a marked improvement over those which were not fluorinated. It was seen to occur that optimum fluorination results in a chrome yellow color in the dielectric, while over fluorination gives a bluish color.

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 INTRODUCTION

The program covering this report consisted of a series of experimental fluorination firings in a small tunnel kiln constructed for this purpose. The preparation of the volatile fluorides and compositions treated are discussed. The problems encountered and suggested methods of solution are also mentioned.

3.2 FLUORINATION PROCEDURES

3.2.1 The kiln used had a hot zone length of 20 inches, width of 3 inches, and a height of 1 1/8 inches. The setters were cut from $2800^{\circ}F$ insulating brick and covered with ZrO_2 grain. These setters measure 5" x 2 1/2" x 1/2". The setters contain the discs to be fluorinated and are pushed through the kiln by means of a mechanical pusher. The fluoride charge is introduced by placing prepared donor tablets on one or more of the setters being pushed through the kiln.

3.3. RAW MATERIALS AND SAMPLE PREPARATION

3.3.1 The $BaTiO_3$ used was Lot 21 obtained from the Titanium Alloy Division of the National Lead Co. and was compounded from West German $BaCO_3$.

3.3.2 Laboratory samples were prepared by wet milling the compositions, drying, granulating, pressing and firing in an electrically heated tunnel kiln to $2450^{\circ}F$, a procedure familiar to all engaged in ceramic capacitor manufacture.

3.3.3 The donor tablets of volatile fluorides were prepared by reacting $BaTiO_3$ with 52% aqueous HF and water in a plastic container in the following amounts: 100 gms $BaTiO_3$ and 50cc H_2O and 25cc 52% HF. The slurry was decanted several times and the powder dried. Donor tablets were then pressed from this powder and used to provide the fluoride atmosphere.

3.3.4 The high K capacitor discs fluorinated were manufactured by Cornell-Dubilier and were fully fired before fluorination. The dielectric constants of the two high K capacitor compositions used are approximately 6,000 (Composition AA) and 7,000 (Composition CC).

3.3.5 Electrical measurements were made on discs coated with DuPont silver paste #6370, fired to 1400°F, as electrodes. Silvered spring contacts were employed to hold the disc during measurements. Insulation resistance measurements were made with a model L-7 Industrial Instruments Megohmmeter at a test voltage of 100 VDC. Capacitance and power factor measurements were made with a model 716C General Radio Capacitance Bridge at a frequency of 1 KC.

3.4 DISCUSSION AND RESULTS

3.4.1 Initial Fluorination Runs

3.4.1.1 Initial runs through the fluorination kiln were made with high K capacitor discs from compositions AA and CC. The kiln temperature was controlled at 2300°F and soaking time was 30 minutes. When the fluoride charge entered the hot zone, rapid volatilization of the donor tablets was visible to the eye. The fluoride vapors showed no swirling movement after initial volatilization and could be seen to settle down at the bottom of the hot zone. These vapors, being heavier than air, cause a vertical gradient to exist which would prevent uniform fluorination treatment in high roofed kilns or settings.

3.4.1.2 The capacitor discs treated during these runs reflected, by color, the problems encountered. The first discs to emerge from the kiln, ahead of the charging setter, were of a normal dark tan color showing little fluoride benefit. On setters No. 3 and 5, before and after the charging setter, the discs were bluish in color and were obviously over fluorinated. AA discs on setters No. 7 and 8 were yellow and optimumly fluorinated while CC discs on setters No. 9 and 10 were at their best. Earlier setters in both cases were over fluorinated, while later ones were definitely under fluorinated.

3.4.1.3 This shift in optimum fluorination position from setters No. 7 and 8 for AA discs to Nos. 9 and 10 for CC discs clearly shows the effect of composition in determining the required fluoride level within the kiln. Composition CC required a lower fluoride level to become optimumly treated.

3.4.1.4 During the run the setters that emerged from the kiln were reloaded with capacitor discs and re-cycled through the kiln. It was observed that the setter plates which were adjacent to the charging setter became heavily loaded with fluorides and upon re-cycling through the kiln released some of the fluoride and in effect acted as a second donor tablet. It becomes obvious that the setters and kiln furniture must be maintained at a constant or uniform fluoride level during its use. The additions of fluoride must be regular and uniform towards creating a constant fluoride level within the kiln.

3.5 CONTINUOUS FLUORINATION

3.5.1 Continuous fluorination runs were performed by including a small amount of donor tablets on each setter along with the discs to be fluorinated. Kiln temperature was maintained at 2300°F and pusher speed was set to allow 30 minutes fluorination time for each setter. The continuous run was successful in that a uniform yellow color was maintained in the AA discs. The CC discs were blue-yellow in color and indicated over fluorination. This difference can only be attributed to their difference in composition. There was no color difference in this run indicating that a constant fluoride level was maintained within the kiln by the continuous addition of donor tablets on each setter.

