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WADC TECHNICAL REPORT 59-190
Part I
AD0226808

SYNTHESIS OF THERMALLY STABLE EPOXY RESINS FOR DIELECTRIC APPLICATIONS

Lee M. Kindley
Richard F. Marshall
Louis P. Glekas
Paul E. Ritt

Melpar, Incorporated

JULY 1959

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WRIGHT AIR DEVELOPMENT CENTER

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NOTICES

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Materials Laboratory
Contract No. AF 33(616)-5518
Project No. 7371

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

400 – September 1959 – 3-113

FOREWORD

This report was prepared by Melpar, Incorporated under USAF Contract No. AF 33(616)-5518. This contract was initiated under Project No. 7371, "Electrical and Electronic Materials," Task No. 73711, "Electrical and Electronic Organic Materials". The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Dr. G. F. L. Ehlers acting as Project Engineer.

This report covers work conducted from March 1, 1958, through February 28, 1959.

ABSTRACT

Literature sources have not revealed any phosphorus epoxide polymers or organo-phosphorus compounds containing more than one epoxide group.

The characteristic thermal properties of commercial epoxy resins were obtained from Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Heat of Distortion values. Resins tested included Dow Epoxy Novalac X2638.3, Eccomold L 266, Stycast 2662, Epoxylite 813, Maraset 617, Sealcast 506, Epon X1310 laminate, Epon 828/PMDA-MA, Epon 828-Epon X1310/Diaminodiphenylsulfone, Epon 828-Triethanol Amine Titanate, and Permacel ST 3994.

It was found that Thermal Gravimetric Analysis (TGA) as compared with Differential Thermal Analysis (DTA) had an inherent advantage for comparing the thermal stabilities of polymers. The (TGA) curves share a common, well-defined "knee" in the temperature range wherein disruptive volatilization first becomes rapid, thus enabling clearer interpretation of degradation temperature.

A number of products resulting from the reaction of tetrakis (hydroxymethyl)phosphonium chloride and epichlorohydrin in the presence of aqueous sodium hydroxide yielded water insoluble foams when cured with anhydride type curing agents. Although positive identification of these products has been a formidable problem, the fact that polymers have been formed from the reaction of a quartenary phosphonium compound and epichlorohydrin is encouraging.

Even more promising results were observed in attempts to prepare a phosphorus containing epoxide by a two step reaction of tris (hydroxymethyl) phosphine oxide and epichlorohydrin. Conditions have been worked out for obtaining satisfactory yields in the first or acid catalyzed step, but more development work is required to define conditions for the second or ring closing step.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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1. INTRODUCTION

This report summarizes the work performed from March 1, 1958 through February 28, 1959 on Contract AF 33(616)-5518. The contract calls for development of new types of epoxy resins, incorporating structures designed to enhance thermal stability and dielectric properties for laminating resins. The goal of this investigation has been to develop phosphorus and titanium containing epoxy polymers that can be cross-linked or chain extended in the curing process to form thermosetting materials more thermally stable than epoxy type resins now commercially available.

Work under this contract was divided into the following phases:

1.1 Phase I Literature Survey

The literature survey was made primarily to furnish information concerning developments of and current trends in epoxy resin research. The survey was conducted in order to eliminate the costly duplication of conducting research investigations already made and to provide additional information on phosphorus and titanium bearing compounds for applications in polymer studies.

1.2 Phase II Testing of Commercial Epoxy Resins

The purpose of this phase was to test commercially available epoxy resins selected from the literature survey. The testing of these resins was confined to determining the temperature at which they break down under thermal stress. Differential Thermal Analysis (DTA), Thermal Gravimetric Analysis (TGA), and Heat of Distortion were used for this purpose.

1.3 Phase III Synthesis

Experimental efforts in the synthesis phase were concentrated in the following general areas:

1) Reactions of tetrakis (hydroxymethyl) phosphonium chloride (THPC).

2) Reactions of tris (hydroxymethyl) phosphine oxide (THPO).

3) The reaction of titanium lactate and epichlorohydrin.

4) Miscellaneous preparations of organo-phosphorus compounds.

Manuscript released by authors 21 May 1959 for publication as a WADC Technical Report.

1.3.1 Reactions of Tetrakis-(Hydroxymethyl) Phosphonium Chloride (THPC)

Initially the reactions of epichlorohydrin and THPC were carried out in the presence of excess sodium hydroxide, which is employed in the commercial epichlorohydrin/bisphenol A reaction as a catalyst and neutralizer for the hydrochloric acid which is formed. These reactions were conducted in a one step operation.

In second phase of the epichlorohydrin-THPC reactions, it was assumed that the hydroxyl groups of THPC behave as alcoholic hydroxyls and the epoxide was formed by a two step reaction. The first step involved the acid catalyzed preparation of the chlorohydrin, and second step involved the dehydrohalogenation with base to close the oxirane ring.

Other reactions considered were with Bisphenol A and Epichlorohydrin.

1.3.2 Reactions of Tris (Hydroxymethyl) Phosphine Oxide (THPO)

These investigations were concerned with reactions of THPO and epichlorohydrin and were divided into the same phases as THPC and epichlorohydrin reactions, the one step reaction in the presence of base and the two step reaction involving the acid catalyzed preparation of chlorohydrin and dehydrohalogenation with base to close the oxirane ring.

Other reactions considered for THPO were 1) reaction with glycidol, 2) reaction with allyl glycidol ether and 3) reaction with phenol. In the reaction of THPO with phenol, the objective was to prepare an intermediate for copolymerization with commercial epoxy resins.

1.3.3 Reactions of Titanium Lactate and Epichlorohydrin

In these reactions, attempts were made to prepare a titanium containing epoxide polymer by reacting titanium lactate with epichlorohydrin under basic conditions.

1.3.4 Miscellaneous Preparations of Organo-Phosphorus Compounds

In addition to THPC and THPO, other organo-phosphorus compounds were considered in the synthesis program of developing a heat stable epoxy resin. The preparation of other phosphorus compounds containing one or more epoxide groups was investigated briefly.

It was proposed that these compounds be self-polymerized or used as reactive modifiers with commercial epoxide resins.

2. DISCUSSION

2.1 Literature Survey (References in this section are on Pages 6 and 7.)

2.1.1 General

The literature survey for thermally stable epoxy type resins was initiated as described in paragraph 1.1. To supplement the literature survey, commercial sources were contacted for those thermally stable epoxy resins which are currently available. It was hoped that a study of these resins by differential thermal analysis, thermo-gravimetric analysis and heat of distortion testing would aid in detecting the mechanism by which epoxy resins are thermally degraded, thus affording a better background in developing thermally stable epoxy resins under this contract.

2.1.2 Patent and Library Search

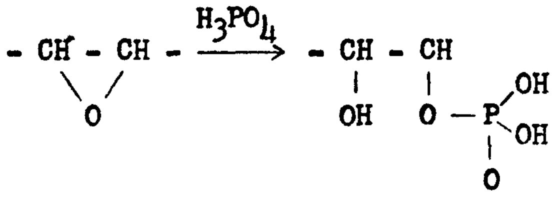
Initial work on epoxy type resins is claimed by de Trey Freres S.A. of Zurich[1] under a patent for the manufacture of thermo-setting resins produced by the reaction of a phenol in alkaline, aqueous or alcoholic solution with epichlorohydrin cured with an anhydride. A further claim by de Trey Freres S.A.[2] incorporated use of 0.1-5 percent of an alkaline catalyst to promote polymerization of products containing at least two ethylene oxide groups, obtained by the reaction of phenolic hydroxyl groups of a dihydric phenol with epichlorohydrin or a dichlorohydrin in the presence of alkali. In the United States S. O. Greenlee is credited with the majority of early patents 3, 4, 5, 6 including claims for methods whereby complex resinous epoxides result from the reaction of bisphenol and epichlorohydrin in the presence of an alkali, epoxides formed from such epoxilating compounds as aliphatic polyepoxides, and curing mechanisms such as boron trifluoride, Fridel-Crafts reagents, polyamine and alkaline. C. E. Bixler has claimed the epoxide formation by polyglycide derivatives of glycerol and epichlorohydrin.[7] Epoxy resins formed by reacting dihydroxy diphenyl[8] and 4,4'- dihydroxydiphenyl sulfone[9] with epoxilating compounds have been reported in patents. The thermal stability of these compounds was not revealed.

For increasing the thermal yield temperatures, work was conducted by Dearborn, et al,[10] on epoxy resins from bis, tris-, and tetrakis - glycidyl ethers. From work for the U. S. Army Signal Corps (contract) No. DA-36-039 SC - 42459) it was concluded that increasing functionality of the anhydride curing agent, and that of the glycidyl ether, increases the thermal yield point. Two epoxy resins developed by Shell Development Company offer good strength to 500°F. These are Epon X-15100, a polyglycidyl ether of tetraphenol, and Epon X12100, a polyglycidyl ether of a phenol-formaldehyde[11].

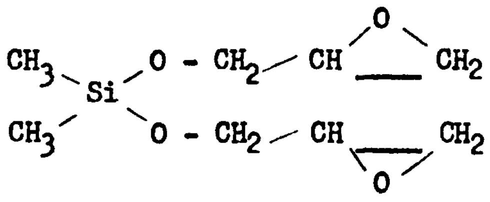
Of interest, with respect to increasing thermal characteristics of epoxy resins, has been blending of this resin with other resins of known high-heat resistance. Work of the National Bureau of Standards for the Department of the Army[12] concludes that thermally stable polymers will have a minumum number of elements involved in their structure, and a high degree of bonding in the chain (greater than single bonds). Areas considered in the study at N.B.S. included theoretical structures of boron, nitrogen, silicon, aluminum and oxygen which would form linear chains. This approach was halted because logical starting materials were not available, and because bond energies were not significantly favorable to the problem. Investigators on this project stated their belief that fluorine is the most promising monofunctional or monovalent element for terminating and saturating bonds not involved in linking the chains of polymer molecules. Reactions for preparing fluorine-containing polyethers which can be used as epoxilating compounds have been studied by Smith, Munch, and Pierce.[13]

Considerable work has been conducted on polymers of boron organo polymers. As reported by Stout and Chamberlain[14], boronic acids do not undergo condensation polymerization similar to the dihydroxy silicones, but decompose to boric acids or the anhydride. It was found that polymeric esters or amides of boron were extremely water sensitive, due to presence of the boron. Work has been conducted by Burg[15] in search of polymeric units of boron and phosphorous, as well as chemical bonding principles for holding these units together.

In the field of organo-phosphorous Reeves and Guthrie[16] report polymers produced from tetrakis (hydroxy-methyl) phosphonium chloride and polybasic carboxylic acids, anhydrides, amines and phenols. A patent by Albright & Wilson, Ltd.[17] reveals a method for replacing a portion of a polyhydric alcohol monomer with tetrakis (hydroxy-methyl) phosphonium chlorides and reacting mixture with a polyfunctional esterificating agent to produce an alkyd type copolymer. Cupery[18] found that the oxirane group will react with phosphoric acid to form phosphoric acid esters according to the following scheme:



Epoxilating compounds containing silicon were prepared by Martin.[19] Martin's patent claims di (2,3-epoxypropoxy) dimethylsilane and di (2,3-epoxypropoxy) diphenylsilane. The structural of di (2-3-epoxypropoxy) dimethylsilane is illustrated below:



Titanium bearing compounds for applications in polymer studies have been prepared by several methods. A method for preparing titanium amines is reported from the reaction of tetrabutyl titanate and piperidine.[20] Similarly an epoxy curing agent has been reported by Beacham and Merz[21] from a mixture of tetrabutyl titanate and ethylene diamine. Commercial quantities of triethanol amine titanate and titanium ortho esters[22] are being produced; they can be used for polymerization. Due to extreme sensitivity of polymers of orthotitanic acid to water, polymeric forms of the organic derivatives may be prepared by reacting monomers with restricted quantities of water (organic solvent medium).[23]

2.1.3 Commercial Epoxy Resins

An additional function of the literature survey included an investigation of current trends in the resin industry to supply thermally stable epoxy resins. Information of this type is considered proprietary by resin manufacturers. To ascertain the state-of-the-art in thermally stable epoxy resins, an inquiry was sent to known vendors of commercial epoxy resins asking if they produce and sell a resin that is stable above 450°F. Vendors and replies are tabulated in Table I. Epoxy resins which vendors claim can withstand 450°F temperature were purchased and made into samples for thermal testing (heat of distortion, differential thermal analysis, and thermo gravimetric analysis).

2.2 Testing of Commercial Epoxy Resins

2.2.1 General

The primary effort in this phase was directed toward obtaining characteristic thermal properties of commercial epoxy resins. With this information, it would then be possible to compare any resins that were developed in the program with these commercial resins.

A secondary effort was directed toward interpretation of the thermal data obtained. The purpose of this effort was to probe the present weaknesses of the commercial epoxy resins and to provide basic background information on the logical starting points for further investigation.

For this investigation, heat distortion temperature, differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) were used.

The techniques used, description of the apparatus, and the results of each test are presented.

2.2.2 Commercial Epoxy Resins

Table II lists commercial epoxy resins obtained from the inquiry (paragraph 2.1.3) to epoxy manufacturers and formulators, with their respective mixing ratios and curing schedules. When specified by the

LITERATURE SURVEY BIBLIOGRAPHY

1. British Patent 518,057, de Trey Freres S. A. of Zurich, Feb. 15, 1940.
2. British Patent 579,698, de Trey Freres S. A. of Zurich, Aug. 13, 1946.
3. U. S. Patent 2,502,145, S. O. Greenlee, March 28, 1950.
4. U. S. Patent 2,521,911, S. O. Greenlee, Sept. 12, 1950.
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7. U. S. Patent 2,512,996, C. E. Bixler, June 27, 1950.
8. U. S. Patent 2,698,315, Dec. 28, 1954.
9. U. S. Patent 2,765,322, E. M. Beaners, Oct. 2, 1956.
10. Dearborn, E. C., Fuoss, R. M., MacKengie, A. K., and Shepherd, R. G., Epoxy Resins from Bis-, Tris-, and Tetrakis - Glycidyl Ethers, Industrial and Engineering Chemistry, Vol. 45, No. 12, 2715 (1953).
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14. Stout, L. E. and Chamberlain, D. F., Investigation of the Synthesis and Testing of Various Possible Boron-Organo and Other Similar Polymers, ASTIA Document No. AD 2149, June 1952.
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16. Reeves, W. A. and Guthrie, J. D., Intermediate for Flame-Resistant Polymers, Industrial and Engineering Chemistry, Vol. 48, No. 1, pp. 64-67, January 1956.
17. British Patent 764, 314, Albright and Wilson, Ltd., Dec. 28, 1956.

18. Canadian Patent 530,492, Cupery, M. E. Sept. 18, 1956.

19. U. S. Patent 2,730,532, Martin, R. W., Jan. 10, 1956.

20. British Patent 783,621, General Electric, Sept. 25, 1957.

21. U. S. Patent 2,742,448, Beacham, H. H. and Merz, K. M., April 17, 1956.

22. DuPont Titanium Organics, Bulletin of E. I. DuPont de Nemours and Co., Inc., Pigments Dept., Wilmington 98, Del.

23. U. S. Patent 2,698,315, December 28, 1954.

TABLE I

RESULTS FROM COMMERCIAL INQUIRY FOR AN EPOXY RESIN WITHSTANDING GREATER THAN 450°F

MANUFACTURER CONTACTED	RECEIVED REPLY	EPOXY AVAILABLE, WITHSTAND 450°F CONT. WORKING	REMARKS
Applied Plastics Co., Inc. 130 Penn. Street El Segundo, California	No		
Aries Laboratory, Inc. 45-33 Davies Street Long Island, New York	No		
Armstrong Products Company Post Office Box 1 Warsaw, Indiana	Yes	No	Currently working on an adhesive which will withstand 450°F.
Bakelite Company Division of Union Carbide Corp. 30 East 42nd Street New York 17, New York	No		
Borden Company, Chemical Division 350 Madison Avenue New York 17, New York	Yes	No	Effort in adhesives.
Chemical Development Corporation Endicott Street Danvers, Massachusetts	No		
Ciba Company, Incorporated 627 Greenwich Street New York 14, New York	Yes	No	

TABLE I (Continued)

RESULTS FROM COMMERCIAL INQUIRY FOR AN EPOXY RESIN WITHSTANDING GREATER THAN 450°F

Cordo Chemical Corporation 34 Smith Street Norwalk, Connecticut	Yes	No	
Dow Chemical Company Plastics Department Midland, Michigan	Yes	Yes	Material procured for testing, epoxy novolac X2638.3 cured with nadic anhydride.
Emerson & Cuming, Incorporated 869 Washington Street Canton, Massachusetts	Yes	Yes	Material procured for testing, Eccomold L266 for 600°F epoxy laminates and Stycast 2662 with a heat of distortion in excess of 500°F.
The Epoxylite Corporation 10829 E. Lentral Avenue El Monte, California	Yes	Yes	Material procured for testing, Epoxylite High Temperature Resin #813, claim heat distortion temperature of 602°F.
Furane Plastics, Incorporated 4516 Brazile Street Los Angeles 39, California	Yes	No	
Houghton Laboratories, Inc. 322 Houghton Avenue Olene, New York	Yes	No	
Jones-Dabney Company 1481 S. 11th Street Louisville 8, Kentucky	Yes	No	
Loven Chemical of California 244 S. Pine Street Newhall, California	No		

TABLE I (Continued)

RESULTS FROM COMMERCIAL INQUIRY FOR AN EPOXY RESIN WITHSTANDING GREATER THAN 450°F

Marblette Corporation 37-21 30th Street Long Island City 1, New York	Yes	Yes	Material procured for testing Maraset Resin #617 and Hardener #886, heat of distortion of 510°F claimed.
Minneapolis Honeywell Regulator Company 2755 4th Avenue, South Minneapolis 8, Minnesota	Yes	Yes	Material procured for testing, Sealcast 506 with hardener Sealset 705, claim service temperature up to 500°F.
C. J. Osborn Company 1301 W. Blancke Street Linden, New Jersey	Yes	No	
Permacel Tape Corporation New Brunswick, New Jersey	Yes	Yes	Submitting a sample of their Epoxy Resin ST3994.
Poly Resins Sun Valley, California	No		
Reichhold Chemical, Incorporated 525 North Broadway White Plains, New York	Yes	No	
Ren Plastics, Incorporated 5422 S. Cedar Street Lansing 17, Michigan	Yes	No	
Rezolin, Incorporated 1651 18th Street Santa Monica, California	Yes	No	

TABLE I (Continued)

RESULTS FROM COMMERCIAL INQUIRY FOR AN EPOXY RESIN WITHSTANDING GREATER THAN 450°F

H. H. Robertson Company 2400 Farmers Bank Building Pittsburgh 22, Pennsylvania	Yes	No	
Shell Development Company Emeryville, California	Yes	Yes	Material procured for testing, Epon 828 and X1310 cured with diaminodi phenylsulfone. Epon X1310 cured with BF3400 in laminate form.
Thalco 765 S. Harvard Boulevard Los Angeles 5, California	Yes	No	Represent Bakelite on their standard epoxy resins.
Tylene Plastics, Inc. Freyer Road Michigan City, Indiana	No		
U. S. Gypsum Company 300 W. Adams Street Chicago 6, Illinois	No		

vendor, laminate samples were prepared only for heat of distortion measurements; castings of the laminating resin were made for thermo-gravimetric and differential thermal analysis.

2.2.3 Heat Distortion Temperature

The Heat Distortion temperature test closely follows ASTM Designation D 648-45T. Figure 1 is a picture of the apparatus.

This test determines the temperature at which an arbitrary deformation (.01 inch was used) occurs, when a sample is subjected to a load of 66 and 264 psi. The test data can be used to predict behavior of plastic materials under conditions of elevated temperatures and stresses.

The test consisted primarily of supporting the sample, applying a load and measuring the deformation. A sample at least 2 inches long was placed across a span of 1.23 inches. The rod carrying the load to the sample was placed halfway between the points of support. The load was calculated by the formula:

$$P = \frac{2Sbd^2}{3L}$$

where: P = load in pounds

S = fiber stress (264 or 66 psi)

b = width of specimen in inches

d = depth of specimen in inches

L = width of span between supports in inches (1.23 inches)

Samples were cut to dimensions of 2 X 1/4 X 1/4 ± .003 inches with care taken to maintain parallel faces. Samples then were conditioned according to ASTM Designation D 618-51T procedure A.

The sample to be tested was submerged in a sesame oil bath (in instances where high heat distortion resins were tested, Dow Corning 710 fluid was used); the bath was continuously stirred using a motor-driven stirring rod; the bath temperature (i.e. the sample) was monitored with a thermometer readable within ± 0.5°C. During the test the heating rate of the bath was 2°C per minute. The deformation of the sample was measured with a dial gauge to ± 0.00002 inches.

The temperature at which the sample deformed 0.01 inch is reported as the heat distortion temperature. The calculated maximum error of this test is about 15 percent. Results of these tests are shown in Table III.

2.2.4 Differential Thermal Analysis

(Figure 2 and 3) To study reactions which involve changes in the enthalapy of a material, Differential Thermal Analysis is used. DTA is a means of determining magnitude and duration of an endothermic or exothermic reaction as a function of sample temperature.

Typical reactions which involve endothermic reactions are dehydration, reduction, melting, boiling, decomposition (such as in a carbonate or sulfate) and some crystalline transitions. Typical exothermic reactions include crystalline transitions, oxidation, and freezing.

Use of DTA for organic compounds has been limited, but some investigators report agreement in values for melting and boiling points for common organic compounds. DTA has been used on cellulose and other organic materials having structures that are not amenable to detailed study by some of the more desirable X-ray techniques.

2.2.4.1 Differential Thermal Analysis Equipment. The sample size, sample holder, and arrangement of measuring equipment has been a subject of discussion in almost all DTA studies. For the study of polymer materials, it was decided that the following functions should be provided:

(1) A means of discarding previous samples without dismantling sample holder.

(2) An easy replacement of thermocouples.

(3) A continuous automatic recording of temperature difference.

(4) A continuous air flow for removing decomposition products.

The first requirement was met by using small procelain crucibles set into a porous holder block. After carbonizing or decomposition of a sample, the crucible can be readily removed for cleaning or replacement.

Use of a thermocouple insulation assembly that permits thermocouples to be replaced without disassembly is advantageous; reaction of the sample with a thermocouple need not affect later runs.

The recording equipment for DTA consists of an X-Y recorder, and a d-c amplifier when required. It was found in early tests that use of an amplifier for the T input was unnecessary since a $2^{\circ}C$ change in sample temperature (with respect to the standard) could be easily detected on the X-Y recorder. Also, the magnitude of the exothermic reactions was such that the recorder could not be maintained on the scale if an amplifier were used.

TABLE II

COMMERCIAL EPOXY RESINS, MIXING RATIO & CURING SCHEDULE

RESIN (TRADE NAME)	MANUFACTURER	MIXING RATIO	CURING RATE
Epoxy Novolac X 2638.3	Dow Chem. Co., Plastics Dpt., Midland, Mich.	X 2638.3 - 100 gm, Nadic Anhydride - 101 gm Pyridine - 0.1 cc	2 Hr. @ 200°F 15 Hr. @ 450°F
Eccomold L266 (Laminate with Garan 181 Glass Cloth)	Emerson & Cumings, Inc. 869 Washington Street Canton, Massachusetts	Eccomold L266 - 100 gm Catalyst 17 - 45 gm	Press Cure Laminate 1 Hr. @ 150°C @ 25 psi Post-Cure 3 Hr. @ 300°F 16 Hr. @ 400°F
Stycast 2662		Stycast 2662 - 90 gm Catalyst 14 - 22.5 gm	48 Hr. @ 25°C 3 Hr. @ 100°C 2 Hr. @ 150°C
Epoxylite #813	The Epoxylite Corp. 10829 E. Lentral Ave. El Monte, California	Epoxylite #813 - 100 gm Catalyst 9 - 39 gm	Gel-0.5 Hr. @ 250°F Cure - 1 Hr. @ 250°F 4 Hr. @ 350°F
Maraset #617	Marblette Corp. 37-21 30th Street Long Island City 1, N.Y.	Maraset #617 - 100 gm Hardener #886 - 18 gm	2 Hr. @ 200°F 5 Hr. @ 400°F

TABLE II (Continued)

COMMERCIAL EPOXY RESINS, MIXING RATIO & CURING SCHEDULE

Sealcast 506	Minneapolis Honeywell Regulator Co., 2755 4th Avenue, S. Minneapolis 8, Minn.	Sealcast 506 - 95.8 gm Sealset 705 - 4.2 gm	3 Hr. @ 250°F 4 Hr. @ 300°F
Epon X1310 (Laminate with Garan 181 Glass Cloth)	Shell Development Co. Emeryville, Calif.	Epon X1310 - 60 gm Acetone - 40 gm Curing Agent - 0.6 gm BF 3400 (Shell)	Press Cure Laminate 1 Hr. @ 150°C @ 25 psi Post-cure 3 Hr. @ 205°C
Epon 828		Epon 828 - 100 gm; Pyromellitic di-anhydride - 17 gm; Maleic Anhydride - 23 gm; Pyridine - 01. cc	1 Hr. @ 100°C 1 Hr. @ 130°C 1 Hr. @ 150°C 1 Hr. @ 170°C 1 Hr. @ 190°C 24 Hr. @ 230°C
Epon X1310 Epon 828		<u>Sample # I</u> Epon X1310 - 60 gm Epon 828 - 40 gm Diaminodiphenylsulfone - 30 gm	2 Hr. @ 100°C 2 Hr. @ 130°C 2 Hr. @ 160°C 1 Hr. @ 200°C
		<u>Sample # II</u> Epon X1310 - 70 gm Epon 828 - 30 gm Diaminodiphenylsulfone - 30 gm	Same as for Sample # I
		<u>Sample # III</u> Epon X1310 - 80 gm Epon 828 - 20 gm Diaminodiphenylsulfone - 30 gm	Same as for Sample # I

TABLE II (Continued)

COMMERCIAL EPOXY RESINS, MIXING RATIO & CURING SCHEDULE

Permacel ST 3994	Permacel-LePage's, Inc. New Brunswick, New Jersey	Permacel ST 2994 - 100 gm Part B - 30 gm	Add part B when ST 3994 has been heated to 130°C Cure: 2 Hr. @ 121°C 4 Hr. @ 150°C 2 Hr. @ 180°C
Epon 828 Triethanol-amine Titanote (TAT-21)	Shell Chemical Co.	Sample I 100 gm 828, 8.3 gm TAT Sample II 100 gm 828, 12.5 gm TAT Sample III 100 gm 828, 16.6 gm TAT	80°C - 3 Hr. 100°C - 3 Hr. 125°C - 2 Hr. 150°C - 2 Hr. Sample I gelled in 44 Hr. Hardened in 68 Hr. Sample II gelled in 24 Hr. Hardened in 44 Hr. Sample III gelled in 20 Hr Hardened in 40 Hr.

