RESEARCH ON BINDER TECHNIQUES FOR HIGH TEMPERATURE RADOME STRUCTURES

Contract No. AF 33(616-8176)
Project No. 1-(670-4161)
Task No. 42039

Interim Engineering Report No. 2

July 18, 1961
October 17, 1961

Project Leader: Henry T. Plant

Associates: P. P. Keenan
W. H. Marks

Project Manager: T. J. Jordan

Report Submitted by: Insulating Materials Dept.
General Electric Company
Schenectady, New York

GENERAL ELECTRIC COMPANY
MANUFACTURING ENGINEERING SERVICE
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ABSTRACT

This interim report contains extensive microwave electrical data on high temperature (1000 F) radome materials, specifically General Electric proprietary mica laminate XS-1342 and silica fiber-reinforced aluminum phosphate. Preliminary data has been gathered about silica fiber-reinforced aluminum phosphate laminates containing glass microspheres. Dielectric characteristics of the materials were measured as a function of temperature (room temperature to 1100 F) at atmospheric pressure and at 650 F in pressure environment simulating 120,000 feet attitude before and after aging for 100 hours. Both materials have dielectric characteristics suitable for 1000 F radome applications. Several materials were water-soaked and tested in vacuum atmospheres. In general, dielectric response of these samples showed a high loss tangent; however, after heating, dielectric characteristics approached that of the sample before soaking.

Use of inorganic glass microspheres as filler for aluminum phosphate binders results in lower processing viscosity, and the microsphere filler allows about half the water to be removed from the formulations without causing high viscosity or premature gelling. No improvement in electrical characteristics was noted; however, one formulation (3GMB3.3-20 H_2O) presented greater laminate flexural strength.

Long-term aging problems exist in the silica fiber-aluminum phosphate laminate system. The laminates lose as much as one-half of their 1000 F flexural strength after exposure for 100 hours at 1000 F. Even more drastic loss in strength occurs between initial room temperature strength and room temperature strength after exposure to elevated temperatures. Loss in strength is probably due to chemical changes in the

phosphate bond and degradation of the silica and asbestos fibers. Although strength of these laminates does not attain the maximum physical strength desired, this inorganic system has good electrical characteristics and its 1000 F physical properties surpass known plastic and semi-organic systems. The mica laminate (XS-1342) does not exhibit this loss at 800 F and therefore appears to be a candidate both physically and electrically for radome material.

SUMMARY OF RECOMMENDATIONS

Further electrical testing should be discontinued. Efforts should be directed toward improving flexural strength of silica fiber-aluminum phosphate systems. General Electric XS-1342 mica laminate is ready to be used as 800 - 1000 F radome material. Radome shapes of both materials should be constructed and tested.

Continued substitution of microspheres, short-fibered small diameter mineral fibers, and removal of water from binder formulations should be made. If significant increase in strength is observed, an aging and electrical test program should be conducted. Studies should be initiated for obtaining flexural strength to greatest extent possible with present binder systems.

TABLE OF CONTENTS

TABLES

FIGURES

ENVIRONMENTAL DATA

DIELECTRIC DATA FOR MICA LAMINATE

DIELECTRIC DATA FOR ALUMINUM PHOSPHATE LAMINATES REINFORCED WITH SILICA FIBERS

DIELECTRIC DATA FOR WATER-SOAKED MICA LAMINATE

FIGURES

DIELECTRIC DATA FOR WATER-SOAKED ALUMINUM PHOSPHATE LAMINATES REINFORCED WITH SILICA FIBERS

SECOND INTERIM ENGINEERING REPORT ON THE DEVELOPMENT OF CERAMIC LAMINATES

ELECTRICAL TESTING

During the course of an investigation performed for the Department of the Navy, Bureau of Weapons,[1] two inorganic laminates, which could be processed by relatively simple means, were found by this laboratory to be possible high temperature (1000 F) radome materials. One was a General Electric proprietary mica laminate, now designated as XS-1342, that was a development of the Insulating Materials Department of the General Electric Company; the other laminate system, which was derived from silica fiber-reinforced aluminum phosphate, was developed directly on the contract. While both these new materials and the processes to produce them resulted in laminated structures that appeared to be suitable for radome construction, there was insufficient data on the electrical properties to verify whether or not these materials were truly radome materials. Consequently, the major share of the effort of the present program has been directed toward obtaining extensive microwave data from these two materials.

In our first interim engineering report very little data had been accumulated since most of the time was used to modify and repair the equipment and prepare samples for testing. As a result, this second interim engineering report is primarily directed to presenting the extensive microwave electrical data that has now been accumulated on these samples. Substantially complete data is now available on the XS-1343 mica laminate and three formulations of silica fiber-reinforced aluminum phosphate laminates. Also, preliminary data has been gathered about the silica fiber-reinforced aluminum phosphate laminates containing glass microspheres in aluminum phosphate binder. The addition of hollow glass microspheres (30 to 300 microns diameter) was an attempt to lower the dielectric constant by the inclusion of more voids in the binder. We also believed this approach might increase laminate strength. This is explained in a following section of the report.

1 - Development of Inorganic Binder NOas 58-850c
8 Quarterly Reports and a Final Report

Table I - Dielectric Tests at Atmospheric Pressure

Material	75°F		600°F		1100°F	
	ϵ'	tan δ	ϵ'	tan δ	ϵ'	tan δ
Mica Laminate No. XS-1342 (not aged) E field parallel to mica lamination	4.7	.0034	4.9	.0058	5.0	.0083
Mica Laminate No. XS-1342 (aged) E field parallel to mica lamination	4.5	.0061	4.6	.0060	4.7	.0058
Mica Lamirnate No. XS-1342 (aged) E field perpendicular to mica lamination	3.1	.0046	3.2	.0036	3.0	.0030
Alum.-Phos.-Silica No. 33Y3 (not aged)	3.25	.0095	3.20	.0015	3.20	.0033
Alum.-Phos-Silica No. 33Y3 (aged)	3.3	.0073	3.3	.003	3.2	.0058
Alum.-Phos.-Silica No. 33Y3 (aged 100 hrs. at 1000°F)	3.3	.0050	3.2	.0027	3.1	.0017
Alum.-Phos.-Silica Form. 3 (not aged)	3.3	.019	3.4	.094*	3.0	.042
Alum.-Phos.-Silica Form. 3 (aged 100 hrs at 1000°F)	2.9	.011	2.9	.013	2.8	.017
Alum.-Phos.-Silica Form. 3-6 Group 7 (not aged)	2.95	.015	2.9	.017	2.65	.010
Alum.-Phos.-Silica Form. 3-6 Group 8 (not aged)	3.0	.011	2.95	.013	2.70	.0079
Alum.-Phos.-Silica Form. 3-6 (aged)	2.8	.0063	2.7	.0061	2.5	.0020
Alum.-Phos.-Silica Form 3GMB (not aged)	2.8	.008	2.8	.016	2.5	.016

*peak of loss

The dielectric constant and loss tangent measurements at 9150 megacycles were obtained for the following conditions:

1. Room temperature to 1100 F.

2. Room temperature to 1100 F after aging 100-hours at 1000 F.

3. Water pick-up and its effect.

4. Time to remove water under simulated "flight conditions".

It appears that we are in an excellent position in regard to the electrical properties of these materials. Both the mica laminate and the silica fiber-reinforced aluminum phosphate laminates meet all the loss tangent target goals. The silica fiber-reinforced aluminum phosphate also meets the required goals as to dielectric constant while the mica laminate has a slightly greater dielectric constant than desired. However, we believe that this greater dielectric constant may be only a small handicap, and it can be compensated for in the radome design. Both laminate systems appear to be stable electrically from room temperature to 1100 F before and after aging for 100-hours at 1000 F. After aging, there is but a slight change and this is for the better. A note of explanation: The graphs depicting both dielectric constant and loss tangent properties might lead one to believe that there are wild gyrations in these values - especially in the case of the loss tangent values- but this is not so. These apparently large changes are due only to the graph scale size. The loss tangent values never exceed those limits set for this project. In most cases the laminates are in the 95% plus transmission range.

Since both laminate materials are porous, it can be expected that they will absorb water after soaking for 24-hours. It is also natural for the water-soaked materials to have higher dielectric constants and higher loss tangent values. It was, therefore, important to determine if this condition was critical and to establish the time required to remove the water under "flight conditions". We also wished to determine whether or not the water soaking had any permanent effect on the electrical properties of the laminates.

Table II - The Effects of Water Absorption

Material	Initial Conditions			Conditions After Soaking			Conditions After Heating		
	ϵ	tan δ	wt (g)	ϵ'	tan δ	wt (g)	ϵ'	tan δ	wt (g)
Mica Laminate No. XS-1342 (aged)*	3.2	.0047	8.6	6.1	.053	9.0	3.0	.001	8.2
Al-Ph-Sil Form 33Y3 (aged)	3.3	.0073	7.9	8.0	.202	9.0	2.9	.0061	7.3
Al-Ph-Sil Form 3 (not aged)	3.3	.019	6.9	8.6	.16	7.9	2.7	.019	6.5
Al-Ph-Sil Form 3 (aged)	2.9	.010	6.6	7.3	.19	8.0	2.7	.011	6.5
Al-Ph-Sil Form 3-6 (not aged)	3.0	.012	6.7	7.7	.16	-	2.2	.004	6.0
Al-Ph-Sil Form 3-6 (aged)	2.9	.0064	7.3	7.3	.26	8.0	2.5	.001	6.5
Al-Ph-Sil Form 3 GMB (not aged)	2.8	.0075	6.7	7.5	.29	8.0	2.5	.001	6.4

*Electric Field perpendicular to plane of mica laminations

In regard to testing conditions, we attempted to simulate flight conditions at 650 F from 45,000 to 70,000 ft. altitude. Unfortunately, we could not effectively control the low pressure. Consequently, we simply placed the laminate sample in the cold waveguide, which was then placed in the 650 F oven. The vacuum pump was then allowed to take its course. As a result, our ultimate pressures are lower than those encountered in flight. The actual pressures would perhaps correspond to 120,000 ft. elevation. We doubt, however, that a few millimeters pressure differential will make any significant change in drying time.

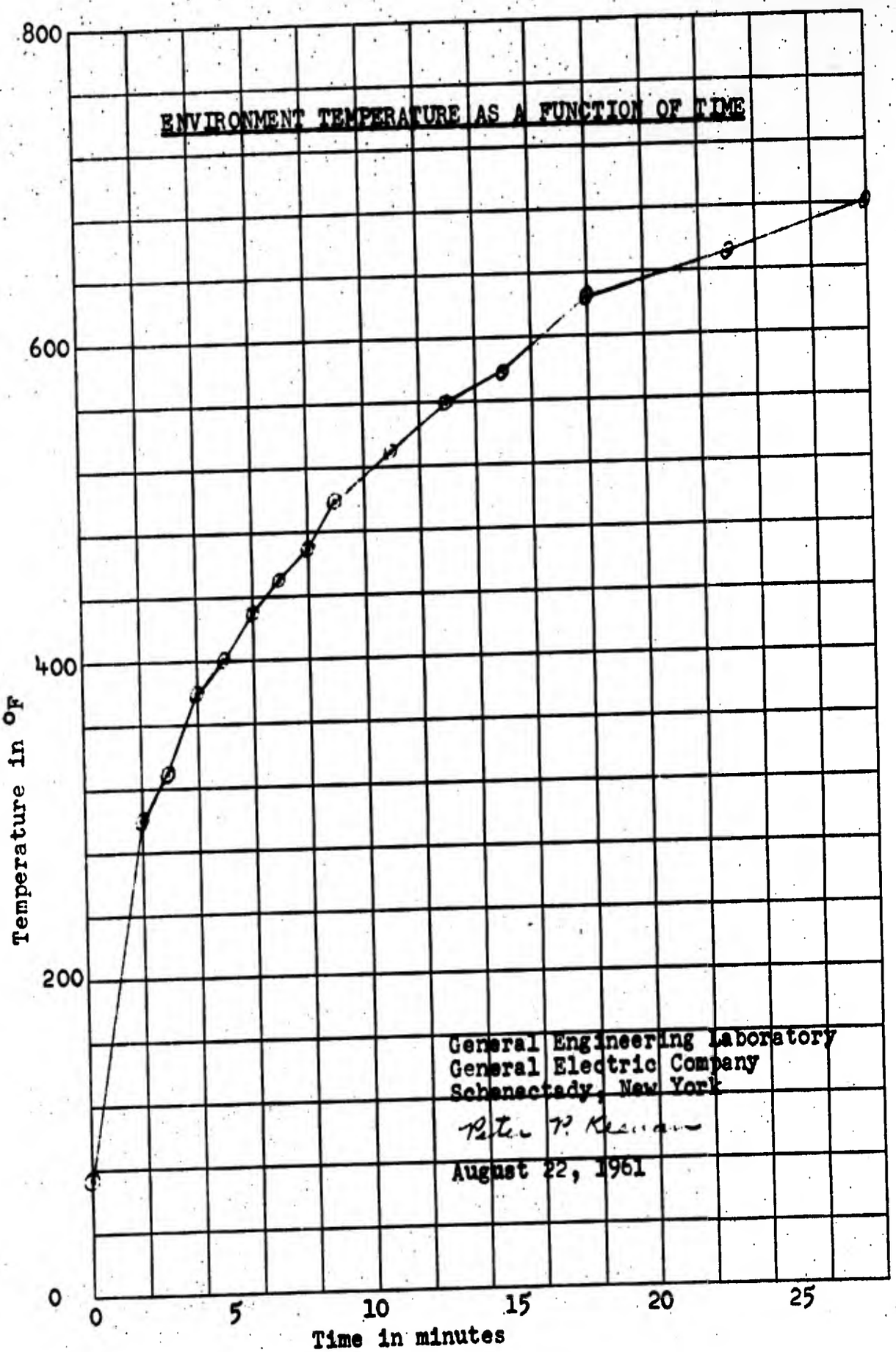
To sum up the results of the water soaked laminate experiments, the soak of 24-hours at room temperature seriously impairs microwave transmission as we anticipated, but both types of laminate recover their excellent initial dielectric properties in less than 15-minutes under the "flight conditions" of 650 F and 120,000 ft. altitude. Furthermore, there are no apparent permanent detrimental losses in dielectric properties; characteristics actually improve.

The data in Table II Page 2a shows that the laminate samples lose weight after drying to a point where they weight less than before they were soaked in water. This does not necessarily mean that something has been leached out of the system. It may simply be a matter of losing original water content, or it may be the result of normal physical attrition by abrasion, etc., due to placing and removing the sample in the waveguide.

The water pick-up problem indicates that some means of coating or impregnating the laminates should be developed, or some means must be used to keep these materials warm and dry during the course of their use in a radome structure.

