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EFFECT OF INORGANIC FILLERS ON COEFFICIENT OF THERMAL EXPANSION OF POLYMERIC MATERIALS

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EFFECT OF INORGANIC FILLERS ON COEFFICIENT OF THERMAL EXPANSION OF POLYMERIC MATERIALS

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EFFECT OF INORGANIC FILLERS ON COEFFICIENT OF THERMAL EXPANSION OF POLYMERIC MATERIALS

INTRODUCTION

Literature lists the thermal expansion of a number of materials over various temperature ranges. Although the thermal expansion of various commercial polymeric materials is available, very little data is available on the thermal expansion of filled polymeric systems. In addition to the lack of empirical data on filled polymeric systems, very little work has been accomplished towards developing mathematical formulas for predicting the thermal expansion of filled polymeric systems based on thermal expansion and other physical properties of their components. Some research performed in this direction by National Bureau of Standards (1) approaches the problem by considering the equilibrium stress-strain conditions between filler particles and polymeric matrix. This treatment fails to account for neither relaxation mechanisms nor possible effects of filler size and shape, while polymer theory and practice indicate that these factors may be extremely important. Hence the purpose of this study and experimentation was to determine to what extent the coefficient of thermal expansion of a cured filled polymeric system can be predicted from the coefficient of thermal expansion of its constituents.

SUMMARY

A semiempirical approach based upon the concept of the mixture rule (2) was utilized to predict the linear thermal expansion coefficients of three different filled polymeric systems. Theoretical curves were computed from the relationship:

$$\alpha^{c}_{s'} = V_p \alpha^{c}_{p'} + V_f \alpha^{c}_{f'}$$

where V_p & V_f = the volume fraction of the polymer and filler respectively; and

$\alpha_{p'}$ & $\alpha_{f'}$ = the linear thermal expansion coefficient of the polymer and filler respectively; and

c is a constant which may vary from -1 to +1, depending on the particular system.

Coefficients of linear thermal expansion were determined experimentally on 75 specimens representing 15 polymer-filler combinations. Data points obtained were plotted along with theoretical curves based on the mixture rule calculations described above.

Comparison of actual and calculated coefficients of linear expansion for the polymer-filler systems indicates that the calculated values can be used within certain limits for predicting coefficient of linear expansion. Differences in actual and calculated values are explained by the fact that the formula does not take into account the effect of filler particle configurations and relaxation processes in the polymer matrix as affected by time and temperature.

EFFECT OF INORGANIC FILLERS ON COEFFICIENT OF THERMAL EXPANSION OF POLYMERIC MATERIALS

OBJECT

To determine to what extent the coefficient of thermal expansion of a cured polymer-filler system can be predicted from the coefficients of thermal expansion of its constituents.

EXPERIMENTAL TECHNIQUES

Specimen Preparation - Epon 828 specimens were prepared by adding the filler (predried at 110°C) to warm Epon 828 resin (65°C) and adding 15 parts of melted metaphenylenediamine (63.5°C) per 100 of the resin. Specimens of approximately .425" in diameter were cast in a steel mold which had been previously coated with Dow Corning 671 to serve as a mold release. The cure was applied in two stages.

1. A two hour cure at 80°C
2. A one hour postcure at 200°C

Cured specimens were removed and machined to about 4" in length.

Paraplex P-43 specimens were prepared by mixing the various filler materials in the polyester resin at room temperature and then adding 0.5 percent benzoyl peroxide to the filled polymer based on the weight of the unfilled polymer. The P-43-filler mixtures were then cast in the mold used to prepare the Epon 828 specimens. The cure applied was as follows:

1. 16 hours at 60°C
2. 1 hour at 80°C
3. 1 hour at 100°C
4. 1 hour at 120°C

Cured specimens were removed and machined to about 4" in length.

Epon 828 - Versamid 115 specimens were prepared by mixing the filler materials into the warm (65°C) Epon 828 resin. Based upon the Epon 828 resin weight, an equal amount of Versamid 115 was added and blended with the filled resin at 50°C. The mixture was then poured into 20 x 150 millimeter

glass test tubes which had been coated on the inside with Dow Corning DC-4. Air was expelled by centrifugation at 1500 RPM for 10 minutes. This was not sufficient to cause the filler materials to settle out. Cure was applied in three stages.

1. 8 hours at room temperature (24°C)
2. 1 hour at 100°C
3. 1 hour at 120°C

The cast specimens were machined to .425" in diameter by about 4" in length. Several of the specimens were machined to 2 inches in length after the original specimens were broken during the machining operation. All specimens prepared for this study were allowed to condition for at least seven days at 25°C and 50 percent relative humidity and were measured to the nearest .001 of an inch by a micrometer, before being tested.

APPARATUS	Source
Potentiometer, Model 3087	Gray Instrument Company Philadelphia, Pa.
Thermocouple Wire (28 gage copper - constantan glass fabric insulated)	Thermo Electric Co., Inc. Saddle Brook, N. J.
Hot Plate (600 watt - Model 1900 110 VAC	Thermo Electric Mfg. Co. Dubuque, Iowa
Powerstat (7.5 amps - 0-140 volts - 50-60 cycles)	The Superior Electric Co. Bristol, Conn.
Voltmeter (A.C. - Model 904 No. 4986 - range 150V Ohms - 7026 -25 - 500 cycles)	Weston Electric Company Newark, N. J.
Stirring Motor	E. H. Sargent & Company Chicago, Ill.
Dewar Flask (4300 cc)	E. H. Sargent & Company
Dilatometer (quartz tube)	Tinius Olsen Testing Machine Company Willow Grove, Pa.
Stripheater (500 Watt Levitron)	Refinery Supply Company Houston, Texas

MATERIALS

	Source
Epon 828, Resin (Lot 9AHJ3)	Shell Chemical Company New York, N. Y.
Paraplex P-43 Resin (Lot K98)	Rohm and Hass Company Philadelphia, Pa.
Versamid 115, Resin	General Mills Chemical Division Kankakee, Ill.
Silicone Fluid S.F. 81 (50)	General Electric Corp. Waterford, N. Y.
Aluminum Powder (325 mesh - MD-105)	Metals Disintegrating Co. Elizabeth, N. J.
Aluminum Oxide (α- fused 320 mesh)	The Carborundum Company Electro-Minerals Div. Niagra Falls, N. Y.
Lithium Aluminum Silicate (325 mesh - Lithafrax 2123)	The Carborundum Company Refractories Div. Latrobe, Pa.
Titanium Dioxide (passes through 325 mesh screen - avg. size 0.35 microns - Titanox RA-10)	Titanium Pigment Corp. New York, N. Y.
Calcium Carbonate (passes through 325 mesh screen - Calwhite)	C. P. Hall Company Chicago, Ill.

DETERMINATION OF COEFFICIENTS OF THERMAL EXPANSION

The equipment used for this purpose was a Tinius Olsen quartz tube dilatometer consisting of two telescoping fused quartz tubes, the inner tube which rests on the specimen being shorter than the outer tube. The expansion was measured by a dial gage, graduated to 0.0001 in., and fastened to the outer quartz tube. The foot of the dial gage rests on the inner tube which in turn rests on the specimen. The temperature was varied by immersing the dilatometer into a silicone fluid S.F. 81 (50) - dry ice bath contained in a Dewar flask in which an electric stirrer and Powerstat controlled strip heater were immersed. The S.F. 81 (50) bath was cooled down below -50°C and the Powerstat regulated such that a temperature rise of approximately 2°C per minute was attained. Temperature of the specimens was measured by means of a Gray Model E-3087 poten-

tiometer (cold junction compensated) connected with calibrated copper-constantan thermocouples which were attached to the approximate center of the specimen. Simultaneous measurements of temperature and extension were obtained by setting the potentiometer at predetermined points and recording the extension when the galvanometer of the potentiometer reached the zero point, i.e., no deflection was produced by opening or closing the circuit. The coefficient of thermal expansion was computed from the standard calculation:

$$\alpha = \frac{\Delta L}{\Delta T \cdot L} \qquad (1)$$

ΔT = Temperature difference over which change was measured (100°C for Paraplex P-43 and Epon 828, Versamid 115, 150°C for Epon 828)

ΔL = Change in length over the temperature range

L = Length of the specimen at room temperature

Results thus obtained were corrected for the expansion of fused-quartz by adding the coefficient of linear thermal expansion of fused quartz, $0.5'' \times 10^{-6}$/deg, C. Since plastic flow and changes in water content of the specimens affect the results, this rapid method, although it does not insure a completely uniform temperature, appears to present a better picture of changes taking place in the specimen which might be masked by long periods at elevated temperatures above room temperature as in the case of conventional test methods. Results obtained from this method were checked by standard ASTM methods and the two compared very well. A method similar to that described above was reported in a paper by Turner (1). Accordingly, it appears that Turner's method compares favorably with classical precision methods.