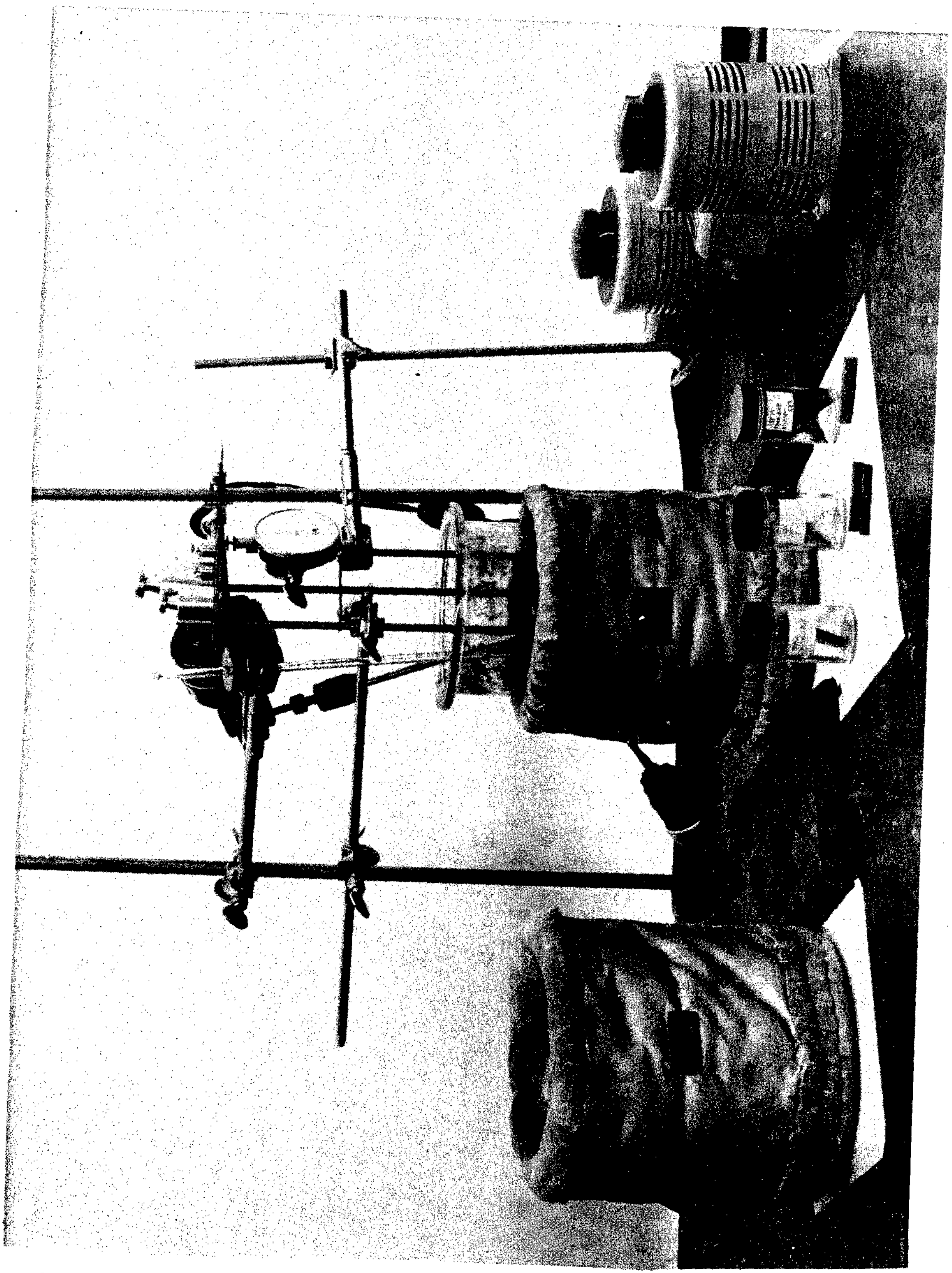

Figure 1. Heat of Distortion Apparatus

TABLE III

COMMERCIAL EPOXIES, HEAT OF DISTORTION (264 psi)

	Sample	Distortion Temperature °C
1.	Dow Epoxy Novalac X2638.3	254°C
2.	Eccomold L 266	350°C
3.	Stycast 2662	No suitable sample
4.	Epoxylite No. 813	290°C
5.	Maraset No. 617	Sample broke at 325°C
6.	Sealcast 506	325°C
7.	Epon X1310 Laminate	350°C
8.	Epon 828/PMDA-MA	No suitable sample
9.	Epon 828 - Epon X1310	
	Sample I	295°C
	Sample II	298°C
	Sample III	303°C
10.	Epon 828 - Triethanol Amine Titanate	
	Sample I	73°C
	Sample II	88°C
	Sample III	82°C
11.	Permacel ST 3994	199°C

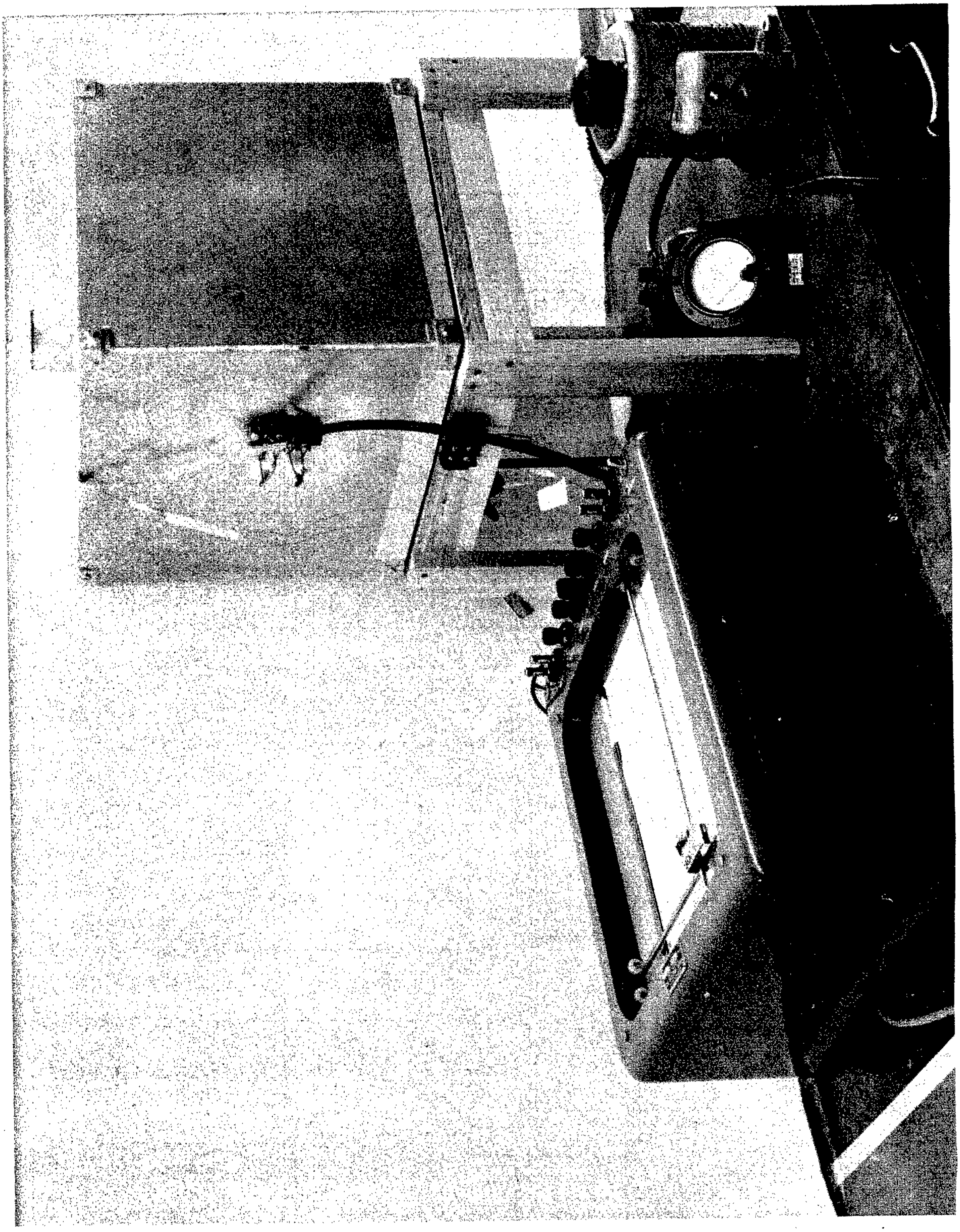

Figure 2. Differential Thermal Analysis Apparatus

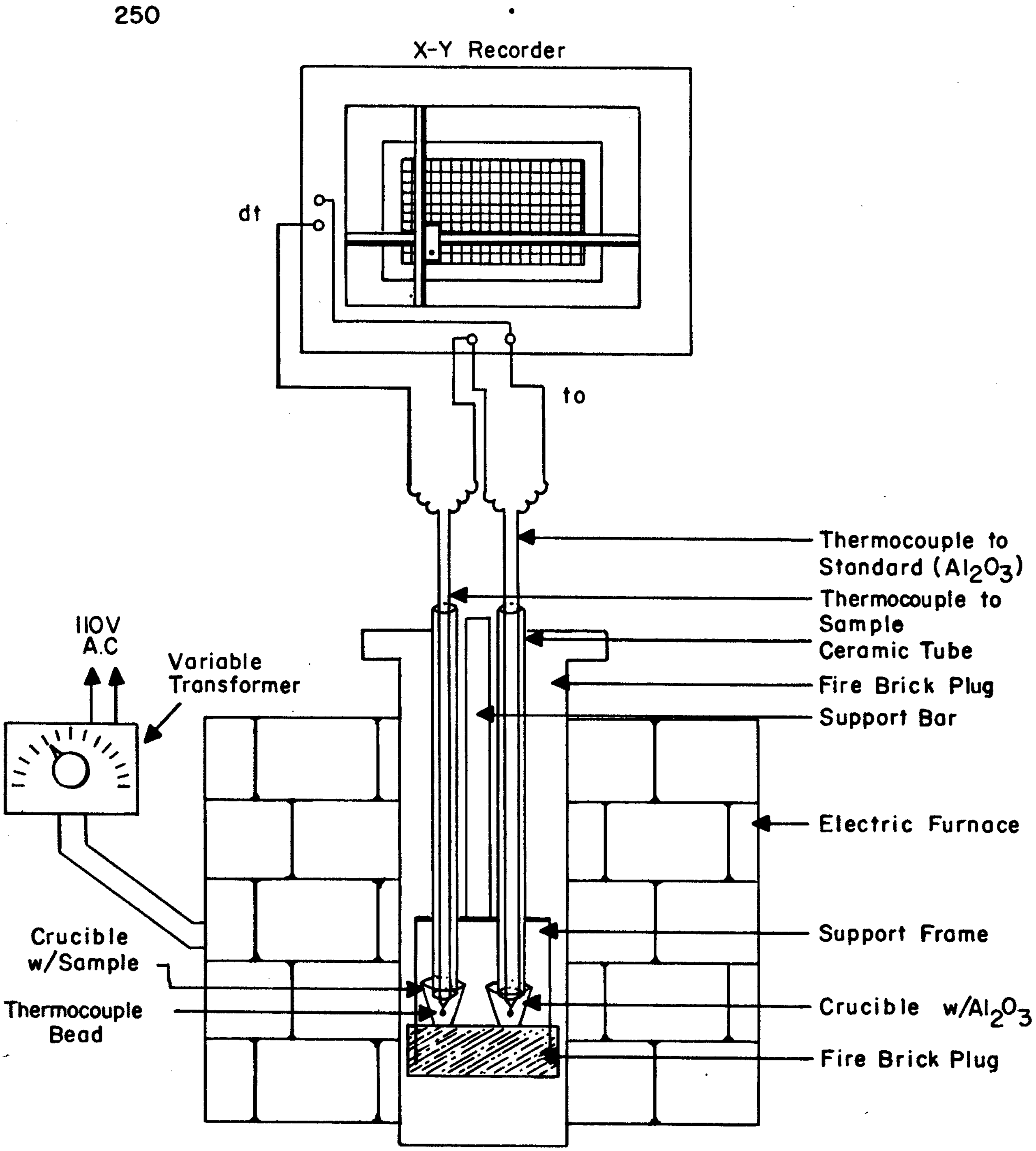

Figure 3. Arrangement of DTA Apparatus

The arrangement of the equipment is shown in schematic form as figure 3. During operation DTA data is recorded directly on the X-Y recorder. The furnace temperature is increased at a rate of 5°C per minute by a programmed increase of power input to the furnace windings. The operator is required only to monitor the temperature (x-input) as a function of time to assure that test conditions are accurately reproduced.

2.2.4.2 Operation of DTA Equipment. In performing DTA, care must be taken in preparing the sample and placing the thermocouple if quantitative results are to be obtained.

2.2.4.3 Sample Preparation. Epoxy resins offer a unique problem in sample preparation. To accurately reproduce sampling and testing conditions, a solid sample of accurately known dimensions is desirable. However, if reactions to be studied involve interaction of the epoxy resin with the atmosphere, a granular sample with greater surface area is desirable. A compromise between the two conditions was made so that a granular sample of pure resin, 16 mesh and finer, was packed into a crucible and the thermocouple embedded into the sample. It was found that this method of sample preparation did not yield uniform sample particle dispersion, and there was some difficulty in reproducing the results obtained.

In order to insure that sample particle dispersion would be as constant as possible, the following method of preparation and packing was adapted. Resin samples were mechanically crushed and passed through a 200 mesh seive. Aluminum oxide was then added as a diluting agent. The resins and the Al_2O_3 were weighed on a balance with a sensitivity of ± 0.01 gm. These were then well mixed in a mortar and pestle and again passed through the 200 mesh seive. This procedure was then repeated in the interest of still better particle dispersion. (The Al_2O_3, used both as a diluting agent and as a standard, was 325 mesh Alcoa A-14.) It was decided after trying varying compositions to use 90% Al_2O_3 and 10% sample. Before being carefully packed in a No. 000000 crucible, the samples were weighed on a balance with a sensitivity of ± 0.0001 gm. The samples were packed into the crucible using a stainless steel spatula; extreme care was taken to keep density as consistent as possible. It is the density of the material near the thermocouple bead and not the total amount of reacting material that determines the peak area. The Differential Thermal Analysis curves for the commercial epoxy resins prepared for testing in this manner are illustrated in figures 5, 6, 7, 8, 9, 10, 11, 12, and 13. With this dilution technique, much more reproducible results were obtained. Since the reproducibility of any given curve was greately improved, the reliability in comparison of several different materials was also improved. Figures 4 and 5 show typical DTA curves obtained for a resin run without and with the Al_2O_3 diluent respectively.

2.2.4.4 Sensitivity. The maximum sensitivity of the Mandrel ER-90 plotter used in the DTA apparatus is 1 mv/inch. By using a d-c amplifier, Kintel model 103, in the Δt circuit, a sensitivity of 100 mv/inch, or 2.5°C/inch is possible.

During the runs with the sample diluted with 90 percent Al_2O_3, the sensitivity of the combined system was set at 0.25 mv/inch, 6.25°C/inch vertical and 2.5 mv/inch, 62.5°C/inch horizontal to achieve suitable gain without excessive noise.

2.2.4.5 Atmosphere. No atmosphere other than normal furnace atmosphere was used during DTA. A slow flow of air was used in several runs to determine if reaction products significantly altered the reaction. Since little difference in the DTA curves was noted, this technique was discarded.

2.2.5 Thermal Gravimetric Analysis (TGA)

Recently TGA has been a useful tool in determining composition changes which occur during heating of a sample. A continuous weighing of the sample at elevated temperatures is necessary. In the case of inorganic compounds, definite conclusions as to what component has been lost or gained may be made.

A photograph of the equipment is shown in figure 14 and a schematic diagram in figure 15. The schematic diagram indicates arrangement; the major components are:

(1) Linear Variable Transformer, Schaevitz Engineering, Type 100 SS-L.

(2) A-C Voltmeter, Ballantine Laboratories Inc., Model 643.

(3) 6.3V a-c power supply.

(4) Size 0 porcelain crucible, Coors Porcelain Co.

(5) Potentiometer, Leeds and Northrup, Type 8657C.

(6) Kanthal wound furnace, 12" x 12" x 12", 2" I.D. Tube.

The linear variable transformer is rigidly supported inside a sealed window box. This arrangement eliminates air drafts which would create oscillations in the transformer slug, supported inside the transformer by a small spring. A chromel wire attached to the bottom of the slug extends through a small opening in the bottom of the window box and supports the porcelain crucible inside the furnace. Firebrick plugs at the top and bottom of the furnace tube eliminate thermal drafts and, in the case of the bottom plug, allow for insertion of a chromel-alumel