The following is a report inserted in toto as it was received from our Microwave Laboratory.

Figure 1


ENVIRONMENT TEMPERATURE AS A FUNCTION OF TIME
800
600
400
200
0
Temperature in °F
0
5
10
15
20
25
Time in minutes
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter T. Keenan
August 22, 1961

MICROWAVE LABORATORY REPORT

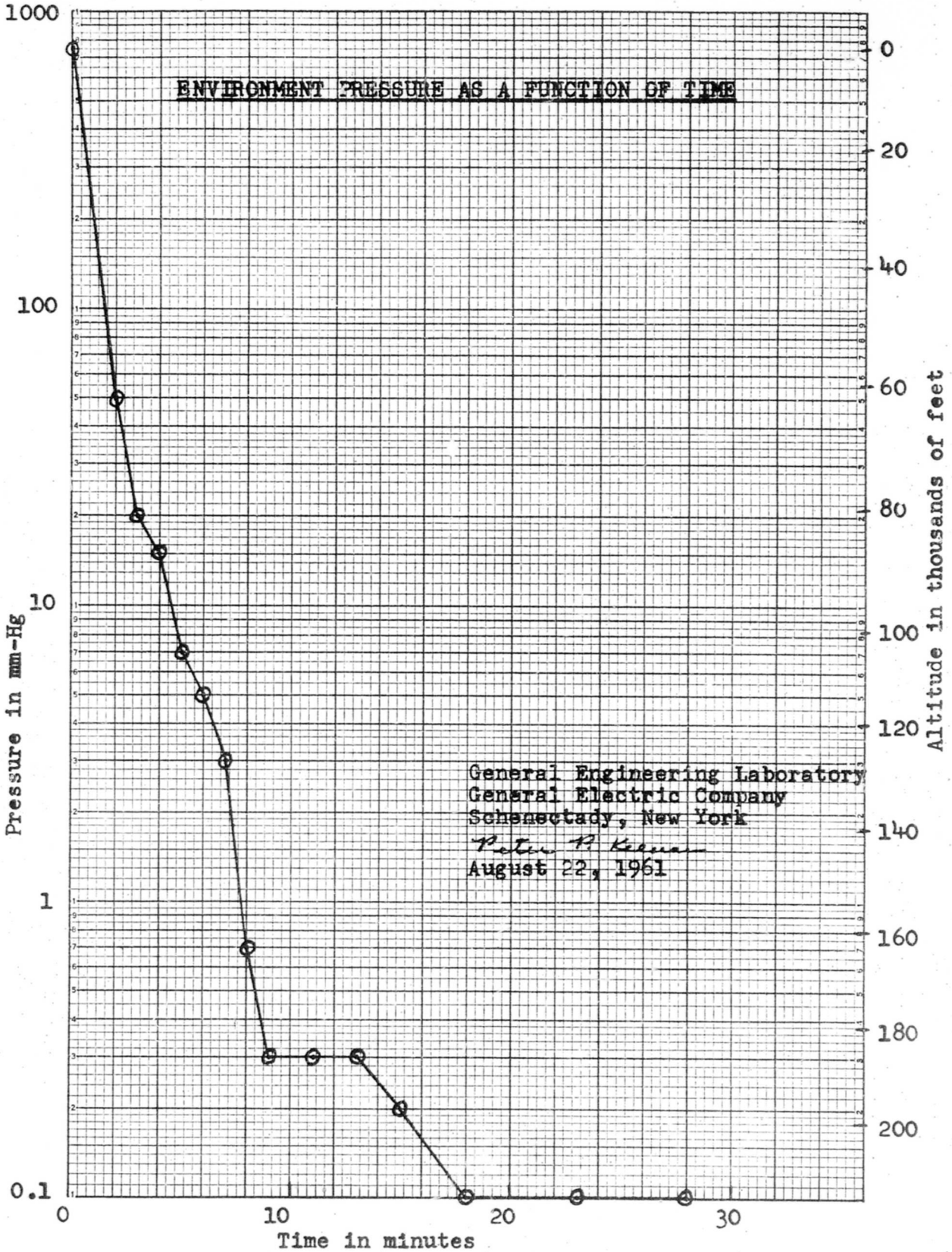
This report summarizes the test results that have been obtained on the dielectric measurements since the last quarterly report.* Two types of dielectric measurements were conducted. In one test the dielectric characteristics of the materials were measured as a function of temperature (from room temperature to 1100 F) while the sample was in air at atmospheric pressure. In the second test the dielectric samples were initially soaked in water prior to testing and were then placed in a waveguide at room temperature. The waveguide with the dielectric samples was then placed in a furnace at 650 F. At the same time, the waveguide is evacuated to pressure simulating altitudes of approximately 120,000 feet. Measurements of dielectric constant (e') and loss tangent (tan δ) are taken as a function of temperature and time as the dielectric sample heats up to the furnace temperature.

The time required for the dielectric characteristics to reach steady state (approximately 10 to 15 minutes) depends on the rapidity with which the waveguide heats; and it is not a characteristic of the dielectric material. The heating curve as a function of time is shown in Fig. 1, Page 3a The true heating response time of the dielectric material (if such information is desired) could be measured by inserting the dielectric sample in an already hot waveguide. Similarly, the pumping capacity is great enough so that the pressure versus time curve is realtively independent of the dielectric material. The environment pressure as a function of time is given in Fig. 2, Page 4a.

The results of the measurements of the dielectric characteristics measured as a function of temperature in air at atmospheric pressure are summarized in Table I. As indicated in Table I, the aluminum-phosphate with silica reinforcement No. 33Y3 has the best dielectric characteristics. The dielectric measurements on the non-aged aluminum-phosphate silica formulation No. 3 showed a loss peak at approximately 600 F (tan δ = 0.094); however, aging for 100-hours at 1000 F removed this high loss. In general, aging 100-hours at 1000 F or heating up the materials to 1100 F improved the dielectric properties. Further, the heating appeared to have no adverse

*"Research on Binder Techniques for High Temperature Radome Structures - Interim Engineering Report No. 1", H.T. Plant and P.P. Keenan, Period Covered - April 17, 1961-July 17, 1961.

Figure 2



effect on the strength of the materials, and the sample dimensions and weights remained essentially the same before and after testing. The effects of water absorption on the materials are summarized in Table II.

Several of the materials have also been water soaked and tested in vacuum atmospheres. In general, the measurements on the water soaked aluminum-phosphate-silica materials showed similar characteristics. The measurements for non-aged aluminum-phosphate-silica formulation 3 (material previously tested in air atmospheric pressure as a function of temperature) are also given in Table II.

In general, the dielectric response of the water soaked samples (with the exception of mica laminates) initially shows a high loss ($\tan\delta \sim .2$) and dielectric constant ($e' \sim 8$). After heating for 10 or 12 minutes, however, the dielectric characteristics ($e' - 2.7$, $\tan\delta = 0.019$) approach that of the sample before soaking in water ($e' \sim 2.5$, $\tan\delta = 0.01$). The strength of the samples appeared to be unaffected by the testing. The mica laminate (XS-1342) had a lower loss tangent ($\sim .05$) after soaking than did the aluminum-phosphate-silica materials.

Detailed information on the dielectric properties as a function of temperature is given in the graphs.(Pages 6-24)

Figure 3

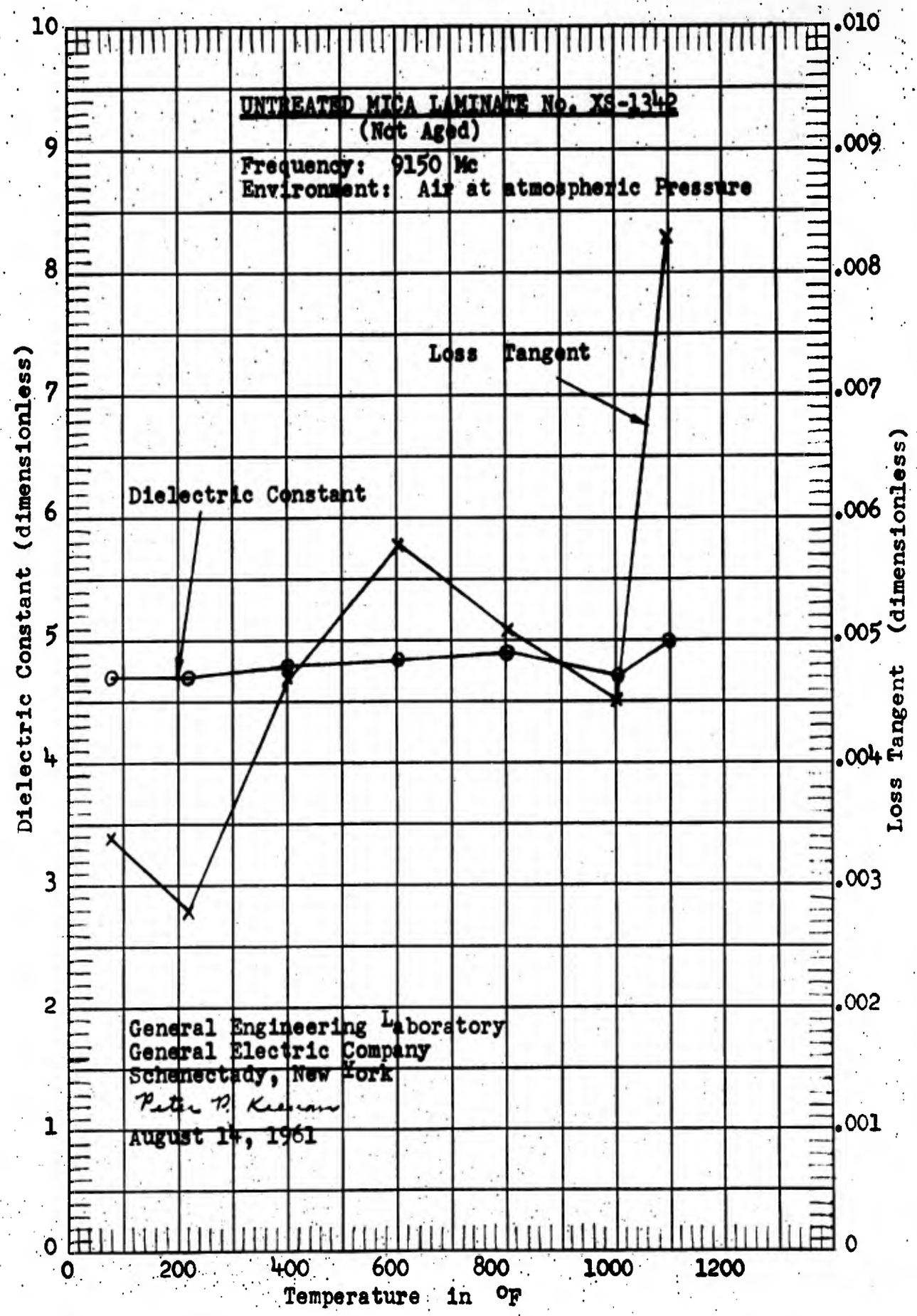

UNTREATED MICA LAMINATE No. XS-1342
(Not Aged)
Frequency: 9150 Mc
Environment: Air at atmospheric Pressure
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.001
.002
.003
.004
.005
.006
.007
.008
.009
.010
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kiernan
August 14, 1961

Figure 4

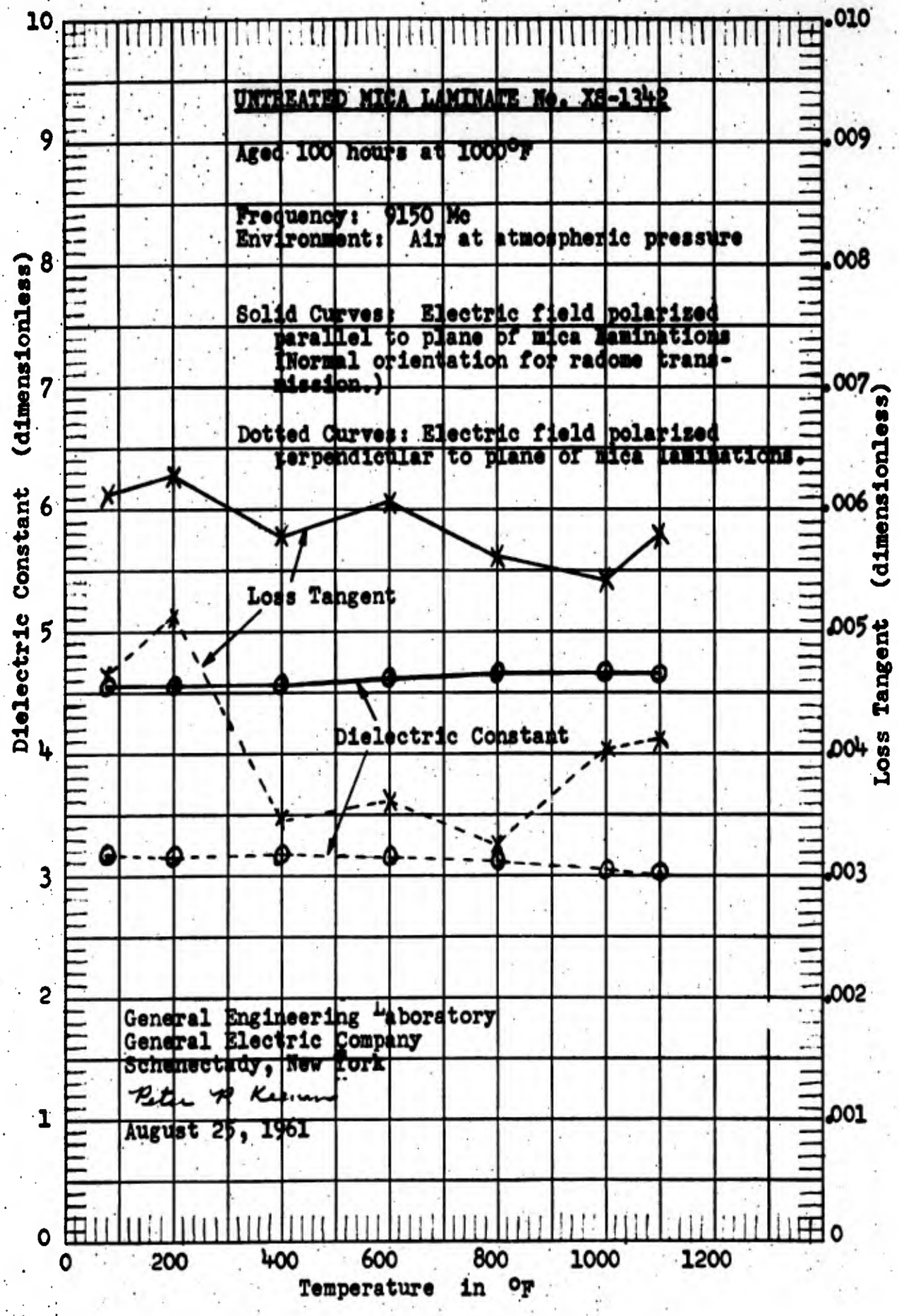

UNTREATED MICA LAMINATE No. XS-1342
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Solid Curves: Electric field polarized parallel to plane of mica laminations (Normal orientation for radome transmission.)
Dotted Curves: Electric field polarized perpendicular to plane of mica laminations.
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.001
.002
.003
.004
.005
.006
.007
.008
.009
.010
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter H Keesom
August 25, 1961