3.5.2 Curves of dielectric constant vs. temperature and volume resistivity for fluorinated and non-fluorinated capacitor discs show the improved quality at elevated temperatures. It should be noted that resistivity curves for CC discs labeled blue represent an over fluorinated condition. The resistivity curves of AA discs from the continuous fluorination run show considerable variation throughout the run; however, all values shown can be considered excellent. Electrical measurements of CC discs from this run were of no value because of this over fluorinated condition. When optimumly fluorinated, each composition shows exceptionally high volume resistivity values at elevated temperatures. A period of extended life testing is necessary to determine if one composition is superior to the other when both are optimumly fluorinated.

3.6 BINARY SERIES

3.6.1 A series of compositions was fluorinated simultaneously to further study the variation in fluoride susceptibility to composition. The majority of compositions involved binary types with $BaTiO_3$ and are shown in Table I. Each setter contained all compositions to be treated. A single large charge of donor tablets was introduced into the kiln and the setters were cycled through. This technique should cause over fluorination of the first setter and under fluorination of the last. It then follows that each composition should receive near optimum fluorination at some point in between these extremes.

3.6.2 The results show strong variations in fluoride susceptibility with composition. The higher the $BaTiO_3$ content, the less fluoride that was required for fluorination. The binary of $BaTiO_3$-$CaZrO_3$ had the longest range of susceptibility of those investigated while the binary with $SrTiO_3$ showed a tendency toward reduction. The binary of $BaTiO_3$ and $CaZrO_3$, showing promise, was further explored with additives of Fe_2O_3, $MgZrO_3$ and Ce_2O_3. These additives changed the fluoride requirements of the composition. The addition of Fe_2O_3 was especially effective in producing a deep yellow color within the disc. No electrical data is available for this series within this report period.

3.7 FLUORIDE CONTROL

3.7.1 It is believed that compositions can be formulated having overlapping fluorination requirements by adjusting the amount of additives. These over-lapping type compositions would then reflect changes, by color, in the fluoride level in the kiln within narrow limits. It can be seen that such compositions could serve as control discs during a prolonged run. To date this offers a possible means of monitoring fluoride concentration within a kiln during a production run.

4. CONCLUSION

4.1 Attempts at fluorinating ceramic capacitor discs have been successful and also were performed in a continuous manner within a tunnel kiln. Insulation resistance values of these fluorinated discs were much higher than those not fluorinated. This improvement is especially noted at elevated temperatures. It was further noted that dielectric composition plays a major role in determining required fluoride level within a kiln. It is expected that a high degree of control can be maintained by observing color changes in control discs whose compositions are such that the required fluoride levels bracket that of the work to be fluorinated.

5. PROGRAM FOR NEXT QUARTER

5.1 The development of an optimum fluorinated composition with respect to life testing at elevated temperatures is the most important consideration. It is not believed that all compositions can be sufficiently improved to withstand the required life testing at 200°F and therefore more knowledge of this phase is required. The next consideration will be to develop a means of accurately monitoring and maintaining a controlled fluoride level within a tunnel kiln during extended runs. This control is necessary to optimumly fluorinate any given composition during a pilot run. Assembly and encapsulating materials and techniques are being investigated and will be discussed in the next report.

6. IDENTIFICATION OF PERSONNEL

ROBERT L. GROVE 48 hrs.

Chief Engineer, Ceramic Division

LAWRENCE E. NORDQUIST 360 hrs.

Project Engineer

JAMES SOUZA 520 hrs.

Electric Engineer

PAUL C. RICARD 352 hrs.

Chemist

Born March 2, 1931

Development, experimental compounding, Ceramic Division, Cornell-Dubilier Electric Corporation, August, 1961 to date

Abroad, 1960 to August 1961

Chemical Engineering Research and Development, Cooper Rubber Co., Findlay, Ohio, 1958 to 1960.

Chemical Engineering Research and Development, Firestone Rubber Co., Akron, Ohio, 1956 to 1958

N. C. State College Graduate School, 1955 to 1956

U. S. Navy, LTJG, Communications, 1953-1955

New Bedford Institute of Technology, 1953, B. S. Chemistry

I. S. LASSOW Clerk-Typist 21 hours

CLAIRE MEDEIROS Clerk 6-1/4 hrs.

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 address of Mr. Cunha, listed as Metuchen, New Jersey on such list, is to be changed to read as follows:

Mr. R. Cunha
Bonn Associates
Metuchen, N. J.

7.1.2 The name of Sandia Corporation is to be deleted from this list because the report previously forwarded to the address listed as Albuquerque, New Mexico, Attn. Dr. T. Kinsley, was returned marked "No Record at Sandia Corporation".

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

Nicholas Zingarelli
c/o Gorham Mfg. Co.
333 Adelaide Ave.
Providence, R. I.

Mr. E. Smoke
Rutgers University
New Brunswick, N. J.