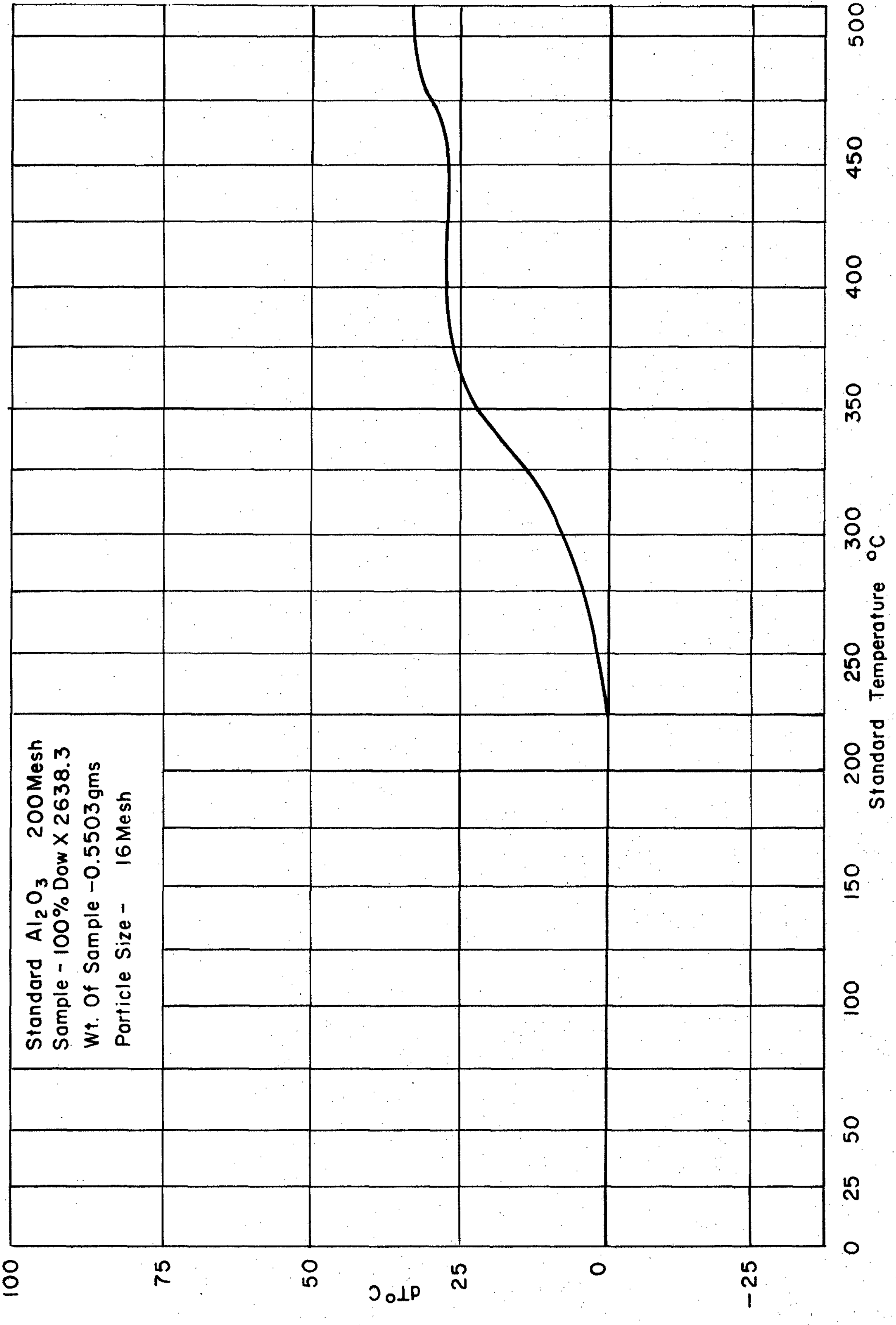

Figure 4. Differential Thermal Analysis of Dow X2638.3

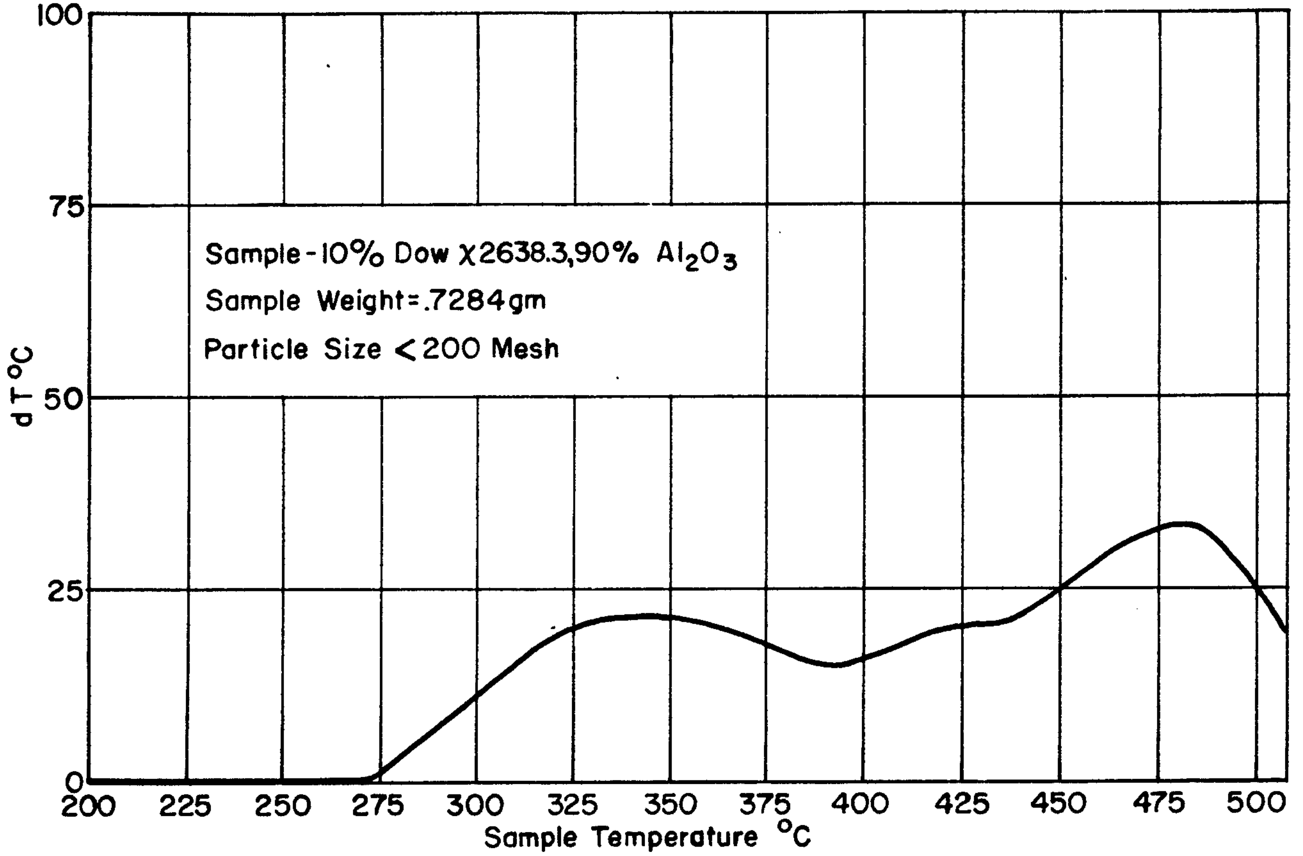

Figure 5. Differential Thermal Analysis of Dow X2638.3

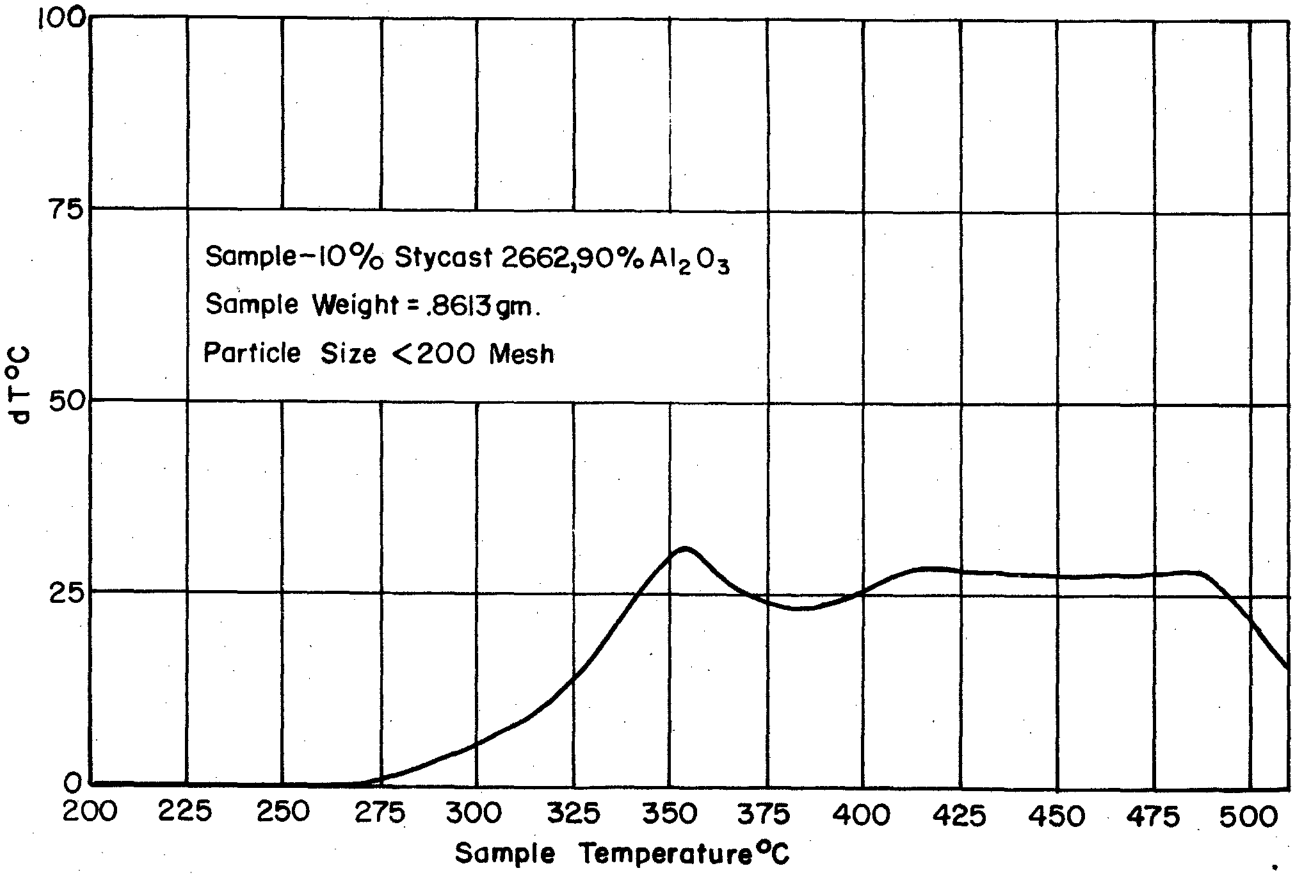

Figure 6. Differential Thermal Analysis of Stycast 2662

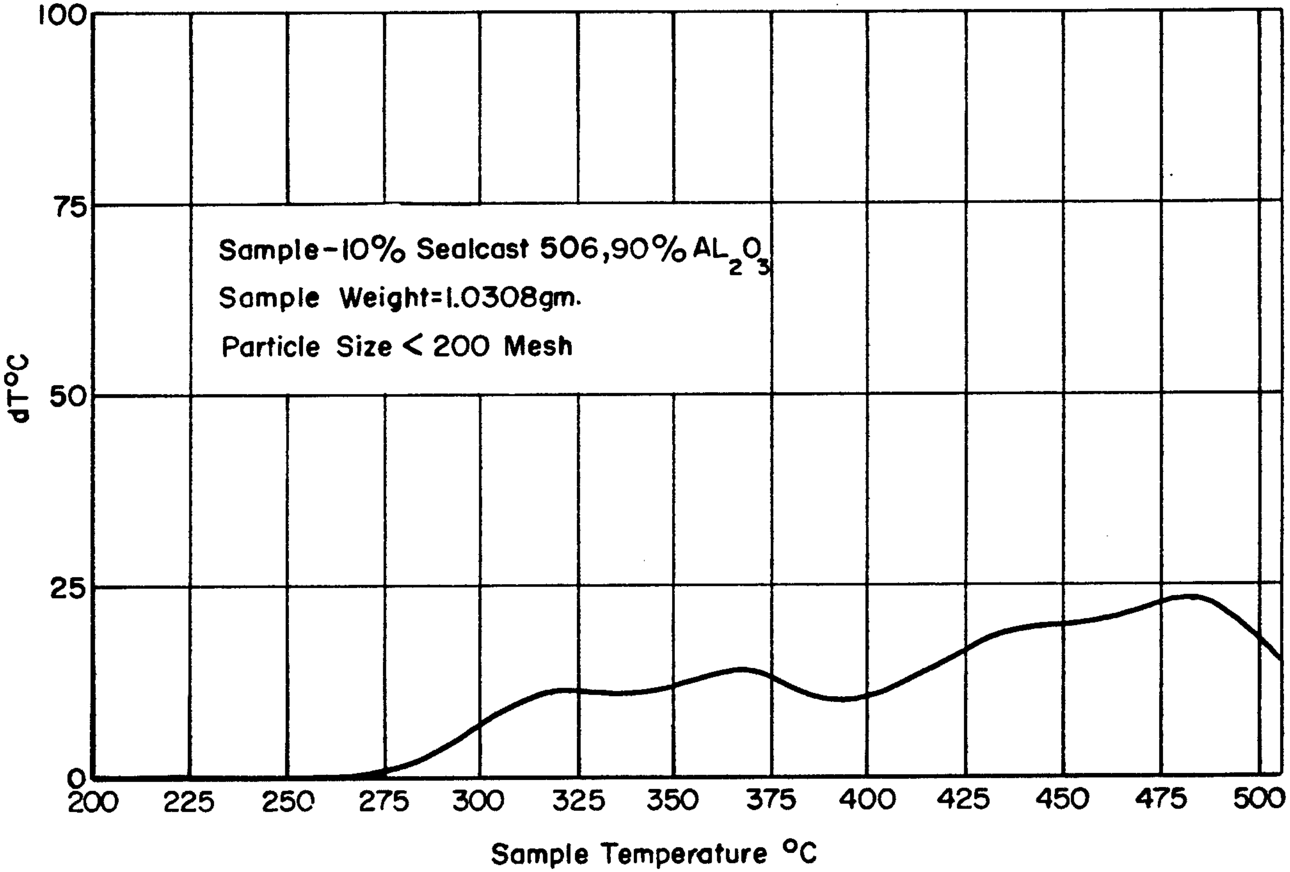

Figure 7. Differential Thermal Analysis of Sealcast 506

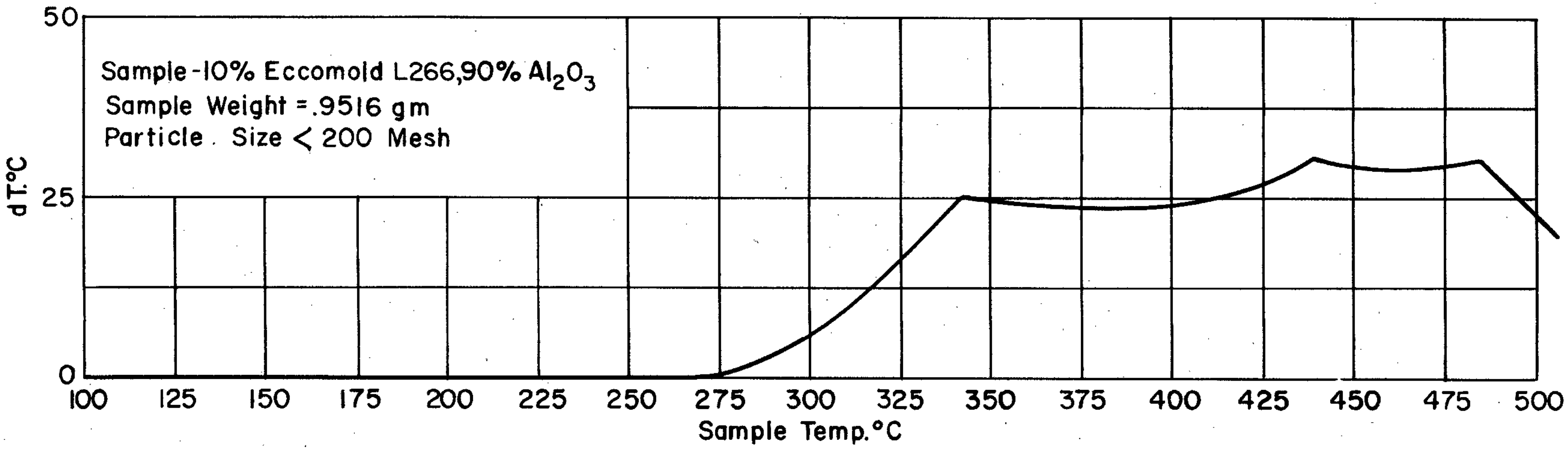

Figure 8. Differential Thermal Analysis of Eccomold 266

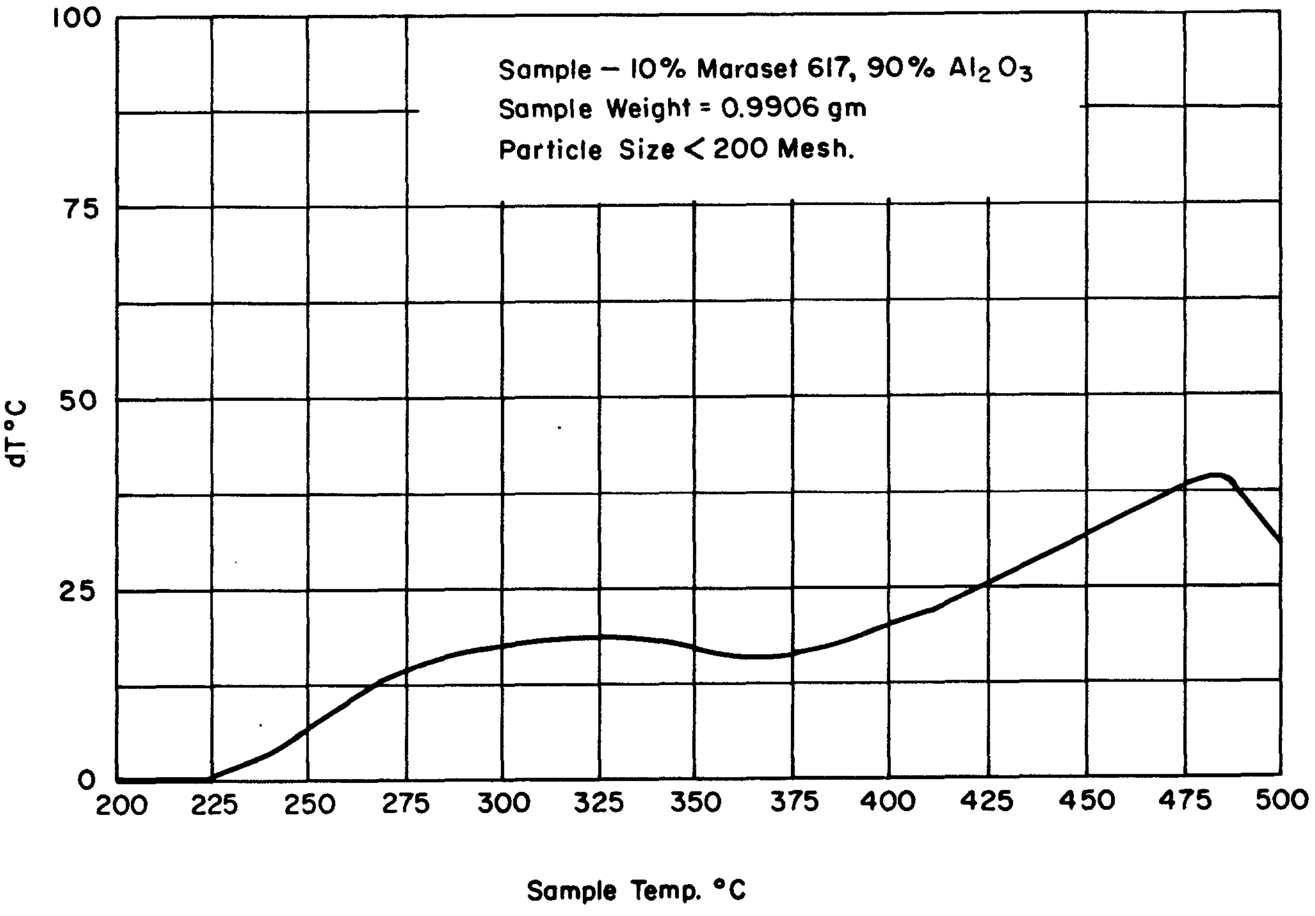

Figure 9. Differential Thermal Analysis of Maraset 617

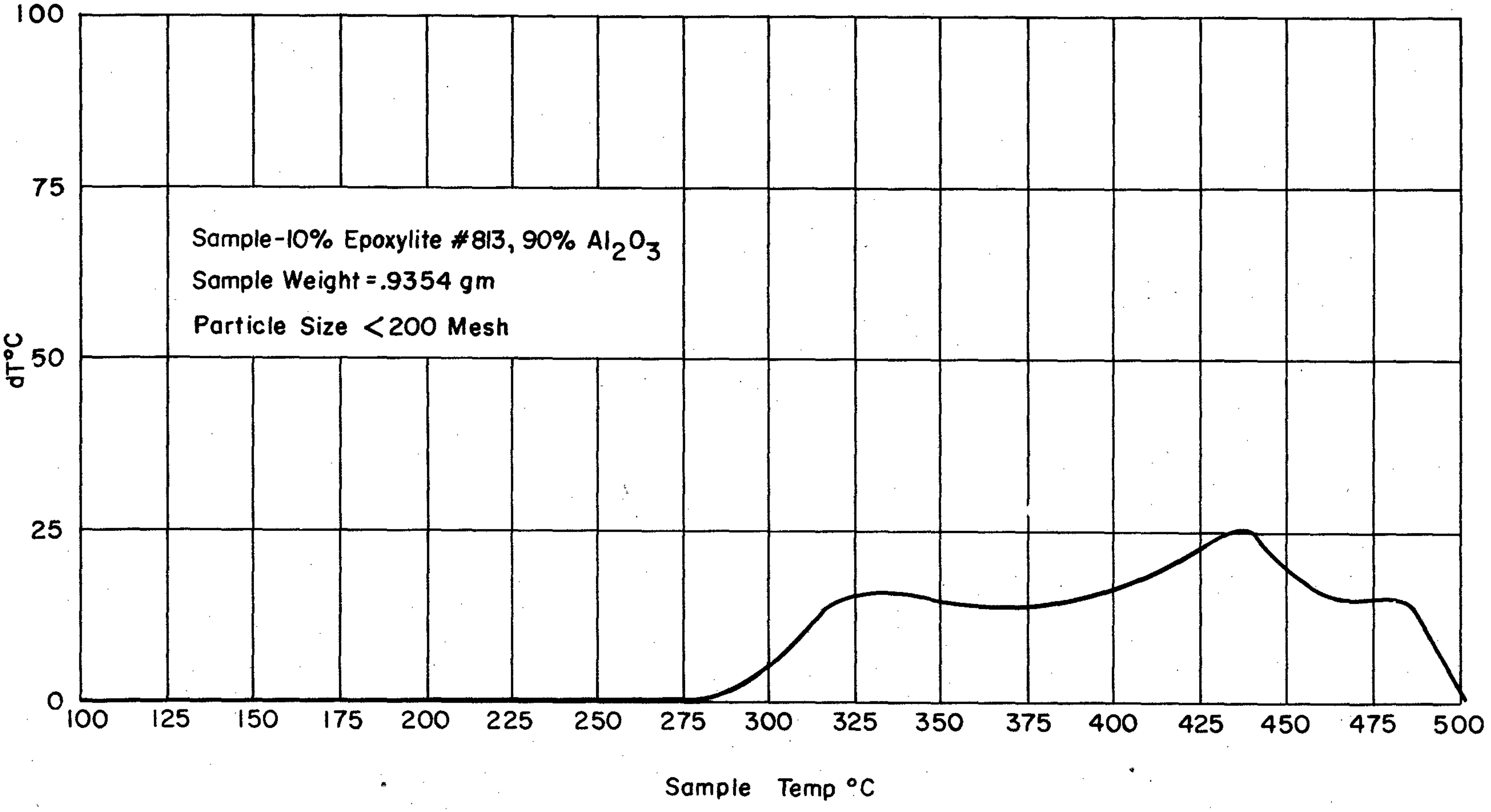

Figure 10. Differential Thermal Analysis of Epoxylite #813

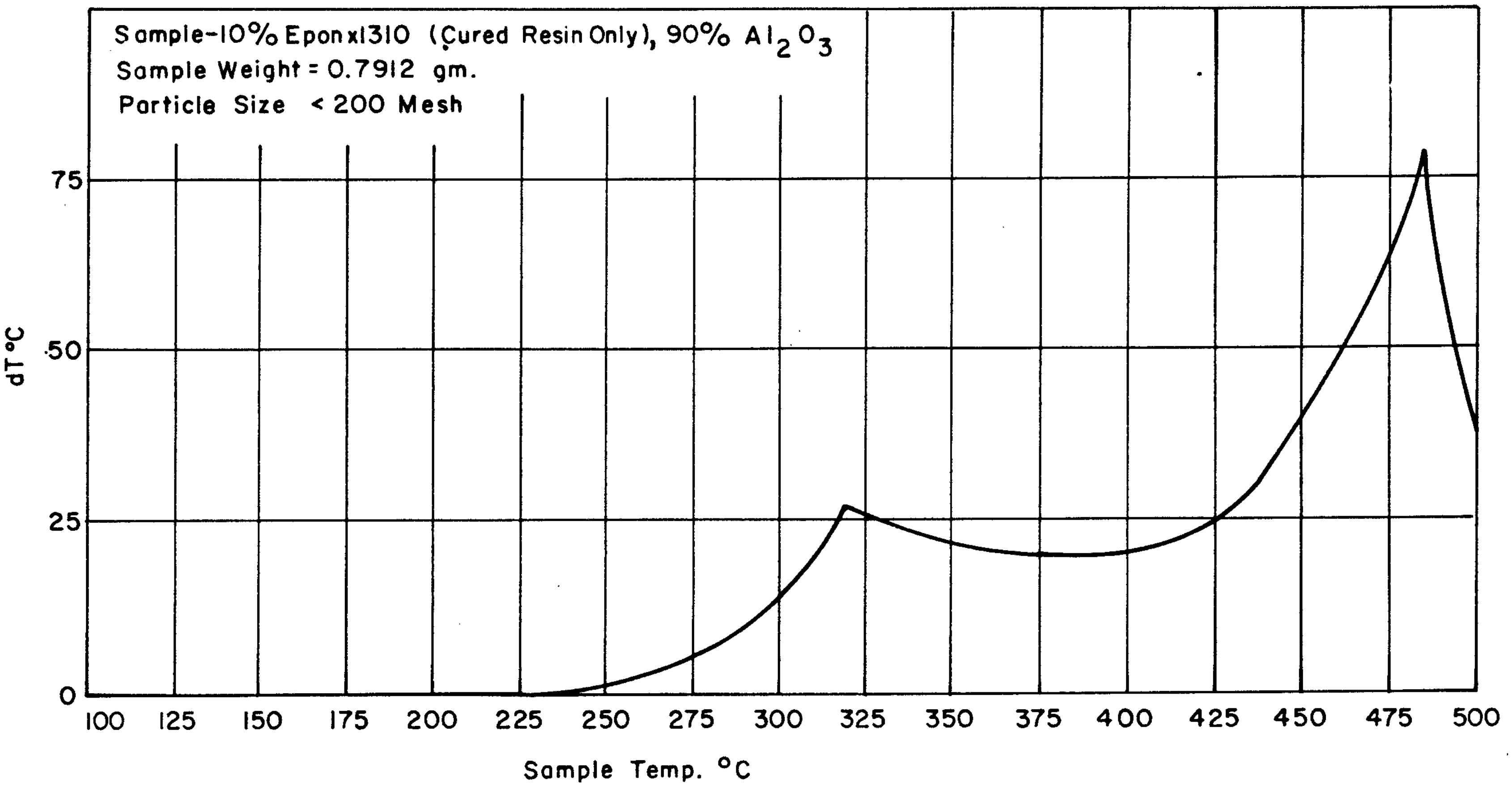

Figure 11. Differential Thermal Analysis of Epon X1310

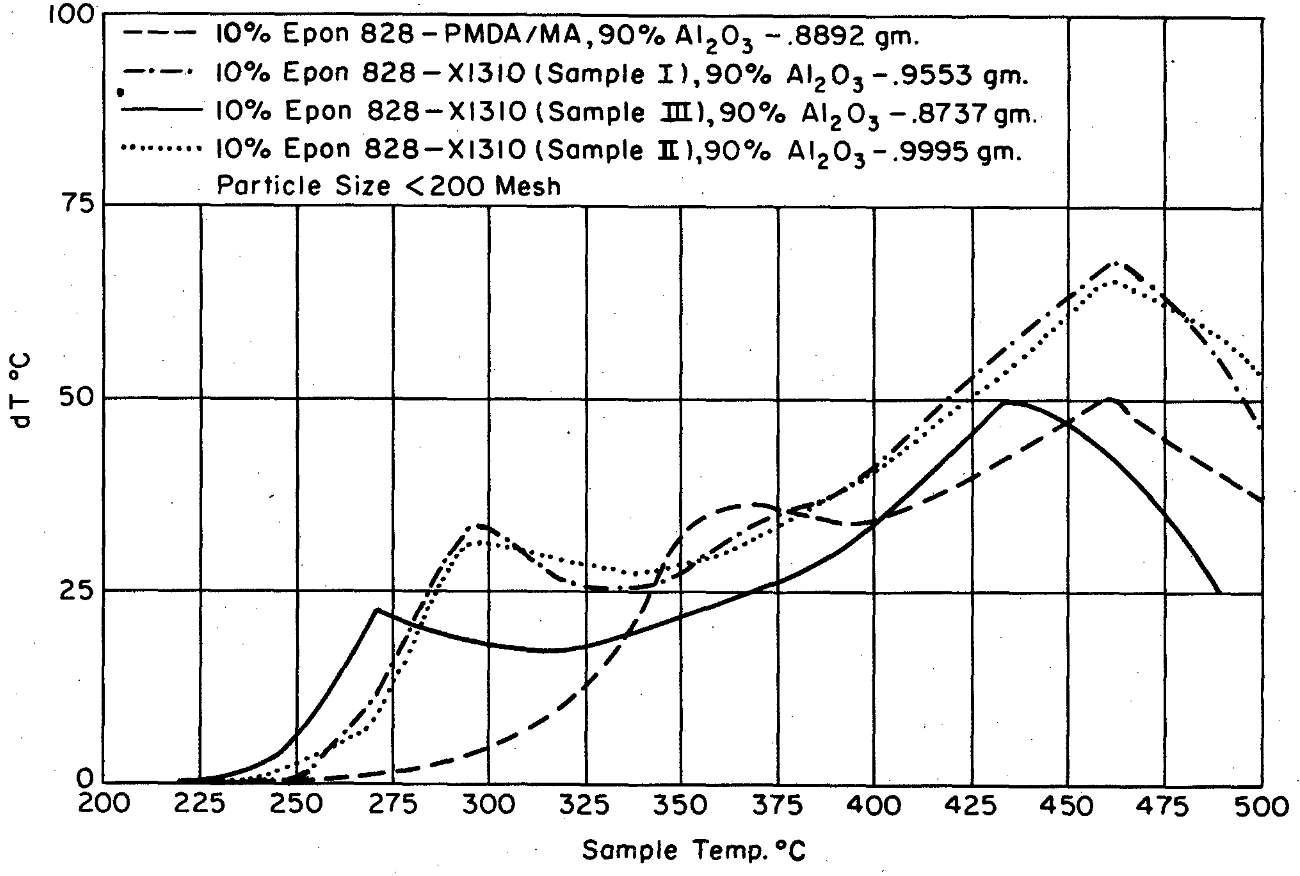

Figure 12. Differential Thermal Analysis of Upon 828 and Epon 828-Epon X1310

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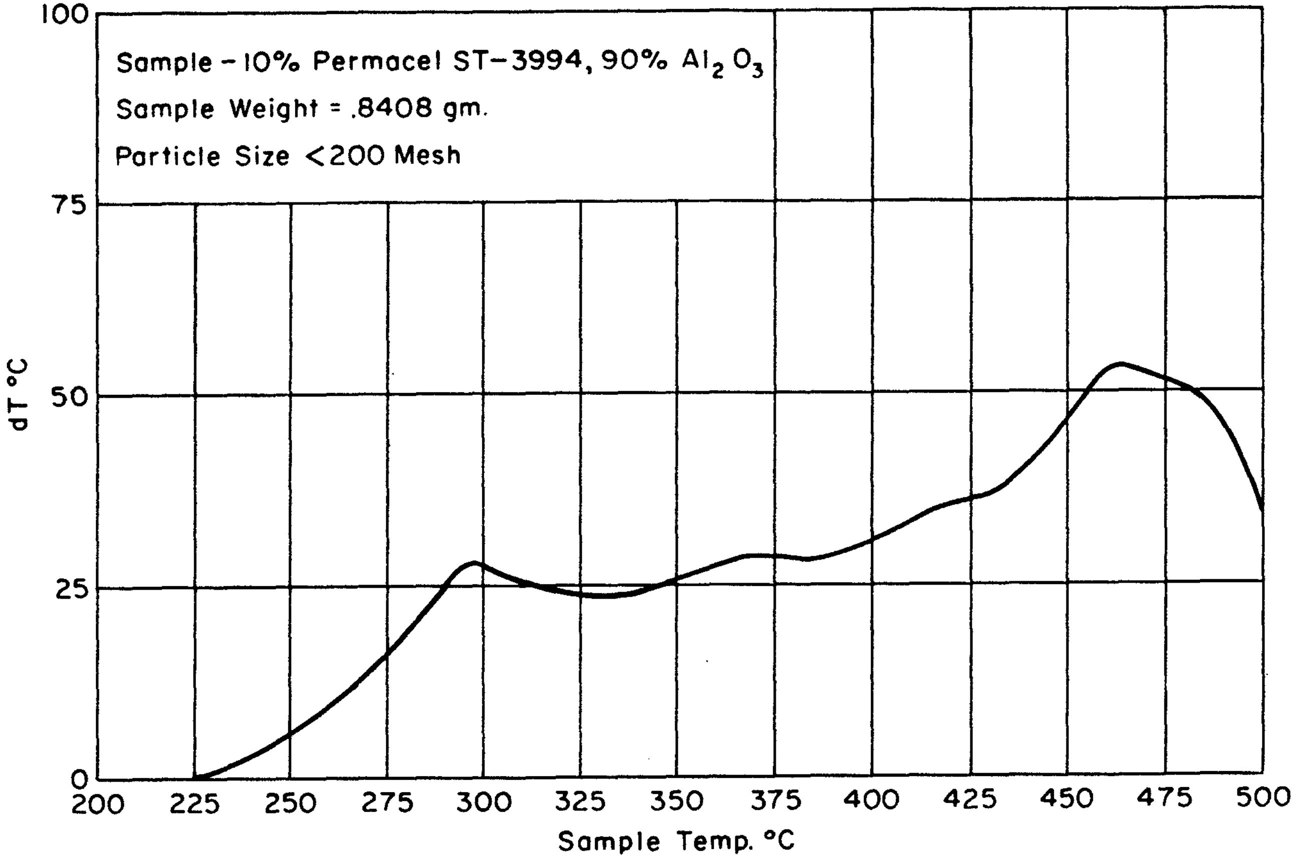


Figure 13. Differential Thermal Analysis of Permacel ST-3994

thermocouple through a porcelain thermocouple protection tube. The window box is supported by rubber shock mounts on a wooden frame above the furnace. A further means of vibration elimination is the magnetic damper which tends to decrease oscillations of the suspension wire. This arrangement has provided oscillation-free operation with a sensitivity of .020 grams.

In operation the slug is adjusted to be slightly above center in the transformer with the sample and crucible held in suspension. The 6 Volt a-c power supply provides operating power to the transformer; output of the slug transformer is indicated on the Ballantine voltmeter. The furnace is heated at roughly 5°C per minute by controlled variac setting. Temperature is indicated to within 1.5°C by the potentiometer. If the sample loses weight, the slug will rise inside the transformer and produce an increased output. If the sample increases in weight, the slug lowers toward the center of the transformer producing, at first, a lower output until the "null" is reached, and then a greater output. This output is entirely linear with weight change, a calibration by known weights indicates a reproducible .003 volt per .050 grams conversion factor. This is shown in Figure 16.

Samples were crushed in a steel impact mortar and the fragments passed through a 16 mesh screen. The sample thus includes a wide range of particle sizes under 16 mesh. Five grams of sample have been used in all cases for each test. See Figures 17-27.

2.2.6 Discussion of Results

Interpretation of the thermal changes in organic resins is a complex field of investigation. However, with the help of DTA, TGA and Heat of Distortion, qualitative interpretations of the thermal behavior of a resin can be simplified. The results of any one of these tests relates little about the thermal degradation processes in a resin. At best, a single test method can be used to measure only relative performance of a resin in high ambient temperatives. Results from the three tests may be viewed as being complimentary and in some cases corrobrating, which lends further reliability to the derived conclusions.

In observing some of the results of the testing the sample of Dow X2638.3 cured with Nadic anhydride and Epon 828 cured with PMDA-MA are interesting examples. Testing of the Dow X2638.3 specimen produced the following results:

1. Significant change (exothermic in the DTA plot at 245°C.)

2. First indication of a weight change (loss) at 245°C.

3. Heat of Distortion occurred at 245°C (264 psi).

The interpretation of this data leads to the conclusion that the thermodynamic phenomenon which occurs at 245°C involves a mass loss and