SEMIEMPIRICAL APPROACH TO PREDICTING COEFFICIENT OF THERMAL EXPANSION OF FILLED POLYMER SYSTEMS

Since the stress analysis theory for explaining the effect of fillers on the coefficient of thermal expansion of filled polymer systems has not been fully substantiated by later research (2), it was believed that the mixture rule (3) which has been found to apply fairly well to such physical properties as conductivity, permeability and permittivity, can also, within limits, be utilized to predict

the thermal expansion coefficient of polymer filler systems. If we assume the consistuents of such a system to occupy a volume fraction V_i and to have a cubical thermal expansion coefficient α_i, the cubical thermal expansion coefficient α_s, of the system is given by

$$\alpha_s^c = \sum_i V_i \alpha_i^c \qquad (2)$$

where c is a constant which may vary from -1 to +1 depending on the particular system. Thus for a binary system:

$$\alpha_s^c = V_p \alpha_p^c + V_f \alpha_f^c \qquad (2a)$$

where V_p & V_f = the volume fraction of the polymer and filler respectively; and

α_p & α_f = the cubical thermal expansion coefficients of the polymer and filler, respectively.

For an isotropic polymer system the cubical expansion coefficient is approximately 3 times that of the linear coefficient.

Hence if $\alpha_{p'}$ & $\alpha_{f'}$ = the linear thermal expansion coefficient of the polymer and filler respectively,

then the formula applied to linear coefficient of thermal expansion would be:

$$\alpha_{s'}^c = V_p \alpha_{p'}^c + V_f \alpha_{f'}^c \qquad (3)$$

If we assume c to be small and use the first two terms in expanding the exponentials in equation (2) when applied to linear coefficient of thermal expansion, we obtain for a binary system:

$$\ln \alpha_{s'} = V_p \ln \alpha_{p'} + V_f \ln \alpha_{f'} \qquad (4)$$

DISCUSSION OF RESULTS

Application Of The Mixture Rule

In Figures 1 - 6 the mixture rule equation has been plotted for twelve binary systems with Epon 828 epoxy, Paraplex

P-43 polyester and Epon 828-Versamid 115 (epoxy - polyamide resins) as the base polymers. For each system, a pair of curves has been drawn with the upper straight portion and the lower curved portions representing the theoretical values when the exponent c is + 1 or -1, respectively. The experimental values of the (various fillers) at the filler percent levels shown in the Table have been plotted except for Lithafrax 2123. The theoretical curves for these Lithafrax 2123 filled systems have such a wide variation as to appear impractical as a method for predicting thermal expansion. As may be observed in Figures 1 - 6, practically all of the experimentally determined values fall within the areas enveloped by their respective theoretical upper and lower limits. Very slight deviations from the theoretical curves are indicated by calcium carbonate and titanium dioxide filled Paraplex P-43 (polyester) system (Figure 4). In Figure 5 the slight deviation of aluminum oxide-Epon 828-Versamid 115 polymer-filler system may also be noted as well as that of calcium carbonate (Figure 6) in the same polymer system. These deviations are so slight as to be negligible; hence the experimental data does follow the theoretical curves.

In Figures 7 - 12 the volume fraction of the filled polymeric systems is plotted against the logarithm of the experimentally determined linear thermal expansion coefficients of the same filled polymer systems as shown in Figures 1 - 6. Experimental data agrees reasonably well with the theoretical curves computed per formula (4) for filled Epon 828 systems; however slight deviations are noted in the filled Paraplex P-43 and filled Epon 828-Versamid 115 systems, with the greatest deviations of the experimental data from the theoretical curves being noted in the aluminum oxide and calcium carbonate (Figures 9 and 10) filled Paraplex P-43 systems and aluminum oxide and Lithafrax 2123 filled Epon 828-Versamid 115 systems (Figures 11 and 12). Since the Epon 828-Versamid 115 systems were quite viscous in nature, the possibility of air entrapment might well have resulted in the slight deviations from the theoretical values noted.

The anomalous behavior of the 4.9 and 9.1 percent concentrations of aluminum oxide in all three polymeric systems would appear on first sight to be an experimental error in determining thermal expansion; however, these systems were checked twice and the probability of this type of error was ruled out. The most logical explanation would seem to be the possibility of air entrapment in these lower concentrations of filler as it is felt that some air entrapment could not be avoided regardless of the care observed in casting the specimens. Air entrapment might markedly effect the thermal expansion of

filled polymer systems. Even though air may be present in slight amounts, it might well escape in higher concentration of filler material where the probability of increased porosity is likely.

Evaluation Of The Mixture Rule As A Means Of Predicting Thermal Expansion

A search of the literature shows that Turner's (1) work proposes a method for predicting thermal expansion of filled polymer systems based upon the theoretical Hookean stress-strain conditions between filler particles and polymer base. This approach appears limited in that it does not account for small amounts of air entrapment or the relaxation mechanisms or particle size and shape. Similar work by Carey (3) using an epoxy system with various fillers did not entirely substantiate the work by Turner but more closely resembles the curve Turner indicated would be found if each component produced only an additive effect on the total thermal coefficient of expansion of the resin-filler system.

For these reasons, a modification of the mixture rule (2) which would include the volume fraction and thermal expansion of the components of a polymer-filler system seemed plausible as a method for predicting thermal expansion of a filled polymeric system. As may be observed from the graphic representation (Figures 1 - 6) the mixture rule can be utilized in predicting thermal expansion of a binary polymer-filler system and all the data obtained in this study very closely approach the areas enveloped by the theoretically computed curves for each polymer-filler system as shown. Although this mixture rule method may be used to predict the thermal expansion of binary polymer-filler systems within certain limits a treatment on a more fundamental basis would possibly be better. It is well known that the stress-strain-time behavior of a polymeric material is determined by an instantaneous elastic, a retarded elastic and a viscous response and the contributions from the latter two processes are proportional to e^{-t/λ_i} where t is the stress action time and λ_1 the relaxation time for the particular process i. Local stresses around the filler particles persist for appreciable times during a determination of thermal expansion; hence, relaxation processes in the polymer matrix in the vicinity of the filler particles play a very important role. The general behavior of the specimen will also be contingent upon any external stress field applied to the system. Thus it would appear that a theoretical approach should consist of a classical calculation of the stress conditions around various geometric configurations of filler particles and a

consideration of the compression relaxation taking place in the proximity of the particles as well as the associated changes in volume.

CONCLUSIONS

1. The thermal expansion of a cured polymer-filler system may be predicted from the coefficients of thermal expansion of its constituents by a modification of the mixture rule.

2. The mixture rule formula, however, fails to take into account particle configuration and the relaxation processes in the polymer matrix, but seems to be adequate for many applications.