Figure 5

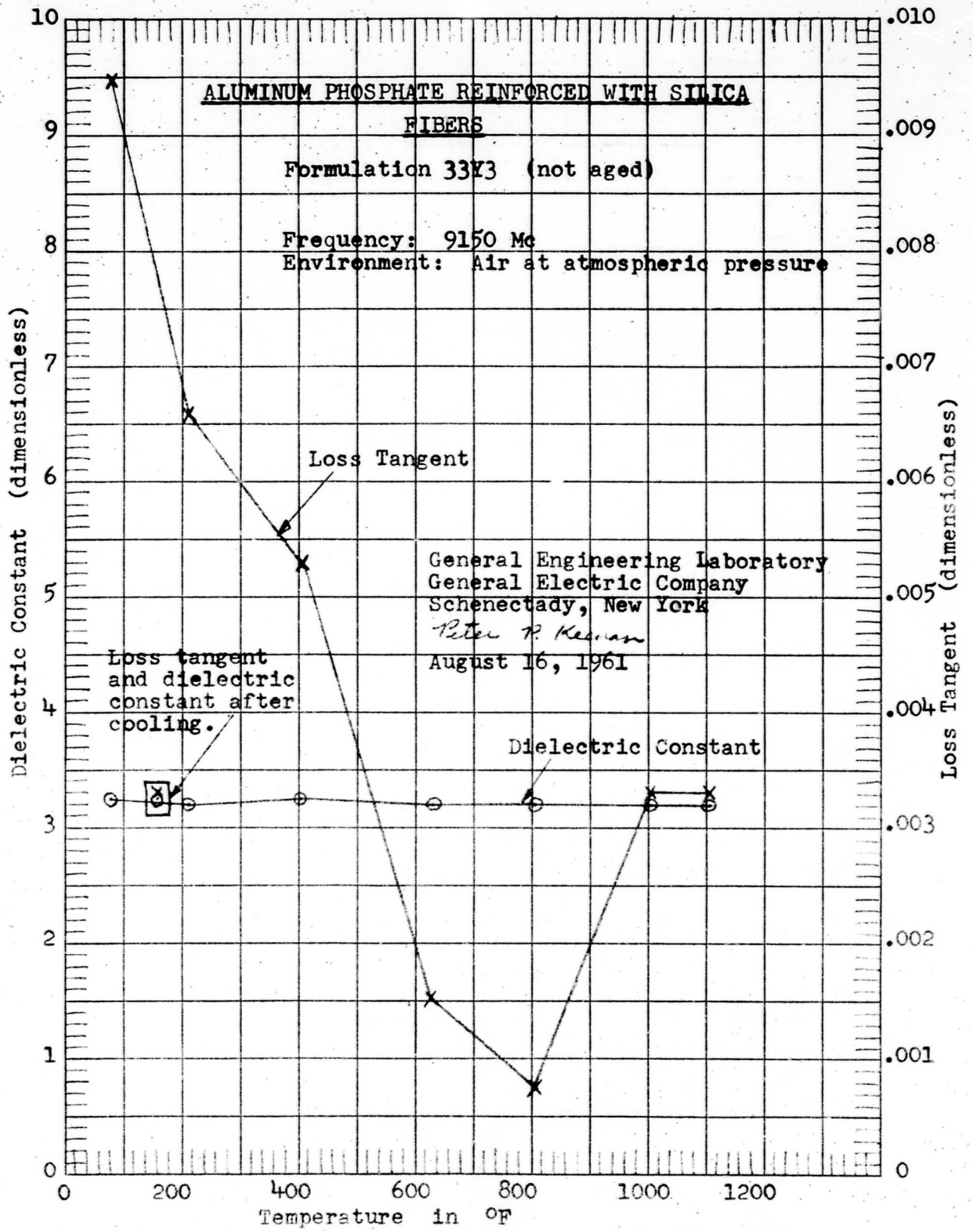

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 33Y3 (not aged)
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Keenan
August 16, 1961
Loss tangent and dielectric constant after cooling.
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.001
.002
.003
.004
.005
.006
.007
.008
.009
.010

Figure 6

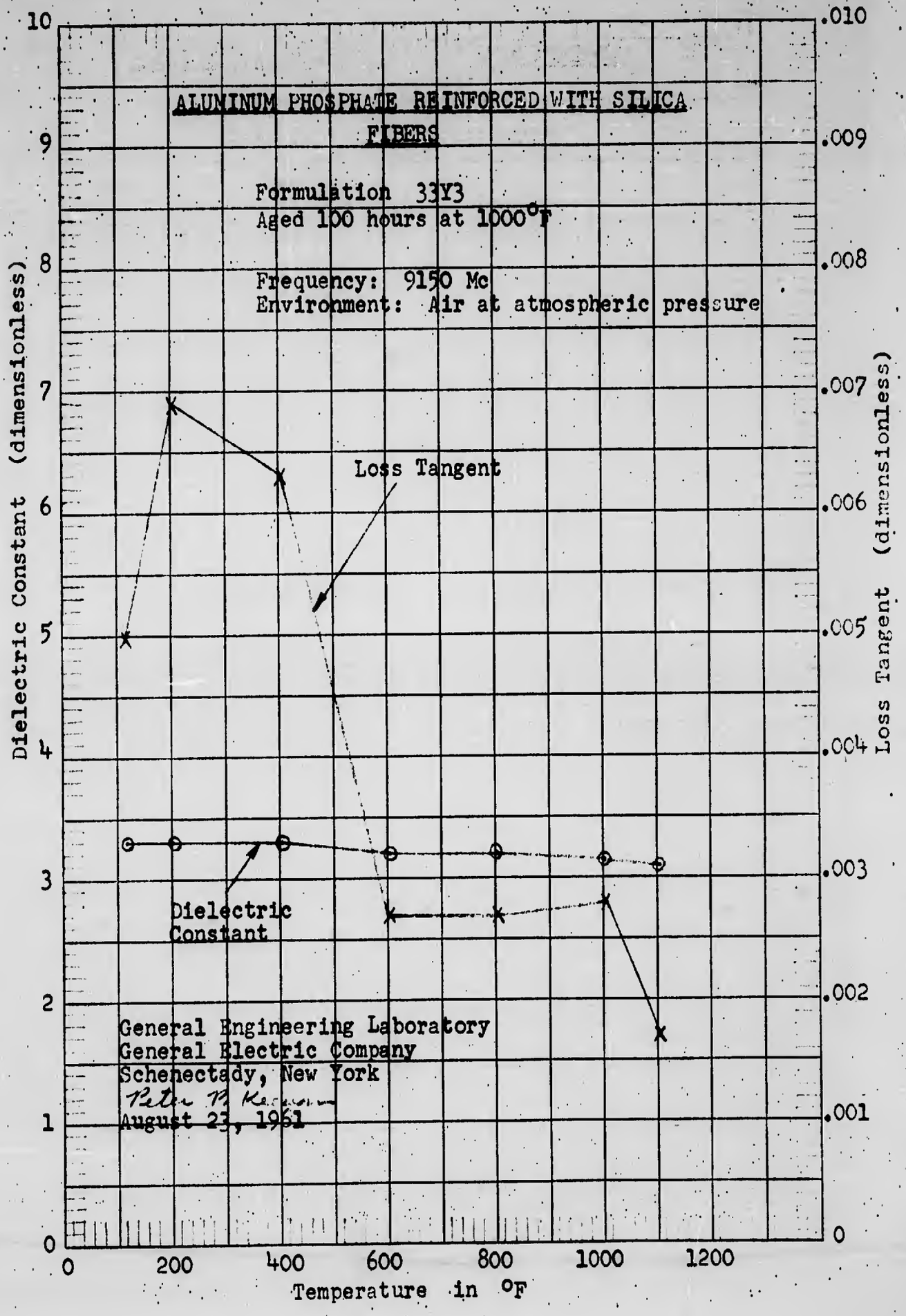

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 33Y3
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.001
.002
.003
.004
.005
.006
.007
.008
.009
.010
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kerson
August 23, 1961

Figure 7

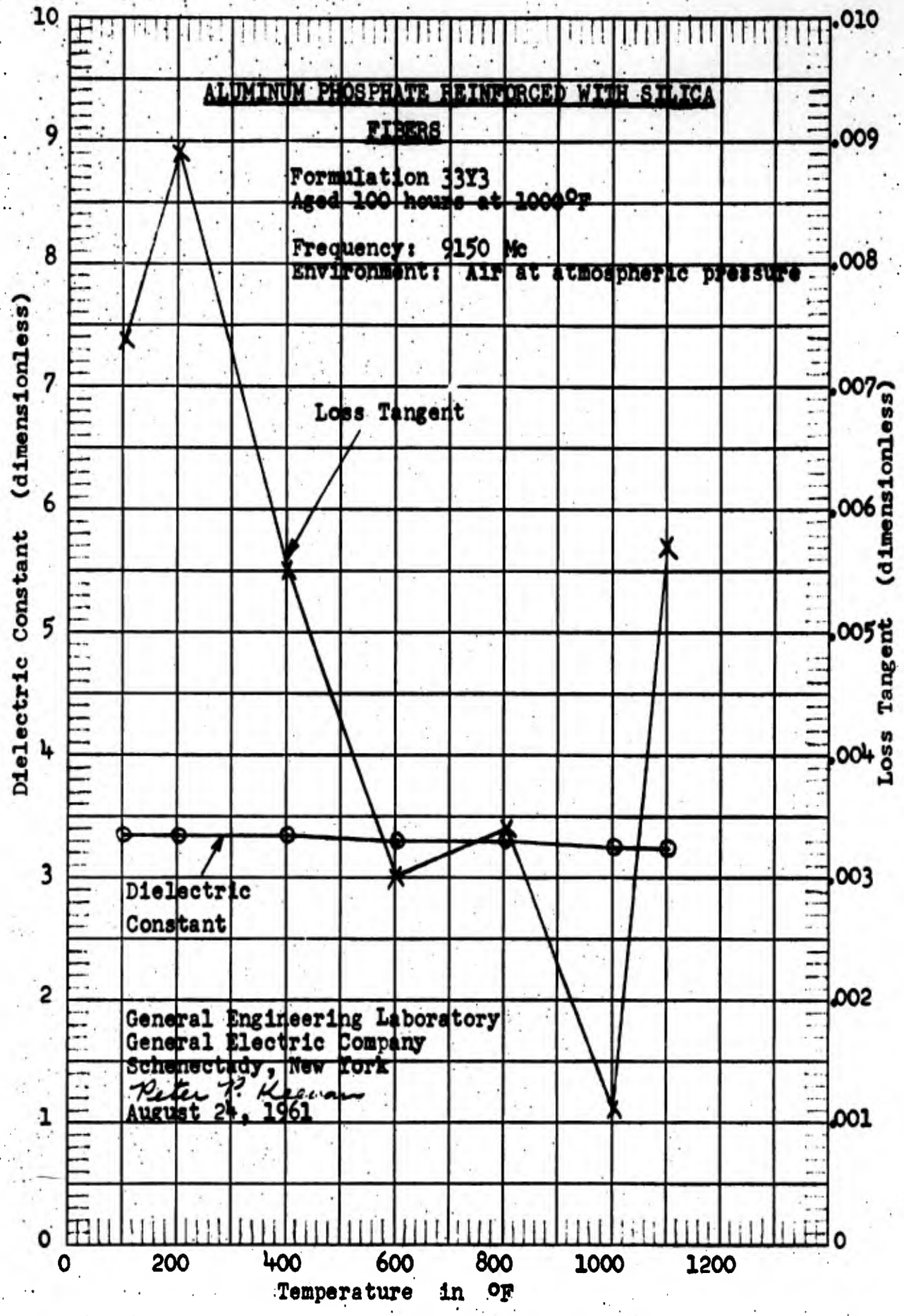

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 33Y3
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.001
.002
.003
.004
.005
.006
.007
.008
.009
.010
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter T. Keegan
August 24, 1961

Figure 8

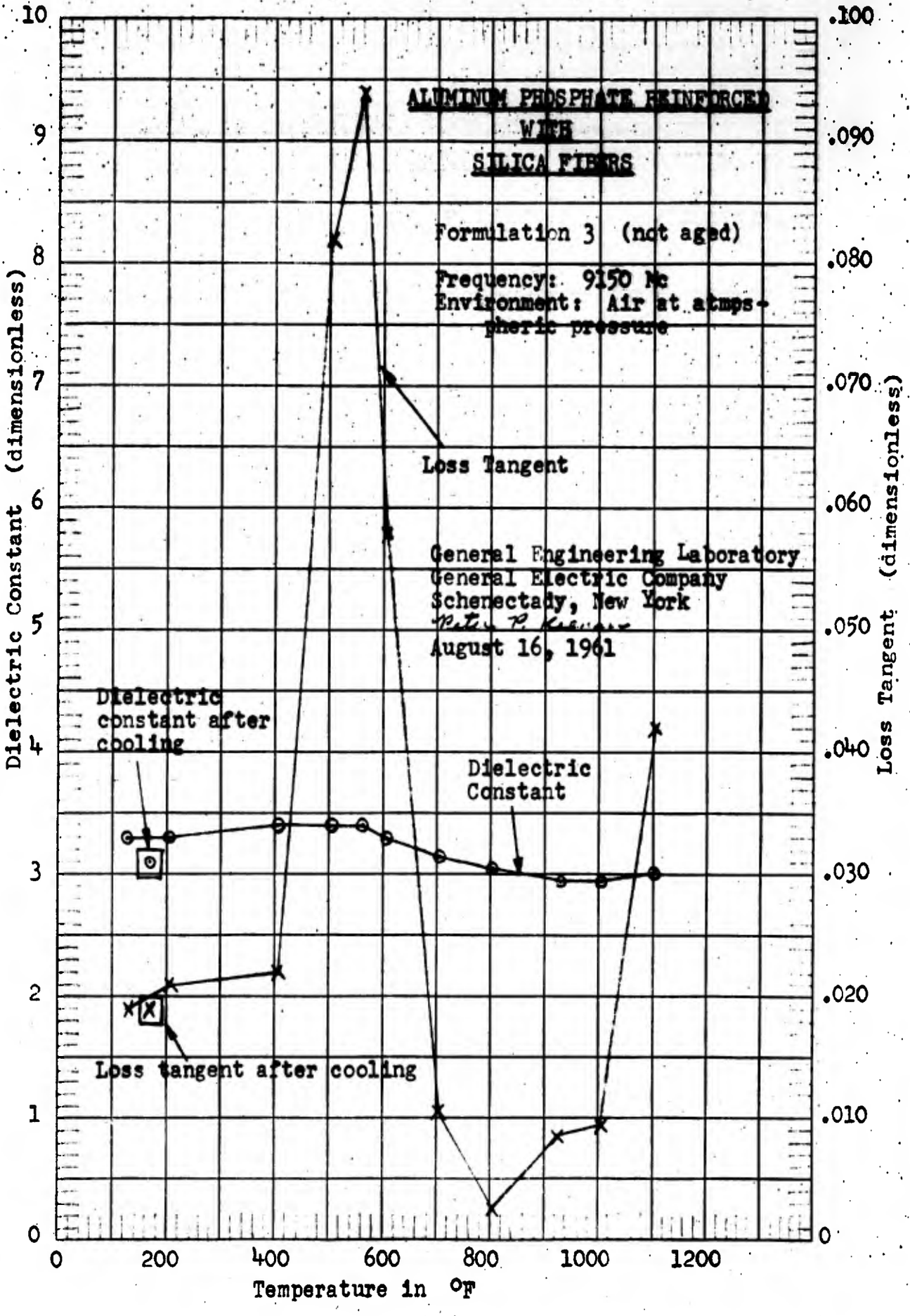

ALUMINUM PHOSPHATE REINFORCED
WITH
SILICA FIBERS
Formulation 3 (not aged)
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
General Engineering Laboratory
General Electric Company
Schenectady, New York
August 16, 1961
Dielectric constant after cooling
Dielectric Constant
Loss tangent after cooling
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.010
.020
.030
.040
.050
.060
.070
.080
.090
.100