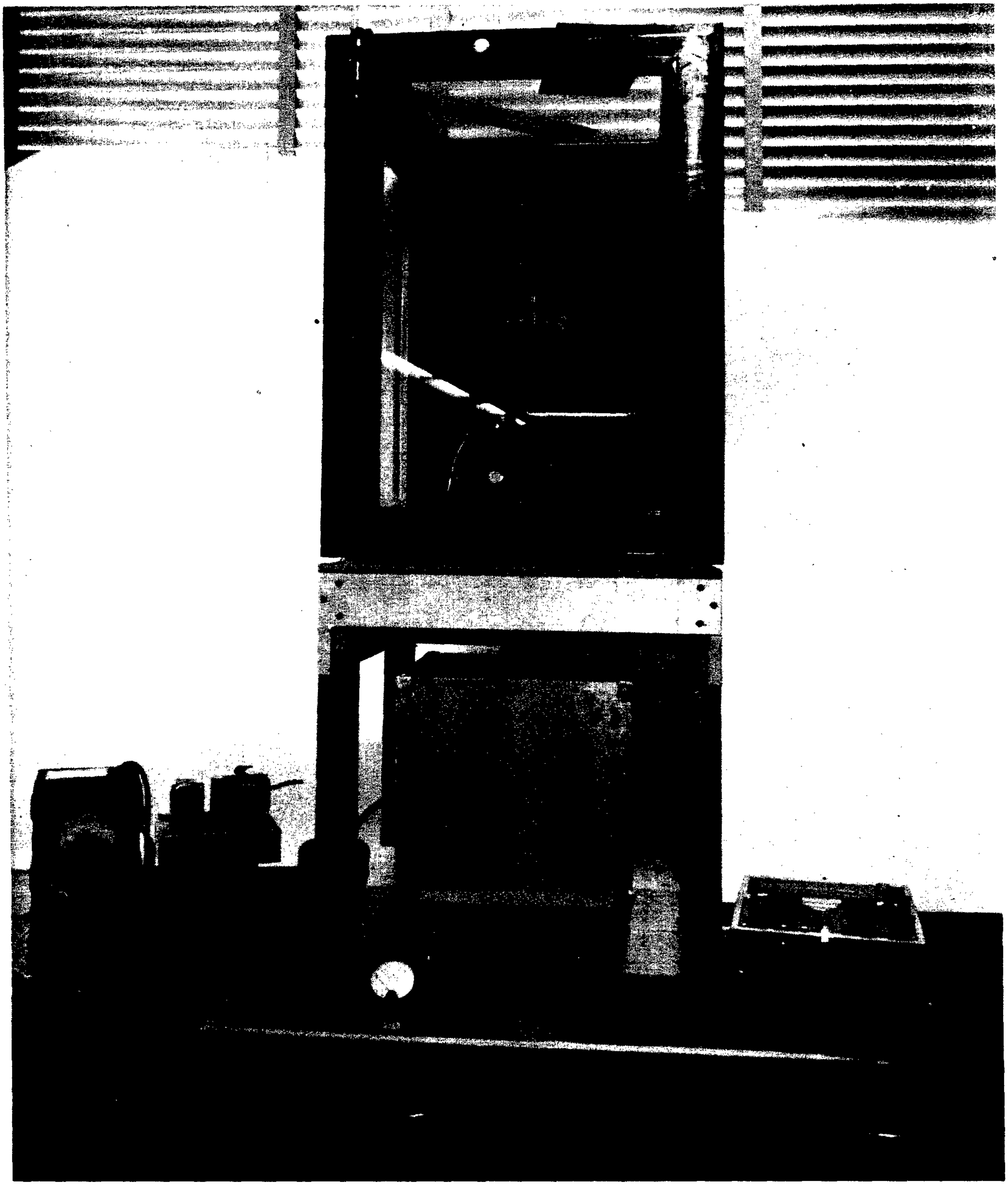


Figure 14. Thermal Gravimetric Analysis Apparatus

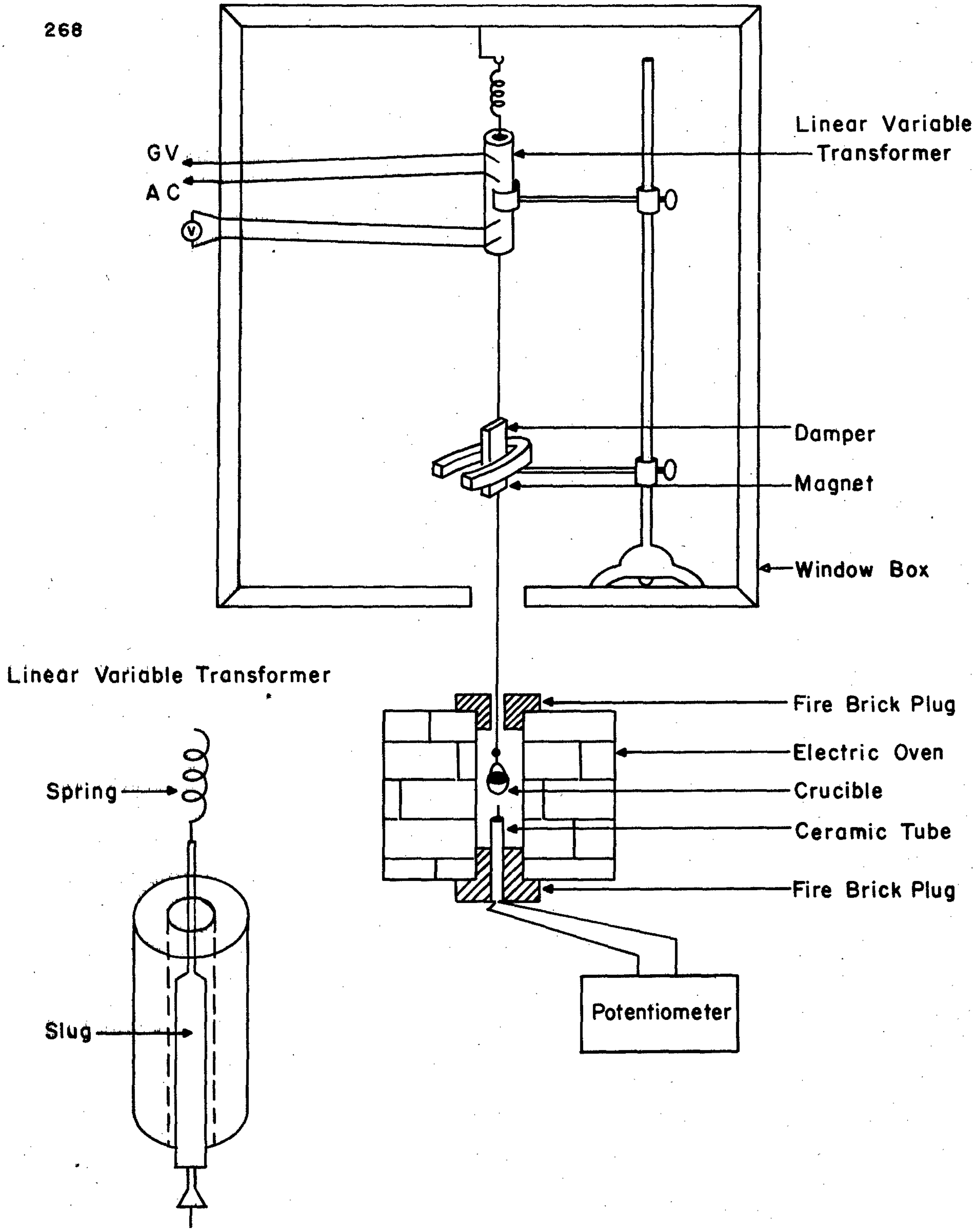


Figure 15. Arrangement of TGA Apparatus

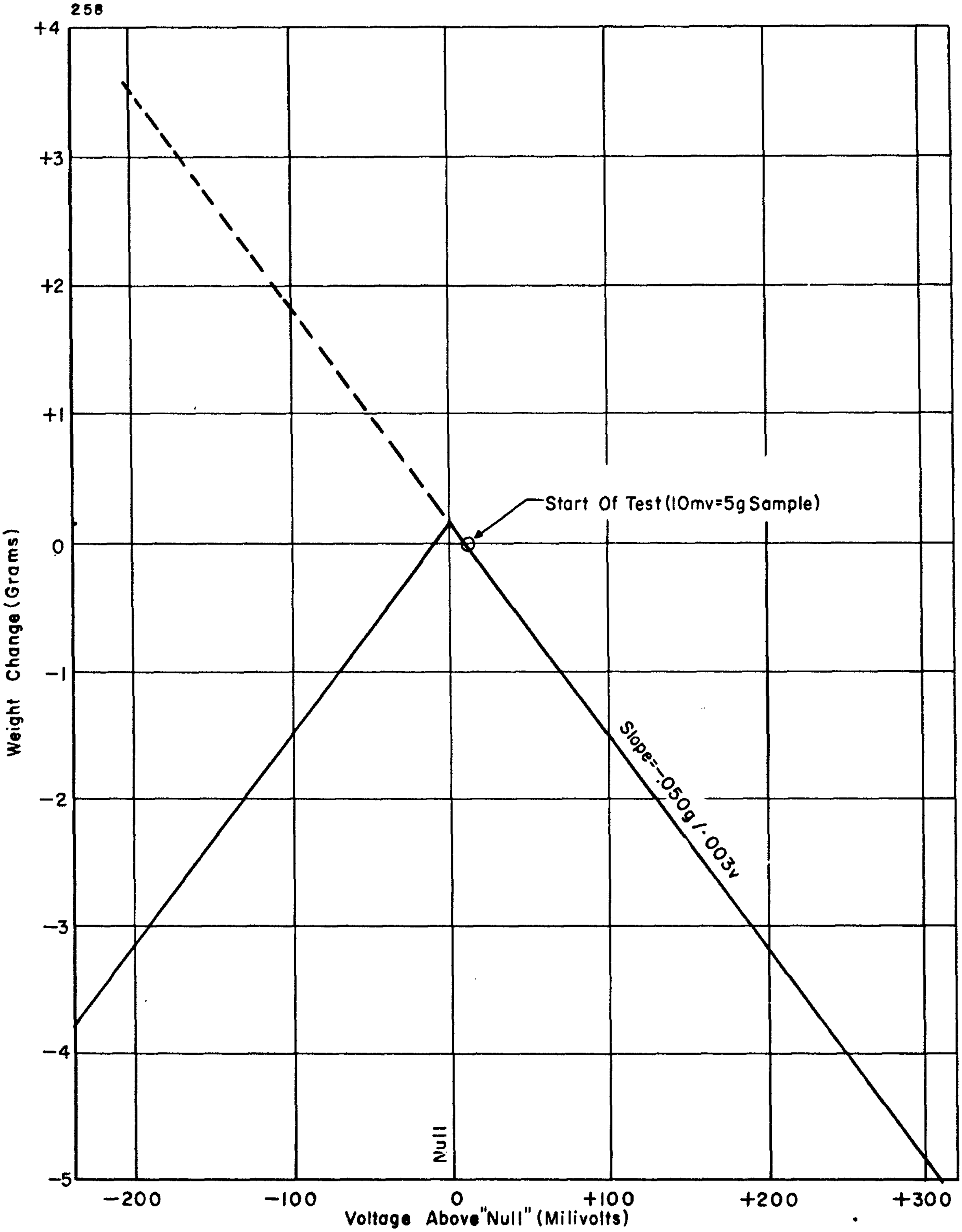


Figure 16. Calibration of Linear Variable Transformer

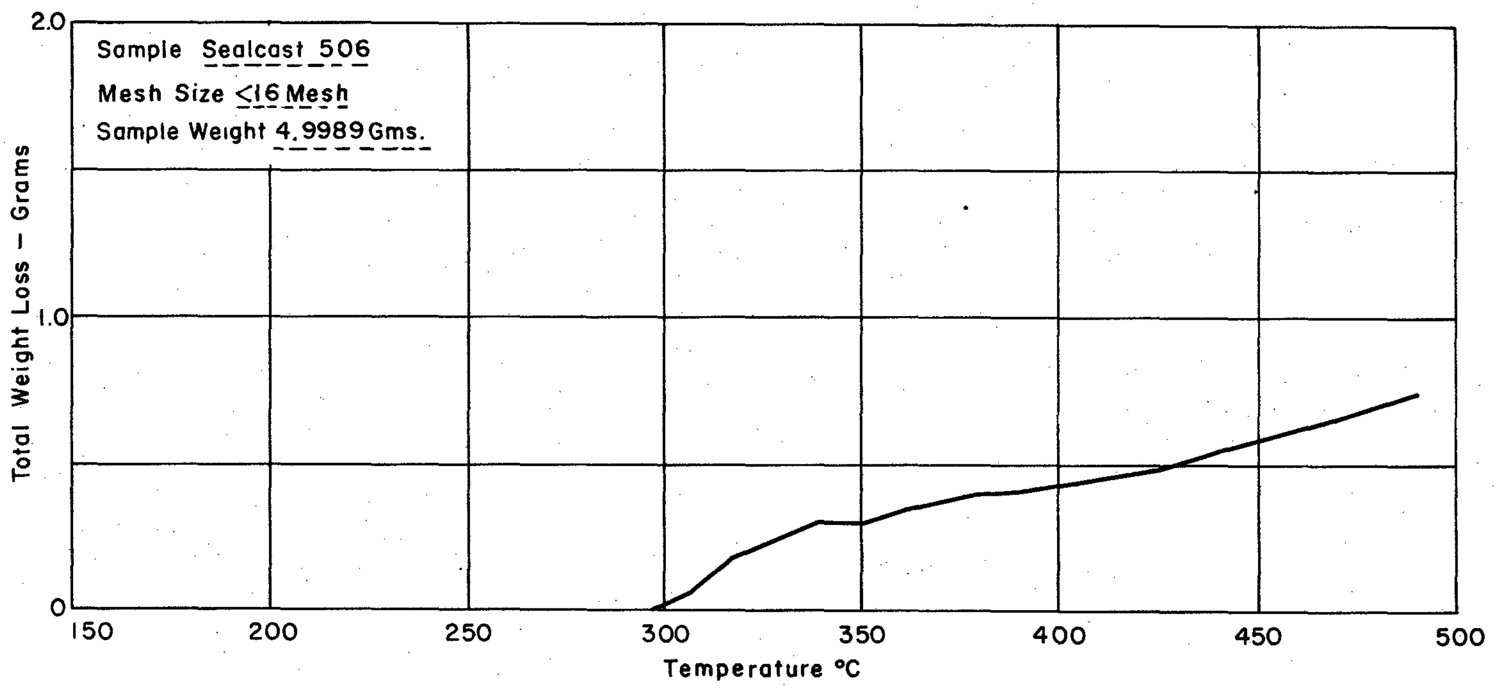


Figure 17. Thermal Gravimetric Analysis of Sealcast 506

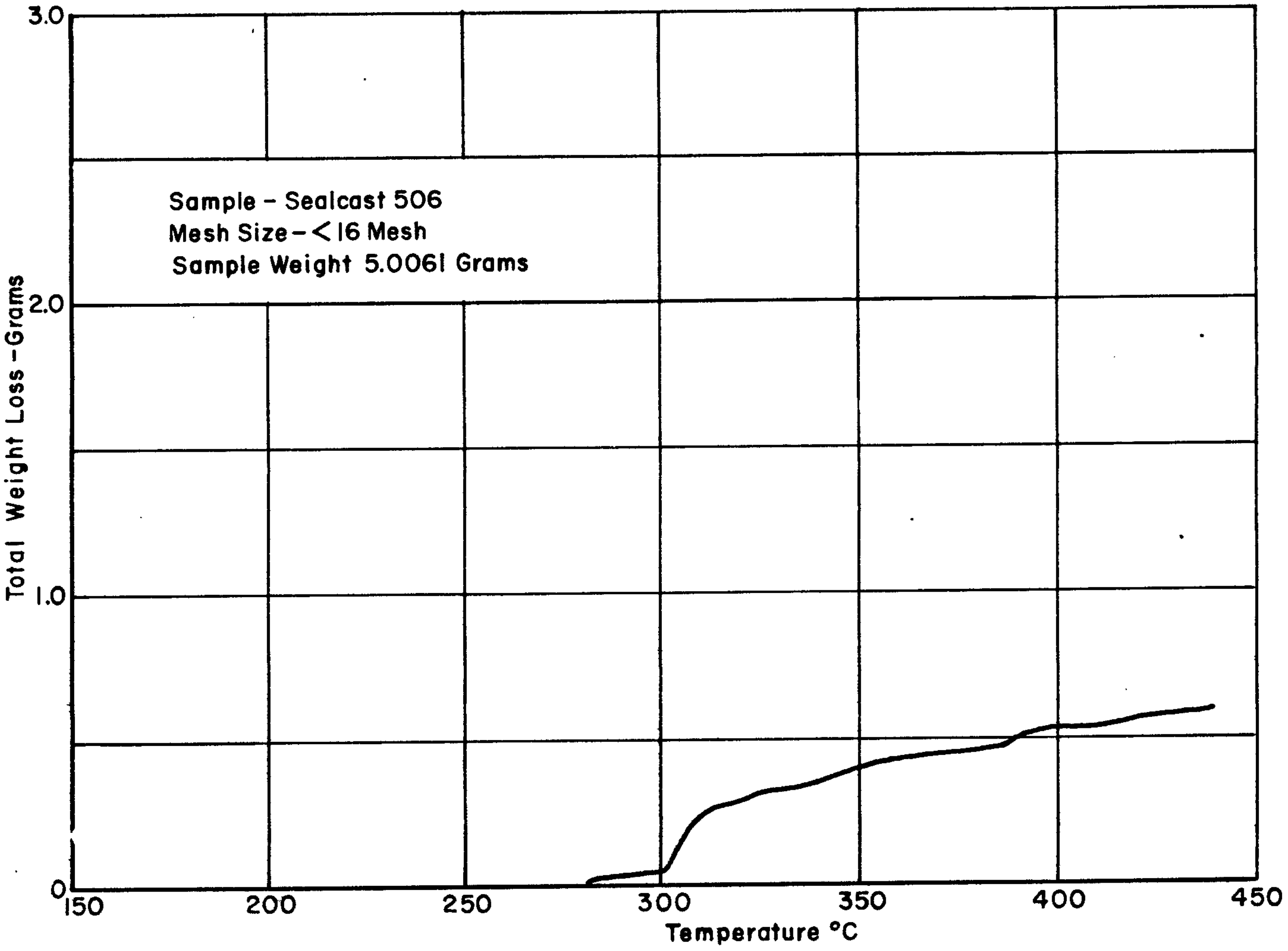


Figure 18. Thermal Gravimetric Analysis of Sealcast 506

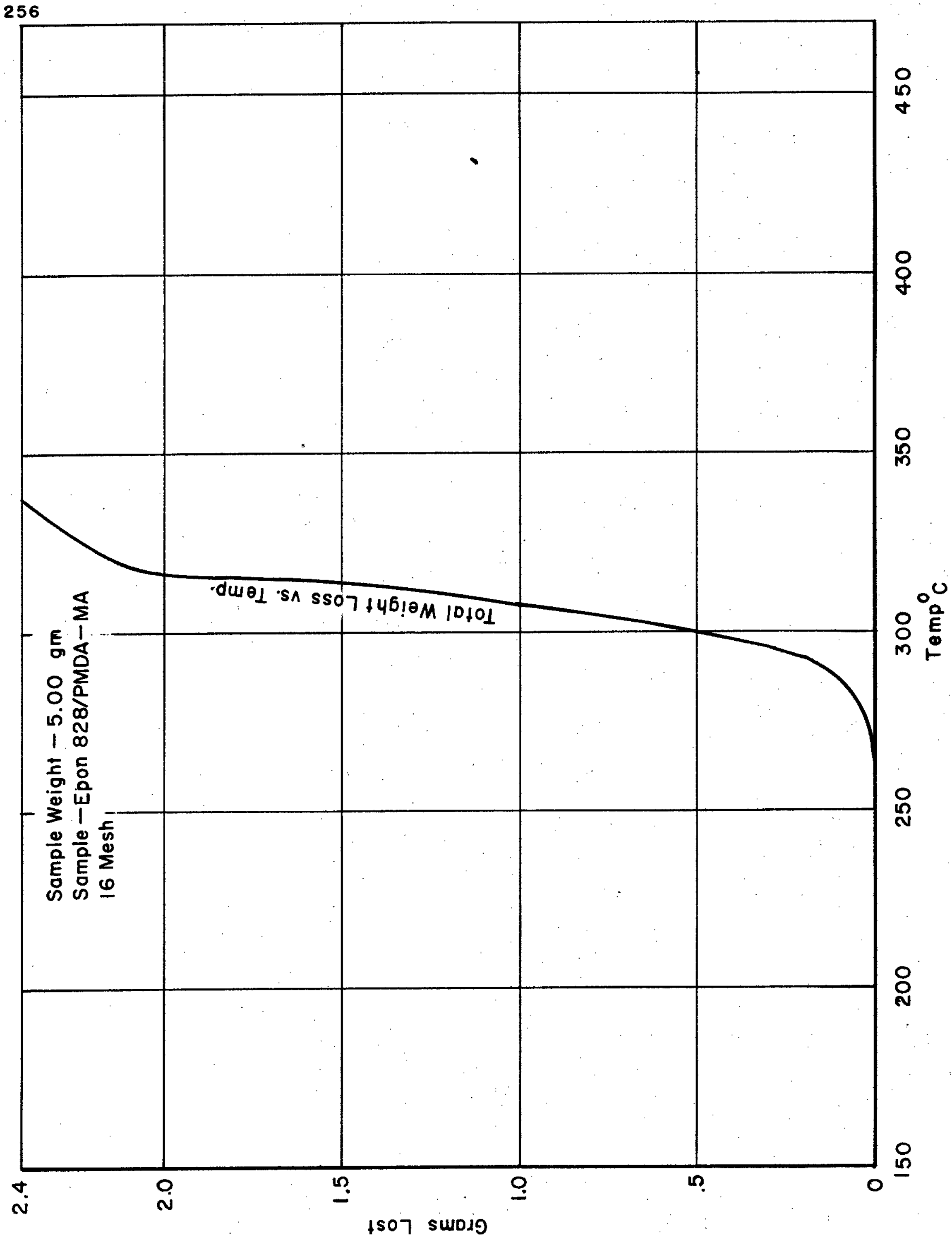


Figure 19. Thermal Gravimetric Analysis of Epon 828/PMDA-MA

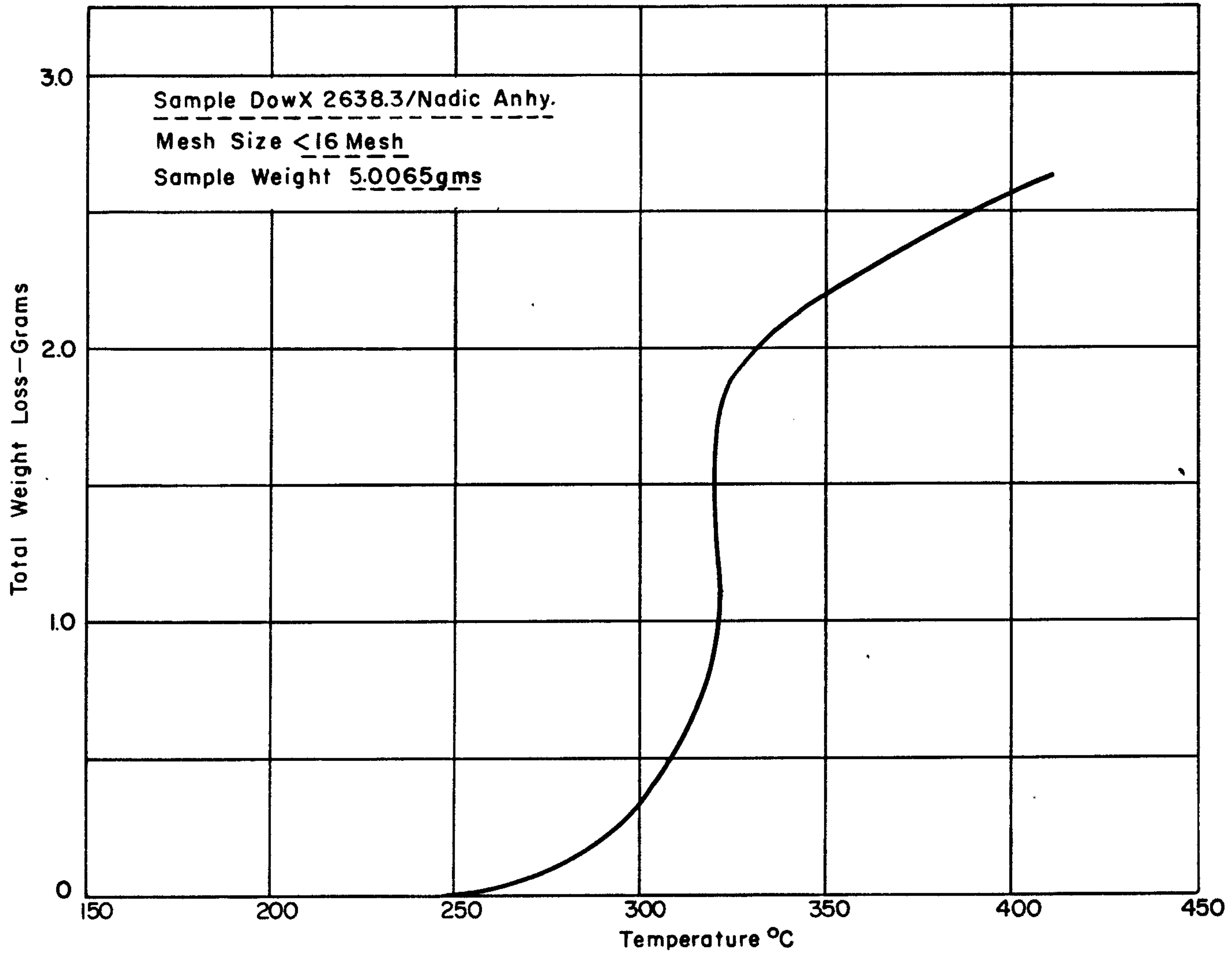


Figure 20. Thermal Gravimetric Analysis of Dow X2638.3 Nadic Anhy.