TABLE

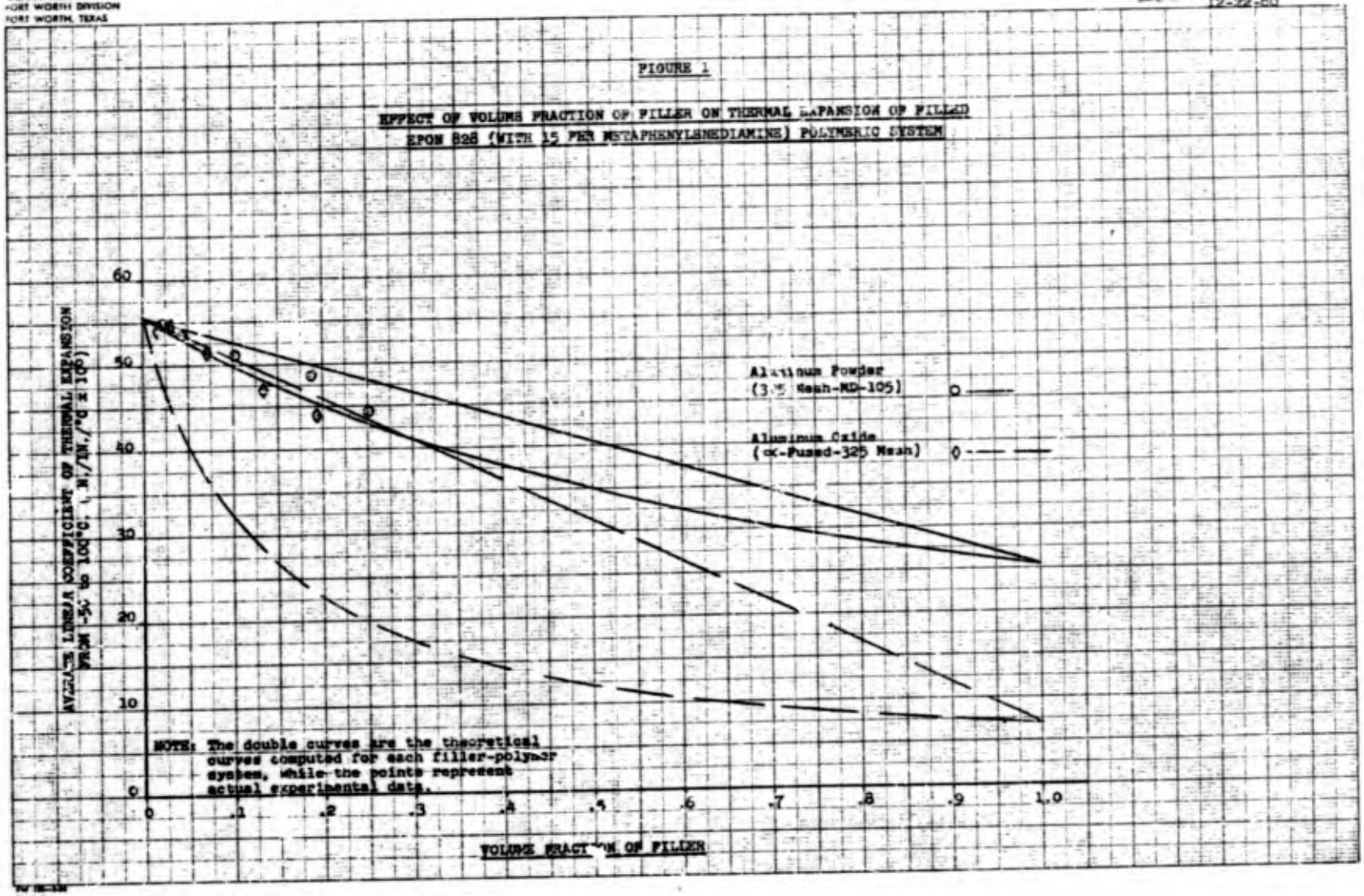
LINEAR COEFFICIENT OF THERMAL EXPANSION AND VOLUME FRACTION OF FILLER FOR EPON 828 WITH 15 PHR METAPHENYLENEDIAMINE, PARAPLEX P-43 AND EPON 828-VERSAMID 115 (50-50 RATIO) FILLED POLYMERIC SYSTEMS WITH AND WITHOUT THE INDICATED FILLERS

FILLER	EPON 828			PARAPLEX P-43			EPON 828 - VERSAMID 115		
	% Filler	Volume Fraction Filler	Thermal Expansion*	% Filler	Volume Fraction Filler	Thermal Expansion*	% Filler	Volume Fraction Filler	Thermal Expansion*
Aluminum Powder (325 Mesh-MD-105)	0		55.5 x 10^{-6}	0		61.6 x 10^{-6}	0		84.1 x 10^{-6}
	4.8	.0219	55.1	4.8	.0226	60.6	4.8	.0199	80.4
	9.1	.0416	53.6	9.1	.0439	58.3	9.1	.0388	79.2
	20.0	.100	51.0	20.0	.103	55.0	20.0	.0916	75.5
	33.3	.187	48.8	33.3	.187	48.5	33.3	.168	74.0
	42.9	.250	43.8	42.9	.257	45.8	42.9	.233	68.2
Aluminum Oxide (α-Fused-325 mesh)	4.8	.015	54.3 x 10^{-6}	4.8	.0158	58.6 x 10^{-6}	4.8	.0139	80.8 x 10^{-6}
	9.1	.029	54.6	9.1	.0309	60.8	9.1	.027	83.1
	20.0	.071	51.5	20.0	.0736	55.1	20.0	.065	81.8
	33.3	.133	46.9	33.3	.137	53.5	33.3	.122	70.5
	42.9	.192	44.0	42.9	.192	48.5	42.9	.174	66.3
Lithium Aluminum Silicate (325 Mesh-Lithafrax 2123)	4.8	.025	54.9 x 10^{-6}	4.8	.026	56.3 x 10^{-6}	4.8	.023	83.7 x 10^{-6}
	9.1	.048	53.0	9.1	.049	53.5	9.1	.044	81.8
	20.0	.112	47.5	20.0	.115	48.3	20.0	.105	75.0
	33.3	.202	42.8	33.3	.207	41.0	33.3	.187	66.5
	42.9	.276	35.9	42.9	.282	34.0	42.9	.257	60.0
Titanium Dioxide (Passes through 325 mesh average particle size 0.35 microns Titanox RA-10)	4.8	.014	54.6 x 10^{-6}	4.8	.0148	57.0 x 10^{-6}	4.8	.013	80.4 x 10^{-6}
	9.1	.028	52.8	9.1	.0289	56.0	9.1	.026	78.0
	20.0	.067	49.4	20.0	[illegible]	54.0	20.0	.061	77.2
	33.3	.126	45.7	33.3	[illegible]	49.0	33.3	.116	67.0
	42.9	.177	43.8	42.9	.183	45.0	42.9	.164	65.8
Calcium Carbonate (Passes through 325 mesh - Calwhite)	4.8	.022	54.1 x 10^{-6}	4.8	.0226	59.2 x 10^{-6}	4.8	.0199	83.8 x 10^{-6}
	9.1	.043	54.0	9.1	.0439	56.3	9.1	.038	80.5
	20.0	.100	49.2	20.0	.103	50.8	20.0	.092	73.0
	33.3	.187	42.5	33.3	.187	40.3	33.3	.168	67.3
	42.9	.250	38.3	42.9	.257	38.0	42.9	.233	61.8

* Thermal expansion was determined over the temperature range of -50 to 100°C for Epon 828 and -50 to 50°C for Paraplex P-43 and Epon 828-Versamid filled polymeric systems.

FIGURE 1

EFFECT OF VOLUME FRACTION OF FILLER ON THERMAL EXPANSION OF FILLED EPON 828 (WITH 15 PER METAPHENYLENEDIAMINE) POLYMERIC SYSTEM



NOTE: The double curves are the theoretical curves computed for each filler-polymer system, while the points represent actual experimental data.

FIGURE 2

EFFECT OF VOLUME FRACTION OF FILLER ON THERMAL EXPANSION OF FILLED EPON 828 (WITH 15 PHR METAPHENYLENEDIAMINE) POLYMERIC SYSTEM