Figure 9

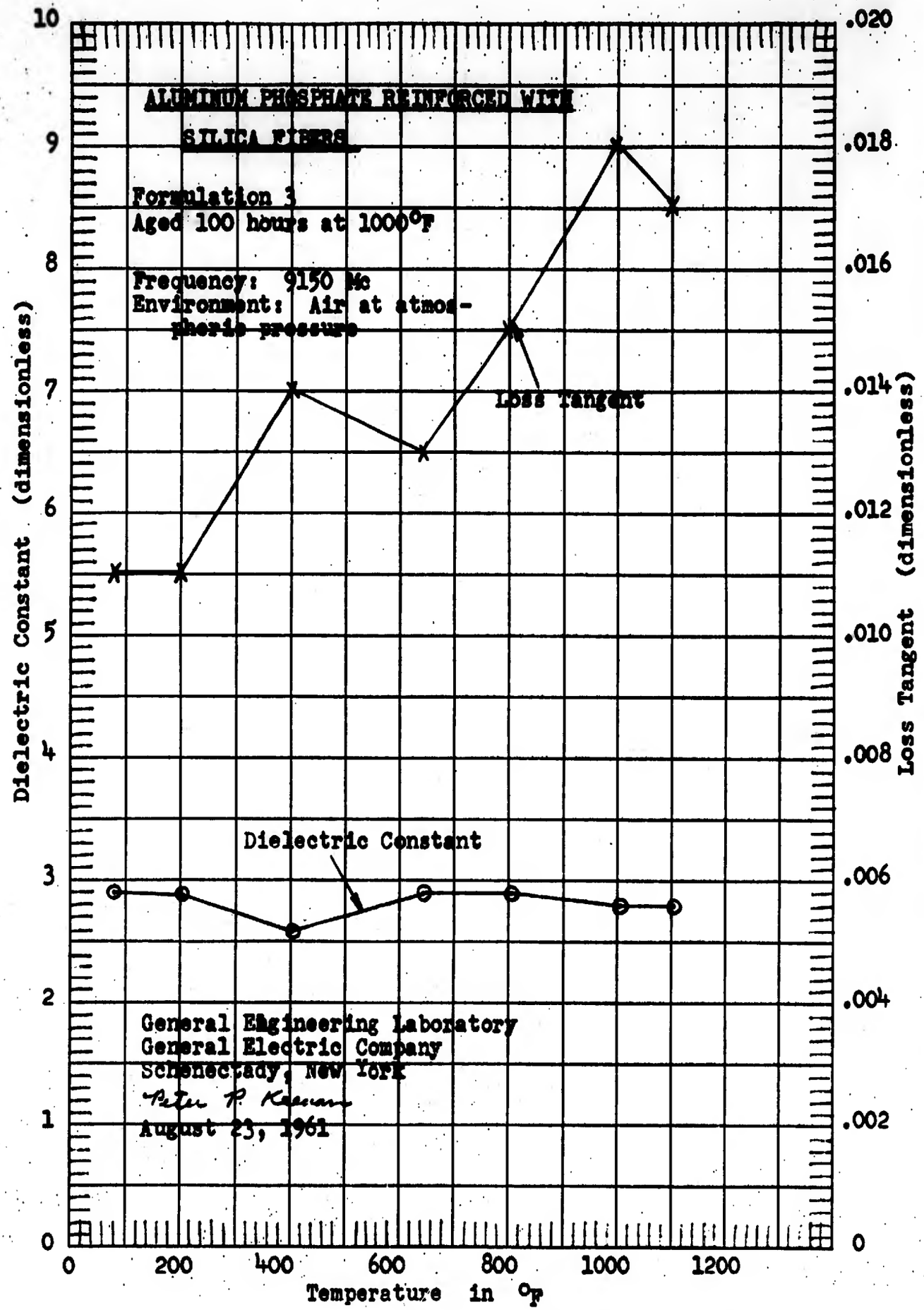

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 3
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.002
.004
.006
.008
.010
.012
.014
.016
.018
.020
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kaelble
August 23, 1961

Figure 10

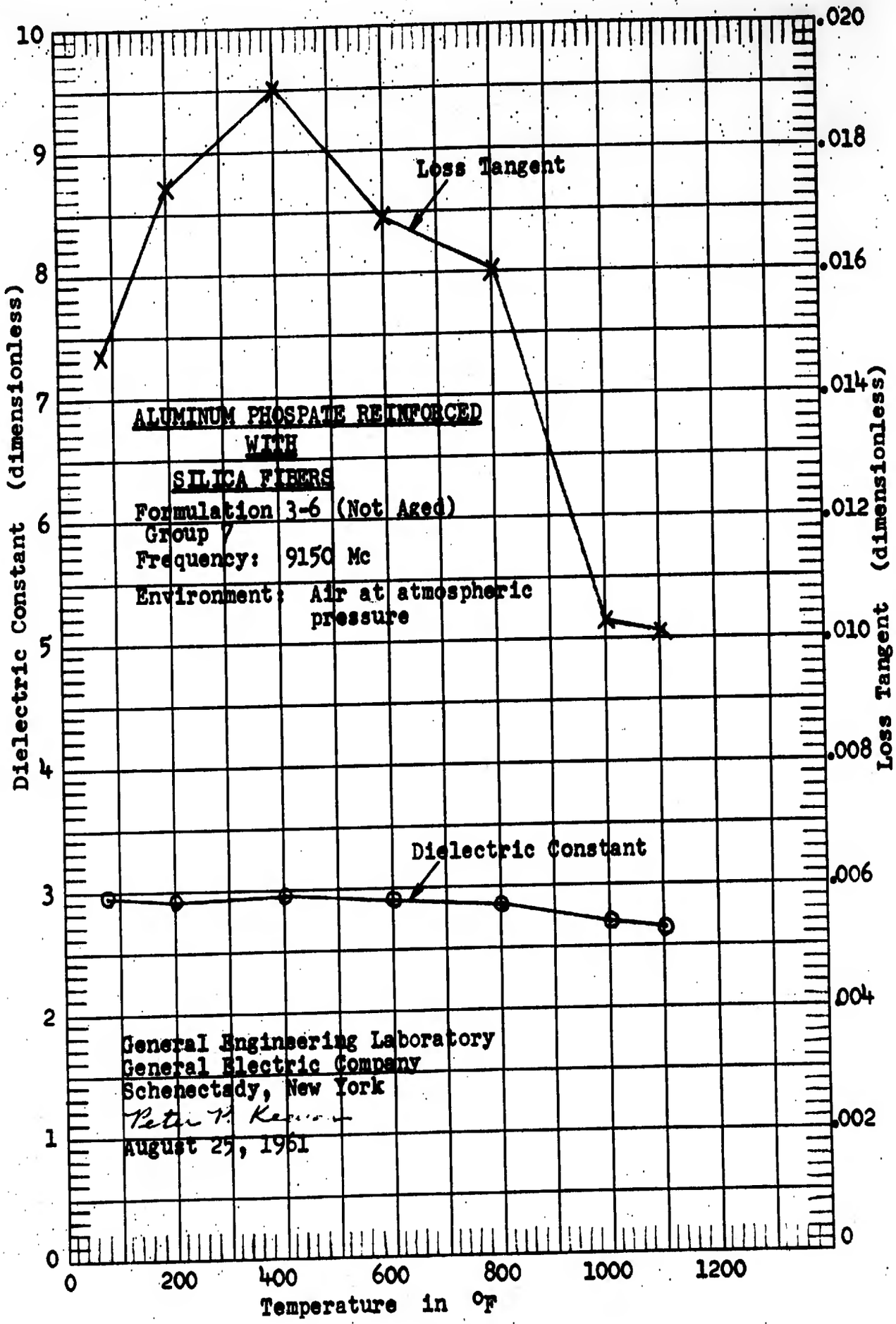

Loss Tangent
Dielectric Constant
ALUMINUM PHOSPATE REINFORCED
WITH
SILICA FIBERS
Formulation 3-6 (Not Aged)
Group 7
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter H. Kerwin
August 25, 1961
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
1
2
3
4
5
6
7
8
9
10
0
200
400
600
800
1000
1200
.020
.018
.016
.014
.012
.010
.008
.006
.004
.002
0

Figure 11

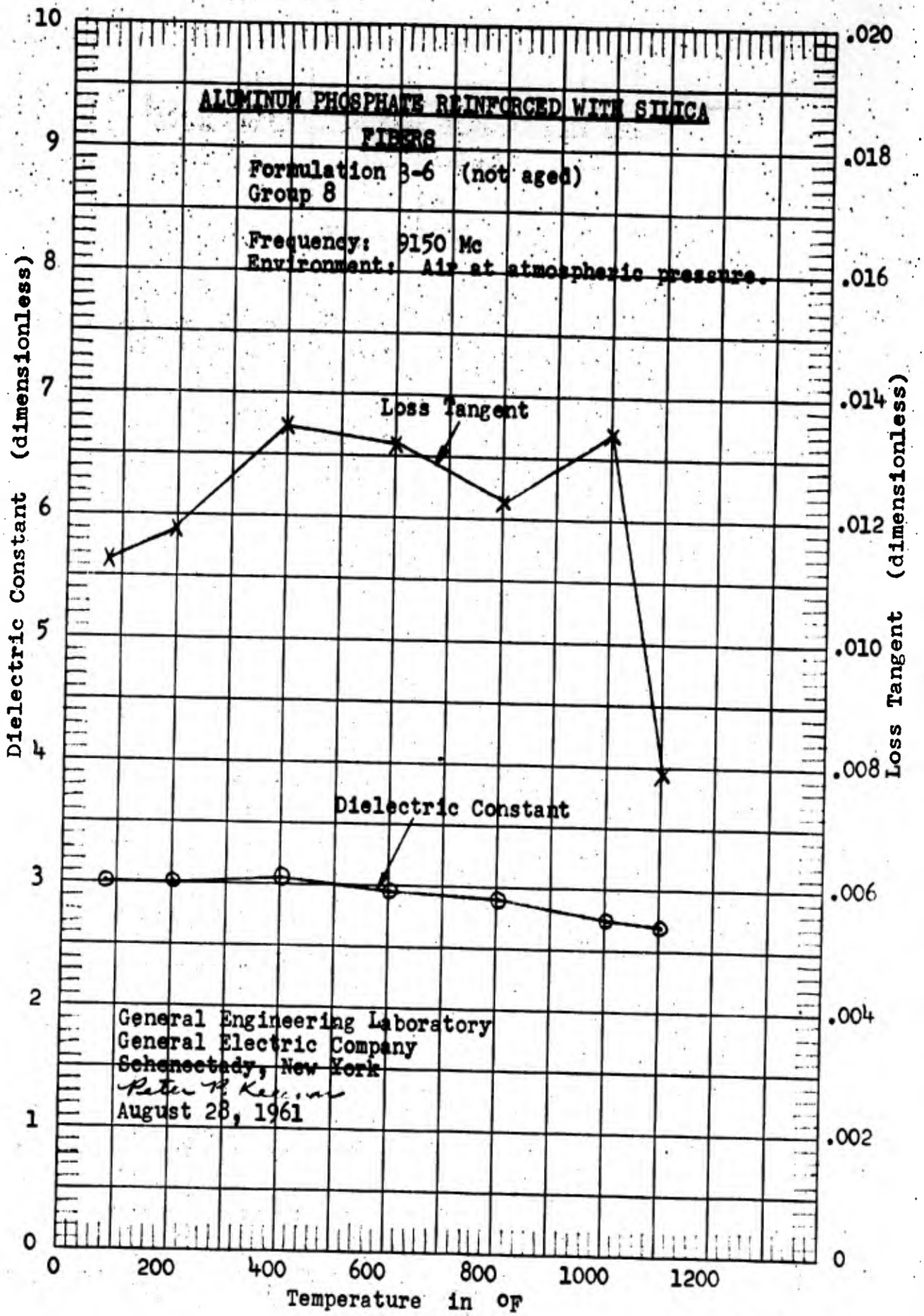

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 3-6 (not aged)
Group 8
Frequency: 9150 Mc
Environment: Air at atmospheric pressure.
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.002
.004
.006
.008
.010
.012
.014
.016
.018
.020
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter K. Kennedy
August 28, 1961