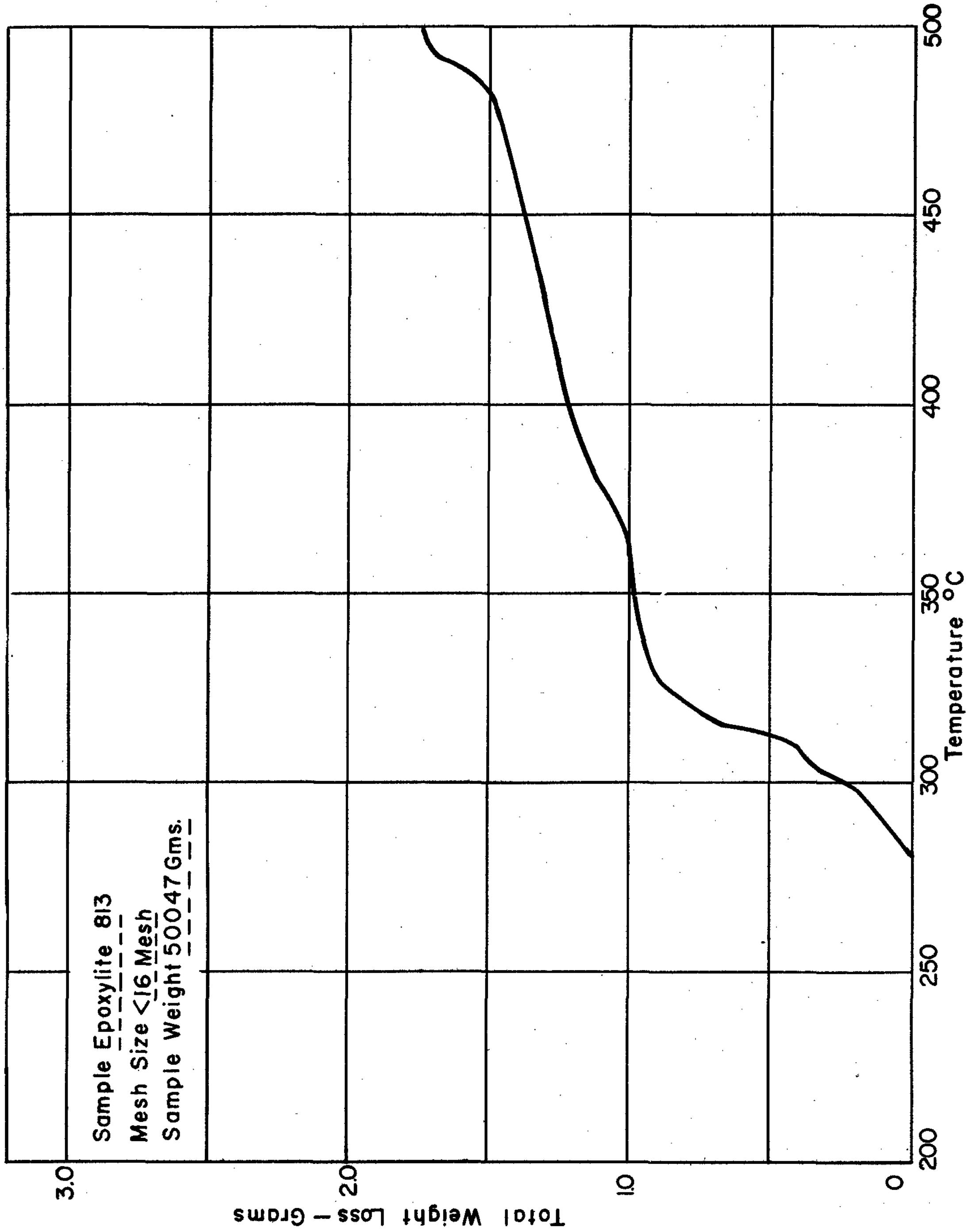


Figure 21. Thermal Gravimetric Analysis of Epoxylite IC

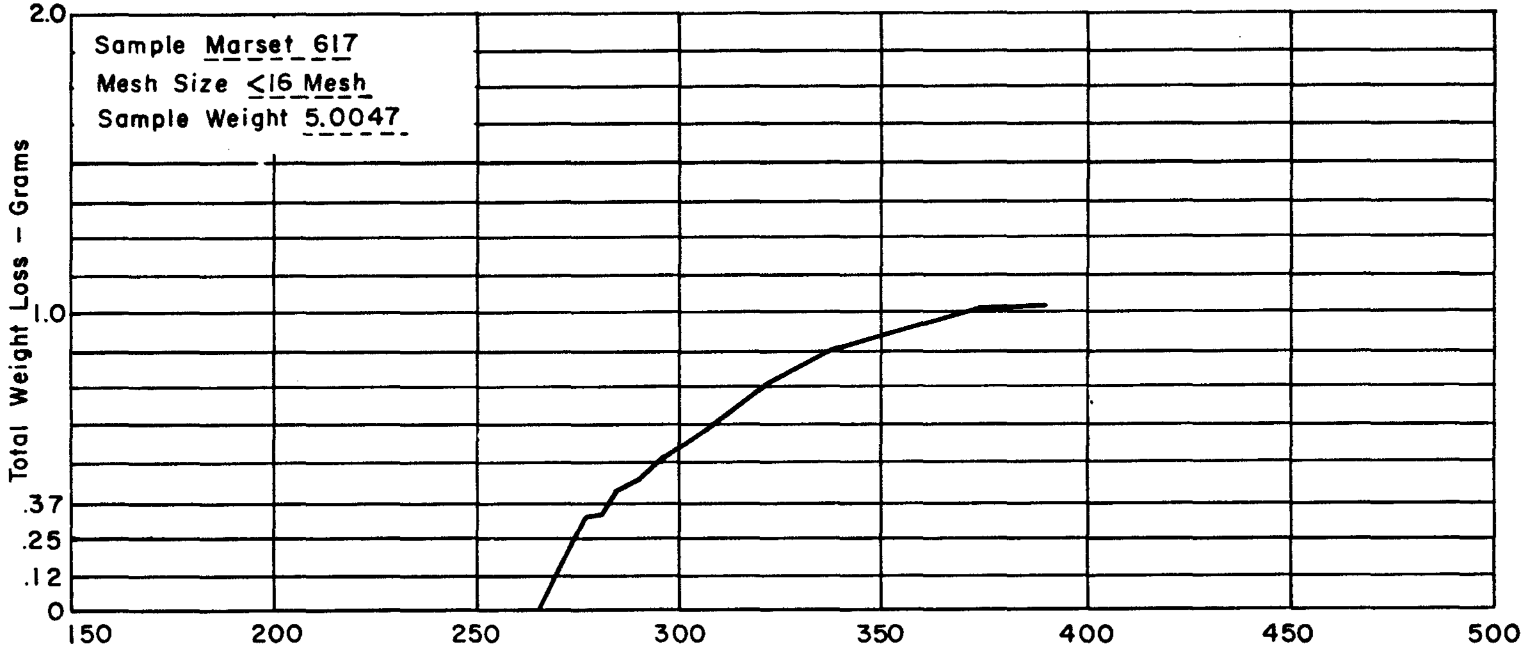


Figure 22. Thermal Gravimetric Analysis of Maraset 617

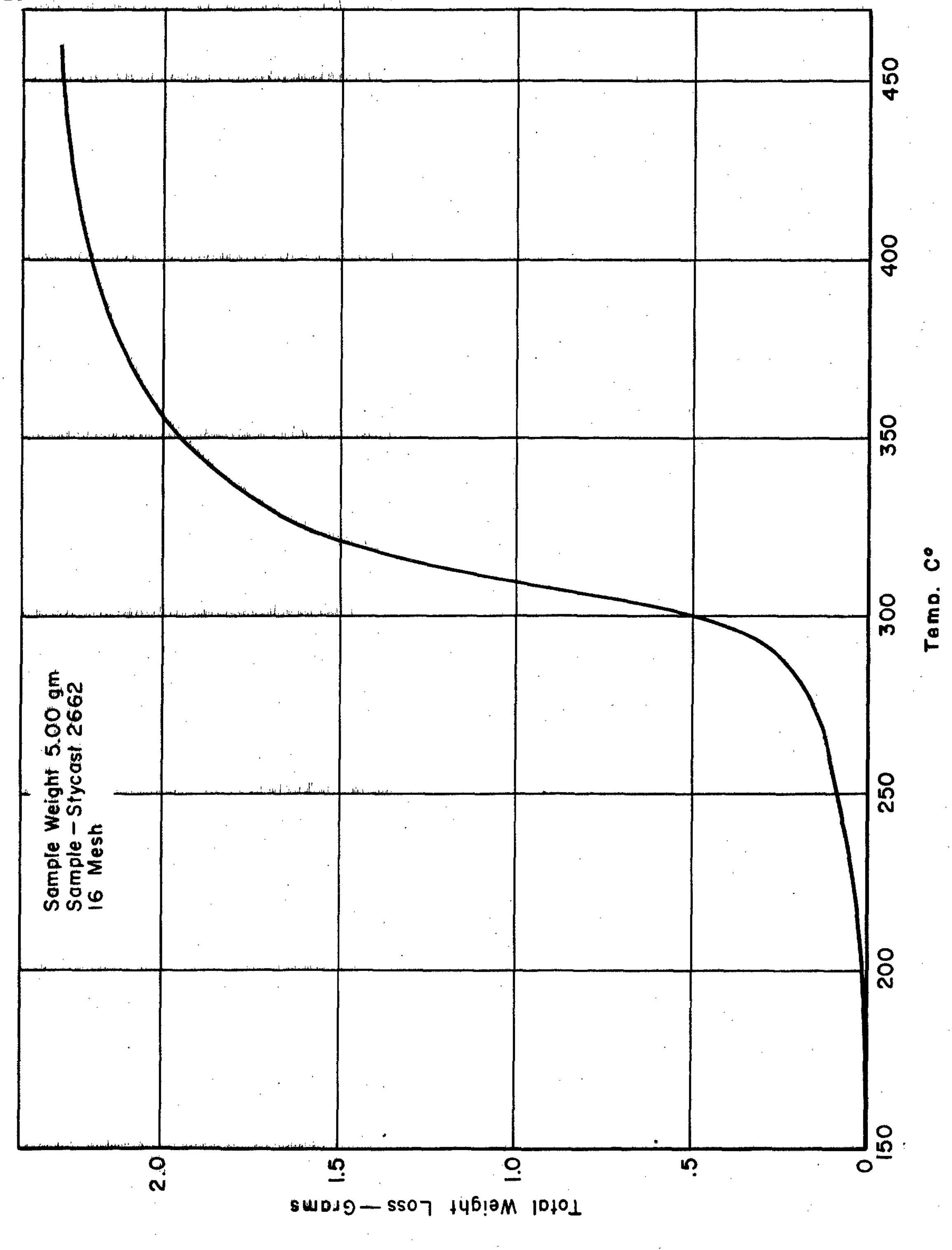


Figure 23. Thermal Gravimetric Analysis of Stycast 2662

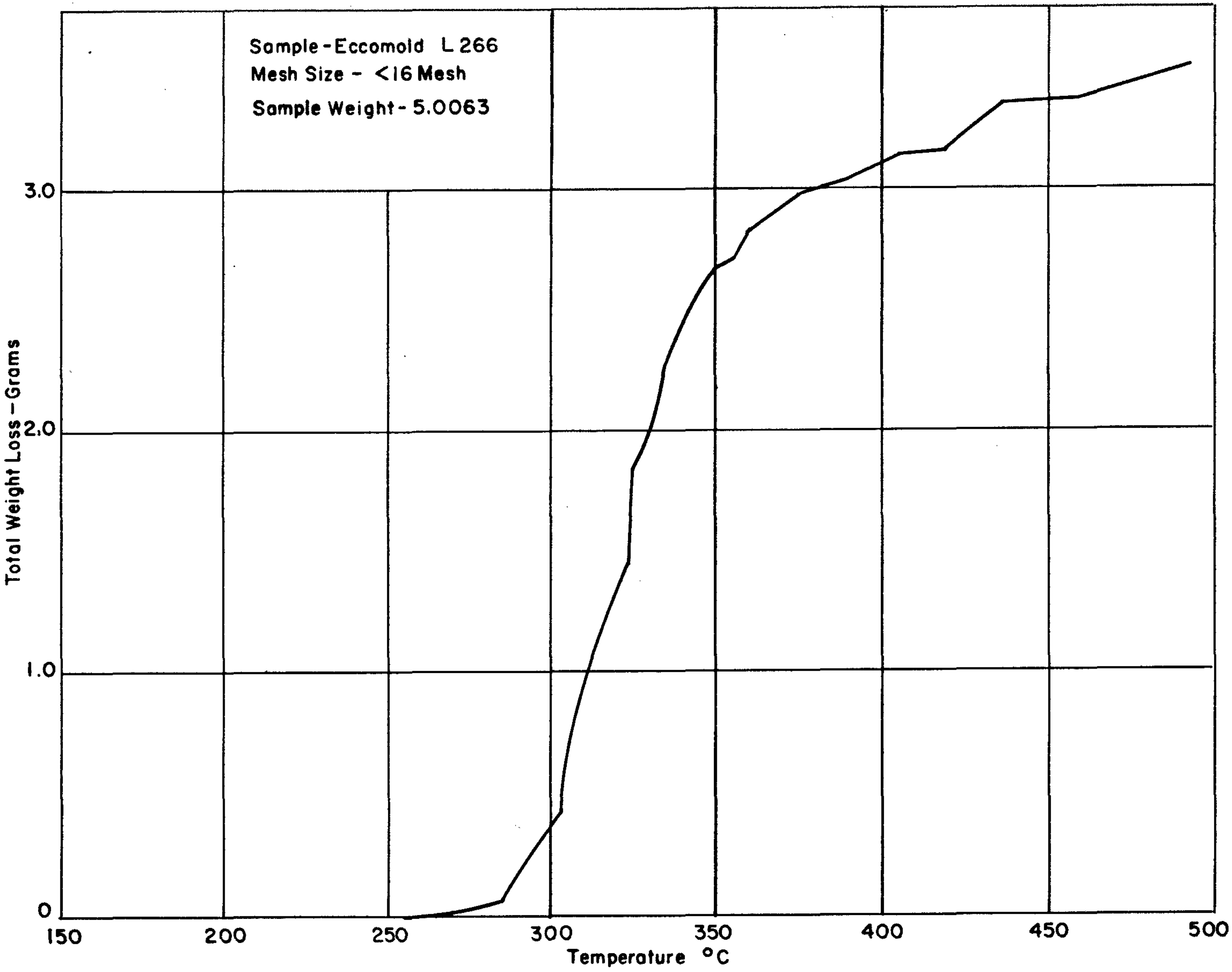


Figure 24. Thermal Gravimetric Analysis of Eccomold L 266

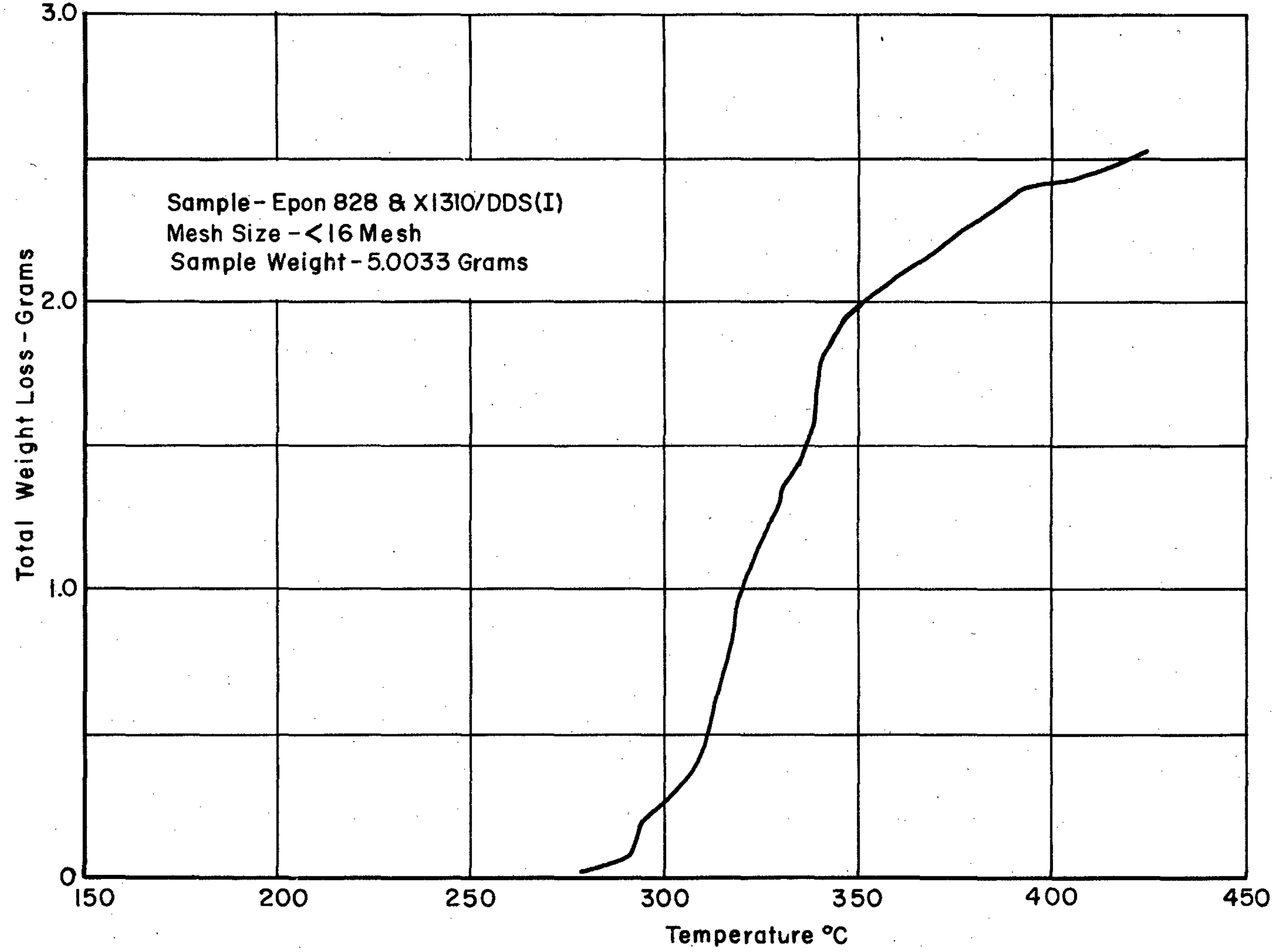


Figure 25. Thermal Gravimetric Analysis of Epon 828 and X1310/DDS

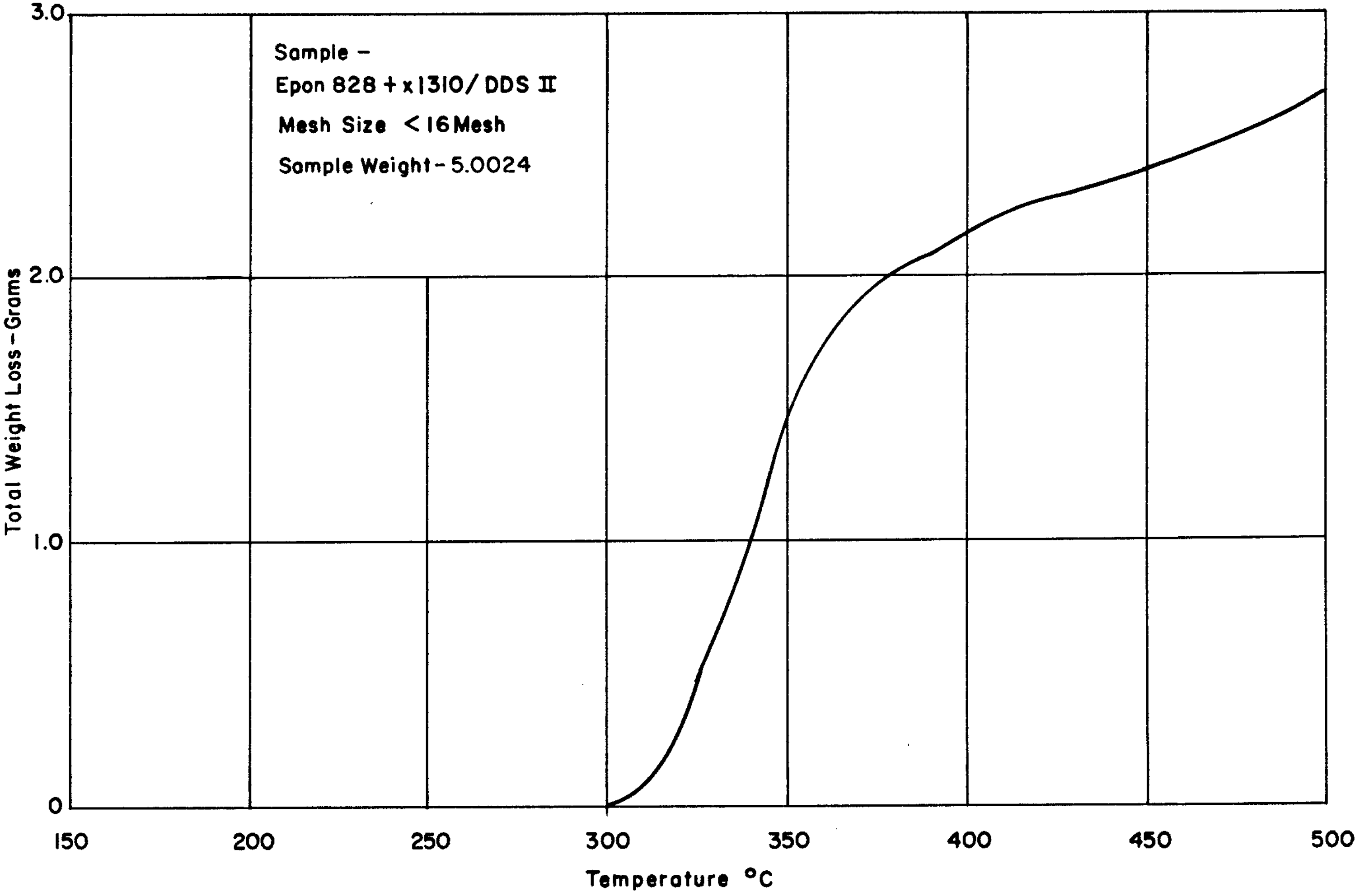


Figure 26. Thermal Gravimetric Analysis of Epon 828 and X1310/DDS

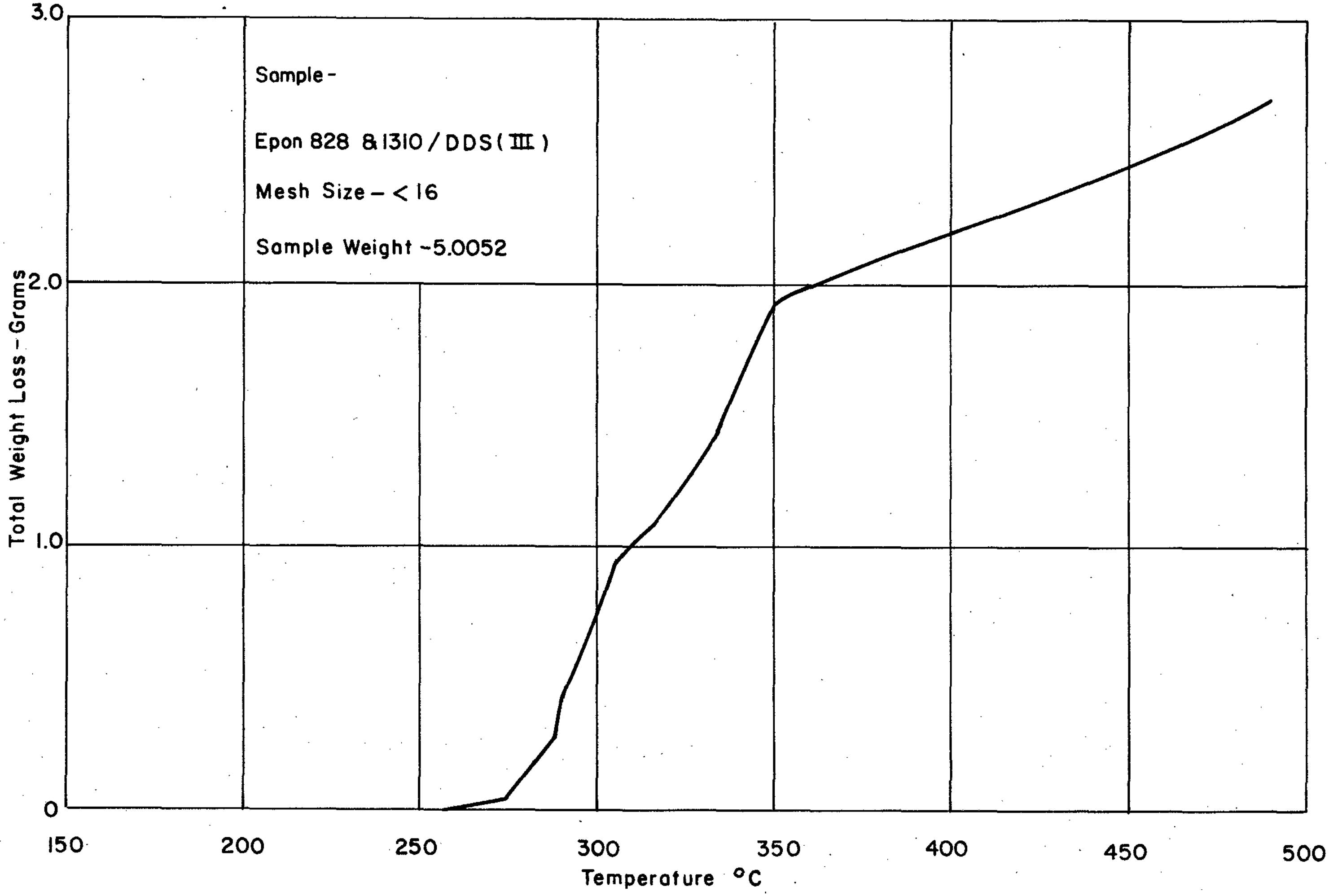


Figure 27. Thermal Gravimetric Analysis of Epon 828 and X1310/DDS

thereby molecular degradation as opposed to rearrangement, and that the degradation adversely affect the flexural strength of the resin (Heat of Distortion Test). It is unlikely that the mass loss is associated with driving off unpolymerized volatiles because such occurrence would have displayed an endotherm in DTA. The opposite was observed.

The results from the Epon 828/PMDA-MA sample indicated the following results:

1. Significant change (exothermic) in DTA plot at 260°C.
2. First indication of a weight change (loss) at 265°C.
3. Heat of Distortion occurred at 127°C (66 psi).

Considering the inherent errors in the methods, the 260° value for DTA and the 265° value for TGA may be considered at agreeing. However, the Heat of Distortion value of 127° is questionable. At this time the only valid conclusion that can be drawn is that the thermodynamic phenomenon which occurs at 260° is a degradation process involving a mass loss. The effect of the phenomenon on the flexural strength of the resin cannot be stated at this time because it is felt that questionable data was obtained from the Heat of Distortion test.

In viewing the possible reasons for discrepancies in the Heat of Distortion test for Epon 828/PMDA-MA sample, it was found that acceptable test samples were difficult to fabricate. The difficulty arose from the brittle nature of this resin which made fabrication to specific dimensions difficult. The cured resin also contained minute cracks which were still present in the ultimate test specimens. It was subsequently found that a reliable Heat of Distortion value, as measured by conventional methods, was not obtained for this resin.

Considering the rather close agreement in the DTA, TGA, and Heat of Distortion values for the Dow X2638.3 resin, it may be possible to draw a close relationship between accepted Heat of Distortion values and the DTA - TGA data. Certainly many more tests would be required before such a relationship can be ascribed any validity, but if it is substantiated it will present a convenient method for reporting "Heat of Distortion" values for those resins which cannot be tested directly. For example, certain resins cannot be cast in solid sections for Heat of Distortion tests. This is generally true of laminating resins where testing is conducted on reinforced structures and the true properties of the raw resin are neglected due to a testing limitation. It may be possible to measure the "Heat of Distortion" of such resins indirectly by measuring the DTA-TGA characteristics. As stated previously, it would be premature to attempt to draw this association with the limited data available, but this interesting possibility is apparent from the tests conducted.

Conclusions

DTA and TGA Analysis

TGA, as contrasted with DTA, has some inherent advantages when comparing the thermal stabilities of polymers. TGA curves have less uncertainty in their interpretation that DTA curves. This is because TGA curves share a common, well-defined knee in the single temperature range, wherein disruptive volatilization first becomes rapid.

For DTA curves, the first prominent peak was taken as the "end-point." For the TGA curves, the "end-point" was taken at maximum slope in the knee of the curve.

Table IV shows the thermal stability of the polymers in decreasing order as interpreted from TGA curves and supplemented with DTA and Heat Distortion data where applicable.

TABLE IV

Thermal Stability of Polymers in Decreasing Order as Interpreted From Thermal Gravimetric Analysis

SAMPLE	TGA DEGRADATION TEMPERATURE	DTA DEGRADATION TEMPERATURE 10% Resin 90% Al_2O_3	HEAT DISTORTION (264 psi)
Eccomold L266	375°C	330°C 340*	350°C
Epon 828 and X1310/DDS II	365	296*	298°C
Stycast 2662	350	300 355*	no sample
Maraset 617	350	325	sample broke 325°C
Epon 828 and X1310/DDS (I)	350	296*	295°C
Epon 828 and X1310/DDS (III)	350	269*	303°C
Dow X2638.3	330	375 340*	254°C
Epoxylite 813	325	330*	290°C
Sealcast 506	312-325	320*	325°C
Epon 828/PMDA-MA	317	313	no sample
Epon X1310	—	320*	350°C
Permacel ST-3994	—	293*	199°C

*10% resin and 90% Al_2O_3

2.3 Synthesis

2.3.1 General

The synthesis phase was directed toward the production of heat stable epoxy resin polymers. Experimental efforts were concentrated in the following general areas:

(1) Reactions of tetrakis-(hydroxymethyl) phosphonium chloride (THPC);

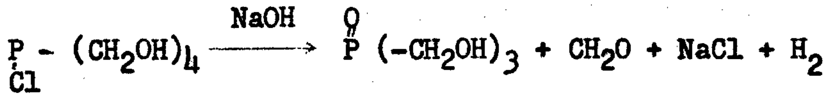
(2) Reactions of tris(hydroxymethyl) phosphine oxide (THPO);

(3) The reaction of titanium lactate and epichlorohydrin; and

(4) Miscellaneous preparations of organo-phosphorus compounds.

2.3.2 Reactions of Tetrakis-(Hydroxymethyl) Phosphonium Chloride (THPC)

Tetrakis-(hydroxymethyl) phosphonium chloride (THPC), is the salt of a weak base and a strong acid, and has a pH in an aqueous solution of approximately 2. In the presence of alkali, THPC liberates formaldehyde and hydrogen to form tris-(hydroxymethyl) phosphine oxide, (THPO).



$$\underset{Cl}{P} - (CH_2OH)_4 \xrightarrow{NaOH} \overset{O}{\overset{\|}{P}} (-CH_2OH)_3 + CH_2O + NaCl + H_2$$

Reeves and Guthrie[1] report that it is most likely that THPC is converted to THPO during reaction in alkaline, neutral or mildly acidic solutions, or when heated. Under these conditions the compound acts as a trifunctional monomer. Both THPC and THPO were supplied by Hooker Electrochemical Co., Niagra Falls, New York.

2.3.2.1 Base Catalyzed Reactions of THPC and Epichlorohydrin (Tables V and VI). Initially the reactions of epichlorohydrin and THPC or THPO were carried out in the presence of excess sodium hydroxide, which is employed in the commercial epichlorohydrin/bisphenol A reaction as a catalyst and as a neutralizer for the hydrochloric acid which is formed.

The postulated structure of the THPC-epichlorohydrin condensation is shown in Figure 28. Use of the trifunctional monomer permits formation of three dimensional polymers. It is important that cross-linking due to the trifunctionality of the monomer be avoided in the initial reaction. During final cure the cross-linking and a significant increase in thermal stability of the resin should result.

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[1] W. A. Reeves and John D. Guthrie, "Intermediates for Flame Resistant Polymers," Ind. and Eng. Chem., 48, No. 1: 64-7 (1956).

The amounts of reactants and the pertinent reaction conditions for each experiment are summarized in Tables V and VI.

Experiments P-1A, P-1B, P-1C and P-1D

These experiments consisted of reacting epichlorohydrin and THPC in aqueous caustic solution (30 percent NaOH solution). The reaction product was vacuum dried and the sodium chloride crystals were filtered from the high viscosity liquid which remained. The vacuum distillate from Experiment P-1D was fractionally distilled at atmospheric pressure to determine the by-products. From the refractive index of this distillate (1.3329) and the distillation temperature, the distillate is doubtlessly water. No higher boiling material was obtained from the vacuum distillate before the flask was dry. This would indicate that all the epichlorohydrin had reacted. The high viscosity materials obtained after vacuum drying the reaction products were found to be water soluble.

The IR spectra of materials from each of these experiments showed some slight indication of the presence of epoxy groups and all the materials showed very intense hydroxyl absorption bands.

All samples absorbed at the same frequencies, however, the intensity of absorption differed depending upon the reactant which was used in excess initially. Samples prepared with an excess of epichlorohydrin showed more intense epoxide absorption indicating the presence of unreacted epichlorohydrin. In addition, a new band at 6.25μ appeared, which may be due to water of hydration.

The complete disappearance of the 6.2μ band during curing supports the assignment of it to water of hydration, since, at the curing temperature, the water would probably volatilize and escape.

Curing

Reaction Product	Curing Agent	Condition of Final Sample
P-1A	BF 3-400 (Shell) (Boron Trifluoride Aminecomplex)	Water soluble Flexible foam
P-1A	Nadic Anhydride	Hard, water insoluble foam.
P-1A	Pyromellitic Anhydride and Maleic Anhydride	Hard, water insoluble foam.
P-1B	Pyromellitic Anhydride and Maleic Anhydride Pyridine Accelerator	Hard foam which absorbed water but did not dissolve.

Curing (Con't.)

Reaction Product	Curing Agent	Condition of Final Sample
P-1C	BF 3-400 (Shell)	Water soluble, flexible foam.
P-1C	Nadic Anhydride	Hard, water insoluble foam.
P-1C	Pyromellitic Anhydride and Maleic Anhydride	Hard, water insoluble foam.

Experiment P-11

This experiment was similar to Experiment P-1A except no sodium hydroxide was employed in the reaction. No syrupy product was formed in the aqueous solution after the reaction. The aqueous solution was vacuum-dried; a high viscosity polymeric material remained. This polymer could be dissolved in water.

The IR spectra of the material from this experiment did not show any characteristic epoxy absorption bands. However, an intense hydroxyl absorption band was observed in the spectra.

Curing

Reaction Product	Curing Agent	Condition of Final Sample
P-11	DDS (Diamino-diphenyl Sulfone	Too viscous to mix with DDS at 132°C.
P-11	BF 3-400 (Shell) Boron trifluoride amine complex	Water soluble, tacky on surface, hard beneath surface.

Experiments P-2 and P-10

These experiments were designed to determine the effect of THPC on the epichlorohydrin - bisphenol A polymer. These reactions were carried out in the presence of sodium hydroxide. Polymers were formed from each of these reactions which were not water soluble.

The IR spectrum of the prepared polymer compared favorably with the IR spectra of Shell Polymer No. 834. Comparison of the two spectra showed that both spectra has absorption bands which could be attributed to epoxy groups. Indications that the THPC had been incorporated into the polymer could not be detected from the spectra.