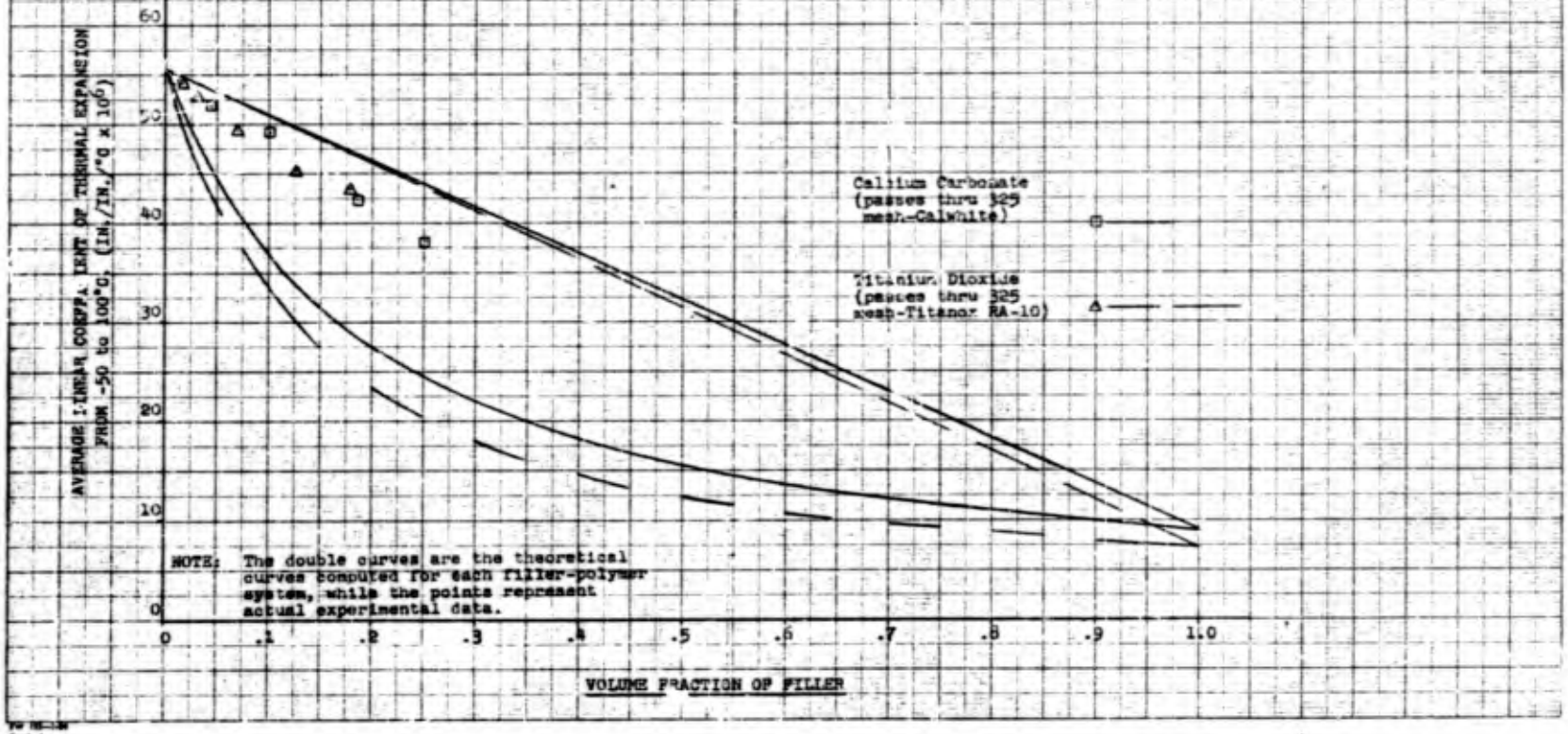


FIGURE 3

EFFECT OF VOLUME FRACTION OF FILLER ON THERMAL EXPANSION OF FILLED PARAPLEX P-43 POLYMERIC SYSTEM

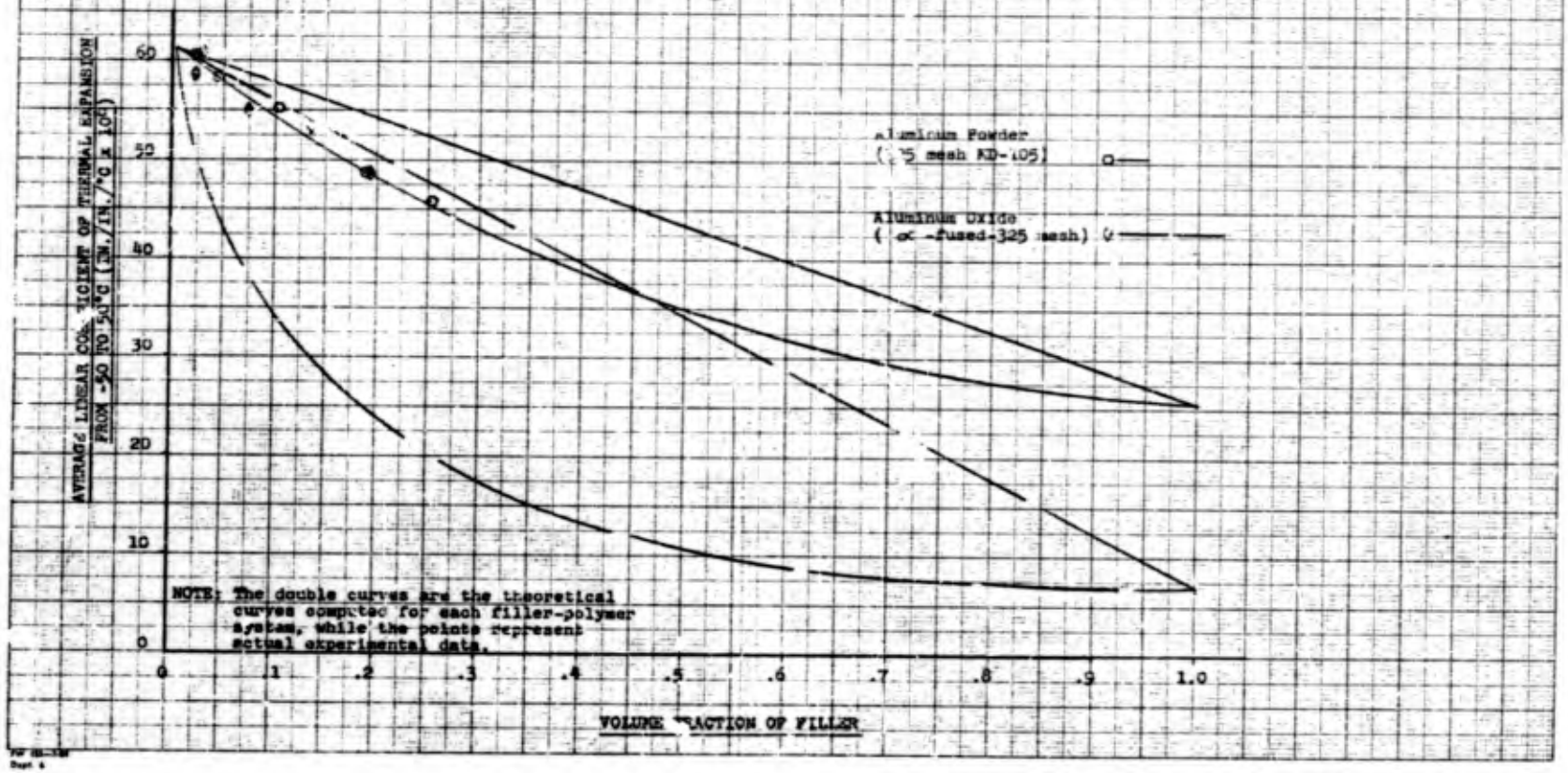


FIGURE A

EFFECT OF VOLUME FRACTION OF FILLER ON THERMAL EXPANSION OF FILLED PARAPLEX P-43 POLYMERIC SYSTEM

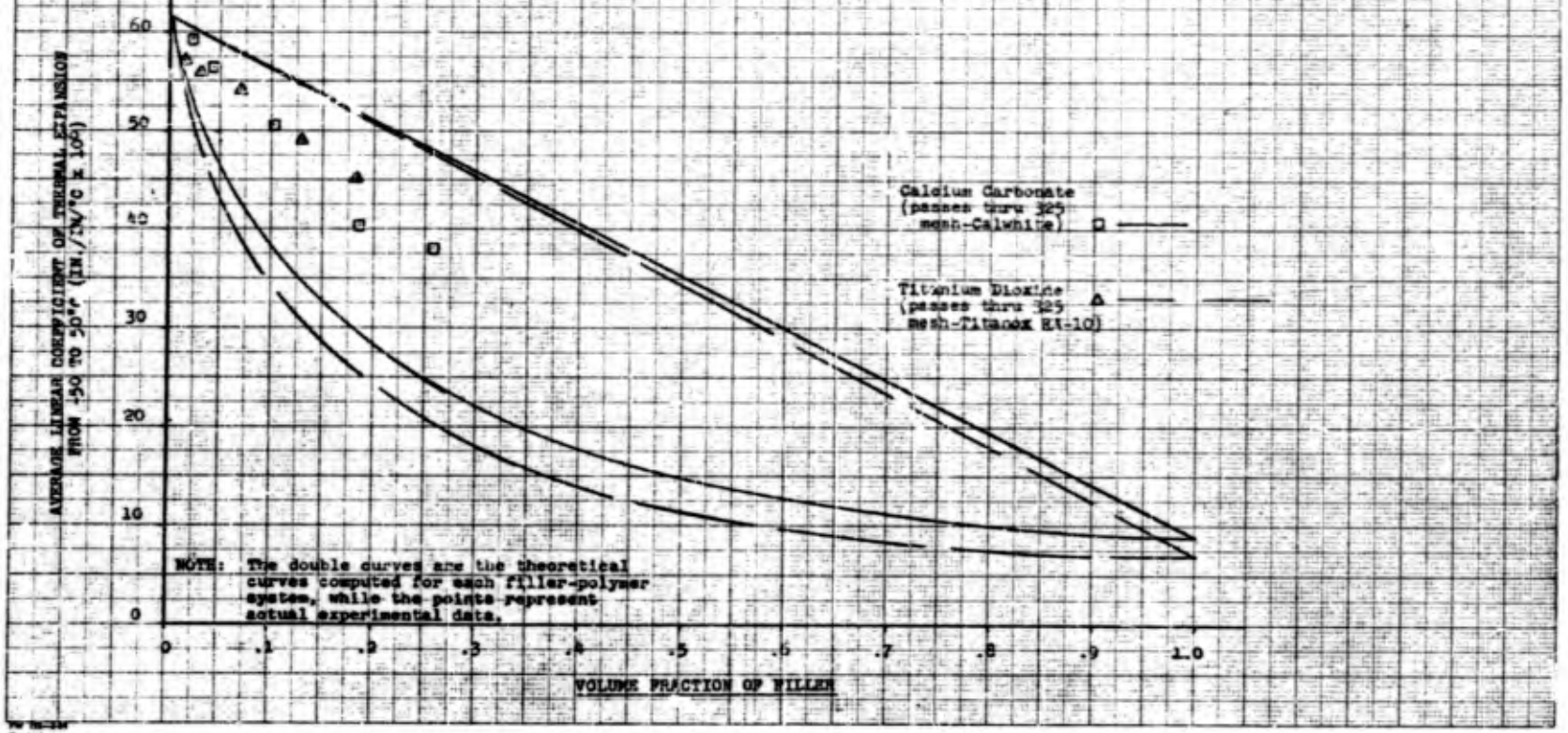