Figure 12

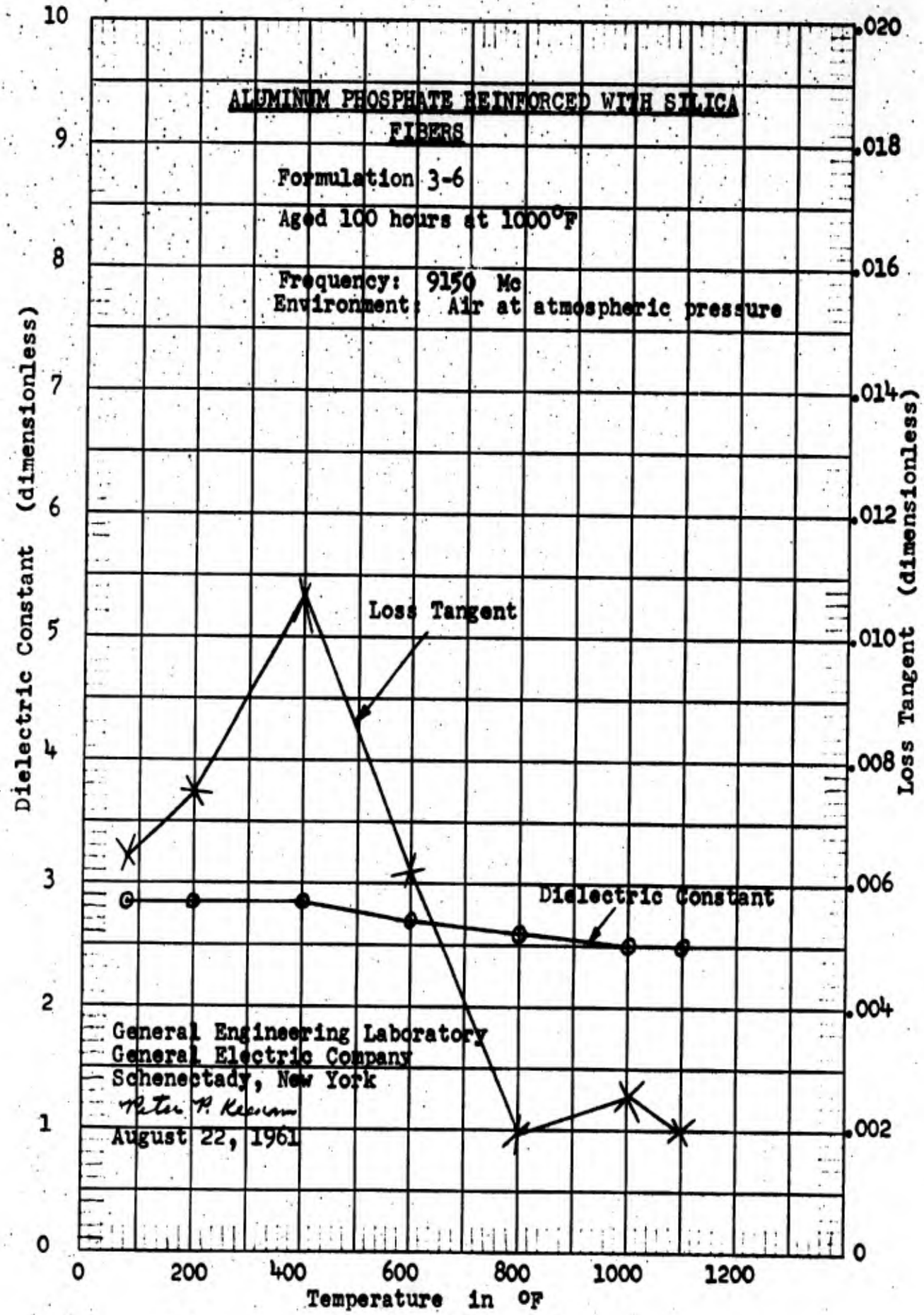

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 3-6
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
0
1
2
3
4
5
6
7
8
9
10
.002
.004
.006
.008
.010
.012
.014
.016
.018
.020
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kerivan
August 22, 1961

Figure 13

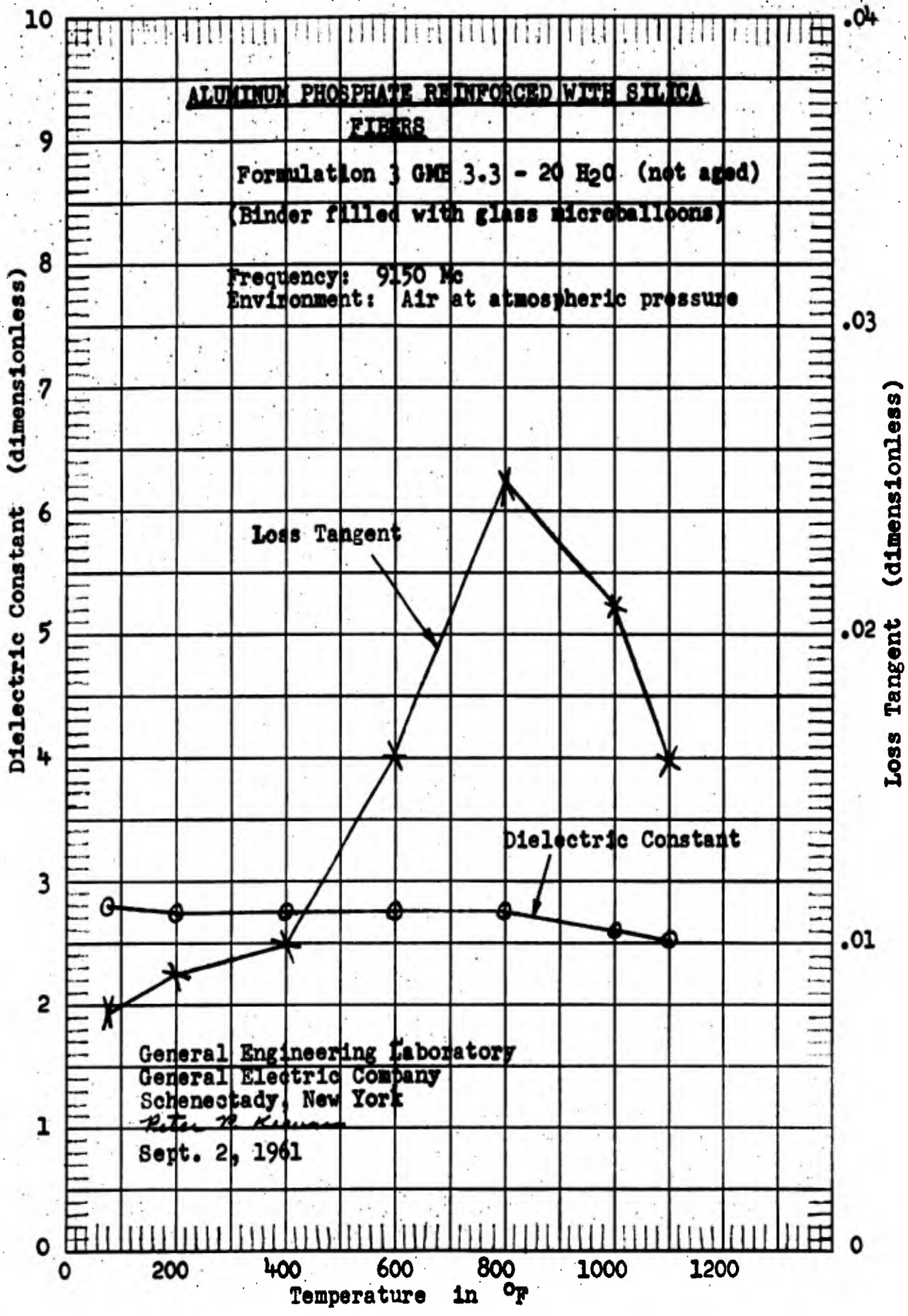
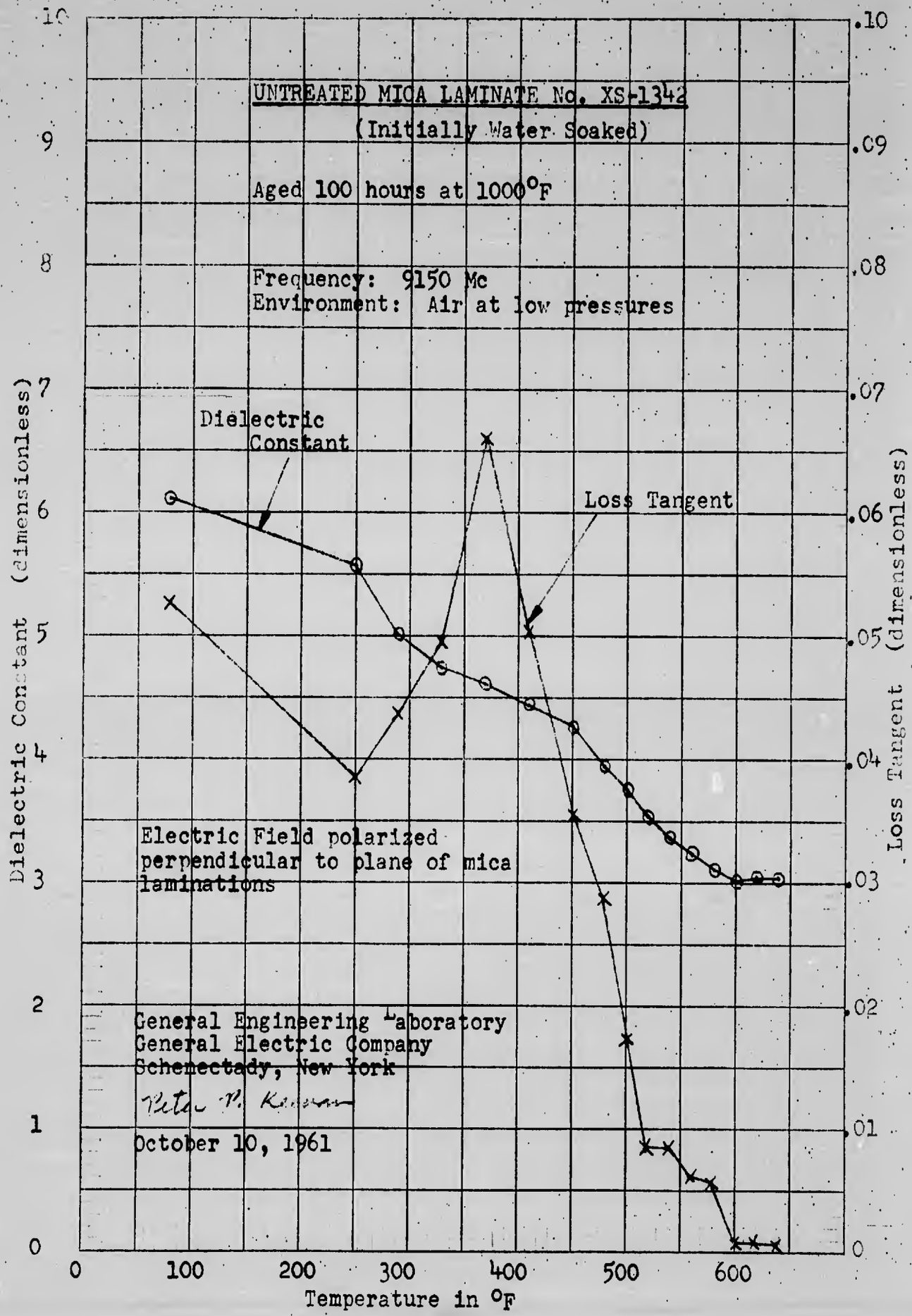

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
Formulation 3 GME 3.3 - 20 H2O (not aged)
(Binder filled with glass microballoons)
Frequency: 9150 Mc
Environment: Air at atmospheric pressure
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
200
400
600
800
1000
1200
1
2
3
4
5
6
7
8
9
10
.01
.02
.03
.04
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kiuman
Sept. 2, 1961

Figure 14


UNTREATED MICA LAMINATE No. XS-1342
(Initially Water Soaked)
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at low pressures
Dielectric Constant
Loss Tangent
Electric Field polarized perpendicular to plane of mica laminations
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kurian
October 10, 1961
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
100
200
300
400
500
600
1
2
3
4
5
6
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8
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10
.01
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Figure 15