TABLE V

Base Catalyzed Reactions of THPC and Epichlorohydrin

Experiment No.	REACTANTS Epichlorohydrin (moles)	Bisphenol A (moles)	THPC (Moles)	30% NaOH Wt. gm.	Water ml.	Time-Temp. hr/°C	REMARKS
P-1	3		1	150		13- 107°	Water solution, crystals identified as NaCl, did not form polymer on drying, viscosity increase noticed.
P-2	5	1	1	266	120	7- 107°	Polymer formed, solid mass, could not be removed from reaction vessel.
P-3	7	2	1	100	170	2- 100°	High viscosity liquid obtained which was water soluble.
P-4	11	4	1	100	366	2- 100°	Polymer
P-5	15	6	1	100	150	2- 100°	Polymer
P-6	19	8	1	100	200	2- 100°	Polymer
P-7	23	10	1	100	170	2- 100°	Polymer
P-8	27	12	1	100	170	2- 100°	Polymer
P-9	31	14	1	100	170	2- 100°	Polymer
P-10	35	16	1	100	170	2- 100°	Polymer
P-11	3		1		50	6.5- 100°	High viscosity liquid obtained after vacuum drying which was water soluble.
P-3B	7	2	1	100	170	2- 100°	Repeat of P-3

TABLE V (Cont.)

Base Catalyzed Reactions of THPC and Epichlorohydrin

Experiment No.	REACTANTS						
	Epichlorohydrin (moles)	Bisphenol A (moles)	THPC (Moles)	30% NaOH Wt. gm.	Water ml.	Time-Temp. Hr/°C	REMARKS
P-11B	3		1		50	6.5-100°	Repeat of P-11
P-1A	1		1/3	150	100	6.5-100°	High viscosity liquid obtained after vacuum drying, which was water soluble; NaCl crystals filtered off from liquid.
P-1B	2		2/3	375	250	94-100°	Same as Exp. P-1A.
P-13[1]	2		.065			6.75-60°	High viscosity liquid obtained after vacuum drying; KCl crystals formed. Liquid portion water soluble.
P-1C	2		2/3	242	250	6.5-100°	Same as Exp. P-1A
P-1D	2		2/3	300	250	7-100°	Same as Exp. P-1A. Distillate from vacuum drying was fractionally distilled. Test by refractive index showed that water was the only by-product of the original distillate.
P-14[2]	1		1/3[2]	204	175	6.5-100°	High viscosity liquid and NaCl crystals obtained after vacuum drying. Liquid portion was water soluble.
P-17	1		1	320	250	12.5-100°	High viscosity liquid was obtained which was water soluble.
P-18	3		0.5	120	450	6.5-100°	High viscosity liquid was obtained which was water soluble.

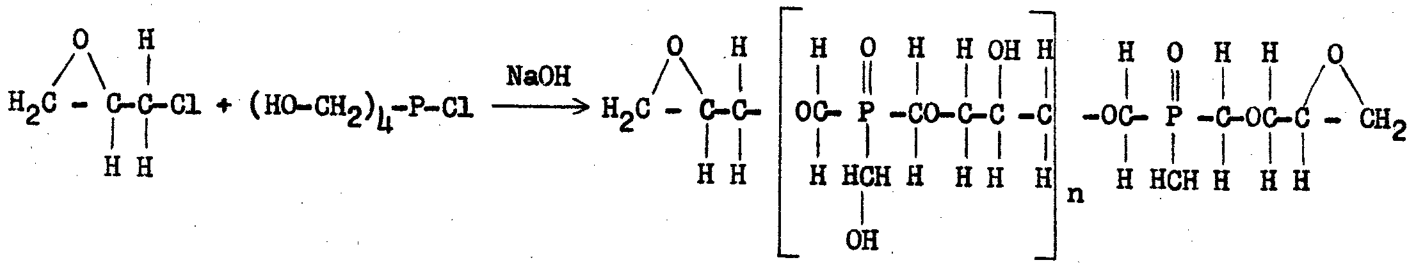
---

[1] 830 ml KOEt solution (13g in 1 l. ethanol) used as the base.
[2] THPO was used as a starting material instead of THPC.

TABLE VI

Base Catalyzed Reactions of THPC and Epichlorohydrin in Presence of Pyridine

Experiment No.	Reactants						Remarks
	Epichlorohydrin Moles	THPC Moles	Pyridine ml.	NaOH gm.	Time hrs.	Temp. °C	
P-19	0.032	.010	40	0.84	2.5	91	A black tar-like product obtained.
P-20	0.032	.010	40	—	1	104	A black tar-like product obtained.
P-21	—	.010	40	—	2	104	No evidence of reaction.
P-22	0.032	—	40	—	1	104	A black tar-like product obtained.
P-23	0.33	0.11	250	—	3.5	100	A dark high viscosity liquid obtained.
P-24	2.0	0.66	400	—	4.5	100	A black tar-like product obtained.



(Epichlorohydrin) (THPC)

FIGURE 28

Formation of Phosphorous Bearing Epoxy Polymers with THPC and Epichlorohydrin

Curing

Reaction Product	Curing Agent	Condition of Final Sample
P-3	DDS (diamino-diphenyl sulfone) BF 3-400 (Shell) Boron trifluoride amine complex	Thermoplastic at 127°C
P-4	DDS BF 3-400	Thermoplastic at 127°C

Experiment P-13

To determine the effect of the reaction medium on the final solubility of the reaction product of epichlorohydrin and THPC this experiment was carried out in a non-aqueous medium. THPC was reacted with epichlorohydrin in ethyl alcohol with potassium ethoxide as the base. The reaction product was vacuum dried and the potassium chloride crystals were filtered from the high viscosity liquid which was obtained. This liquid was found to be water soluble. Attempts were made to produce an insoluble mass through effective cross-linking with acid anhydrides.

The IR spectra of the reaction product was obtained; however, no indications of the epoxy groupings could be detected in the spectra. The reaction product was also water soluble.

Curing

Reaction Product	Curing Agent	Condition of Final Sample
P-13	Pyromellitic Anhydride and Maleic Anhydride Pyridine accelerator	Hard foam which absorbed water, but did not dissolve.

Experiments P-17 and P-18

Further variations in the reaction of epichlorohydrin and THPC in the presence of strong base were studied.

Past reactions with epichlorohydrin and THPC were primarily concerned with varying the reaction time, temperature, and amount of NaOH but maintaining stoichiometric amounts of the reactants.

In experiments P-17 and P-18, variations were made in the molar ratios. In experiment P-17, the amount of THPC added is in excess of the required stoichiometric amount, while in experiment P-18, the amount of epichlorohydrin is in excess of the stoichiometric requirement. The primary objective in each case was to increase the number of available reactive sites.

In both experiments it was desirable to reduce the water solubility of the resultant product by increasing its molecular weight through chain lengthening. The ratio of epichlorohydrin to THPC for the reaction is shown in Table V. All of the reactions were very exothermic and products of high viscosity were obtained after removing water by vacuum distillation. The products were water soluble and not significantly different in appearance from those reported previously. (See Experiments P-1A, P-1B, P-1C, and P-1D.)

Analysis P-17 and P-18

The IR spectra of materials from each of these experiments showed some slight indication of the presence of epoxy groups and very intense hydroxyl absorption bands.

Experiments P-19, P-20, P-21, P-22, P-23, and P-24

The reaction of THPC and epichlorohydrin in pyridine was investigated more fully. It was hoped that pyridine would function both as an acid acceptor and a non-aqueous solvent for the reaction.

Epichlorohydrin and THPC in pyridine were heated with and without NaOH. In both reactions, a dark water soluble liquid of high viscosity was obtained. No reaction was observed when THPC alone was heated with pyridine. However, epichlorohydrin and pyridine yielded a dark liquid similar in appearance to the product obtained previously from epichlorohydrin and THPC in pyridine. Since amines are known to catalyze the cleavage of epoxide rings, it might be concluded that the only reaction observed is a reaction between pyridine and epichlorohydrin and that THPC does not enter into the reaction.

Analysis of samples P-20 and P-22 was conducted in order to determine the functional groups present. The spectrum of sample P-20 obtained from the reaction of THPC, epichlorohydrin, and pyridine showed hydroxyl absorption. The hydroxyl band was very strong and broad, indicating the occurrence of hydrogen bonding which has been evident in pure THPC and pure THPO. Phosphoryl absorption similar to that noted with pure THPO suggests that the THPC has undergone decomposition to THPO during the course of the reaction due perhaps to heating of the reaction mixture.

Epoxide absorption of sample P-20 was not evident, which indicates cleavage of the epoxide ring. The spectrum of sample P-22 was recorded in order to determine whether cleavage of the epoxide ring could be due to a reaction between epichlorohydrin and pyridine only. This spectrum showed strong hydroxyl absorption and no absorption due to the epoxide ring. This suggests that in sample P-20 cleavage of the epoxide ring was catalyzed by the pyridine present, and the THPC may not have taken part in the reaction but rather decomposed to THPO upon heating the reaction mixture.

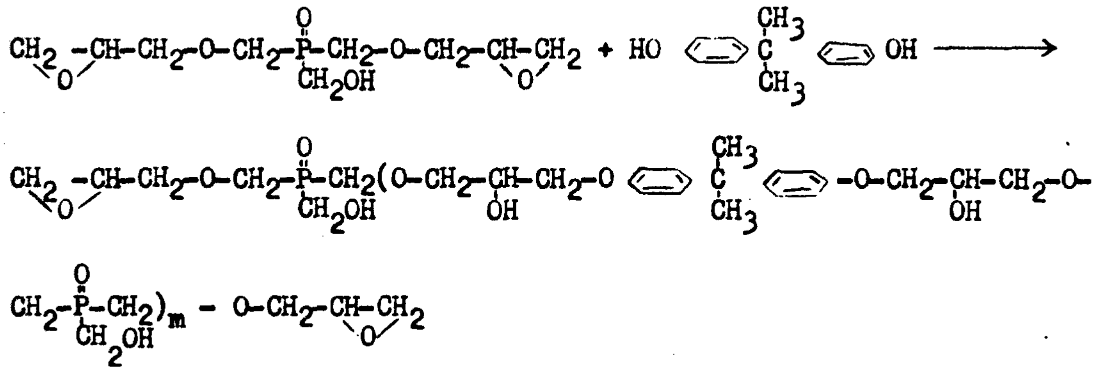
Curing

Reaction Product	Curing Agent	Condition of Final Product
P-24	Pyromellitic Anhydride and Maleic Anhydride Pyridine Accelerator	Water soluble tar.

2.3.2.2 Reaction of Bis-phenol A and the Reaction Product of THPC and Epichlorohydrin (See Experiment P-1D)

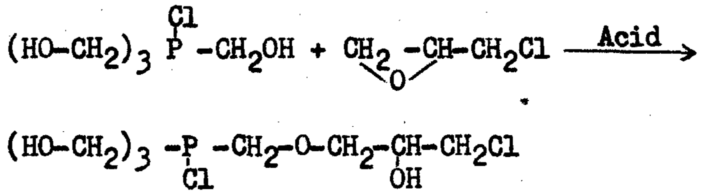
Experiment P-26

The reaction products of THPC and epichlorohydrin in the presence of aqueous NaOH have all been water soluble. The product of Experiment P-1C is typical of these preparations. If these products contained reactive epoxide groups, it was reasonable to expect it to react with Bis-phenol A in the presence of base to give a water-insoluble polymer. This polymer could then be cross-linked through the hydroxyl groups formed and the epoxide groups at the ends of the chains. Assuming a di-epoxide structure for the reaction product of THPC and epichlorohydrin, the proposed reaction might be represented as follows:



The reaction product of THPC and epichlorohydrin was heated with Bis-phenol A in the presence of aqueous NaOH. There was no evidence of reaction and a crystalline material resembling the original Bis-phenol A came out of solution on cooling. No spectrum was obtained.

2.3.2.3 Acid Catalyzed Condensation of THPC and Epichlorohydrin (Table VII). In these reactions it was assumed that the hydroxyl groups of THPC behave as alcoholic hydroxyls[1]. An acid-catalyzed reaction of THPC with epichlorohydrin might, therfore, be expected to proceed as follows[1]:

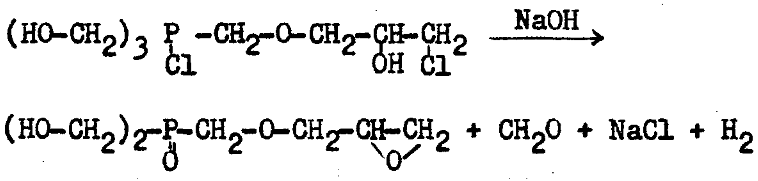


$$(HO\text{-}CH_2)_3\overset{Cl}{P}\text{-}CH_2OH + \underbrace{CH_2\text{-}CH}_{O}\text{-}CH_2Cl \xrightarrow{Acid}$$

$$(HO\text{-}CH_2)_3\text{-}\underset{Cl}{P}\text{-}CH_2\text{-}O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2Cl$$

The reaction is not limited to the condensation of one mole of epichlorohydrin with a mole of THPC, as shown above. Theoretically, each of the hydroxyl groups of the THPC is capable of reacting with a mole of epichlorohydrin.

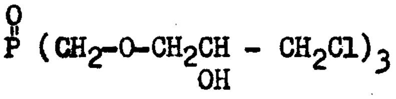
The subsequent treatment of the chlorohydrin with strong NaOH should effect ring closure to give the epoxide. It is known[2] that THPC in aqueous base is converted to THPO. It is postulated, therefore, that the second step of the reaction might proceed as follows:



$$(HO\text{-}CH_2)_3\underset{Cl}{P}\text{-}CH_2\text{-}O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}\underset{Cl}{CH_2} \xrightarrow{NaOH}$$

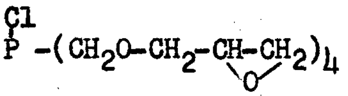
$$(HO\text{-}CH_2)_2\text{-}\underset{O}{P}\text{-}CH_2\text{-}O\text{-}CH_2\text{-}\underbrace{CH\text{-}CH_2}_{O} + CH_2O + NaCl + H_2$$

The instability of THPC raises certain questions concerning the probable course of the reaction. Decomposition to THPO may occur during the initial acid catalyzed reaction, in which case only three hydroxyl groups would react and the final product after reaction with three moles of epichlorohydrin would be:



$$\overset{O}{P}\ (CH_2\text{-}O\text{-}CH_2\underset{OH}{CH} - CH_2Cl)_3$$

On the other hand, it is quite possible that under mild anhydrous conditions, all four hydroxyls would react. In this case, decomposition to the tertiary phosphine oxide may not occur even during the ring-closing step with base, and the final product would have the structure:



$$\overset{Cl}{P}\text{-}(CH_2O\text{-}CH_2\text{-}\underbrace{CH\text{-}CH_2}_{O})_4$$

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[1] Technical Booklet SC: 49-35 "Epichlorohydrin" Shell Chemical Corp.

[2] W. A. Reeves and John D. Guthrie, Ind. and Eng. Chem. 48, No. 1, 64-7, 1958.

The stability of this proposed structure is unknown.

Experiment K-1

A catalytic amount of concentrated H_2SO_4 was added to 1 mole of epichlorohydrin and THPC was added gradually to the stirring mixture. After 0.25 mole of THPC had been added, the reaction mixture was heated gradually and the THPC appeared to dissolve slowly. At 40°C an exothermic reaction took place with explosive violence and the temperature rose suddenly to 140°C. A sample of the resulting product was salvaged. It was light yellow, viscous liquid almost completely soluble in water. A sample was submitted for spectral analysis.

Since the spectrum obtained was very poorly resolved, the purity of the sample was considered to be questionable. Nevertheless, the spectrum obtained was compared to the spectrum of pure THPC and epichlorohydrin. Although the spectrum was not identical to that of pure THPC, several similarities were evident. There were no sharp absorption peaks characteristic of the oxirane group. Several broad bands suggest additive absorption from a mixture of components. It is concluded, therefore, that the sample is a mixture of unreacted THPC and intermediate addition products from the reaction of THPC and epichlorohydrin.

Experiment K-3

The experiment above (K-1) was repeated with 0.25 moles of epichlorohydrin in 150 ml of benzene. After an equimolar quantity of THPC had been added, the reaction mixture was heated slowly to 80°C then allowed to cool. There was no evidence of an exothermic reaction. No solids remained but the reaction mixture consisted of two phases. The upper phase included the benzene and probably some unreacted epichlorohydrin. The lower phase was a viscous liquid almost completely soluble in methanol. Quantitative analysis of the lower phase indicated the absence of epoxide groups.

Experiment K-5, K-8, K-11, K-16, K-19, K-22, K-27, and K-31

In spite of the exothermic nature of the acid-catalyzed reaction of THPC and epichlorohydrin, it was found possible to control it by adding the THPC very slowly and cooling the reaction mixture during the initial stages of exothermic reaction. Using this technique, several runs were made in which the ratio of epichlorohydrin to THPC was varied from 0.5 mole epichlorohydrin per mole THPC to 8.0 moles epichlorohydrin per mole of THPC. In all cases a highly exothermic reaction was observed and the final product was a clear viscous syrup. With a higher ratio of epichlorohydrin, the reaction appeared to be more vigorous and a less viscous product was obtained. With $FeCl_3$ as the acid catalyst, the reaction was equally vigorous and the product obtained was similar although darker in color.

Analysis K-8

In general, the characteristics of this spectrum were similar to those of the spectrum from sample K-1. In addition, a marked increase in the intensity of several bands due to THPC indicates the presence of a greater percentage of unreacted THPC than in sample K-1. This would be expected, since an excess of THPC was used initially.

Analysis K-11

New peaks in the spectrum of K-11 are indicative of a reaction product with a longer chain length and an ether linkage. The peaks, however, were not as well resolved as would be expected if a pure compound were present. Therefore, this sample was again probably a mixture of components. The absence of a strong absorption at 8.8 eliminates the possibility of the THPC havingundergone decomposition to THPO under these conditions. A reaction had occurred through the oxirane group since the characteristic oxirane absorption bands were absent.

Analysis K-22 (Before and after vacuum distillation)

The two spectra are for practical purposes identical, however, two very weak bands which appeared before vacuum distillation were not present after the distillation. These bands are due to the excess epichlorohydrin and are therefore absent after the epichlorohydrin has been removed by distillation in this sample.

The hydroxyl band at 3.1 indicates that there is still a considerable degree of hydrogen bonding (See Section 2.3.6, P. 90 (1)). Therefore, the conclusion is that all of the $-CH_2OH$ groups of THPC have not reacted. However, that at least one, and possibly more, $-CH_2OH$ groups have reacted was evident by the shift in the $-CH_2OH$ absorption band from 9.58μ in this sample. This shift in frequency of absorption indicated that there was an increase in the mass of the molecule containing a primary alcohol group.

A band adhering at 9.25μ is assigned to C-O-C and/or secondary hydroxyl absorption, and additional bands are assigned to C-C and C-H deformations, supporting the presence of a molecule with an increased carbon chain. The C-Cl absorption is further support of the presence of an addition product since the only source of C-Cl bonds prior to reaction is epichlorohydrin which has been removed in this sample. On the basis of the spectral evidence a reaction has taken place between THPC and epichlorohydrin.

Analysis K-27

The spectrum obtained gave no indication of the presence of unreacted THPC. The $-CH_2OH$ absorption has shifted indicating an increase in mass and chain length. The strong band at 9.25μ was due to ether and/or secondary alcohol absorption and C-Cl absorption was strong. On the basis of the spectral evidence, a reaction has occurred between the THPC and epichlorohydrin.

A typical run (Experiment K-19) was carried out as follows:

Materials:			
	(1)	Epichlorohydrin	0.8 mole (73.6g)
	(2)	THPC	0.1 mole (19.0g)
	(3)	H_2SO_4 (conc.)	0.08 ml.

Apparatus: 500 ml., round-bottom flask equipped with a mercury-seal stirrer, thermometer, and reflux condenser.

Procedure: Epichlorohydrin was added to the flask and stirring was started. The H_2SO_4 was introduced. There was a slight hissing and fuming as the drops of H_2SO_4 contacted the epichlorohydrin. The THPC was added in 3-5 gram increments over a period of 5 hours. After addition of each portion of THPC, heat was applied very slowly until an exothermic reaction occurred. This was usually observed at about 40°C. External heat was removed and reaction was allowed to continue between 40° and 50°C until the exothermic reaction ceased and the reaction mixture became clear. It was necessary to cool the reaction with ice water to keep the temperature from rising above 50°C. After all the THPC had been added and there was no further evidence of exothermic reaction, the remaining product, a clear light yellow viscous liquid, was vacuum topped to remove excess epichlorohydrin and any other low-boiling material. The vacuum topping was accomplished by distillation through a simple still at 20 mm until the pot temperature reached 50°C. The bath was then allowed to cool and the pressure was lowered to less that 1 mm. Distillation was continued until the pot temperature reached 50°C. The final product was a viscous yellow liquid, soluble in water, methanol, acetone, and chloroform but insoluble in benzene, ether, and dioxane.

2.3.2.4 Epoxide Ring Closing Experiments (Table VIII). Although the structure of the acid-catalyzed condensation product of THPC and epichlorohydrin had not been confirmed, the presence of chlorohydrin groups was assumed and preliminary ring-closing experiments were carried out.

Experiment K-7

Materials: (1) Reaction Product from Experiment K-5 (See Table VIII) - 35.2 g. and (2) 30% NaOH aqueous solution 80 g. (0.6 mole NaOH).

Apparatus: 500 ml, round bottom flask, equipped with a mercury-seal stirrer, thermometer, and reflux condenser.

TABLE VII

ACID CATALYZED CONDENSATION OF EPICHLOROHYDRIN AND THPC

Experiment No.	Epichlorohydrin (Moles)	THPC (Moles)	Catalyst	Time Hrs.	Temp. °C	Results
K-1	1.0	0.25	H_2SO_4 (0.2 ml)	0.6	Max. 140	Explosive reaction clear yellow viscous liquid obtained.
K-3	0.25[1]	0.25	H_2SO_4 (0.1 ml)	3	Max. 75	Clear viscous liquid obtained.
K-5	0.2	0.1	H_2SO_4 (0.1 ml)	4.5	Max. 115	Clear yellow, viscous liquid obtained.
K-8	0.2	0.1	H_2SO_4 (0.1 ml)	4.5	Max. 85	Clear yellow, viscous liquid obtained.
K-11	0.4	0.1	H_2SO_4 (0.1 ml)	7.0	Max. 58	Clear yellow viscous liquid obtained.
K-16	0.1	0.2	H_2SO_4 (0.01 ml)	5.3	Max. 54	Clear viscous liquid obtained.
K-19	0.8	0.1	H_2SO_4 (0.08 ml)	5.6	Max. 55	Clear yellow, viscous liquid obtained.
K-22	0.8	0.1	$FeCl_3$ (0.25 g)	6.1	Max. 140	Clear brown, viscous liquid obtained.
K-27	0.8	0.1	H_2SO_4 (0.08 ml)	7.0	Max. 90	Clear brownish yellow viscous liquid obtained.
K-31	0.8	None	H_2SO_4 (0.08 ml)	2.0	Max. 90	Unchanged epichlorohydrin recovered.

[1] Benzene solvent (150 ml)

Procedure: The reaction product from Experiment K-5 was treated with the NaOH solution. Almost immediately there was a violent exothermic reaction accompanied by bubbling and a rapid rise of temperature to 85°C. The mixture was cooled to 40°C and stirred for 1.3 hours, then heated to 90°C and stirred at that temperature for 15 minutes. The reaction mixture on cooling consisted of a solid and liquid phase. The solid was filtered off, washed with water and acetone, and dried. The dried product was a brown, crystalline material completely infusible and insoluble - apparently a crosslinked polymer.

Experiment K-9

By slowly adding 30% NaOH solution to the reaction product of Experiment K-8, the exothermic reaction could be satisfactorily controlled. The resulting product was an insoluble, infusible solid similar in appearance to the material obtained in Experiment K-7.

Experiment K-13

Materials: (1) Reaction Product from Experiment K-11 - 56g. (2) Sodium aluminate 49g (0.6 mole). (3) Dioxane 150 ml.

Apparatus: 500 ml, round-bottom flask, equipped with a mercury-seal stirrer, thermometer, and reflux condenser.

Procedure: The product from Experiment K-11 was only partially soluble in dioxane. Sodium aluminate was added to the stirring two-phase system. The temperature was raised gradually to 90°C over a period of one hour and held at that temperature for 3 hours. The mixture was filtered to remove inorganic salts. The residue was quite gummy and there appeared to be a significant amount of organic material which was not soluble in dioxane. The residue was washed thoroughly with methanol to separate the organic material from salts. The methanol was removed by vacuum distillation through a simple still until the pot temperature was 100°C. at <1 mm. The material recovered was brown viscous liquid soluble in water.

The original dioxane filtrate was vacuum distilled to remove dioxane and any other low-boiling materials. Only a very small amount of black, viscous liquid remained after the pot temperature reached 100°C at <1 mm. The product was water soluble.

Attempts were made to cure the products recovered from methanol and dioxane solution. Neither of these materials could be cured with diethylene triamine. An attempt to cure the dioxane-soluble product by heating it with phthalic anhydride at 120°C. for 12 hours was not successful. It was assumed from these results that ring closure did not occur with sodium aluminate under the conditions used.

Analysis K-13

The spectrum of the sample gave poor resolution showing evidence of an impure sample. The strong broad absorption between 8.7 and 9.8 microns, with no discernible sharp peaks, makes definite structural assignment difficult since ethers and primary and secondary alcohols all absorb in this range.

Curing

Reaction Product	Curing Agent	Condition of Final Product
K-13	Diethylene Triamine	Failed to harden
K-13	Phthalic Anhydride	Failed to harden

2.3.3 Reactions of Tris(Hydroxymethyl) Phosphine Oxide (THPO)

It has been pointed out that THPC is converted to THPO during reaction under alkaline, neutral or mildly acidic conditions or when heated. During the latter part of the contract, purified THPO became available from the Hooker Electro-Chemical Company. By using this compound as a starting material, it was reasoned that some of the complications caused by the instability of THPC could be eliminated and a clearer picture of the expected reactions could be realized.

2.3.3.1 Reaction of Glycidol and THPO

Experiment P-12

Water solubility of the polymer formed in previous experiments was thought to be due to the presence of chlorine, either in the reaction medium or in the dried polymer. To eliminate chlorine from the reaction glycidol (glycide or epihydrin alcohol), $O{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}OH$, was reacted with tris-(hydroxymethyl) phosphine oxide. The tris-(hydroxymethyl) phosphine oxide was prepared by heating tetrakis-(hydroxymethyl) phosphonium chloride in the presence of sodium hydroxide solution between 60 - 70°C for three hours. This solution was vacuum dried, dissolved in methyl alcohol (the sodium chloride being relatively insoluble in methyl alcohol and the THPO soluble) and the undissolved sodium chloride crystals were filtered from the solution. The THPO dissolved in methyl alcohol was vacuum distilled to remove the alcohol and then 3 moles reacted with 1 mole of glycidol in a water medium. The reaction products were not syrupy polymers suspended in the aqueous solution, but instead produced a transparent amber solution which on vacuum drying formed a polymer like substance. This polymeric material could be re-dissolved in water; in this respect it did not show improvement over those previously prepared.

2.3.3.2 Reaction of THPO and Allyl Glycidyl Ether

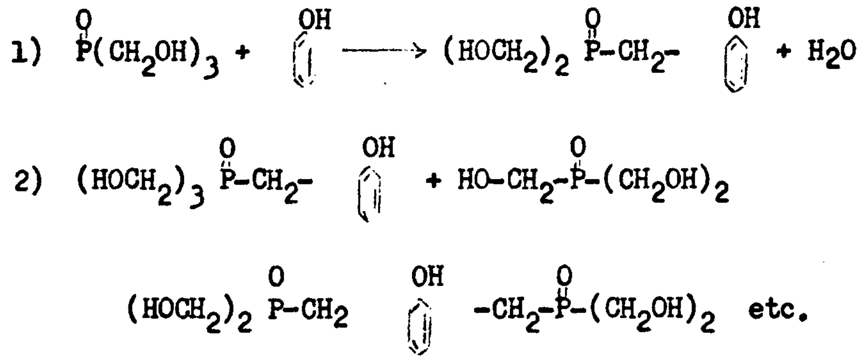
Experiment P-25

In order to further study the mechanism by which epoxide groups might react with the hydroxyl groups of THPC and THPO, allyl glycidyl ether was heated with an equivalent amount of THPO for 2 hours at 200°C. There was an increase in the viscosity of the solution and a sample was submitted for analysis.