FIGURE 5

EFFECT OF VOLUME FRACTION OF FILLER ON THERMAL EXPANSION OF FILLED EPON 828 - VERSAMID 115 (50-50 RATIO) POLYMERIC SYSTEM

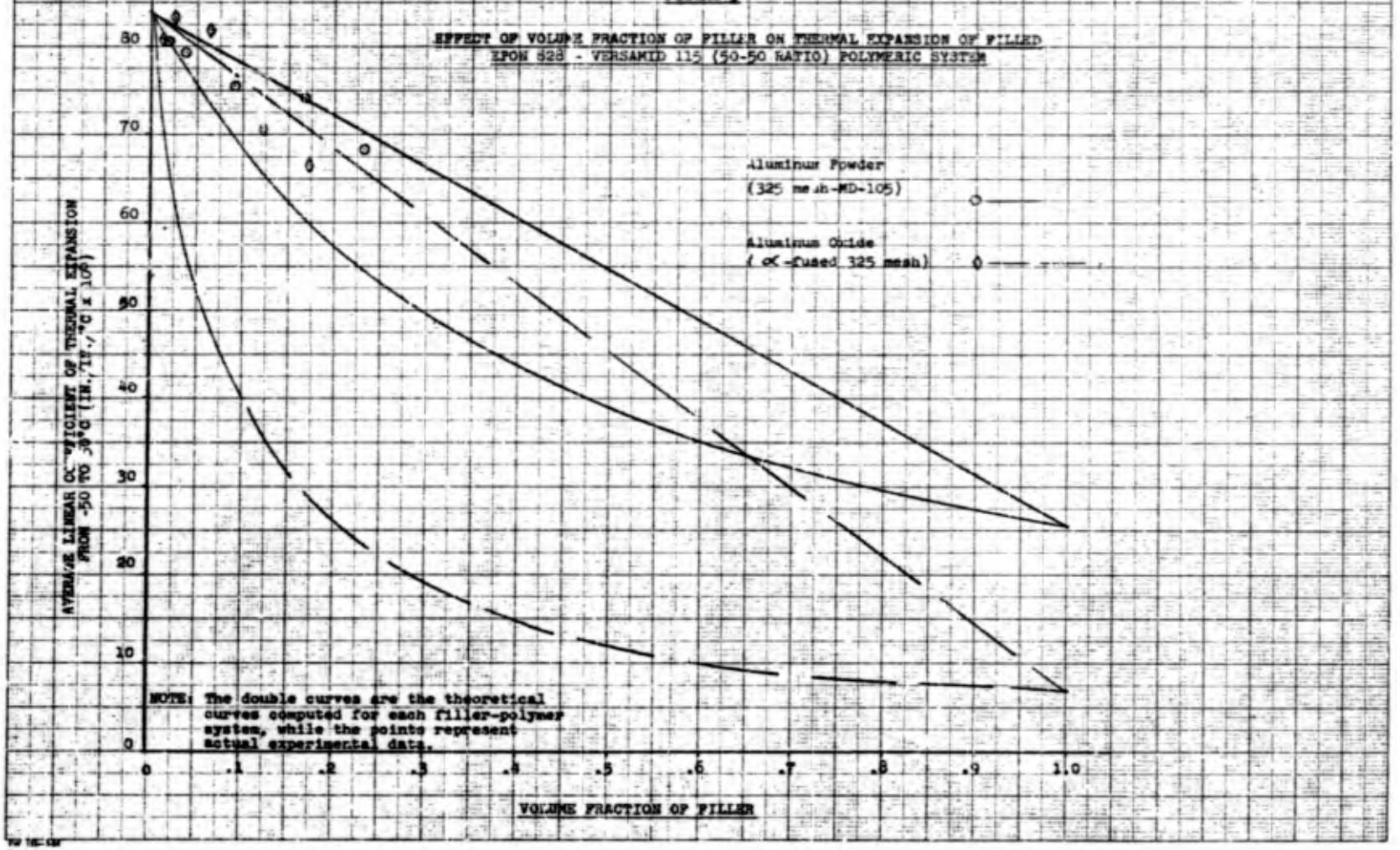


FIGURE 6

EFFECT OF VOLUME FRACTION OF FILLER ON THERMAL EXPANSION OF FILLED EPON 828 - VERSAMID 115 (50-50 RATIO) POLYMERIC SYSTEM