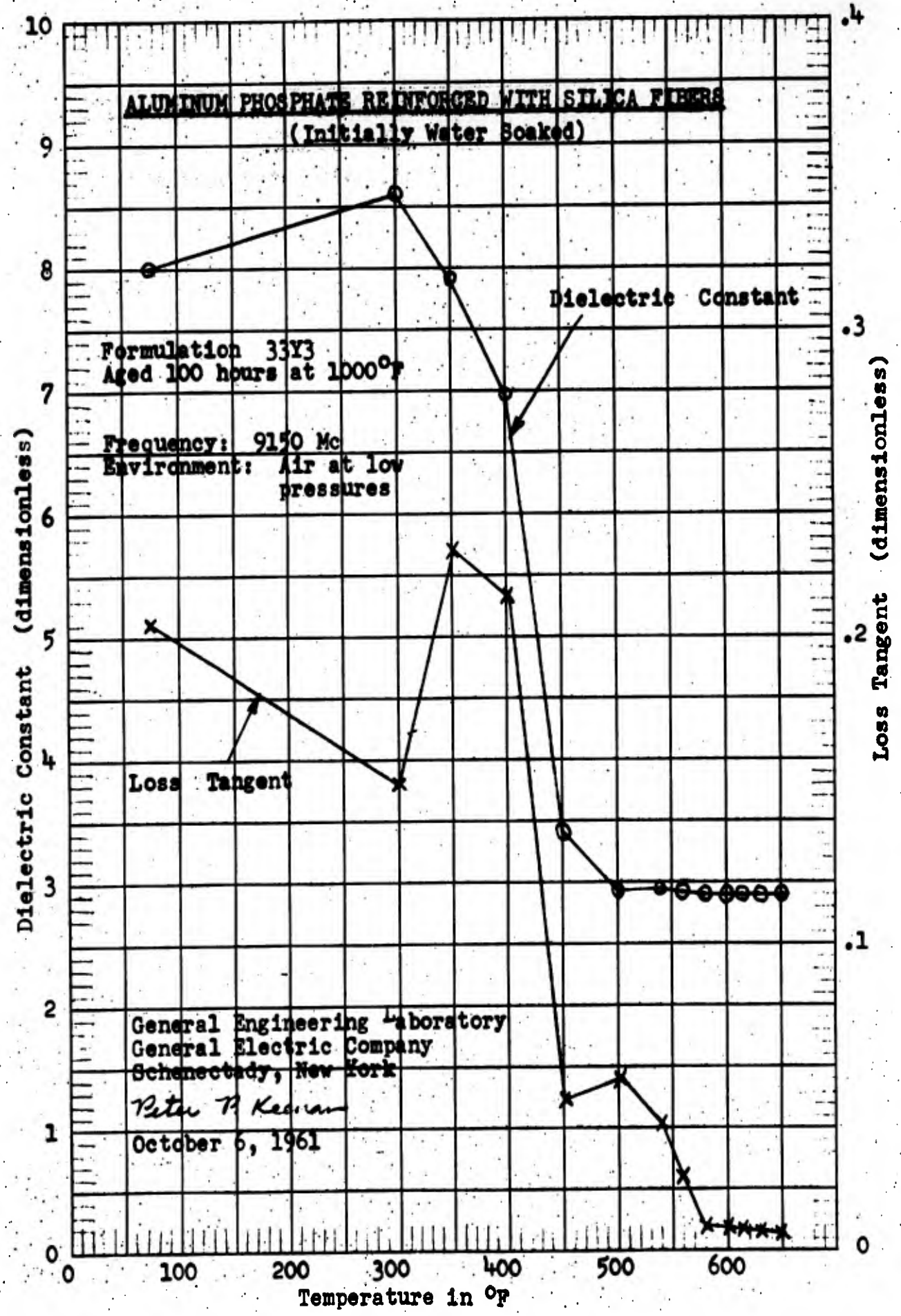
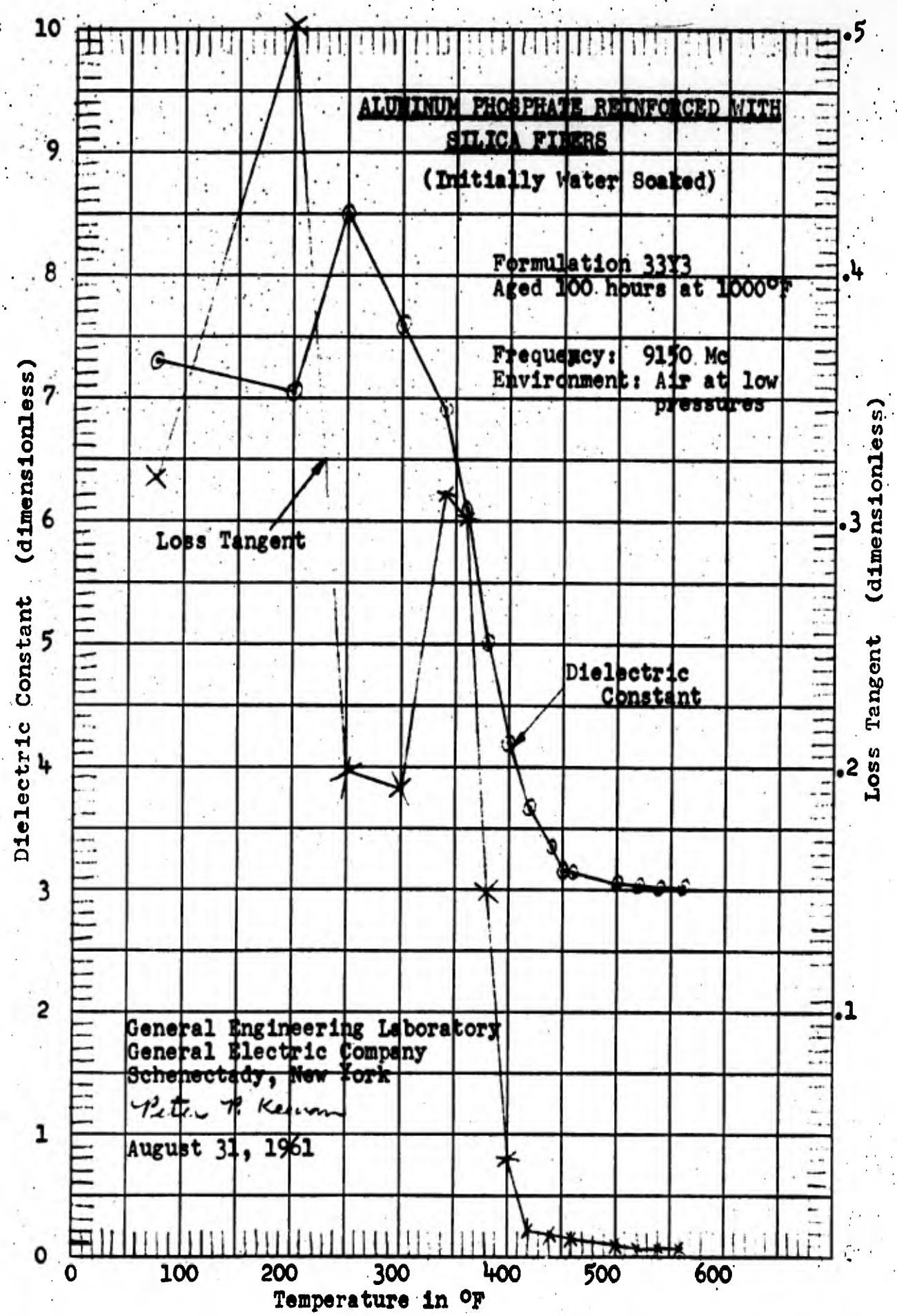

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
(Initially Water Soaked)
Dielectric Constant
Formulation 33Y3
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at low pressures
Loss Tangent
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
1
2
3
4
5
6
7
8
9
10
.1
.2
.3
.4
100
200
300
400
500
600
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P Kedian
October 6, 1961

Figure 16


ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
(Initially Water Soaked)
Formulation 33Y3
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at low pressures
Loss Tangent
Dielectric Constant
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
100
200
300
400
500
600
1
2
3
4
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6
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10
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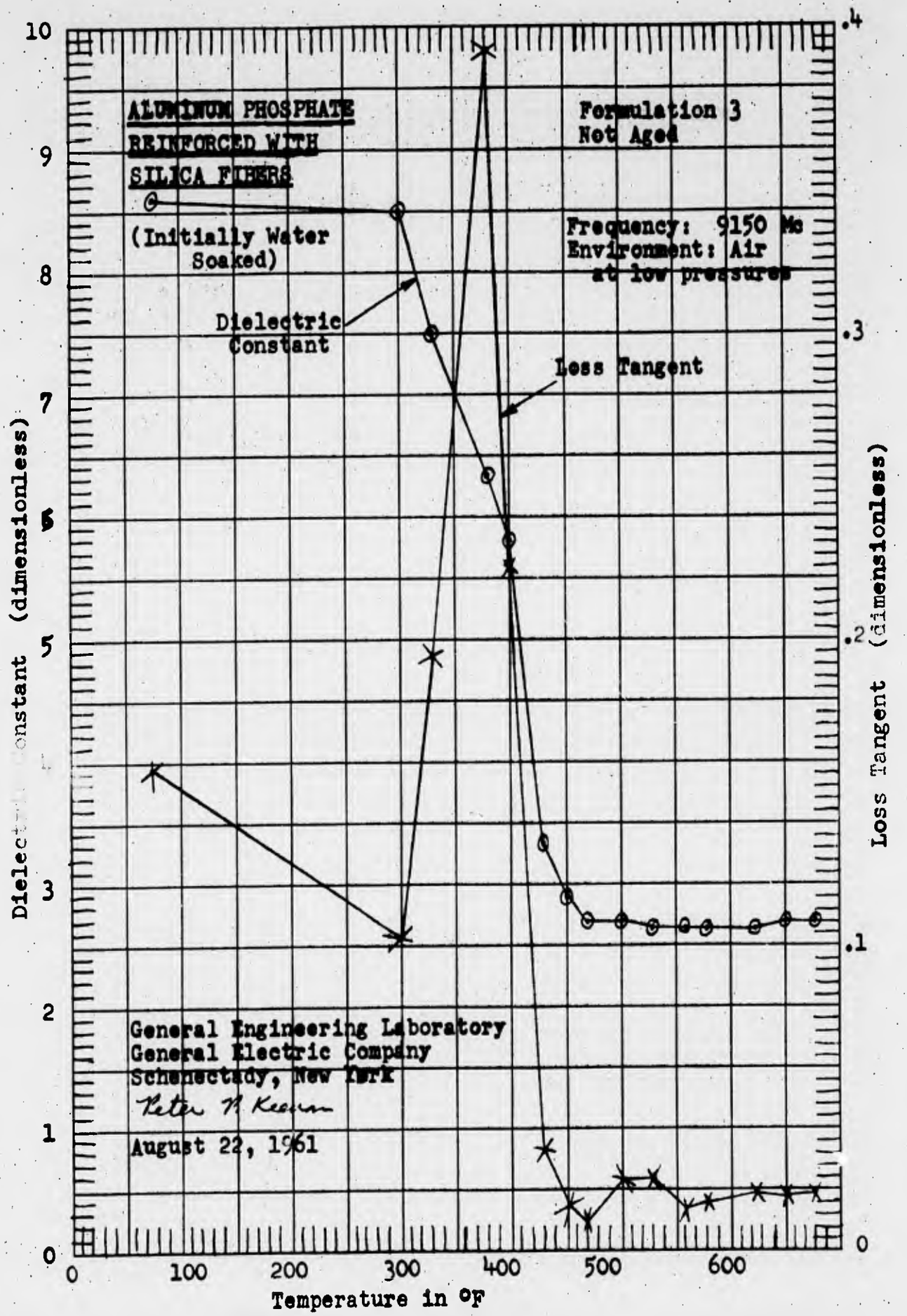
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter M. Kelly
August 31, 1961

Figure 17


ALUMINUM PHOSPHATE
REINFORCED WITH
SILICA FIBERS
(Initially Water Soaked)
Formulation 3
Not Aged
Frequency: 9150 Mc
Environment: Air at low pressures
Dielectric Constant
Loss Tangent
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
100
200
300
400
500
600
1
2
3
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.1
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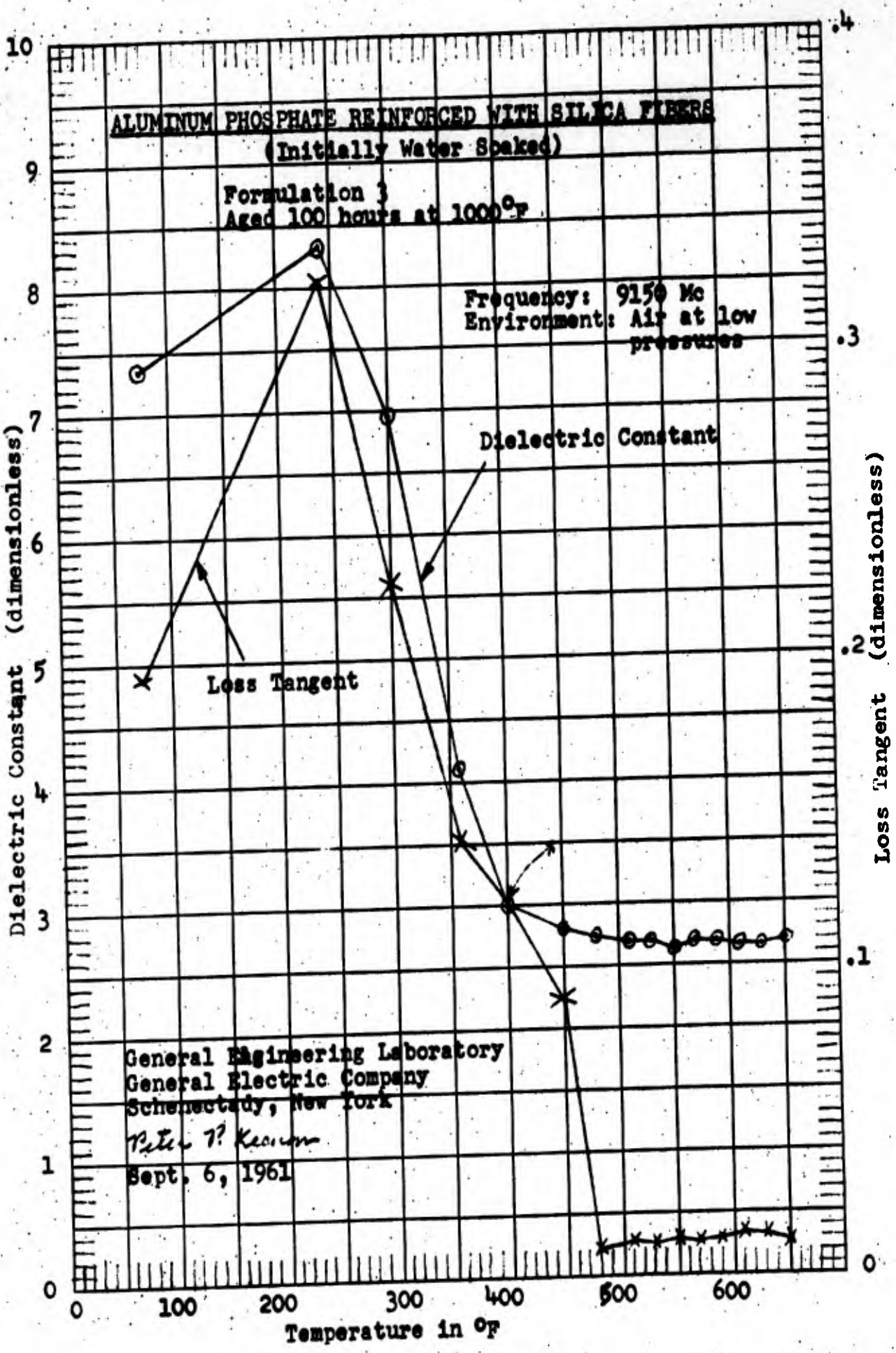
.4
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter N. Keehn
August 22, 1961

Figure 18


ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
(Initially Water Soaked)
Formulation 3
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at low pressures
Dielectric Constant
Loss Tangent
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
100
200
300
400
500
600
1
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General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter T. Kearns
Sept. 6, 1961