Spectral Analysis of Sample P-25

A spectrum of pure allyl glycidyl ether was recorded for comparison purposes. Since ether linkages were present initially, it was difficult to verify the formation of new ether linkages in this reaction. No definite conclusions can be made concerning the formation of new ether bonds since the spectrum showed broad absorption in the 8-10μ region with few discernible peaks.

2.3.3.3 Reaction of Phenol and THPO. In an effort to prepare a phosphorus containing epoxy modifier, THPO was condensed with phenol. This material could then be copolymerized with a commercial epoxide resin.

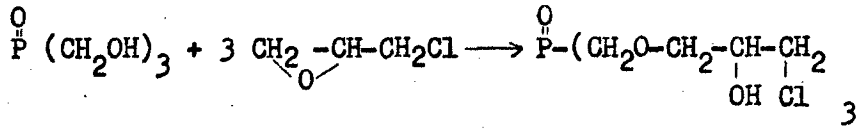


Experiment K-86

The reaction was carried out by heating the two reagents in the presence of NaOH for a short period of time followed by further heating at a lower pH with H_3PO_4 as the acid catalyst. The final product after vacuum topping to remove water was not compatible with a commercial epoxide resin.

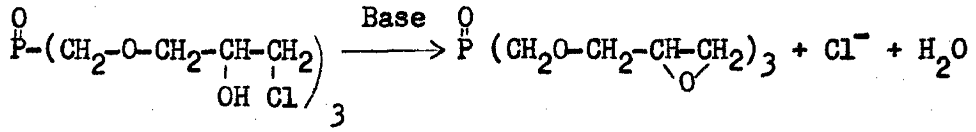
2.3.3.4 Reactions of THPO and Epichlorohydrin. It was proposed that a phosphorus containing epoxide might be prepared by a two step reaction of THPO and epichlorohydrin. It will be noted that these reactions are practically identical to the reactions proposed for THPC and epichlorohydrin in a previous section of the report. However, the reaction in which THPC decomposes to THPO is eliminated if THPO is the starting material.

The first step of the reaction is represented by the acid catalyzed condensation of THPO and epichlorohydrin under anhydrous conditions:



$$\overset{O}{\overset{\|}{P}}(CH_2OH)_3 + 3\ \underset{\diagdown O \diagup}{CH_2\text{-}CH}\text{-}CH_2Cl \longrightarrow \overset{O}{\overset{\|}{P}}\text{-}\left(CH_2O\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}\underset{Cl}{\underset{|}{CH_2}}\right)_3$$

Subsequent treatment of the chlorohydrin with base should effect ring closure to give the epoxide:



$$\overset{O}{\overset{\|}{P}}\text{-}\left(CH_2\text{-}O\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}\underset{Cl}{\underset{|}{CH_2}}\right)_3 \xrightarrow{\text{Base}} \overset{O}{\overset{\|}{P}}\ (CH_2O\text{-}CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2})_3 + Cl^- + H_2O$$

2.3.3.4.1 Acid Catalyzed Condensation of THPO and Epichlorohydrin.

Experiments K-33 and K-42

Reactions were carried out by heating THPO and epichlorohydrin in the presence of a catalytic amount of H_2SO_4. The molar ratios of epichlorohydrin to THPO were 8:1 (K-33) and 6:1 (K-42). The reaction mixture started as a two phase system of solid THPO and epichlorohydrin. Upon heating to about 60°C, the THPO melted to give a liquid which at first did not appear to dissolve in the epichlorohydrin. The two phase liquid mixture was stirred and gradually heated to 100°C for 6.5 to 9 hours. The reaction was considered to be complete when it, rather abruptly, became clear and homogeneous. There was no evidence of an exotherm during the reaction. Following the reaction, unreacted epichlorohydrin and other low boiling components were removed by vacuum distillation until pot temperature reached 100°C at less than 1 mm. The viscous, yellow taffy-like residue was presumed to contain the desired product.

Analysis K-33 (Before and after vacuum distillation)

The strong absorptions due to oxirane groups in the sample before vacuum distillation were due to the presence of considerable unreacted epichlorohydrin. That the sample was a mixture was confirmed by its spectrum. Therefore, interpretation was simplified by removal of the excess epichlorohydrin and the spectrum after vacuum distillation was obtained. In this sample, partial reaction has taken place to form an intermediate product. The hydroxyl stretch and the phosphoryl frequency has shifted indicating less intermolecular hydrogen bonding. (See Section 2.3.6, P. 90.)

The band at 9.05μ is due to ether and/or secondary alcohol absorption and the presence of the C-Cl band is further evidence of an addition product.

Analysis K-42 (Before and after vacuum distillation)

The spectrum before distillation was similar to that of K-33 before distillation; a spectrum of the sample after distillation was recorded and was very poorly resolved indicating the presence of a mixture. The various absorption bands in the spectrum suggest the presence of unreacted THPO and addition products from the reaction of THPO with epichlorohydrin.

Experiments K-50 and K-62

Reactions of THPO and epichlorohydrin were conducted in the absence of a catalyst. The molar ratios of epichlorohydrin to THPO were 6:1 (K-50) and 3:1 (K-62). The reaction mixture became homogeneous after heating to 100°C over a period of 5 to 15 hours. There was no evidence of an exotherm. The product from Experiment K-50 was not vacuum distilled to remove unreacted epichlorohydrin and low boilers. Following the reaction in Experiment K-62, unreacted epichlorohydrin and other low boiling components were removed by vacuum distillation until pot temperature reached 100°C at less than 1 mm. pressure. The distillate was redistilled to recover unreacted epichlorohydrin and an unidentified fraction boiling at 49-50°C at 5 mm. This compound contained no phosphorus. The viscous taffy-like residue was presumed to contain the desired product.

Analysis K-62 (After vacuum distillation)

The spectrum obtained from K-62 was identical to that of K-72 (see below) after distillation and the same conclusions are drawn: the material was unreacted THPO with a small amount of addition product.

Unidentified fractions boiling at 49-50°C, 5 mm from K-62, K-72 and K-76 all gave identical spectra. Hydroxyl absorption was evident; and very weak absorption bands at 8.0μ and 11μ indicate a slight amount of epoxide, probably as an impurity. Absorptions at 9.18, 9.31, and 9.52μ confirmed the presence of the hydroxyl and these frequencies suggest a primary alcohol. C-Cl absorption was also present.

Experiment K-56

Dioxane was used as a solvent for a mixture of 1 mole of epichlorohydrin and 0.33 mole of THPO. It was reasonable to expect a more satisfactory reaction of the reaction mixture consisted of one homogeneous liquid phase. Stannic chloride was used as a catalyst. The reactants were not completely soluble in dioxane and even after heating to 100°C over a period of 21 hours, the reaction mixture was not entirely homogeneous. The solvent, unreacted epichlorohydrin and low boilers were not removed prior to the ring closing step.

Experiments K-68 and K-72

Boron trifluoride etherate was used as a catalyst in these experiments. The molar ratio of epichlorohydrin to THPO was 3:1. The reaction mixture became homogeneous after heating at 100°C for 5 to 9 hours. There was no evidence of an exotherm. Following the reaction, unreacted epichlorohydrin and other low boiling components were removed by vacuum distillation until pot temperature reached 100°C at less than 1 mm. The distillate in Experiment K-72 was redistilled to recover unreacted epichlorohydrin and an unidentified fraction boiling at 49-50°C at 5 mm. This compound contained no phosphorus. The viscous taffy-like residue was presumed to contain the desired product.

Analysis K-68 (After distillation)

This compound absorbed at the same frequencies as K-72 after distillation and the conclusion is that unreacted THPO was present, however, partial reaction has taken place to form a secondary alcohol and/or ether linkage.

Analysis K-72 (After distillation)

The hydroxyl absorption and characteristic absorptions in the remainder of the spectrum were due to the presence of unreacted THPO. A slight broadening of the 8.8μ band down to approximately 9.2μ suggested the presence of a small amount of addition product.

Experiments K-76, K-98, and K-114

Stannic chloride was used as a catalyst in these experiments. The molar ratio of epichlorohydrin to THPO was 3:1. The reaction mixture became homogeneous after heating at 100°C for 6 to 11 hours. There was a slight exotherm near the end of the heating period. In Experiment K-98 and K-114, the reaction temperature was raised to 150°C over a period of 1 hour before allowing to cool. Following the reaction, unreacted epichlorohydrin and other low boiling components were removed by vacuum distillation until pot temperature reached 100°C at less than 1 mm. The distillate in Experiment K-76 was redistilled to recover unreacted epichlorohydrin and an unidentified fraction boiling at 49-50°C at 5 mm. This compound contained no phosphorus. The viscous taffy-like residue was presumed to contain the desired product. In experiment K-98 an attempt was made to fractionate this final product by extracting it first with dioxane then with tetrahydrofuran. Approximately 15 percent of the product was extracted with each of these solvents.

Analysis K-76 (After distillation)

The absence of several bands due to THPO in the spectrum of K-76 (after distillation) indicate that there was very little unreacted THPO present in the sample. There was evidence from the spectrum to suggest that the sample was a mixture consisting of addition products of THPO and one, two and three moles of epichlorohydrin. An increase in the resolution and number of C-H absorption bands suggests an increase in chain length. A distinct band at 9.05μ, attributed to ether and/or secondary hydroxyl absorption, and C-Cl absorption 6μ was further evidence of the presence of an addition product between THPO and epichlorohydrin.

Analysis K-98 - Dioxane Extracted Material

The spectrum of this sample was recorded both as a thin film and dissolved in CCl_4. The spectrum from a thin film of the sample as received for analysis showed indications that the film was a mixture of reaction products.

Although the sample was practically insoluble in CCl_4, a considerable amount of the sample was allowed to stand in CCl_4 for a period of time and the CCl_4 was decanted. This was placed in a liquid cell and the spectrum recorded. In addition, some of the CCl_4 solution was placed on a warmed sodium chloride window and the CCl_4 was allowed to evaporate leaving a thin film. Indications from the spectrum obtained are that this procedure was, in reality, a step in fractionation. It is believed that this fraction contained the final, completely reacted product for the following reasons:

(1) No bonded phosphoryl band was present although there were indications of unbound phosphoryl.

(2) The hydroxyl absorption had shifted. There were strong peaks attributed to ether and/or secondary alcohol absorption.

Residue After Dioxane Treatment

The conclusion to be drawn from this spectrum is the same as that from the film of sample of dioxane extracted material as-received, namely, that the sample was a mixture of partially and completely reacted components. There was no evidence of pure unreacted THPO. A better resolved and seemingly more intense absorption at 8.75 and a more intense hydroxyl band as compared to the C-H band suggest there is a greater percentage of partially reacted product as opposed to completely reacted product than in the sample (as-received) before extraction.

Tetrahydrofuran Extracted Material

This sample was treated in a manner similar to that of dioxane extracted material and similar conclusions can be drawn.

Residue from Dioxane and Tetrahydrofuran Extraction

The resolution was poor, supporting the belief that a mixture was present. The 8.75μ band was very well resolved and intense and therefore, bonded phosphoryl was present. Although some unbound phosphoryl (see Section 2.3.6, P. 90) was present and was causing the broadness at 8-8.6μ, there was a large percentage of partially reacted products. This is reasonable since the fractionating methods should have removed the more completely reacted products.

Experiment K-120

The procedure used in this experiment gave the best results and is therefore described in detail as the recommended procedure for the acid catalyzed reaction of THPO and epichlorohydrin. By using an excess of epichlorohydrin, it was hoped that the reaction would give the best yield of completely reacted material.

Materials:	(1)	Epichlorohydrin	2.0 moles (185g)
	(2)	THPO	0.33 moles (46.6g)
	(3)	$SnCl_4$	0.25 ml.

Apparatus: 500 ml, 3-neck round bottom flask equipped with a mercury-seal stirrer, thermometer, and reflux condenser.

Procedure: Epichlorohydrin and THPO were added to the flask and stirring started. The reaction mixture started as a two phase system of solid THPO and epichlorohydrin. Upon heating to 60°C, the THPO melted to give a liquid which, at first did not appear to dissolve in the epichlorohydrin. The two phase liquid mixture was stirred and heated at 100°C for 10 hours, at which time the reaction mixture became completely homogeneous. The reaction mixture was allowed to cool to room temperature and the $SnCl_4$ catalyst was added. The temperature was then gradually increased to 150°C over a period of 4 hours. When a temperature of 150°C had been reached, heating was discontinued and mixture was allowed to cool. Unreacted epichlorohydrin and other low boiling components were removed by vacuum distillation until pot temperature reached 100°C at less than 1 mm pressure. The distillate recovered weighed 98g and the very viscous taffy-like residue, presumed to be the desired product, weighed 130g. The residue could not be further fractionated.

Analysis K-120

The spectrum gave no evidence of unreacted THPO. Absorption bands due to both bonded and unbound phosphoryl gave evidence that this sample was a mixture. However, the comparison of the intensity of the hydroxyl stretch with that of the C-H stretch gave strong indications that the sample had a large percent of the addition product from the reaction of THPO with either two or three moles of epichlorohydrin.

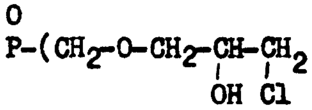
Found	**Theoretical for**  $\overset{O}{P}-(CH_2-O-CH_2-\underset{OH}{CH}-\underset{Cl}{CH_2}$
% P - 7.39	7.43
% Cl - 16.2	25.6

TABLE VIII

ACID CATALYZED CONDENSATION OF EPICHLOROHYDRIN AND THPO

Experiment No.	Epichlorohydrin	THPO	Catalyst	Time (Hrs.)	Temp °C	Fractionation		Calculated Weight of Product g (Residue)
						Low Boilers g	Product (residue) g	
K-33	0.8 moles (73.6g)	0.1 mole (14g)	H_2SO_4 (0.08 ml)	6.5	120° Max.	31g	40g	41.7
K-42	3.0 moles (277.5g)	0.5 moles (70g)	H_2SO_4 (0.4 ml)	9.5	126° Max.	198	139	208.5
K-50	3.0 moles (277.5g)	0.5 moles (70g)	None	15.5	120° Max.	No Fractionation		208.5
K-62	1.0 moles (92.5g)	0.33 moles (46.6g)	None	5.0	102° Max.	51[2]	81	139.0
K-56	1.0 moles (92.5g)	0.33 moles (46.6g)	S_nCl_4 (0.25 ml)	21.0	101° Max.	No Fractionation		139.0
K-68	1.0 moles (92.5g)	0.33 moles (46.6g)	BF_3 in ether (1 ml 4.5% solution)	5.0	110° Max.	64.5	73	139.0
K-72	1.0 moles (92.5g)	0.33 moles (46.6g)	BF_3 in ether (3 ml 4.5% solution)	9.0	101° Max.	53.8[3]	75.6	139.0

1. The Calculated Weight of Product (Residue) is based on the reaction of 3 moles of epichlorohydrin with 1 mole of THPO. The assumption is made that all of the product was contained in the residue.

2. Unreacted epichlorohydrin 45 - 7°C/50 mm - 35g
   Intermediate fraction 51 - 7°C/5 mm - 16g

3. Unreacted epichlorohydrin 43 - 5°C/50 mm - 32.2g
   Intermediate fraction 47 - 9°C/5 mm - 21.6g

TABLE VIII (Cont.)

ACID CATALYZED CONDENSATION OF EPICHLOROHYDRIN AND THPO

Experiment No.	Epichlorohydrin	THPO	Catalyst	Time (Hrs.)	Temp. °C	Fractionation		Calculated Weight of Product g (Residue)
						Low Boilers g	Product (residue) g	
K-76	1.0 moles (92.5g)	0.33 moles (46.6g)	$SnCl_4$ (0.25 ml)	11	140° Max.	36.7[4]	102.5	139.0
K-78	1.0 moles (92.5g)	0.33 moles (46.6g)	$SnCl_4$ (0.25 ml)	12.5	150° Max.	---	101.4	139.0
K-114	1.0 moles (92.5g)	0.33 moles (46.6g)	$SnCl_4$ (0.25 ml)	6.5	150° Max.	---	----	139.0
K-120	2.0 moles (92.5g)	0.33 moles (46.6g)	SnCl (0.25 ml)	15.0	150° Max.	98	130	139.0

[4] Unreacted epichlorohydrin 44 - 5°/50 mm - 917g
Intermediate fraction 51°/5 mm - 27g

2.3.3.4.2 Condensation of THPO and Epichlorohydrin in Presence of Sodium Hydroxide

Experiment P-14: This experiment consisted of the reaction of epichlorohydrin with purified THPO from Hooker Electrochemical Company in aqueous caustic solution (30% NaOH solution). The reaction product was vacuum dried and the sodium chloride crystals filtered from the high viscosity liquid which remained. This liquid was found to be water soluble.

Analysis P-14: In the interpretation of the spectral evidence, there are several possibilities to consider, namely: (1) the spectrum may have been the result of a mixture of epichlorohydrin and partially decomposed THPO; (2) a reaction may have occurred to some extent, leaving a mixture of reactants and products; and (3) epichlorohydrin may have undergone self-polymerization. The broadness and poor resolution of certain bands suggests that the sample was a mixture of components:

The spectra of the sample which had been cured with pyromellitic dianhydride gave new bands at:

Frequency	Assignment
5.8 - μ	Carbonyl (ester)
8.95- μ	Terminal cyclic anhydride
8.75- μ	C - = C (ring)
9.13- μ	Ester linkages

A marked decrease in the CH_2OH absorption at 9.53 μ and the epoxide absorption at 10.9 and 11.6 suggests that curing may have occurred through these functional groups.

Curing:

Reaction Product	Curing Agent	Condition of Final Product
P-14	Pyromellitic Anhydride and Maleic Anhydride Pyridine accelerator	Hard, water-insoluble foam. Foam structure destroyed in water.

2.3.3.4.3 Epoxide Ring Closing Experiments. Ring closing experiments have not proved too successful in spite of many variations in technique. The products recovered as the residue in the acid catalyzed condensations of epichlorohydrin and THPO described above were all soluble in water, lower alcohols, and N-N' dimethyl formamide, but essentially insoluble in nonpolar solvents. The polar nature of the product made it difficult to find a suitable solvent in which to carry out the ring closing experiments. The products from the acid catalyzed reaction could not be conveniently handled in the absence of a solvent because of their high viscosities. Several different polar solvents were used, but none of these were completely satisfactory.

Water was avoided as a solvent because of the great possibility of alkaline hydrolysis of the chlorine of the chlorohydrin or the hydrolysis of the epoxide as soon as it formed. The lower alcohols were used, but the possibility of reaction with the newly formed epoxides had to be considered. N-N' dimethyl formamide proved to be the most convenient solvent, but its possible reactivity in the presence of bases was a factor to consider. Its high boiling point and well known difficulty of separation by fractional distillation were other disadvantages.

Sodium aluminate and 30%-50% aqueous sodium hydroxide were tried as dehydrohalogenating agents in the ring closing step. In reactions where sodium aluminate was used, part of the final reaction mixture hardened and could not be removed from the flask. The liquid portion consisting mainly of solvent contained only a small amount of a viscous water soluble material. Attempts were made to extract the hardened portion with various solvents, but with little success. When concentrated sodium hydroxide was used, vigorous exothermic reactions resulted in the formation of insoluble and infusible products (apparently) cross-linked polymeric substances) and a small amount of very viscous water soluble material. Attempts to identify the products obtained in the ring closing step have been complicated by the difficulty of isolating even a reasonably pure sample.

Experiment K-36 The product from Experiment K-33 was dissolved in N-N' dimethyl formamide and a calculated excess of sodium aluminate was added. The mixture was stirred and heated at 50-58°C for 6 hours and at 85-90°C for 10 hours. After filtration and vacuum distillation to remove the dimethyl formamide, a viscous, taffy-like product was recovered in about 40% yield on a weight basis.

Analysis % Cl - 10.6 which indicates that little or no ring closure in the compound.

Experiment K-46 The product from Experiment K-42 was stirred at room temperature and 30% NaOH was added dropwise. After approximately one-half of the calculated amount of NaOH had been added, a sudded exothermic reaction occurred and the reaction mixture gelled into a rubbery mass.

Experiment K-52 The product from Experiment K-50, which had not been distilled to remove unreacted epichlorohydrin, was stirred at room temperature and a calculate excess of 30% NaOH was added dropwise over a period of 16 hours. On standing overnight, the reaction gelled to a rubbery mass. A small amount of yellow, viscous material was extracted with CH_3OH.

Analysis % Cl - 8.0 which indicates very little ring closure in the compound.

Experiment K-58 The product from Experiment K-56, which was prepared in dioxane, consisted of a lower layer of very viscous material and a top layer of low viscosity (probably the dioxane). A calculated excess of sodium aluminate was added. This formed a thick paste on the botton of the flask which could not be easily stirred. After heating for 4.5 hours at 100°C and attempting to stir, the botton layer hardened. Attempts to extract a reasonably pure sample were unsuccessful and the experiment was discontinued.

Experiment K-75 The product from Experiment K-72 was dissolved in a mixture of methyl and isopropyl alcohol. A calculated excess of sodium aluminate was added and the mixture was heated and stirred. On standing over night, the solid hardened to a putty like material which settled at the botton of the flask. By adding more methanol and heating, it was possible to remove the solid and filter off the solid material. A very viscous yellow material was recovered by removing the methyl and isopropyl alcohol from the filtrate.

Analysis K-75

This spectrum was similar to that of K-72 after distillation, although the bands were not as well resolved. Because the spectrum of K-72 (after distillation) indicated the presence of a very small percentage of addition product, treatment with sodium aluminate would not alter the mixture composition to any great extent. Therefore, the spectrum obtained was still indicative of the presence of unreacted THPO. No strong bands due to epoxide absorption were present.

% Cl-9.2 which indicates that very little ring closure has occurred.

Experiment K-80 The product from Experiment K-76 was dissolved in methyl alcohol. A calculated excess of sodium aluminate was added and the mixture was stirred and heated at 69°C for 11 hours. On cooling, the reaction mixture became a thick, pasty mass which was impossible to filter. Acetone was added to break up the gel-like structure so that separation of the solid by filtration was possible. The filtrate was distilled to remove solvent. A dark yellow, viscous material was recovered as the residue from the distillation.

Analysis K-80

Compared to K-76 (after distillation) the hydroxyl absorption had decreased considerably relative to the C-H absorption. This means that there has been a decrease in hydroxyl in going from sample K-76 to K-80, and therefore a reaction with sodium aluminate had occurred. Oxirane groups may have been formed, however, these groups were not observed in they spectrum. This could be due to the fact that the phosphoryl, ether, and alcohol absorptions were so intense that they conceal any expected oxirane absorption. A small amount of C-Cl absorption was still evident which indicated that reaction with sodium aluminate was not complete.

% Cl - 10.44 which indicated that very little ring closure has occurred.

Experiment K-116 The product from Experiment K-114 was cooled to 0-2°C and dissolved in just enough water to permit stirring. A calculated excess of aqueous 50% NaOH was added over a period of 6 hours, keeping the temperature of the reaction mixture as close as possible to 0°C. With each small addition of NaOH an exothermic reaction took place which caused the temperature to increase to about 15°C. After the addition of NaOH was complete, the very viscous reaction mixture was extracted with diisopropyl ether keeping the temperature at about 0° during the extraction. Only a trace of material remained as a residue after removal of the solvent indicating the poor solubility of the product in a relatively non-polar solvent. The presence of NaOH made separation by solvent extraction very difficult.

Experiment K-123 The product from Experiment K-120 was dissolved in N-N' dimethyl formamide and a calculated amount of sodium aluminate was added. The mixture was stirred and heated at 100°C for 5 hours. After cooling, the reaction mixture was filtered to remove the inorganic salts. Considerable difficulty was encountered in filtration due to the pasty nature of the mixture. By adding more dimethyl formamide, it was possible to achieve a fair degree of separation by filtration. In the removal of dimethyl formamide by vacuum distillation, the reaction mixture suddenly polymerized (at about 100°C) very rapidly, accompanied by an exotherm which raised the temperature to 300°C and caused the mixture to char and foam and finally harden to a black mass.

TABLE IX

EPOXIDE RING CLOSING EXPERIMENTS

Experiment No.	Reactants				Results
	Reaction Product of Experiment No.	Base	Time (Hrs.)	Temp. °C	
K-6	K-5 (35.2g)	30% NaOH (0.6 mole)	1.5	Max. 90	Highly exothermic reaction Solid product.
K-9	K-8 (36.1g)	30% NaOH (0.6 mole)	5	Max. 90	Exothermic reaction controlled by slow addition of NaOH. Solid product isolated.
K-13[1]	K-11 (56g)	Sodium Aluminate (49g)	3	Max. 90	Very viscous water soluble liquid isolated.
K-36	K-33 (20g)	Sodium Aluminate (20g)	6 10	50-58 85-90	Approx. 8g viscous taffy-like material. Water soluble.
K-46	K-42 (84g)	30% NaOH (39g)	--	Rm. Temp.	Rubbery gel.
K-52	K-50 (174g)	30% NaOH (98g)	16	Rm. Temp.	Rubbery gel.
K-58	K-56 in dioxane	Sodium Aluminate (90g)	4.5	100°	Thick, pasty mass which could not be removed from flask. Water soluble.
K-75	K-72 (65.8g)	Sodium Aluminate (90g)	--	---	Thick pasty mass and a viscous, yellow material.
K-80	K-76 (102.5g)	Sodium Aluminate (90g)	11	69°	Yellow, viscous material. Water soluble.
K-116	K-114 (80g in 30 ml water)	50% NaOH (78g)	--	0-15°	Trace of material soluble in diisopropyl ether. Large amount of emulsified liquid which was not fractionated.
K-123	K-120 (130g)	Sodium Aluminate (90g)	100	5.	Highly exothermic reaction occurred during vacuum distillation. Charred and hardened.

[1] Reaction carried out in 150 ml dioxane.

2.3.4 Reactions of Titanium Lactate and Epichlorohydrin and the Preparation of One Titanium Containing Intermediate (Table X)

Titanium lactate, a chelate of titanium was reacted with epichlorohydrin to form the epoxy polymer containing titanium. The structure for titanium lactate, as proposed by the Pigments Department of E. I. du Pont de Nemours and Company, follows:

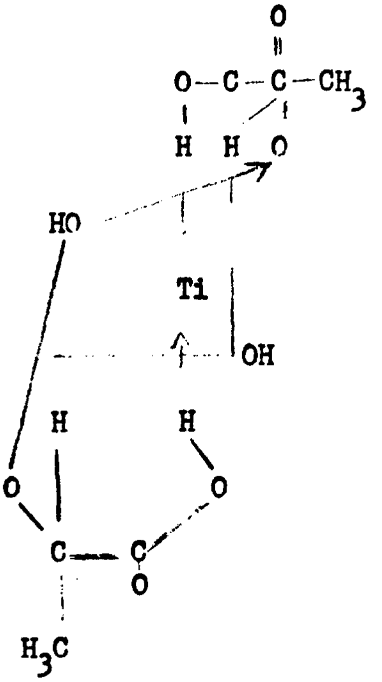


FIGURE 29

Structure of Titanium Lactate

Titanium lactate is a solid material, very soluble in water, slightly soluble in ethyl alcohol, and insoluble in other hydrocarbons. Titanium lactate forms stable aqueous solutions which are acidic. Titanium hydrate is formed if the solution is made alkaline. If the solution is neutralized cautiously with alkali however, a precipitate of titanium hydrate will not form. The probable structure of titanium lactate in a aqueous solution is shown in Figure 30.

The structure of the linear polymer formed from the reaction of epichlorohydrin and titanium lactate is depicted in Figure 31. As titanium has a valence of four and a maximum co-ordination number of six, the chelate structure demonstrates hydrogen bonding, or two secondary bonds. It is possible in the polymerization reaction that primary (valence) bonds may be formed. The hydroxyl group attached directly to the titanium has ionic bonding and would be less likely to undergo the polymerization reaction.