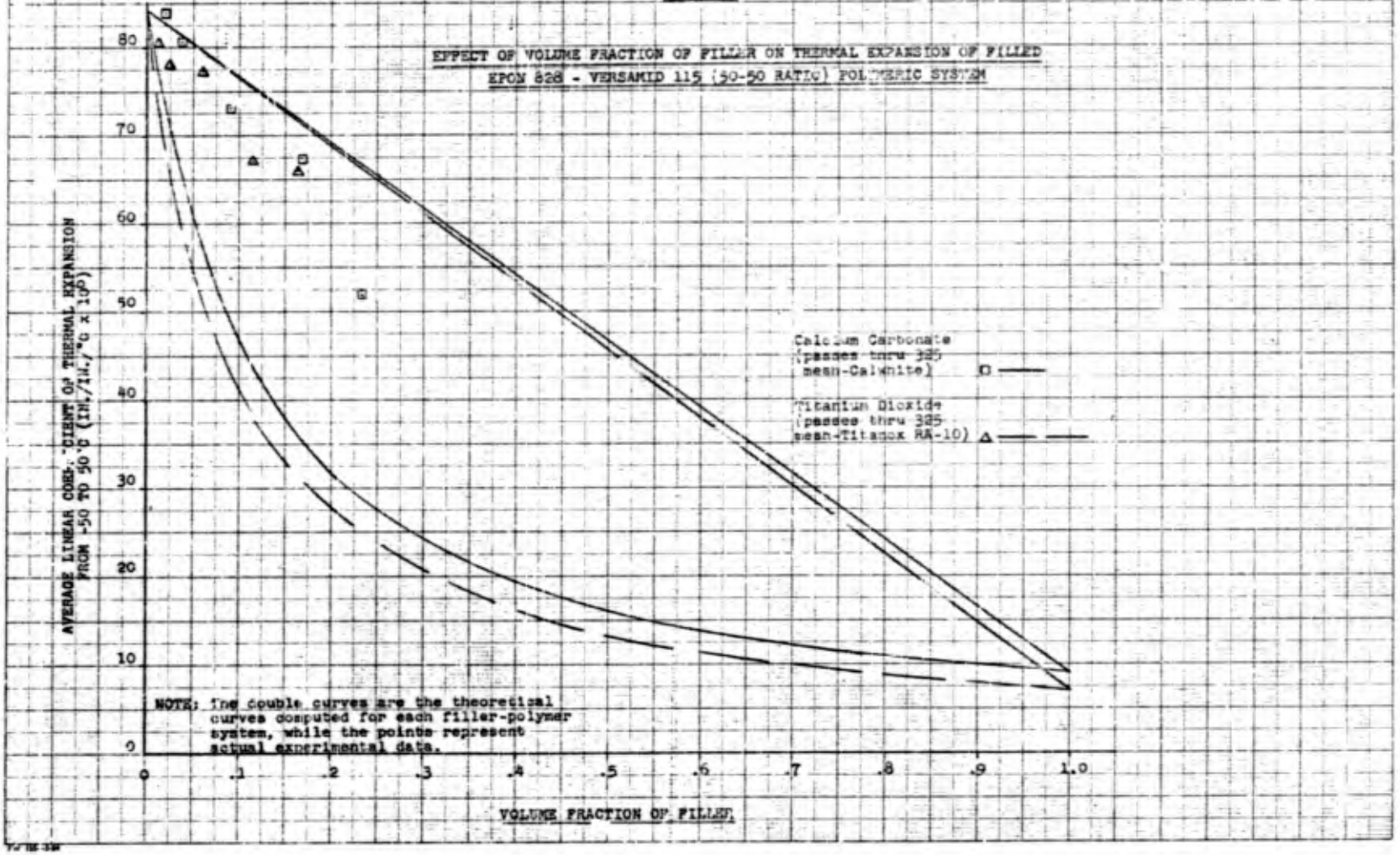


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FIGURE 7
EFFECT OF VOLUME FRACTION OF A FILLER ON THE LINEAR THERMAL EXPANSION COEFFICIENT OF EPON 828 WITH METAPHENYLENEDIAMINE AND THE INDICATED FILLERS

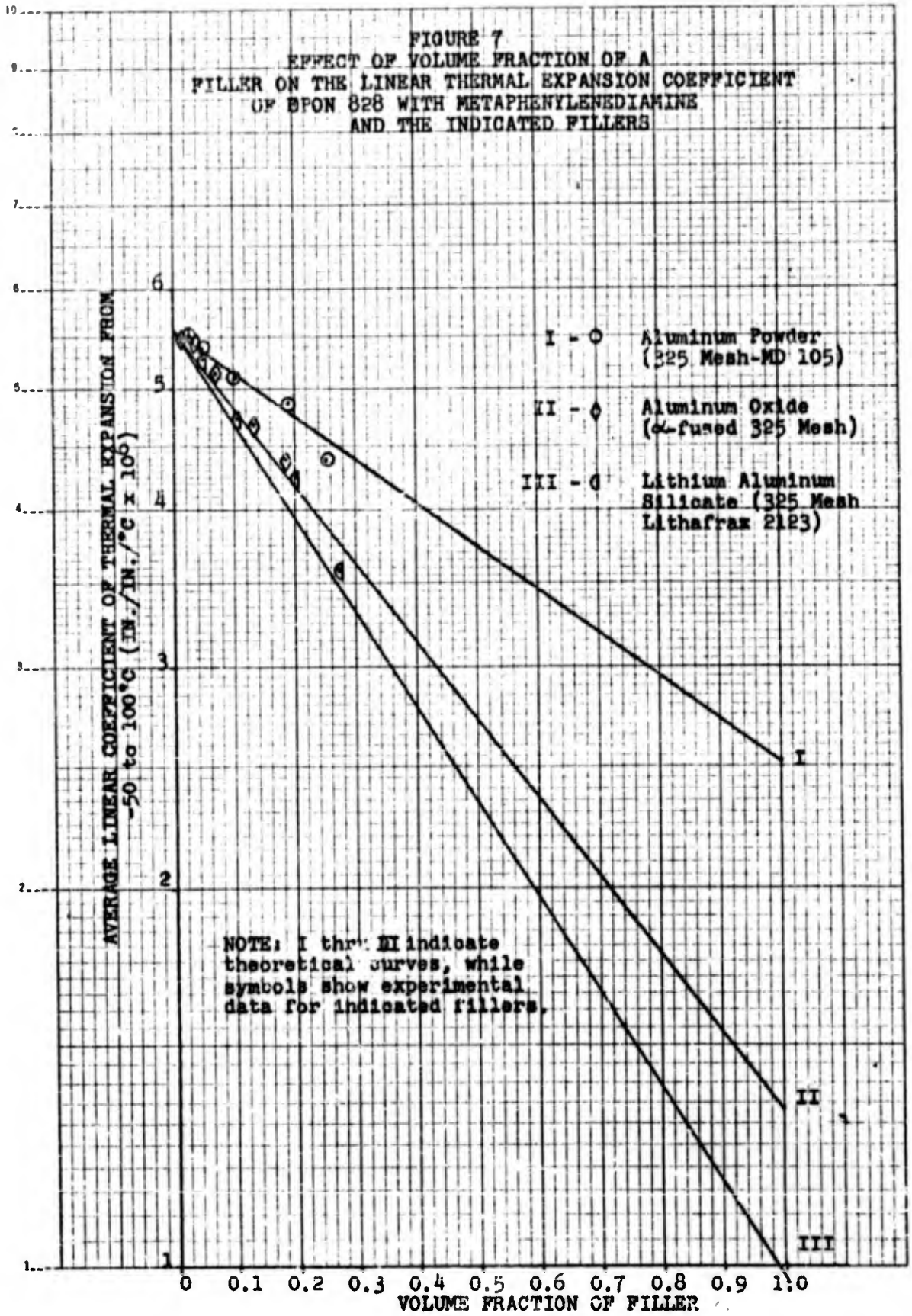


FIGURE 8
EFFECT OF VOLUME FRACTION OF A FILLER ON THE LINEAR THERMAL EXPANSION COEFFICIENT OF EPON 828 WITH METAPHENYLENEDIAMINE AND THE INDICATED FILLERS

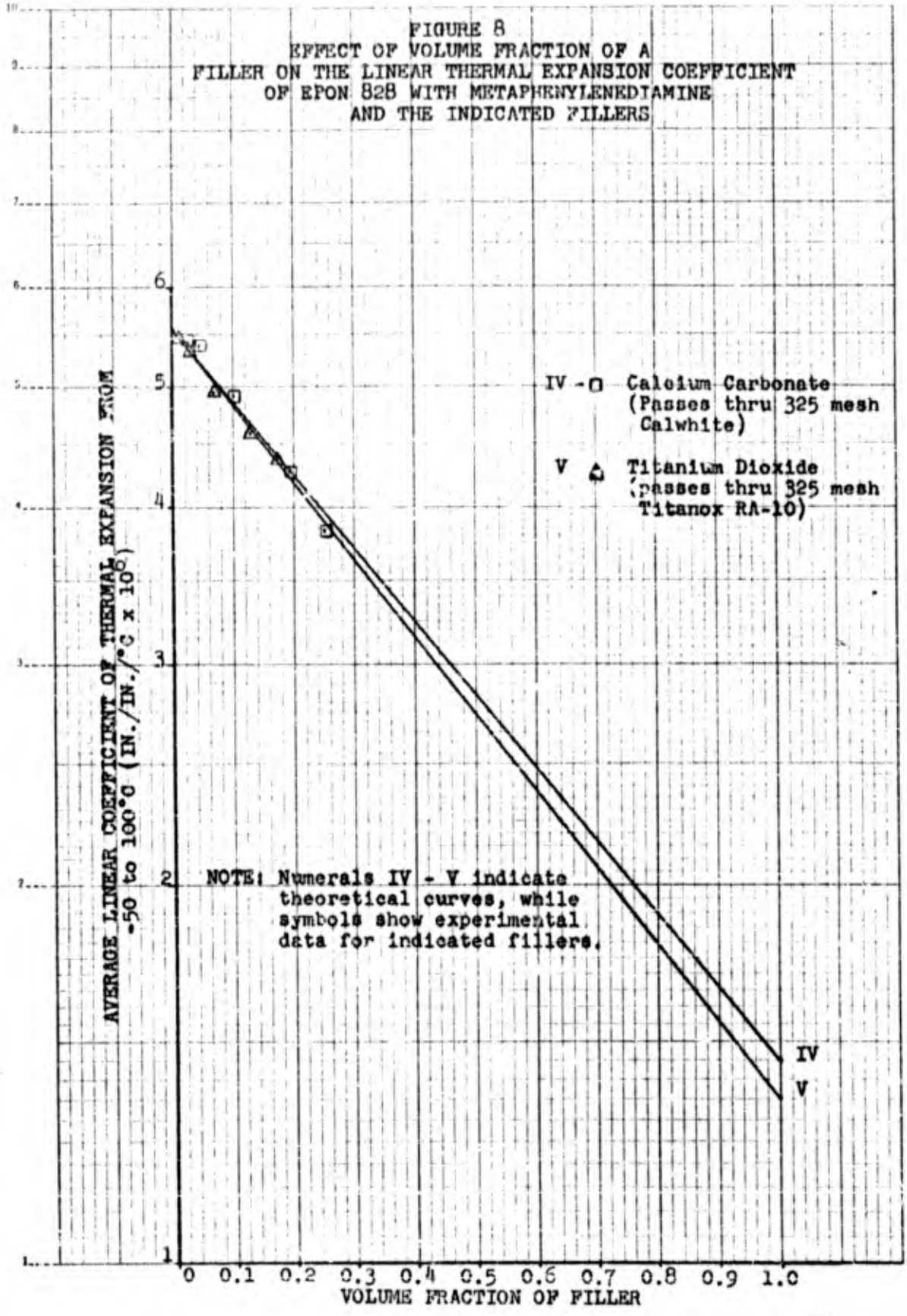


FIGURE 9
EFFECT OF VOLUME FRACTION OF A FILLER ON THE LINEAR THERMAL EXPANSION COEFFICIENT OF PARAPLEX P-43 WITH THE INDICATED FILLERS