Mr. J. McHugh
Cornell-Dubilier Electric Corp.
55 Cromwell Street
Providence 7, Rhode Island

Mr. H. Pickett.
Aerovox Corporation
New Bedford,
Massachusetts

TABLE I

COMPOSITIONS INVESTIGATED - WEIGHT PERCENT

	$BaTiO_3$	$CaTiO_3$	$CaZrO_3$	$SrTiO_3$	Fe_2O_3	$MgZrO_3$	Ce_2O_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

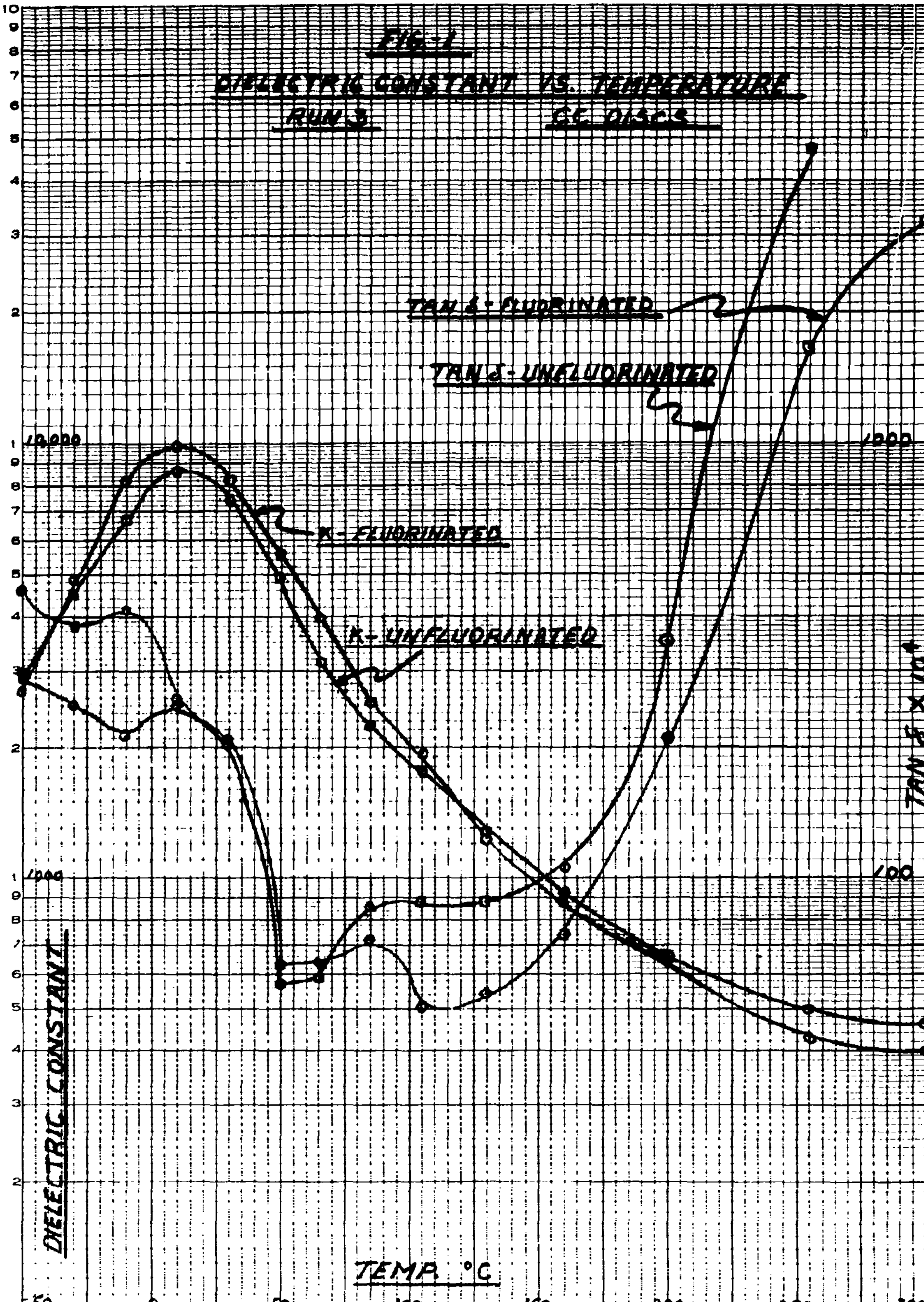
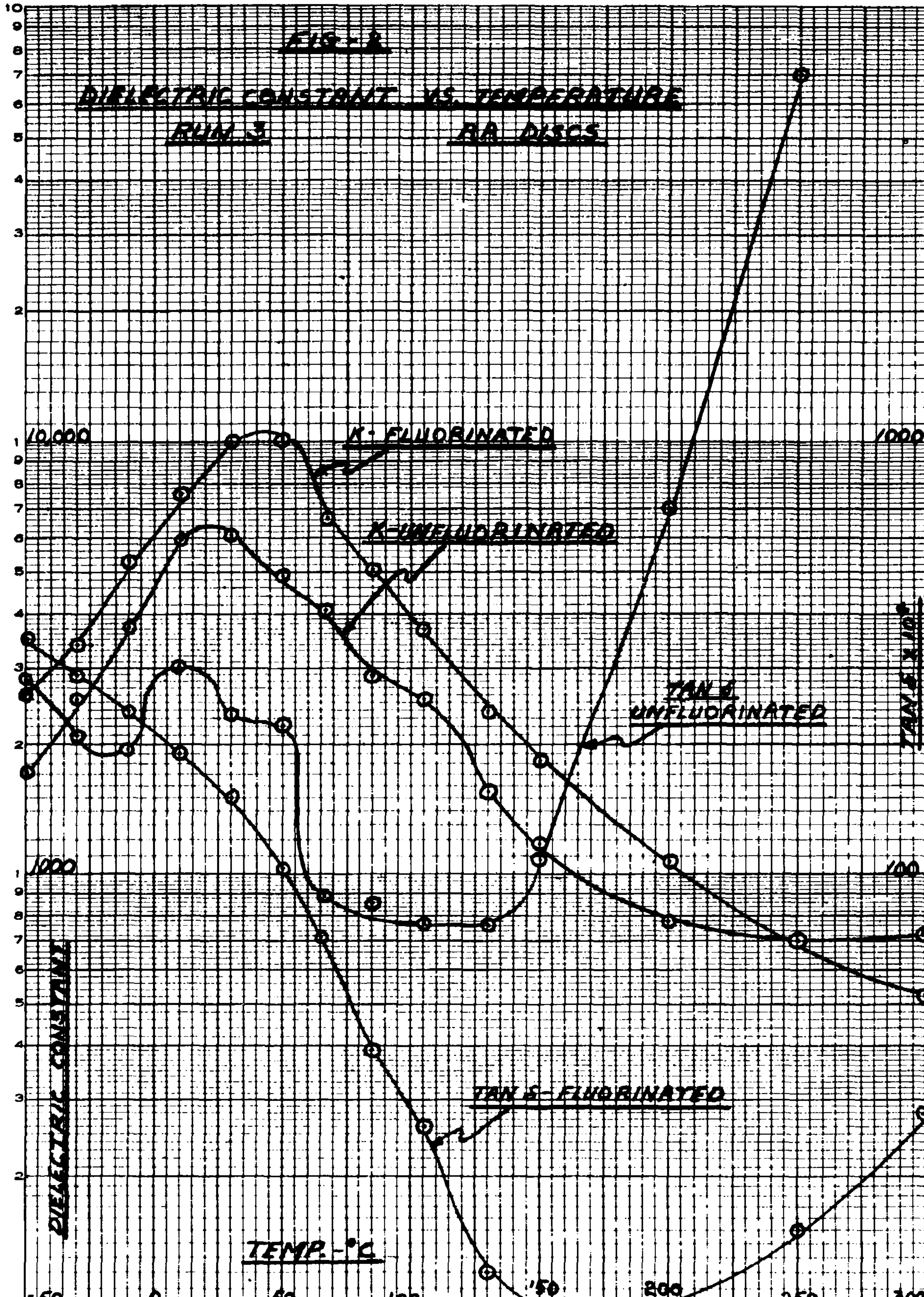