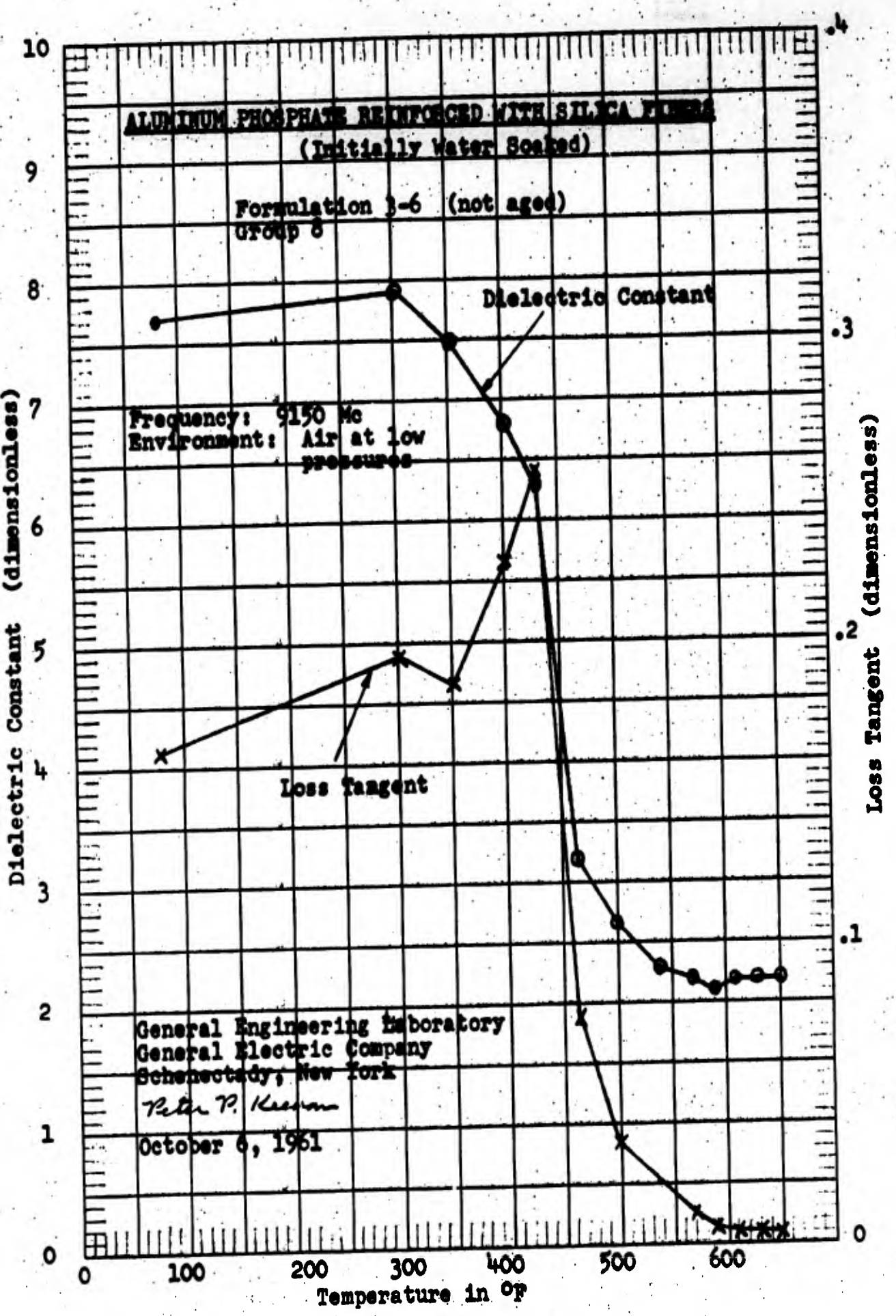
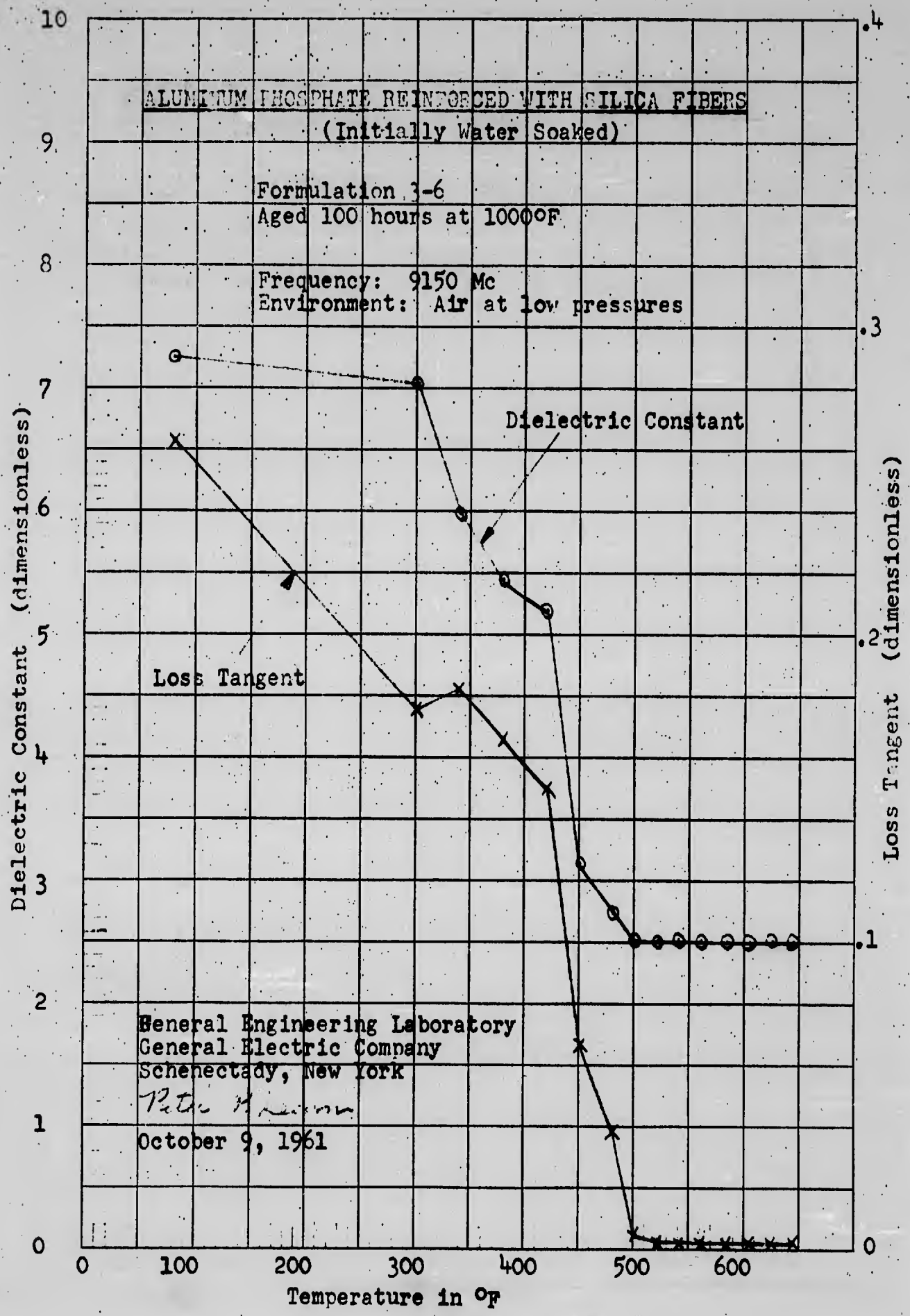

ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
(Initially Water Soaked)
Formulation 3-6 (not aged)
Group 8
Dielectric Constant
Frequency: 9150 Mc
Environment: Air at low pressures
Loss Tangent
General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Kerrn
October 6, 1961
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
1
2
3
4
5
6
7
8
9
10
.1
.2
.3
.4
100
200
300
400
500
600

Figure 20


ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
(Initially Water Soaked)
Formulation 3-6
Aged 100 hours at 1000°F
Frequency: 9150 Mc
Environment: Air at low pressures
Dielectric Constant
Loss Tangent
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
100
200
300
400
500
600
1
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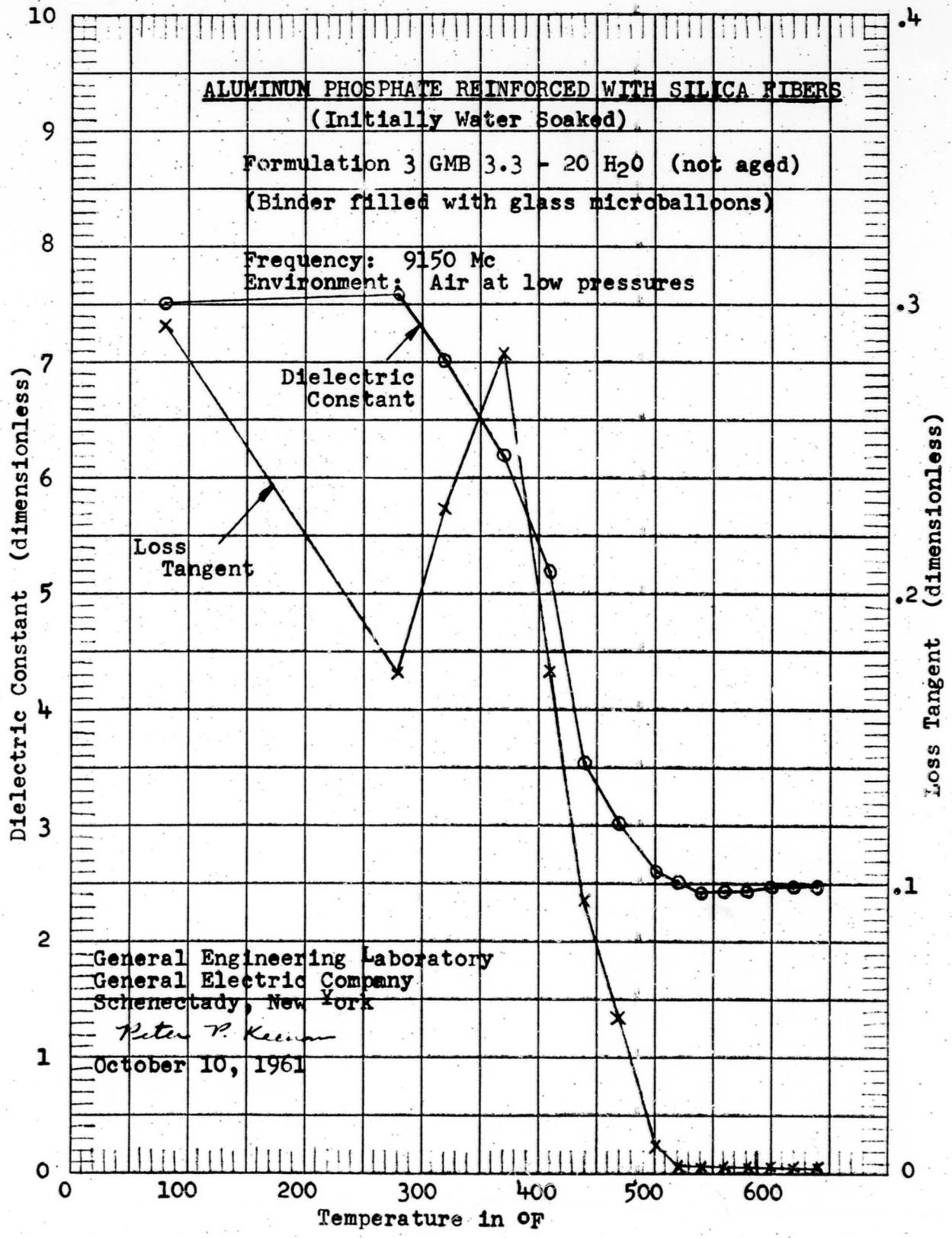
General Engineering Laboratory
General Electric Company
Schenectady, New York
October 9, 1961

Figure 21


ALUMINUM PHOSPHATE REINFORCED WITH SILICA FIBERS
(Initially Water Soaked)
Formulation 3 GMB 3.3 - 20 H_2O (not aged)
(Binder filled with glass microballoons)
Frequency: 9150 Mc
Environment: Air at low pressures
Dielectric Constant
Loss Tangent
Dielectric Constant (dimensionless)
Loss Tangent (dimensionless)
Temperature in °F
0
100
200
300
400
500
600
1
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General Engineering Laboratory
General Electric Company
Schenectady, New York
Peter P. Keenan
October 10, 1961

CONCLUSIONS

1. The 9150 megacycle dielectric properties of both the silica fiber reinforced aluminum phosphate laminates and the General Electric proprietary XS-1342 mica laminate make these materials strong contenders for 1000 F radome applications so far as electrical properties are concerned.

2. The 100-hours aging at 1000 F has no detrimental effect on the 9150 megacycle dielectric properties of these materials either at room temperature or up to 1000 F. Prolonged exposure at the elevated temperature may tend to improve these properties.

RECOMMENDATIONS

1. A study of methods to prevent moisture pick-up should be initiated for both materials.

2. Further electrical testing should be discontinued since these materials have been characterized sufficiently to deem them applicable electrically for 1000 F radome systems. The efforts of the program should now be directed toward improving the flexural strength of the silica fiber-aluminum phosphate systems.

3. Simple radome shapes, based on mica laminate, should be designed, constructed, and tested since the XS-1342 is stable electrically as well as physically.[1] In our opinion, it is ready to be used as a 800 - 1000 F radome material.

4. A simple filament wound radome shape (cylinder) should be constructed using the aluminum phosphate silica fiber system to demonstrate the process applicability to larger shapes.

1 - See Interim Engineering Report No. 1, Page 30A.

TABLE III
BINDER COMPOSITION
(SUBSTITUTING MICROSPHERES AND REMOVING WATER)

Formulation	Hydrated Alumina (C-730 Alcoa) grams	H_2O cc	Ortho Phosphoric Acid 85% cc	Milled Zircon (325 Mesh) Titanium Alloy Mfg. Div. National Lead Co. grams	Aluminum Oxide (900 Mesh) (Alundum 38-900 Norton Co.) grams	Glass Microspheres Emerson and Cuming, Inc. grams	Comments
3	40	40	60	80	40	-	A standard formulation.
3GMB3.3-10H_2O	"	30	"	"	-	3.3[1]	Handles well. Makes into laminates worthy of testing.
3GMB3.3-20H_2O	"	20	"	"	-	"	Handles well. Have already tested laminates.Looks good.
3GMB3.3-30H_2O	"	10	"	"	-	"	Very viscous. Laminates poorly. Bonded-weak-warped.
3GMB3.3-40H_2O	"	-	"	"	-	"	Gelled during preparation of the binder.
Z	40	40	60	-	-	-	Very low viscosity. Binder ran out of laminates. Laminates weak.
ZGMB3.3-40H_2O	"	-	"	-	-	3.3	Became so viscous only 1 sample could be made. Laminate weak and warped.
ZGMB8.4-10H_2O	"	30	"	-	-	8.4[2]	Handles well. Laminates weak. Poorly bonded.
ZGMB8.4-20H_2O	"	20	"	-	-	"	Handles well. Only a few laminates were worthy of testing. Laminates weak.
ZGMB8.4-30H_2O	"	10	"	-	-	"	Too viscous to make samples.

1 - Approximately the same volume as the alumina.
2 - Approximately the same volume as the alumina and zircon.

BINDER FORMULATIONS CONTAINING MICROSPHERES

The use of inorganic microspheres as a filler for aluminum phosphate binders was investigated in an attempt to improve electrical properties and reduce weight of silica fiber-reinforced laminates. There was also the possibility that the hollow glass spheres would impart elongation to the aluminum phosphate binder so that more efficient use of the reinforcing fibers could be obtained, thereby resulting in subsequent higher laminate flexural strength.