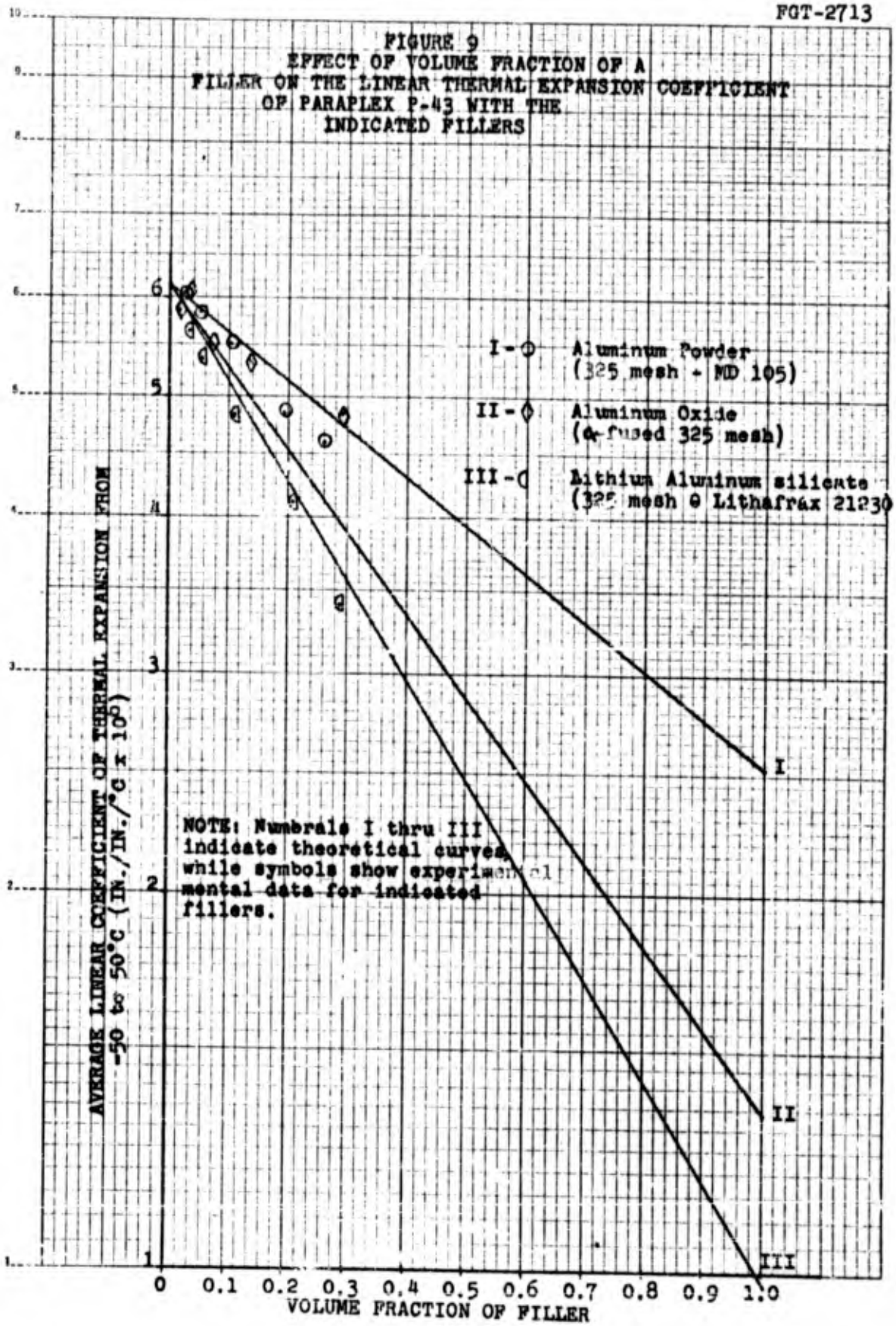


FIGURE 10
EFFECT OF VOLUME FRACTION OF A FILLER
ON THE LINEAR THERMAL EXPANSION COEFFICIENT
OF PARAPLEX P-43 WITH THE
INDICATED FILLERS

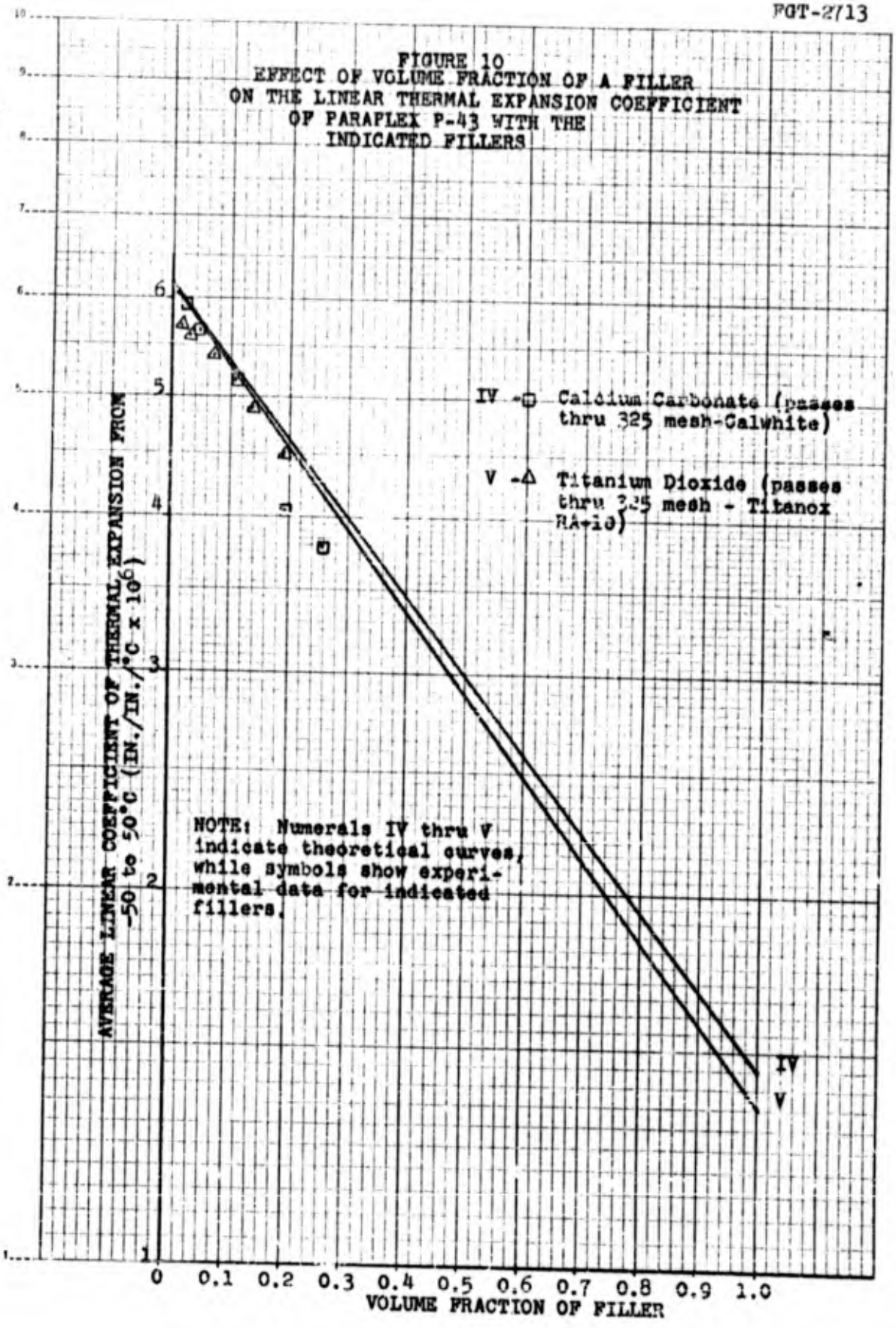


FIGURE 11
EFFECT OF VOLUME FRACTION OF A FILLER ON THE LINEAR THERMAL EXPANSION COEFFICIENT OF EPON 828 - VERSAMID 115 (50-50 RATIO) WITH INDICATED FILLERS