FIG. 1
DIELECTRIC CONSTANT VS. TEMPERATURE
RUN 3
C.C. DISCS
TAN δ - FLUORINATED
TAN δ - UNFLUORINATED
K - FLUORINATED
K - UNFLUORINATED
10,000
1000
1000
100
DIELECTRIC CONSTANT
TAN δ × 10⁴
TEMP. °C
-50
0
50
100
150
200
250
300


DIELECTRIC CONSTANT VS. TEMPERATURE
RUN 3
RA DISCS
K- FLUORINATED
K-UNFLUORINATED
TAN δ
UNFLUORINATED
TAN δ- FLUORINATED
TAN δ X 10⁴
DIELECTRIC CONSTANT
TEMP. - °C
10,000
1000
1000
100
-50
0
50
100
150
200
250
300

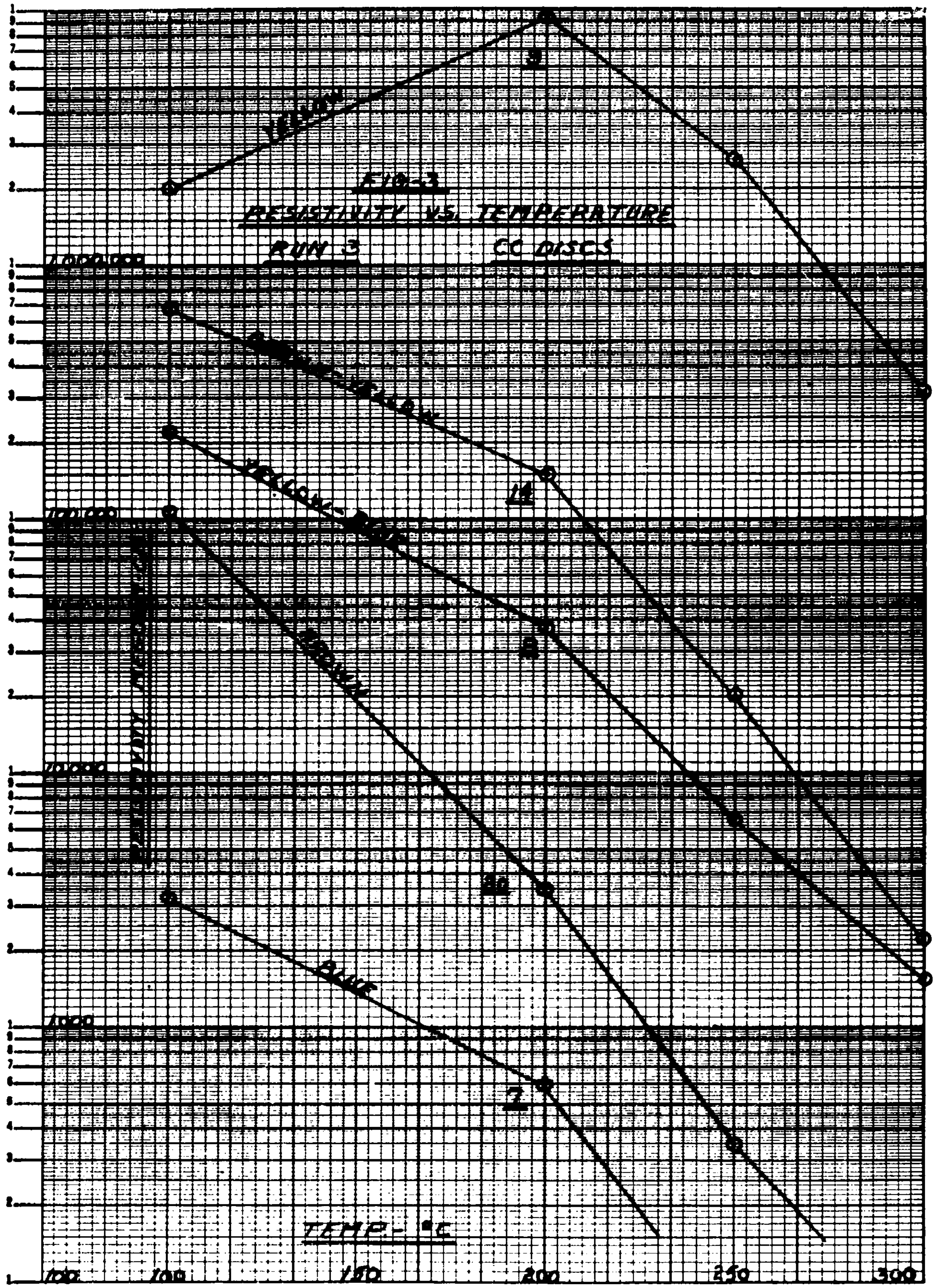
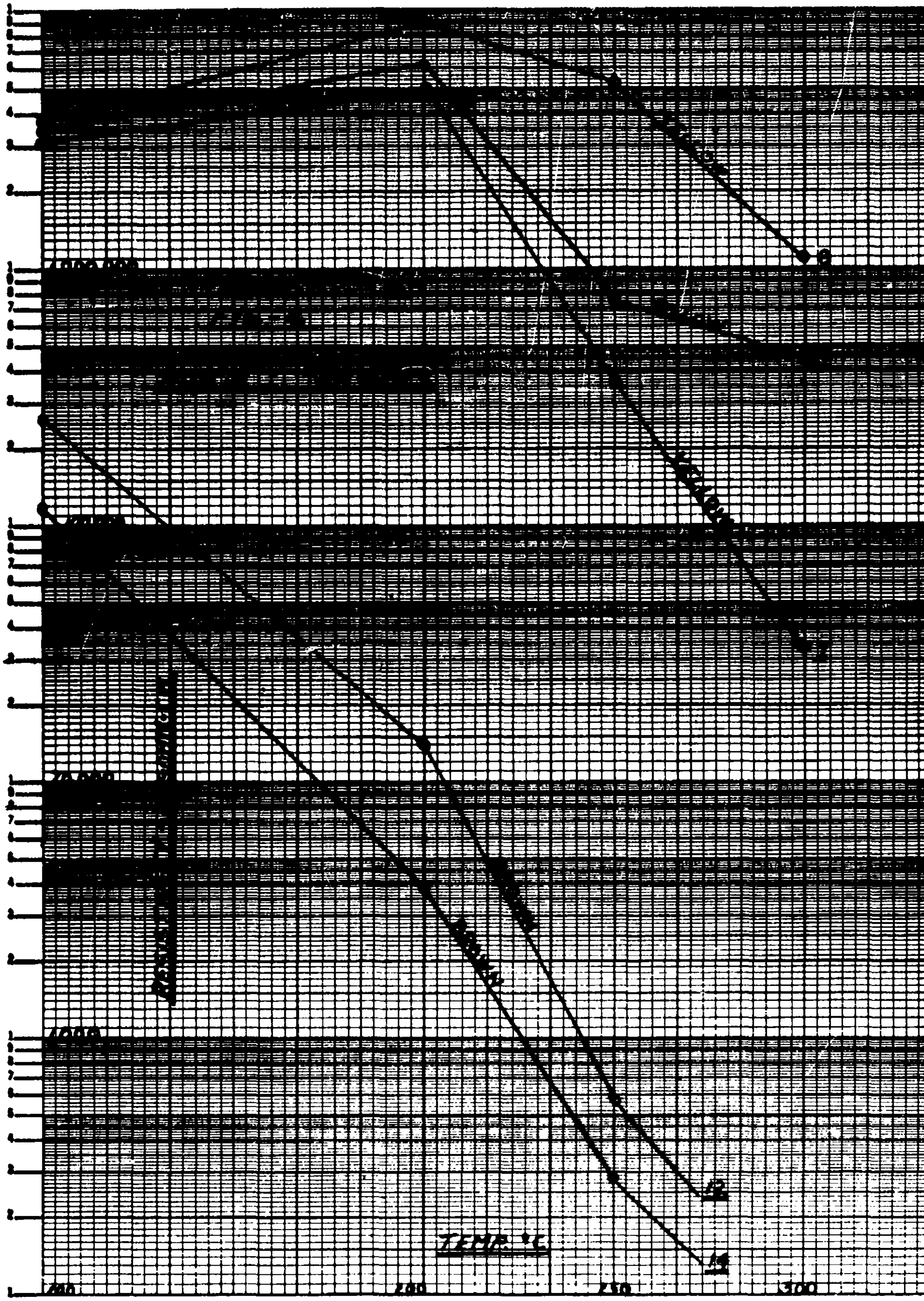
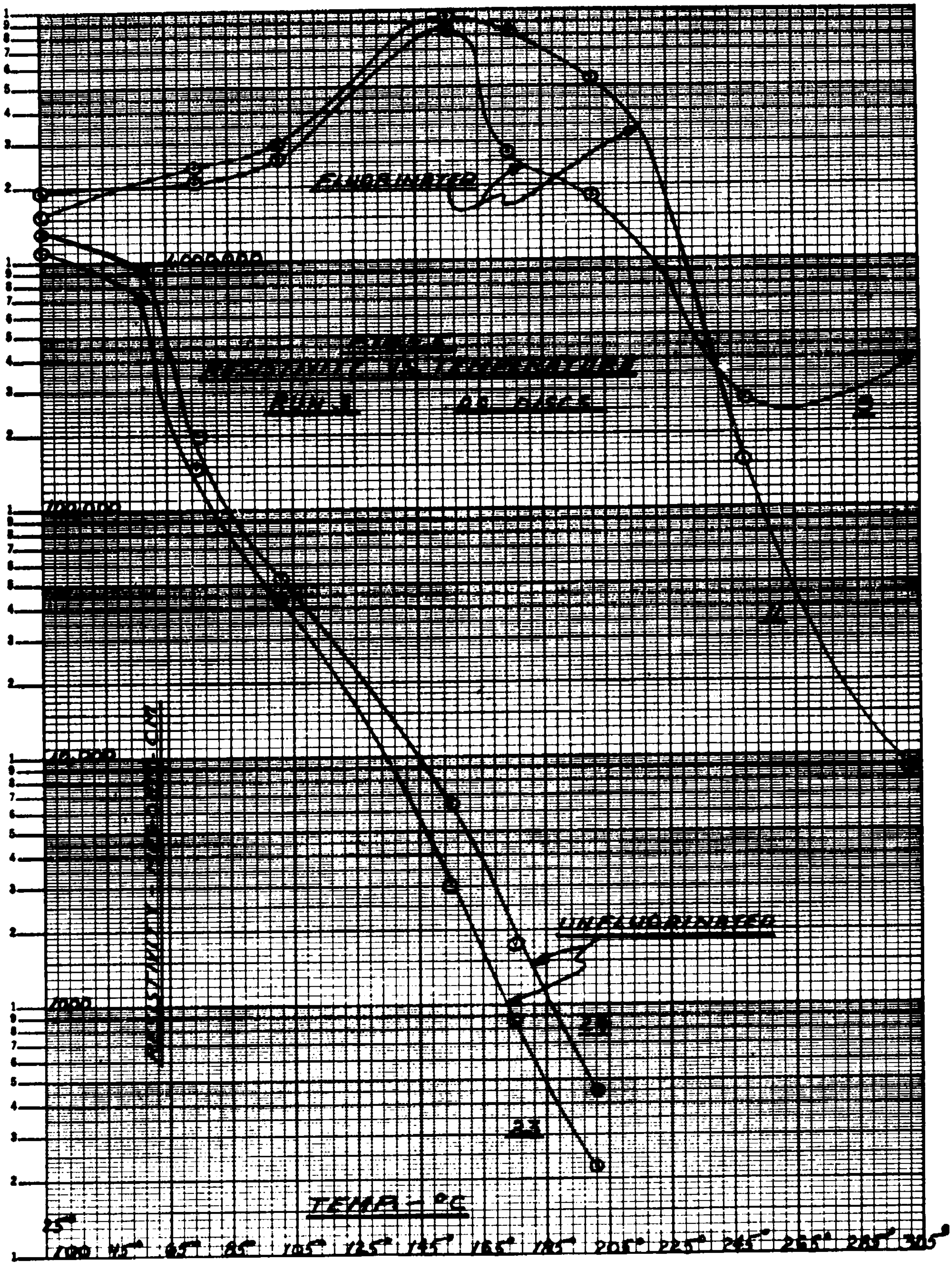
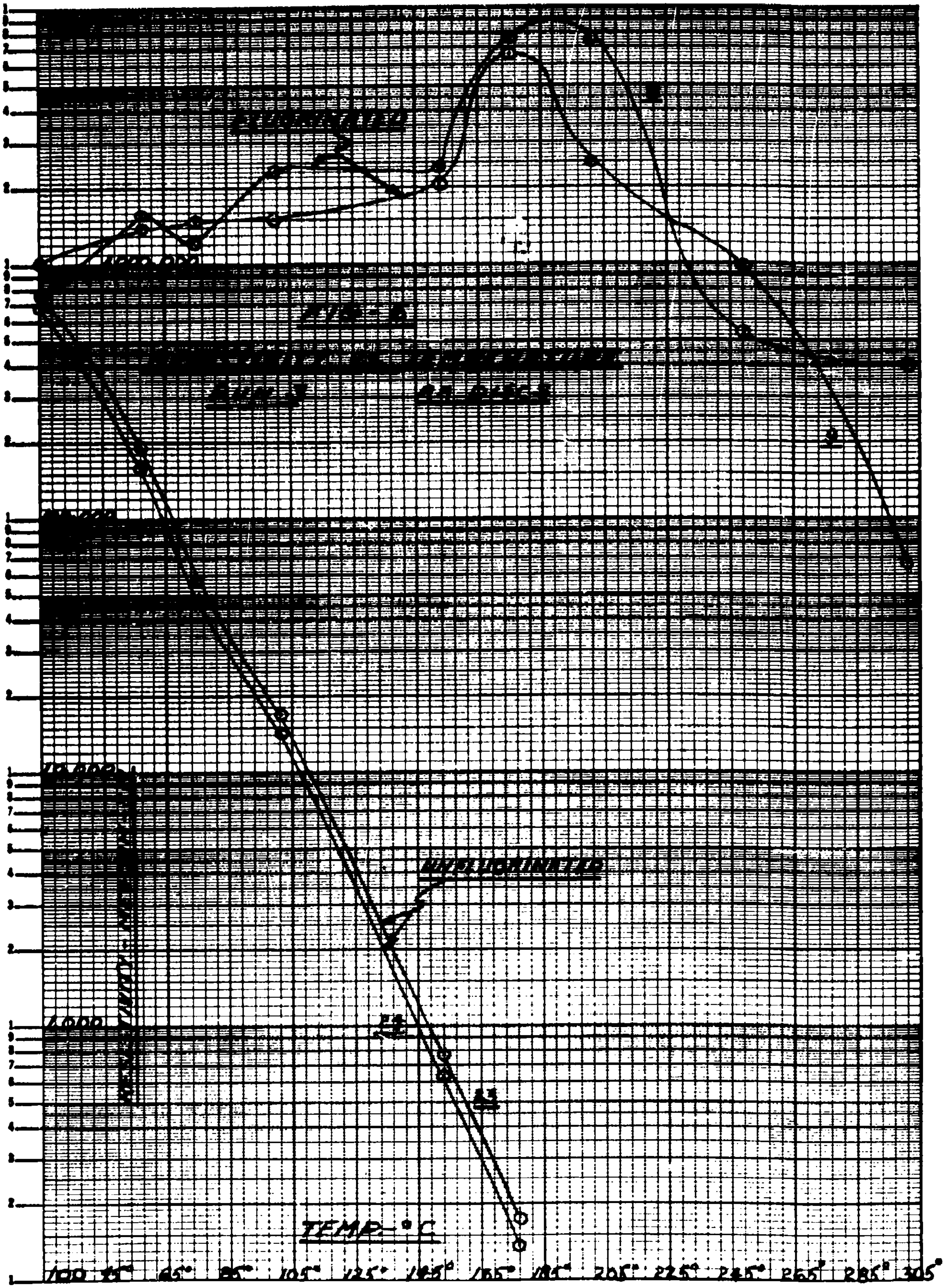