The initial experiments demonstrated that the binders containing the microspheres had a much lower viscosity than binders containing the solid high density fillers. This is undoubtedly due in part to the relatively large size and small surface area of the microspheres. This lower viscosity enabled us to remove water from the formulation and still maintain a workable binder viscosity. Lowering the water content is an objective that we have tried to accomplish for some time since large water content means that the laminate will be highly porous. An overly porous system is physically weak, and it is subject to much water absorption, which is detrimental to the electrical properties. It appeared that we also had the means to reduce the porosity while maintaining low density of the laminate system. In general, about half the water could be removed from the formulations without encountering high viscosity or premature gelling of the binder.

In most cases laminates could be made from these binders, but until recently we met with continued failure in making structurally satisfactory laminates. The laminates were usually warped, weak and poorly bonded; and the binder was powdery. Table III on Page 25a shows the various formulations investigated and lists some comments concerning the performance of these binders. It appears that if we substitute a volume-for-volume quantity of glass microspheres for alumina and we remove half of the water, we can make laminates that look good, feel good, and perform good. This is a singular formulation, for most of the other formulations resulted in extremely poor laminates. One other formulation was deemed worthy of testing, but it was found to be extremely weak.

1 - Emerson and Cuming, Inc. glass and silica microspheres 30-300 microns diameter

TABLE IV
BINDER COMPOSITION
(ORIGINAL FORMULATIONS)

CONSTITUENTS	FORMULATION		
	3	3-6	33Y3[1]
Hydrated Alumina (C-730) Alcoa	40 g	40 g	40 g
Ortho Phosphoric Acid (85%)	60 cc	60 cc	52.2 cc
Water	40 cc	40 cc	121.3 cc
Milled Zircon (325 mesh) (Titanium Alloy Mfg. Div.) National Lead Co.	80 g	80 g	
Aluminum Oxide (900 mesh) (Alundum 38-900) Norton Co.	40 g		
Aluminum Oxide (500 mesh) Norton Co.			212 g
Asbestos Floats GR7TF1 Johns-Manville Co.		15.6 g	

1 - Prepared by mixing 69.5 g of H_2O with the hydrated alumina and the ortho phosphoric acid. Heat the mix 90 C for 2 1/4 hrs., cool and cut back with water to bring weight of mix to 213.5 g. Then add the alumina.

A recently made sample has not yet been tested, but it looks good. So far, we know that we can use microspheres for part of the binder filler, and we can remove approximately half of the water in the binder. Removal of more water is not good. Removal of all fillers and removal of no water is not good. Removal of all water and addition of microspheres is not good. Removal of half the water and total substitution of microspheres for the fillers is not good. All this negative work tends to make us suspicious of the few formulations that do turn out well.

Table IV Page 26a gives some limited flexural strength data on two microsphere-containing laminates at room temperature and at 1000 F after one-half hour exposure at 1000 F. These are the only two samples that have been deemed worthy of testing thus far. One formulation certainly does not appear promising; however, formulation 3GMB3.3-20H_2O appears most interesting. Here again, we see the typical scatter evidenced in most of our laminates. But interestingly, we see strengths considerably greater than those made with our standard formulation 3, which contained no microspheres and more water. While the evidence is scant, there is some hope that these higher strengths do indicate that the presence of the glass microspheres is in effect making the aluminum phosphate binder system more extensible, and, therefore, more load is placed on the reinforcing fibers. This approach is certainly worthy of further investigation. Better results at the elevated temperature may be obtained if silica microspheres are used in liew of glass microspheres. It will also be interesting to investigate the effect of adding asbestos fibers to binders containing microspheres. Work in this direction is already being pursued.

In Table II on Page 2a in the previous section of electrical testing, we see that the desired improvement in electrical properties apparently did not materialize as the result of adding microspheres to the binder. (Formulation 3GMB3.3-20H_2O). A significant improvement may be difficult to achieve since all the laminates possessed excellent electrical characteristics using the original formulations shown in Table IV on Page 26a. The water pick-up values for this material are tabulated along with those for silica fiber-aluminum phosphate laminates in Table II. We had believed that the removal of half the water from the binder formulation would result in a less porous structure; the water pick-up data belies this expectation. There is no drastic reduction

in water absorption. Thus far, the only improved aspect is the high strength feature as can be observed by comparing the data in Tables V and VI. Upon further examination and experimentation, improvements in water absorption and microwave performance may evolve.

CONCLUSIONS

1. The substitution of glass microspheres for the alumina filler has not as yet led to improved electrical performance.

2. Thus far, attempts to replace all particulate high density fillers with microspheres have not led to good structural laminates.

3. The removal of water from formulations does not result in any apparent decrease in porosity or subsequent water absorption.

4. There is some evidence that the presence of glass microspheres in the binder does increase laminate flexural strength.

RECOMMENDATIONS

1. Continued study should be made of the substitution of microspheres for particulate fillers and the removal of water from the binder formulation.

2. Use should be made of silica microspheres rather than glass microspheres in attempt to obtain better high temperature performance.

3. Use of short fibered small diameter mineral fibers in conjunction with the microspheres should be investigated.

4. If significant increases in strength are observed, an aging program as well as electrical testing program should be conducted for these materials.

TABLE V
FLEXURAL STRENGTH OF LAMINATES
(BASED ON BINDERS CONTAINING GLASS MICROSPHERES
REINFORCED WITH 150 4/3 SILICA FIBER YARN)

	Flexural Strength PSI[1]					
	Hi	Av	Lo	Hi	Av	Lo
Form. 3GMB3.3-20H_2O	14,400	13,500	12,200	20,000	17,300	15,900
Form. ZGMB8.4-20H_2O	3,500	3,200	2,700	6,200	5,000[2]	3,400
Form. 3		10,700			15,200	

1 - Five samples tested.
2 - Only three samples tested.

EFFECT OF 100-HOUR AGING AT 1000 F ON LAMINATE FLEXURAL STRENGTHS

Our previous work for the Bureau of Weapons, Department of the Navy, resulted in the development of the silica fiber-aluminum phosphate laminate system. Since the nature of that work was exploratory, only short term 1000 F aging flexural strength data was obtained. In the current test series, we found that in laminates based on binder formulations 3 and 33Y3, a definite long term aging problem existed. Our first interim engineering report states that formulation 3 loses approximately one-half of its 1000 F flexural strength after exposure for 100-hours at 1000 F; there is a much smaller loss in laminates based on formulation 33Y3. However, these were not strong originally, and they were hardly worth considering. These first attempts showed us that we had a problem with long term aging of which we were not previously aware. We were, therefore, anxious to determine if laminates based on formulation 3-6, which gave us the highest flexural strengths (approaching 25,000 psi), would also deteriorate upon long term exposure at 1000 F. Samples for flexural testing were made according to the directions given in the first interim engineering report, which describes both the binder and sample preparation.[1]

Before we discuss the laminate flexural strengths, we will first discuss sample uniformity or, more correctly, non-uniformity. This has hounded us throughout the program, and it is most evident in the samples based on formulation 3-6 which produces the highest strengths. Any aberations in the binder or laminate preparation is revealed by a more drastic change in strength. Formulations for the three binders are given on Page 28a in Table V .

On the brighter side, the large differences in sample-to-sample strength does not appear to be due to some unknown factor. It was easy to visually discern which samples would be good and which would be poor. Sample preparation technique apparently is the answer. We feel that greater care in winding may eliminate most of these deviations.

Another reason that the sample-to-sample discrepancy is accentuated with formulation 3-6 is the high viscosity of this binder. Unless constant slow agitation of the binder is

TABLE VI

FLEXURAL STRENGTH OF LAMINATES

(BASED ON ALUMINUM PHOSPHATE BINDERS)

REINFORCED WITH 150 4/3 SILICA FIBER YARN

TEST CONDITIONS	FLEXURAL STRENGTH PSI Formulation			
	3	3 3Y3		3-6
Room Temperature	10,700	4,800	Hi	14,400
			Av	8,800
			Lo	6,200
RT after ½ hr. at 1000 F	4,800	4,800	Hi	10,000
			Av	8,200
			Lo	6,800
RT after 25 hrs. at 1000 F	3,100	4,400	Hi	4,800
			Av	4,300
			Lo	3,100
RT after 100 hrs. at 1000 F	2,600	5,200	Hi	4,900
			Av	3,800
			Lo	2,800
1000 F after ½ hr. at 1000 F	15,200	9,100	Hi	24,700[2]
			Av	19,100
			Lo	10,000
1000 F after 25 hrs. at 1000 F	9,800	8,400	Hi	15,100
			Av	11,200
			Lo	7,700
1000 F after 100 hrs. at 1000 F	7,900	6,800	Hi	14,300
			Av	11,200
			lo	7,900

1 - Each data point is an average of 5-6 samples.
2 - 3 out of 6 samples over 22,000 psi.

maintained, the silica yarn will "tunnel through" the viscous binder and pick up little or no binder. Knowing this condition and taking proper precaution, we hope to minimize this cause of sample non-uniformity.

Because sample non-uniformity is present, data is listed as high, average, and low. In Table VI, on Page 29a we have presented the previously obtained flexural strength data for laminates based on formulations 33Y3 and 3 for comparison with the new data on formulation 3-6.

These data show that we have, in effect, duplicated the exploratory work which we did under the contract for the Bureau of Weapons, Department of the Navy. Silica fiber laminates based on binder formulation 3-6 (containing asbestos) are best by far. The fact that we have been able to duplicate our previous work is reassuring. More significant is that we approach the 1000 F goals for short duration, but we fall far short of the goals on long term aging. From previous experience with this system, we were aware of the more drastic drop in room temperature strength even after short exposure to elevated temperature. These new data verifies this, and it shows longer exposure leads to even greater loss of room temperature flexural strength.

The greatest problem in silica fiber-reinforced aluminum phosphate laminates does not lie in its electrical properties, but it occurs in its physical strength properties and its instability to a continued high temperature environment. We must find means to improve the physical strength and means to maintain strength at 1000 F and at room temperature after aging. Even the best material, silica fiber-reinforced formulation 3-6 which approaches 25,000 psi at 1000 F for short term - loses nearly 50% of its strength at 1000 F after exposure for 100-hours at 1000 F. There is an even more drastic drop in strength between the initial room temperature strength after exposure to elevated temperatures.

Even though this easily processed inorganic materials system shows a marked decline in strength after exposure for long periods at elevated temperature, any plastic or semi-

organic system would be completely destroyed under similar circumstances. This does not mean that we can ignore the obvious faults of this inorganic system, and every effort must be made to upgrade the physical properties and thermal stability of the system. It does mean, however, that there does exist an inorganic material having suitable microwave transmission properties. It can be made in complex shapes with simple tooling, and it does possess at least 10,000 psi flexural strength after 100-hours exposure at 1000 F. Even with these confining physical properties, there may be some applications where this minimal material could be used. One such instance might be in the high temperature radome or high temperature electrical area where the environmental temperatures are just beyond the capabilities of reinforced plastics or where the size or complex shape precludes the use of conventional ceramic systems.

The loss in strength of these laminates is probably due to the changing nature of the aluminum phosphate binder. As originally made, the binder is a relatively extensible glassy bond. It changes with temperature (to a more crystalline brittle material) by the loss of chemically bound water. The progressive reduction in binder elongation means that the reinforcing fibers cannot be loaded to their full strength. The brittle bond breaks before the full load can be applied to the reinforcing fibers.

The reinforcing silica fiber itself degrades after long term exposure at 1000 F. This was learned in our original work for the Bureau of Weapons.[1] Nevertheless, this may not be the major source of difficulty in the laminate system as the binder - not the fibers - appears to break in all cases. However, the fibers do appear to be much more brittle after the long term aging. The asbestos fibers in formulation 3-6 undoubtedly embrittle due to the loss of water after long term aging, and therefore this embrittlement probably contributes to the lower laminate strength.

CONCLUSIONS

1. Data on the short term flexural strength (of the silica fiber-reinforced aluminum phosphate systems) at room temperature and at 1000 F presently being evaluated, essentially reproduce the exploratory work for the Bureau of Weapons, Department of the Navy.

1 - Development of inorganic binders NOas 58-850C.

2. Even the highest strength laminates suffer a 40-45% drop in 1000 F flexural strength after 100-hours exposure to 1000 F, and room temperature strength loss of 55-60% occurs after similar aging at 1000 F.

3. Much of the loss in strength after high temperature aging is probably due to chemical changes in the phosphate bond which make the binder less extensible.

4. The silica and asbestos fibers also degrade, and this contributes to the loss of laminate strength after prolonged high temperature exposure.

5. Future work must be directed toward overcoming these difficulties.

6. Even with its physical limitations, there may be applications where this system's unique electrical and potential processing advantages may make it the only candidate.

RECOMMENDATIONS

1. High modulus fibers must be investigated as a reinforcement, for even with the present relatively inextensible binders, a higher modulus reinforcement would accept a greater load. This would undoubtedly give us the higher strengths we seek. The commercial availability of such high modulus fibers, in any quantity, is unfortunately in doubt. Aluminum oxide fibers are being made in short lengths as are several other types of fibers. Therefore, our present investigation will be limited to the use of such short fibers, for it is doubtful that continuous lengths of high modulus fibers will be available in time for use in this contract.

2. Studies should be initiated to obtain a more extensible high temperature binder. We shall attempt to do such things as we can with our present binder system to perhaps extend the flexural strength range into the 30,000-40,000 psi range. This might be accomplished by means such as the inclusion of glassy fillers, typically represented by our studies of glass and silica microspheres in the binder.

While this may enable us to raise the overall flexural strength, it is doubtful that this will result in obtaining permanent high temperature flexural strength, since the changing nature of the basic phosphate binder at high temperature continues to function even with these extensible materials present. Moreover, the problem of making an extensible binder actually is a much more fundamental research effort that we feel is beyond the scope of the present project. A study of the dehydration of the aluminum phosphate binder at elevated temperatures is needed, followed by a study of methods for dehydration prevention such as the substitution of more thermally stable groups for hydroxyl groups. It is possible that the reaction of organo-aluminum compounds with P_2O_5 might also hold some promise.

3. The addition of asbestos fiber to formulation 3-6 significantly upgrades the short term flexural strength of the laminate, but asbestos has temperature limitations (650-700 F). It would, therefore, seem wise to look for other more thermally stable fine diameter mineral fibers that would perform the same function as the asbestos does in formulation 3-6. There are not very many materials in this category. One of the most intriguing to us is a mineral called palygorskite, also known as mountain leather. It is a sort of second cousin to asbestos, having definite fiber properties but much higher temperature stability than asbestos. Work is underway using this material.

ACKNOWLEDGEMENTS

The authors wish to thank T. Collins of the Materials and Processes Laboratory for the flexural testing of ceramic laminates during this quarter.

UNCLASSIFIED