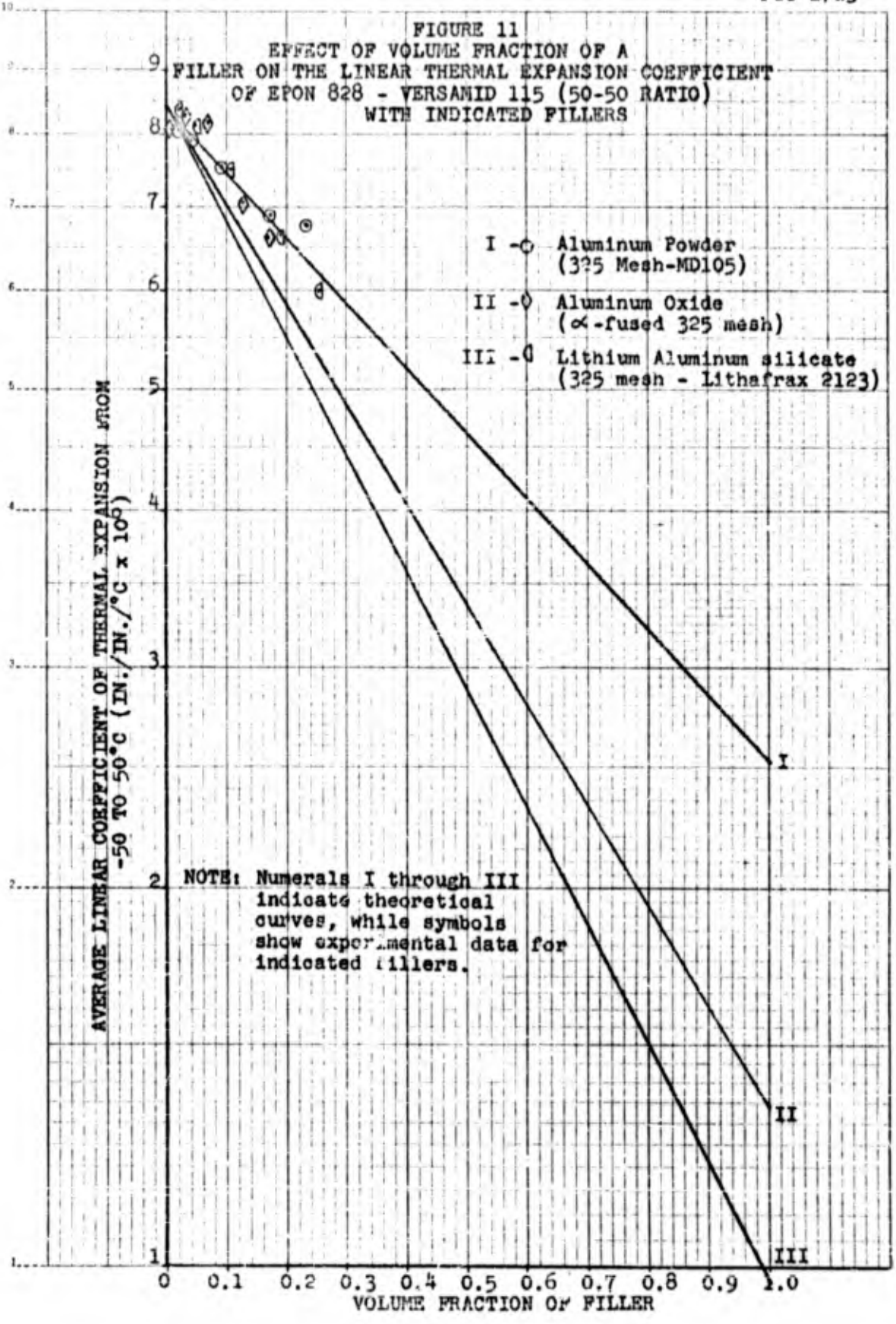
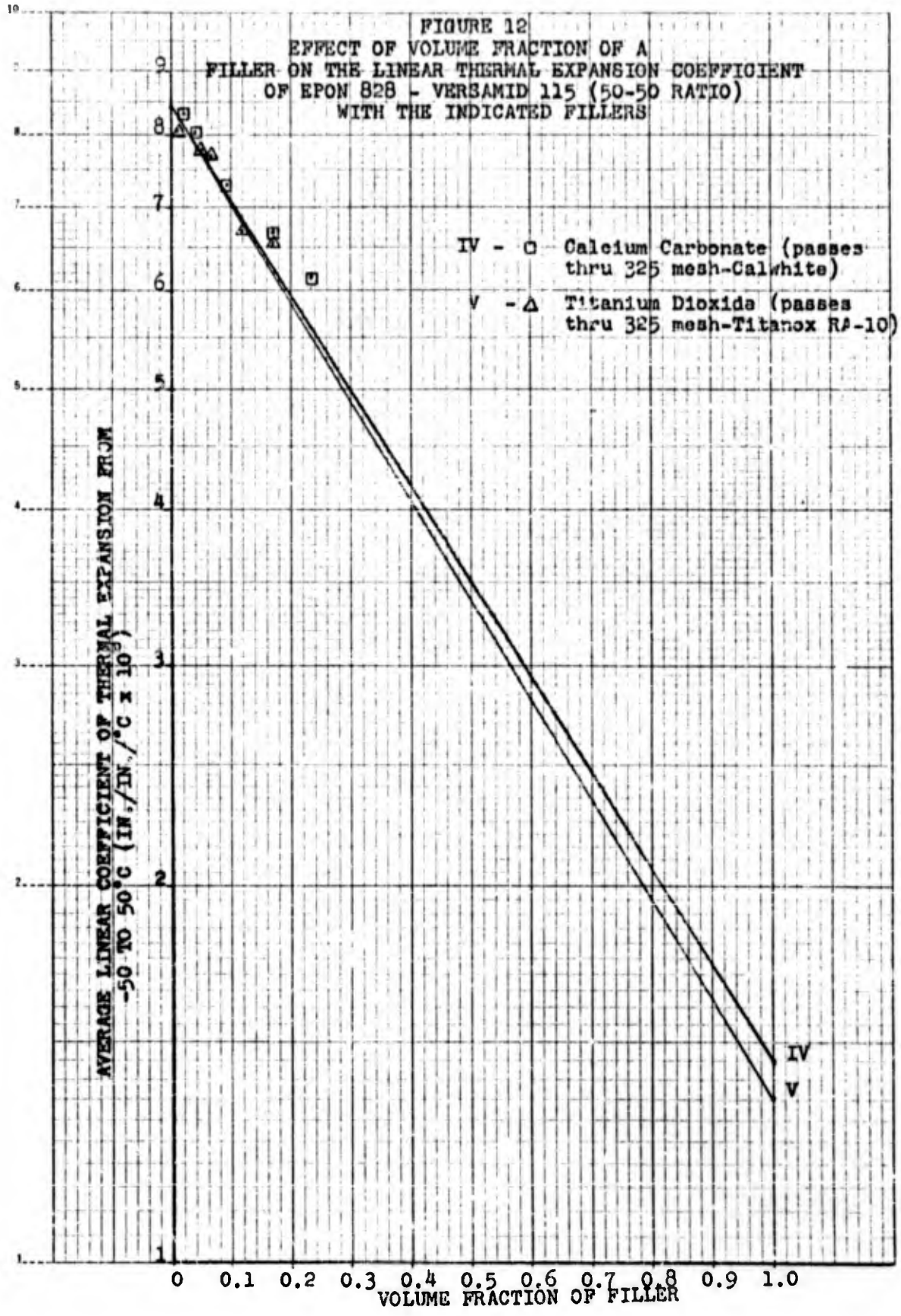


FIGURE 12
EFFECT OF VOLUME FRACTION OF A FILLER ON THE LINEAR THERMAL EXPANSION COEFFICIENT OF EPON 828 - VERSAMID 115 (50-50 RATIO) WITH THE INDICATED FILLERS



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