FIG-3
RESISTIVITY VS. TEMPERATURE
RUN 3
CC DISCS
YELLOW
BROWN-YELLOW
YELLOW-BLUE
BROWN
BLUE
1000000
100000
10000
1000
TEMP - °C
100
150
200
250
300



1,000,000
10,000
10,000
1000
TEMP. °C
200
250
300


FLUORINATED
1,000,000
100,000
10,000
1000
UNFLUORINATED
TEMP - °C
25°
100 45° 65° 85° 105° 125° 145° 165° 185° 205° 225° 245° 265° 285° 305°



TEMP - °C
1,000
125°
145°
165°
185°
205°
225°
245°
265°
285°
305°

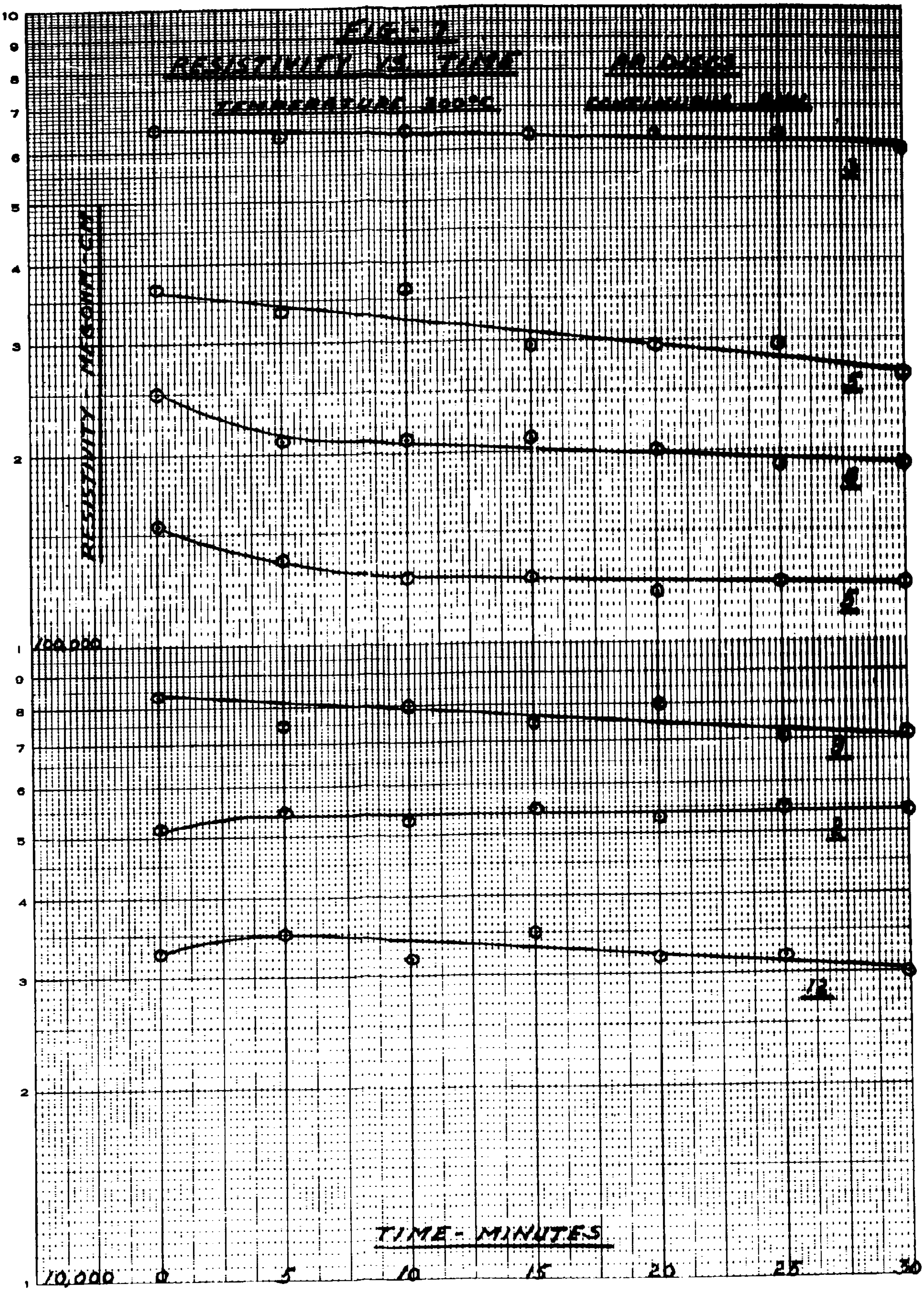


FIG. 2
RESISTIVITY VS. TIME
RESISTIVITY
100,000
10,000
TIME - MINUTES
0
5
10
15
20
25
30