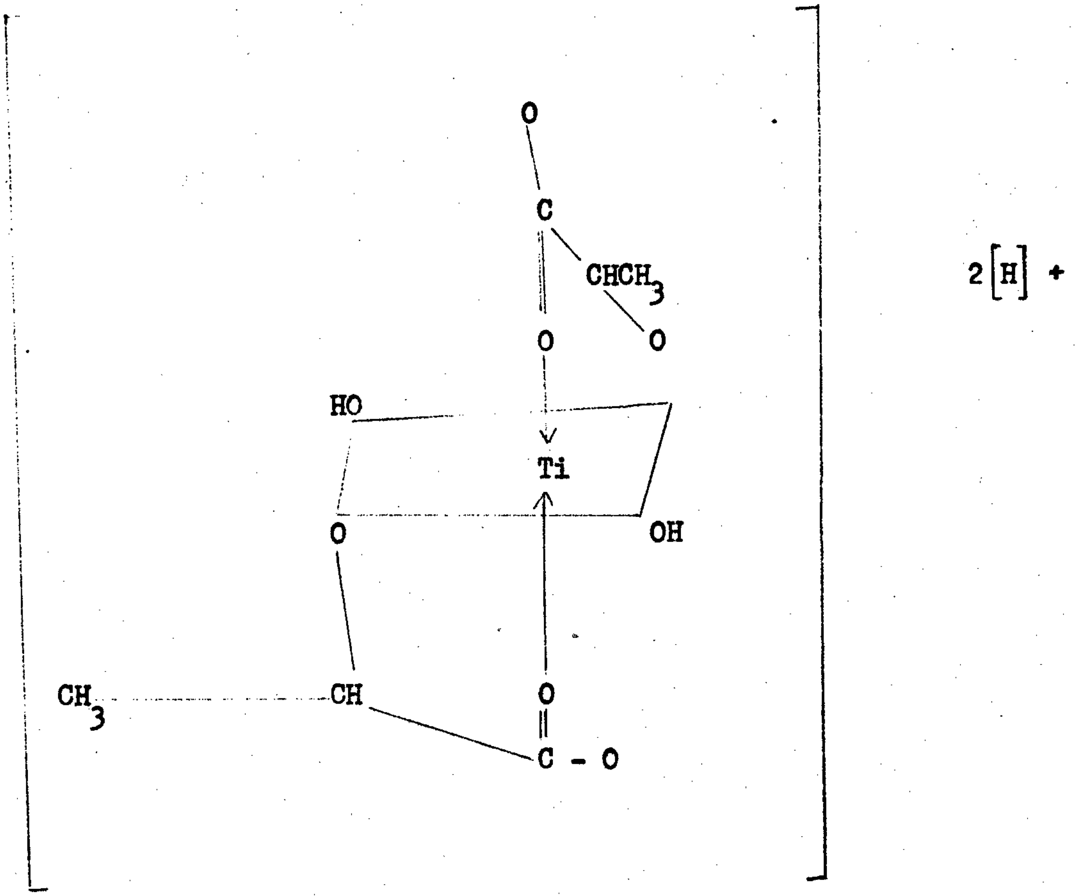


FIGURE 30

Titanium Lactate Ionized In Water

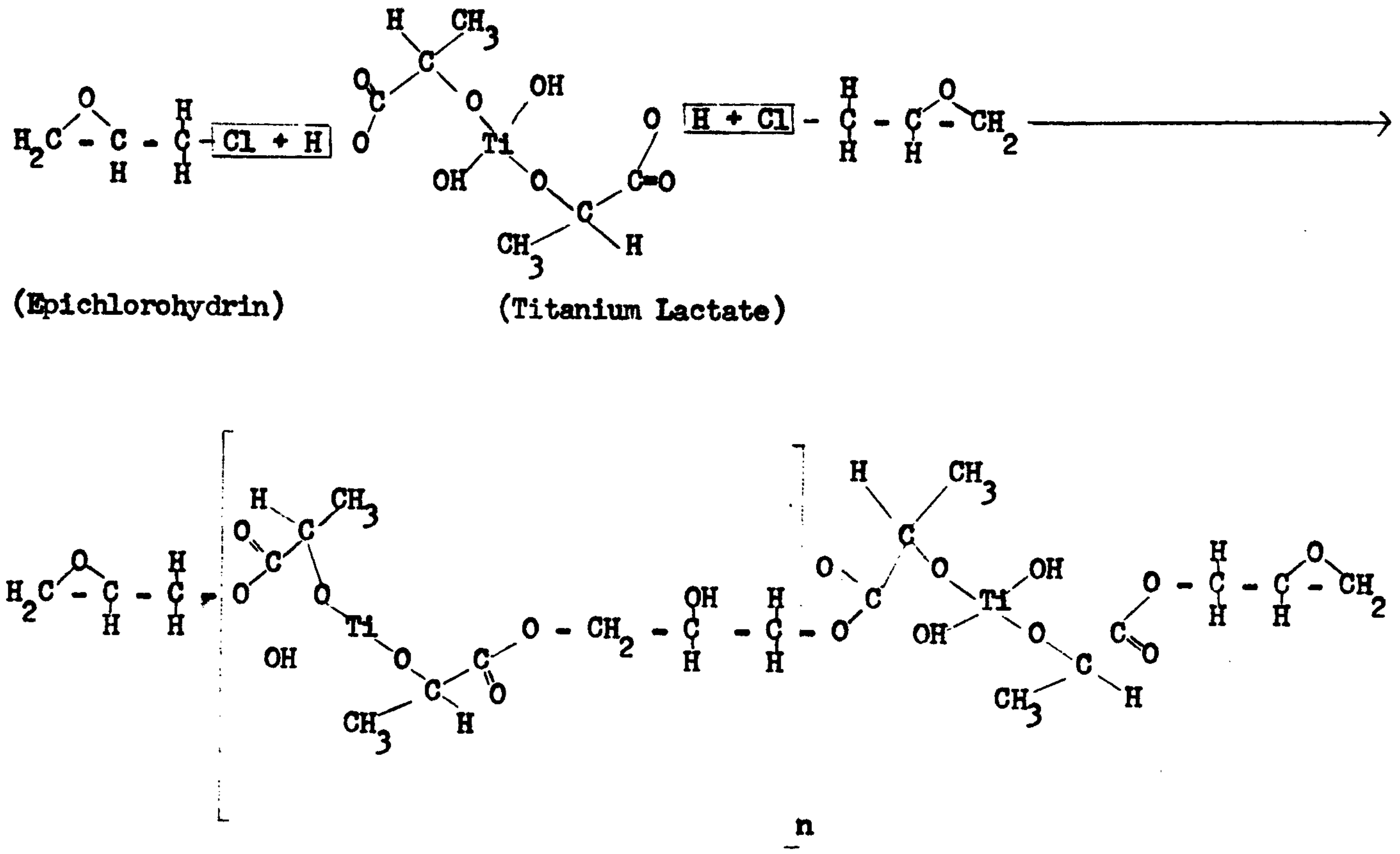


FIGURE 31

Formation of Titanium Bearing Epoxy Polymer with Titanium Lactate and Epichlorohydrin

Experiment T-1

This reaction with titanium lactate and epichlorohydrin was carried out in a sodium hydroxide solution. On the addition of sodium hydroxide to the aqueous solution of titanium lactate, a precipitate was formed which was probably titanium hydrate. Analysis of the dried precipitate indicated a higher titanium content than the original titanium lactate. Had a polymer been formed, the titanium content would have been lower due to the separation effect in the polymer molecule by the epichlorohydrin.

Experiment T-2

As titanium hydrate is formed from addition of sodium hydroxide to titanium lactate, this epichlorohydrin/titanium lactate reaction was carried out in the absence of sodium hydroxide. No precipitate was formed as in the absence of sodium hydroxide. No precipitate was formed as in Experiment T-1, and no syrupy polymer resulted from the reaction. On vacuum-drying of the reaction solution, a polymeric substance was formed which could be dissolved in water.

Analysis: T-2

The spectra obtained on material from Experiment T-2 was of particular interest. This material (T-2) shows a strong hydroxyl absorption band. Since the IR spectra of Pure Tilac and pure Epichlorohydrin show negligible hydroxy absorption bands, it can be assumed that the hydroxyl groups are formed during the reaction. The appearance of these hydroxyl bands could be attributed to the reaction of the epoxy groups with water. Each of the materials obtained from the experiments was water soluble.

Curing:

Reaction Product	Curing Agent	Condition of Final Sample
T-2	BF 3-400 (Shell) Boron Trifluoride Amine Complex	Failed to harden

Experiment T-3

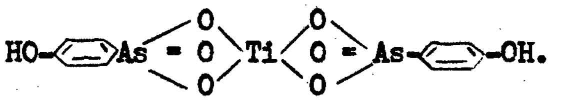
This reaction is similar to Experiment T-2 except benzene was used as a reaction medium instead of water. Titanium lactate is insoluble in benzene so epichlorohydrin was added dropwise to the dispersion of titanium lactate in benzene. After completing the reaction there was a precipitate which was dried under vacuum. The reason for carrying out the reaction in benzene is explained in the Literature Survey Section which reports preparations of polymeric organic derivatives of ortho-titanic acid in restricted quantities of water (organic solvent medium). This reaction was carried out in an organic solvent medium due to the extreme sensitivity of polymers of ortho-titanic acid to water.

TABLE X

REACTIONS OF TITANIUM LACTATE AND EPICHLOROHYDRIN

Experiment Number	Reactants					
	Epichlorohydrin (moles)	Titanium Lactate (moles)	30% NaOH (grams)	Water (ml)	Time-Temp. (hr/°C)	Remarks
T-1	2	1	100	200	4.5-96°	Ppt. formed on addition of NaOH solution, after reaction Ti content greater than in Tilac.
T-2	2	1		120	7-100°	Polymer
T-3	2	1		Benzene 100	7-100°	Tilac would not dissolve in benzene; to Tilac suspended in benzene, added epichlorohydrin.
T-2B	2	1		120	7-100°	Repeat of T-2. High viscosity liquid obtained after vacuum drying which was water soluble.

Experiment T-4 Preparation of a Titanium Derivative of p-hydroxyphinylarsonic acid

A solution of p-hydroxyphenylarsonic acid was acidified with nitric acid. To this solution titanium tetra-chloride was added to form a precipitate believed to be  When the washed precipitate was placed in an alkaline solution a white insoluble precipitate formed which was believed to have been titanium hydrate since it was insoluble in water. Such a result makes the prepared use of this compound as a replacement for bisphenol in a epoxy resin synthesis appear impractical. The formation of the hydrate in aqueous alkali appears to be a familiar tendency of the organotitanium compounds investigated to date.

2.3.5 Miscellaneous Preparations of Organo-Phosphorus Compounds

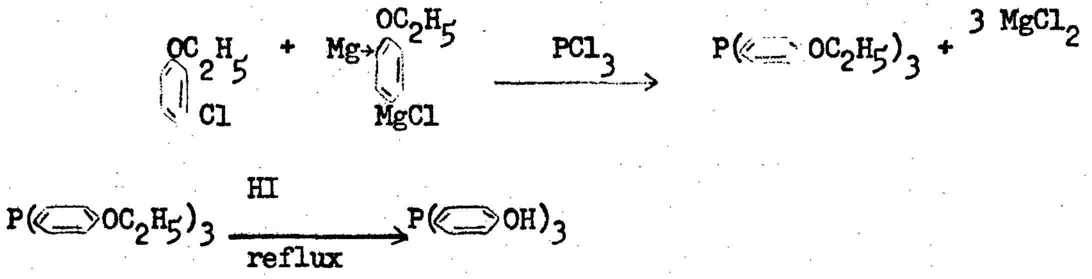
In addition to THPC and THPO, other organo-phosphorus compounds were considered in the synthesis program of developing a heat stable epoxy resin. The preparation of other phosphorus compounds containing one or more epoxide groups was investigated briefly. It was proposed that these compounds be self-polymerized or used as reactive modifiers with commercial epoxide resins.

Organic compounds of phosphorus containing multiple functional groups capable of reacting with epichlorohydrin to yield epoxide polymers were also of special interest. Attempts to synthesize several such intermediates are described below.

Finally, organo-phosphorus compounds which might serve as curing agents for epoxide polymers were briefly explored.

2.3.5.1 Experiment P-30, Preparation of Tris (p-hydroxyphenyl) Phosphine

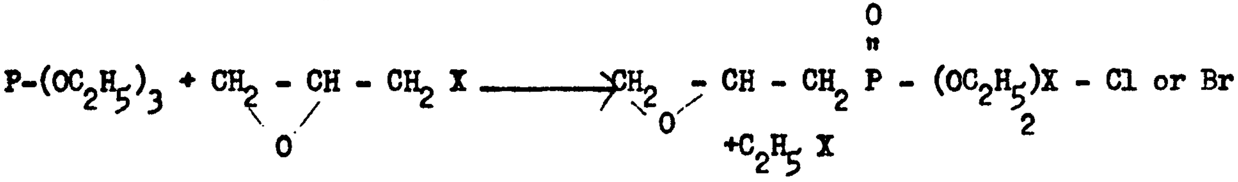
This experiment was designed to prepare an organo phosphorus intermediate which might react with epichlorohydrin to give a phosphorus - containing epoxide resin. The steps involved in the proposed synthesis were:



Attempts to from a Gringnard reagent with p-chlorophenetole proved to be unsuccessful. Apparently the chlorine derivative is no sufficiently active.

2.3.5.2 Preparation of Diethyl 2.3 Epoxy Propane Phosphonate.

Diethyl 2,3 Epoxy Propane Phosphonate was prepared as a phosphorus containing epoxide compound which might prove useful as a reactive resin modifier. The compound is made by reacting triethyl phosphite with epichlorohydrin or epibromohydrin:[1]



Experiment K-104

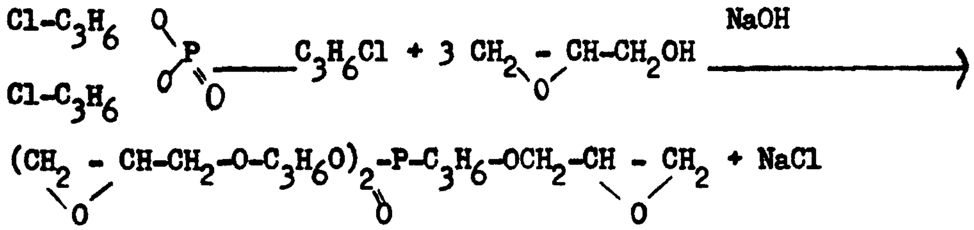
Triethyl phosphite and the epichlorohydrin were mixed in equimolar porportions to form a homogeneous mixture. The apparatus was assembled so that the epichlorohydrin refluxed and the ethyl halide was condensed and removed continuously from the reaction mixture. Heating was discontinued when the ethyl halide no longer appeared in the condenser. (See Figure 32) The reaction mixture was then fractionally distilled to recover the product. With epichlorohydrin, the reaction was very slow and only a trace of product was isolated. The reaction went smoothly with epibromohydrin and about a 50% yield of essentially pure product was obtained boiling at 101°/35 mm.

Curing:

Reaction Product	Curing Agent	Condition of Final Product
Epon 828 (Shell)	Diethylene	Hard, water-insoluble
Diethyl 2,3 epoxyphosphonate	Triamine	Plastic
K-104		Heat distortion was disappointing - 155°C compared to 255°C for Epon 828 without modifier.

2.3.5.3 Reaction of Bis-(chloropropyl) Chloropropane Phosphonate and Glycidol.

The reaction proposed was:



(1.) U. S. Pat. 2,770, 610 (Nov. 13, 1956)

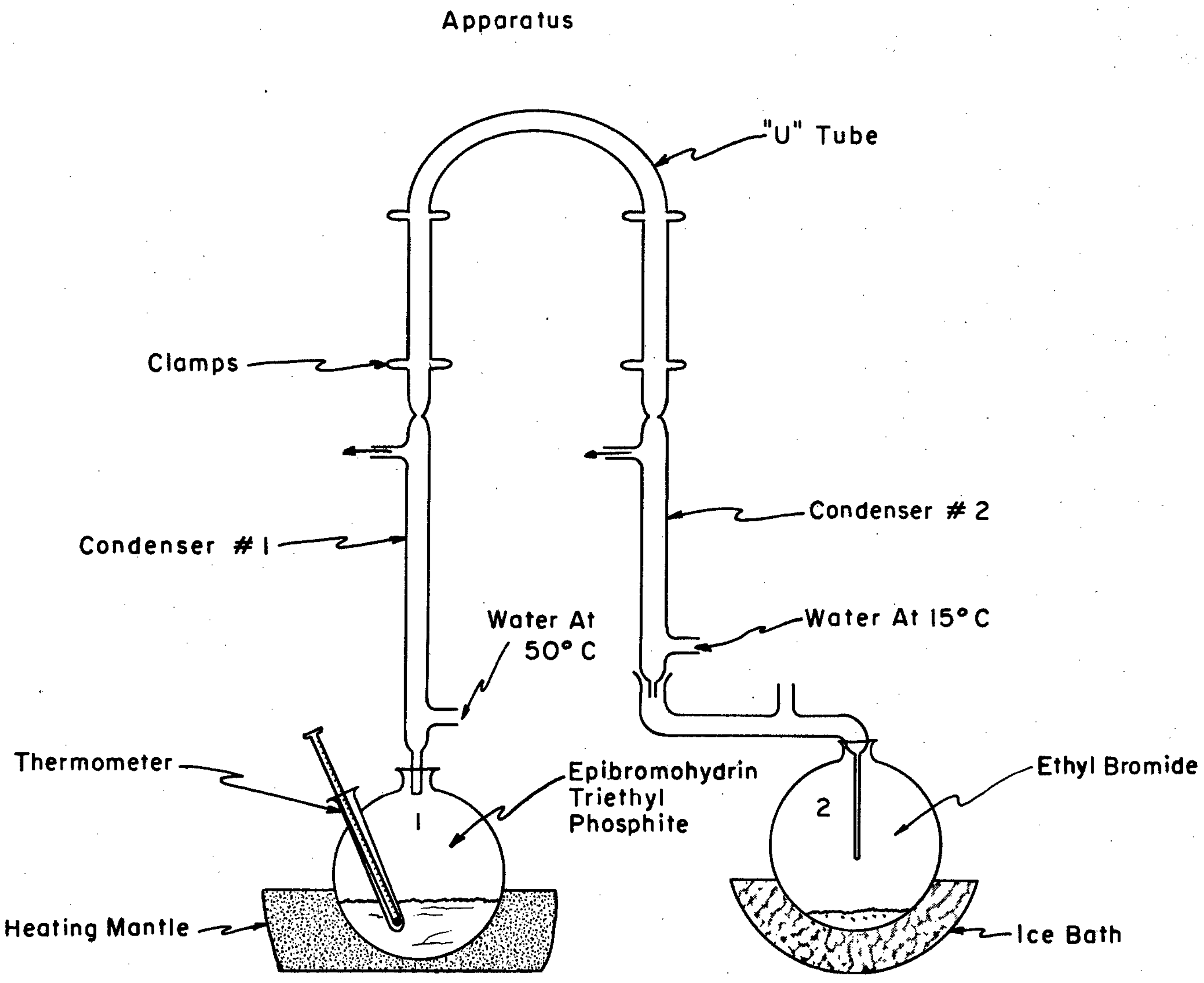


Figure 32. Apparatus For Preparation of Diethyl 2,3 Epoxy Propane Phosphonate

Experiment K-108

One tenth of a mole of bis-(chloropropyl) chloropropane phosphonate and 0.3 mole of glycidol were dissolved in 50 ml of benzene to form a homogeneous solution. Solid NaOH (0.3 mole) was added and the entire mixture was refluxed. A heavy, brown, viscous material formed almost immediately. This material was not miscible with the benzene solution and could be readily separated by decanation. It was quite soluble in water. No further effort was made to determine the structure. Under the conditions of the reaction, it seemed likely that the water-soluble material resulted from the self-polymerization of glycidol.

2.3.6 Analytical

This section of the report is concerned with the analytical techniques used for the analysis and study of the products formed from the various reactions which are mentioned throughout the test. The techniques used to perform the required analytical work are divided into two categories for purposes of presentation. These categories are infrared spectroscopy and classical analytical procedure for the determination of phosphorous, chloride, epoxide equivalents, carbon, hydrogen and oxygen. Each of these categories is discussed below, while the actual results of the analytical work are reported in the appropriate position in the test of this report.

2.3.6.1 Infra-red Spectroscopy. The success of infra-red spectroscopy as a qualitative tool has been due primarily to the fact that various functional groups in organic compounds exhibit characteristic absorption frequencies in certain regions of the infra-red spectrum. This feature of infra-red spectroscopy has led to its utilization at Melpar as a means of analysis of unknown compounds.

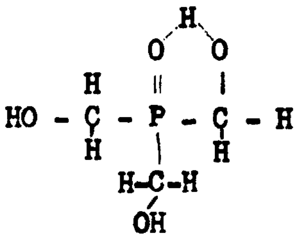
The absorption frequencies (converted to wavelengths for convenience in expressing numerical values) is tabulated for the functional groups of interest in this project.

Nature of Vibration	Wavelength Range
O-H Stretching frequency	
Free O-H	2.7 - 2.8 μ
Bonded O-H	2.8 - 4.0
O-H Deformations	
Primary alcohol - CH_2OH-	9.1-9 near 9.5
Secondary alcohol - CHOH-	8.6-5 near 9.0

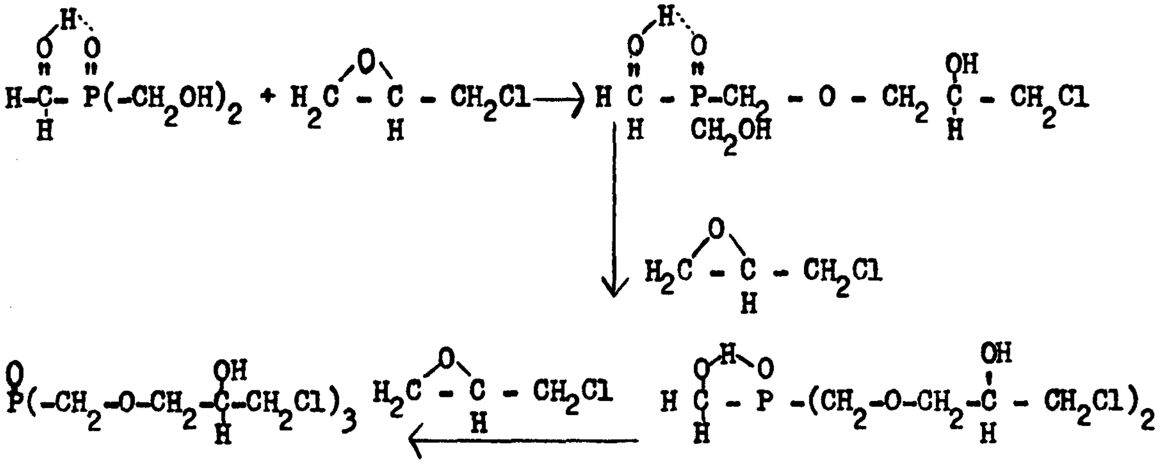
Ethers	
Alkyl - CH_2-O-CH	8.6-9.5 μ
Cyclic, Epoxy  $\overset{O}{C - C}$	near 8.0
	10.8 - 11.4
	12 - 12.2
Phosphorous-oxygen links	
P = o, free	7.0 - 8.5
P = o, hydrogen-bonded	near 8.7
C-Cl	12.5 - 16.7

The range of absorption frequencies of a particular functional group in a compound can normally be obtained from charts which are available both in the literature and commercially. This range of absorption frequencies of a particular functional group may be narrowed considerably if the spectra of pure compounds containing this functional group are available for study. Therefore, preliminary investigations of the spectra of pure materials related to this project were conducted and the observed absorption bands were correlated with the various functional groups within the molecules. A comparison of the absorption frequencies of the unknown materials with those of the pure materials then leads to certain conclusions concerning the nature of the unknown material, i.e., the appearance of new absorption bands or a shift in frequency of absorption of the original bands suggests a change in molecular structure and the occurence of a chemical reaction. A detailed example of this type of reasoning is given below.

In pure THPO, there are many sites for hydrogen bonding, either between two hydroxyl groups of the same or neighboring molecules, or between a phosphoryl group and a hydroxyl group. The shift in frequency of absorption from the normal hydroxyl absorption at approximately 2.7 to 3.1 microns in THPO, and the broad shoulder at 3.75 microns suggests the presence of hydrogen bonding, both intramolecular and intermolecular. Likewise, the frequency of the P = O absorption at 8.85 microns suggests the possibility of hydrogen bonding through this group, since the unbound phosphoryl absorption frequency is normally in the 7 - 8.5 microns region. In addition, a weak absorption band at approximately 6 microns is present in the spectrum of THPO; a band at 6 microns is often attributed to intramolecular hydrogen bonding. The 9.58 microns band in the spectrum of THPO is attributed to the C-O stretching frequency of the primary alcohol group - CH_2OH. Consideration of these spectral characteristics suggests the following type of intramolecular bonding:



Furthermore, if the reaction between THPO and epichlorohydrin proceeds as indicated. the following spectral changes should be evident.



(1) The secondary hydroxyl group will still give rise to a band in the three micron region. However, as the reaction proceeds, the sites for hydrogen bonding, although still present, will become influenced by steric factors resulting from the increase in chain length of the molecule. This steric hinderance will reduce the amount of hydrogen bonding and this decrease in the amount of hydrogen bonding will cause a shift in the hydroxyl stretching abosrption frequency to shorter wavelengths. Compare Figures 33, 34, 35.

(2) A decrease in the intensity of the 3 micron hydroxyl absorption band relative to the C-H absorption band at approximately 3.4 microns should be observed. This is due to the fact that as the reaction proceeds the hydroxyl group becomes a smaller percentage of the entire molecule whereas the percentage of carbon and hydrogen increases. An example of this is shown in Fig. 34.

(3) The spectral region between 8 to 10 microns is by far the most complex region to study since many structural assignments may be made in this area of the spectrum. Included in this region are the C-O stretching frequencies of ethers and primary and secondary alcohols. Definite absorption frequencies are difficult to assign since factors such as molecular size and molecular symmetry influence the band position. In addition, many of the absorption bands observed in this area are very broad or doublets and triplets.

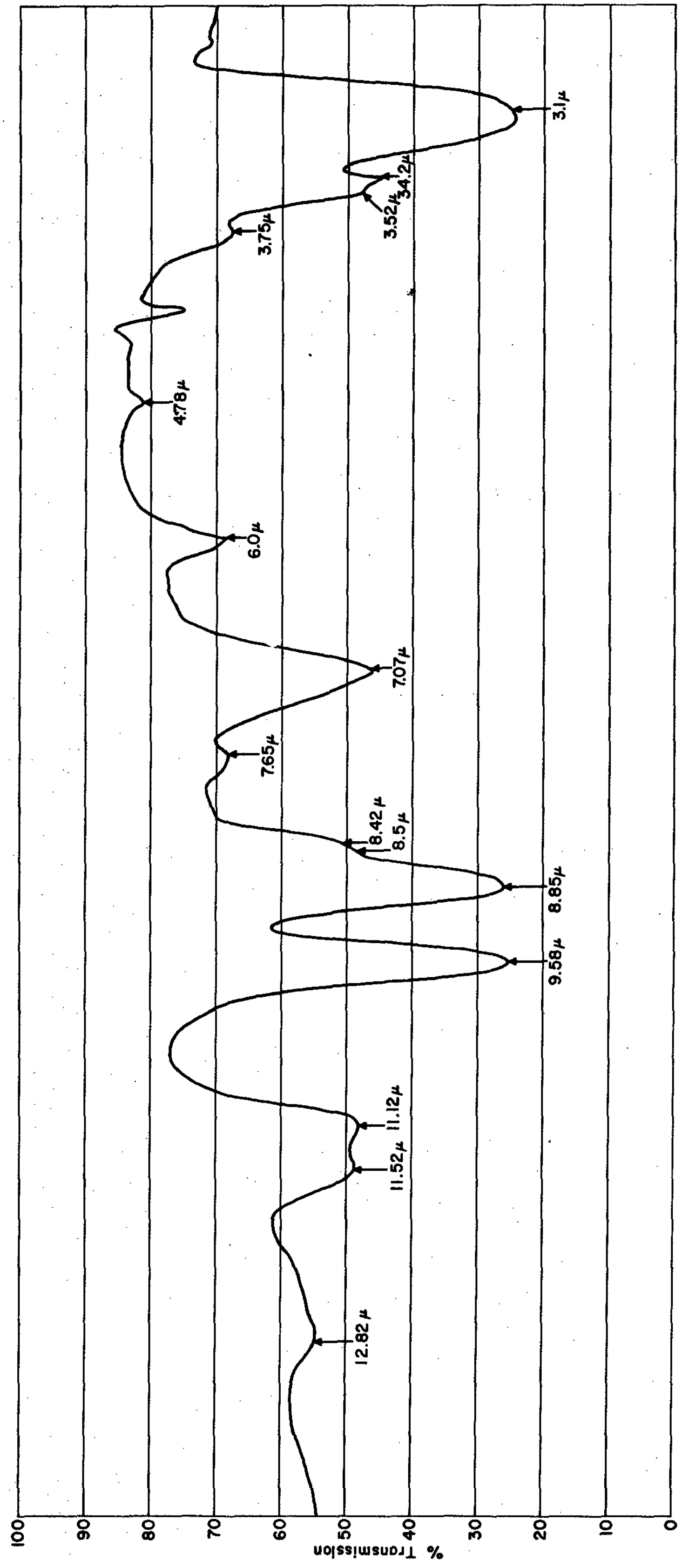


Figure 33. Infrared Spectra of Pure THPO (thin film)

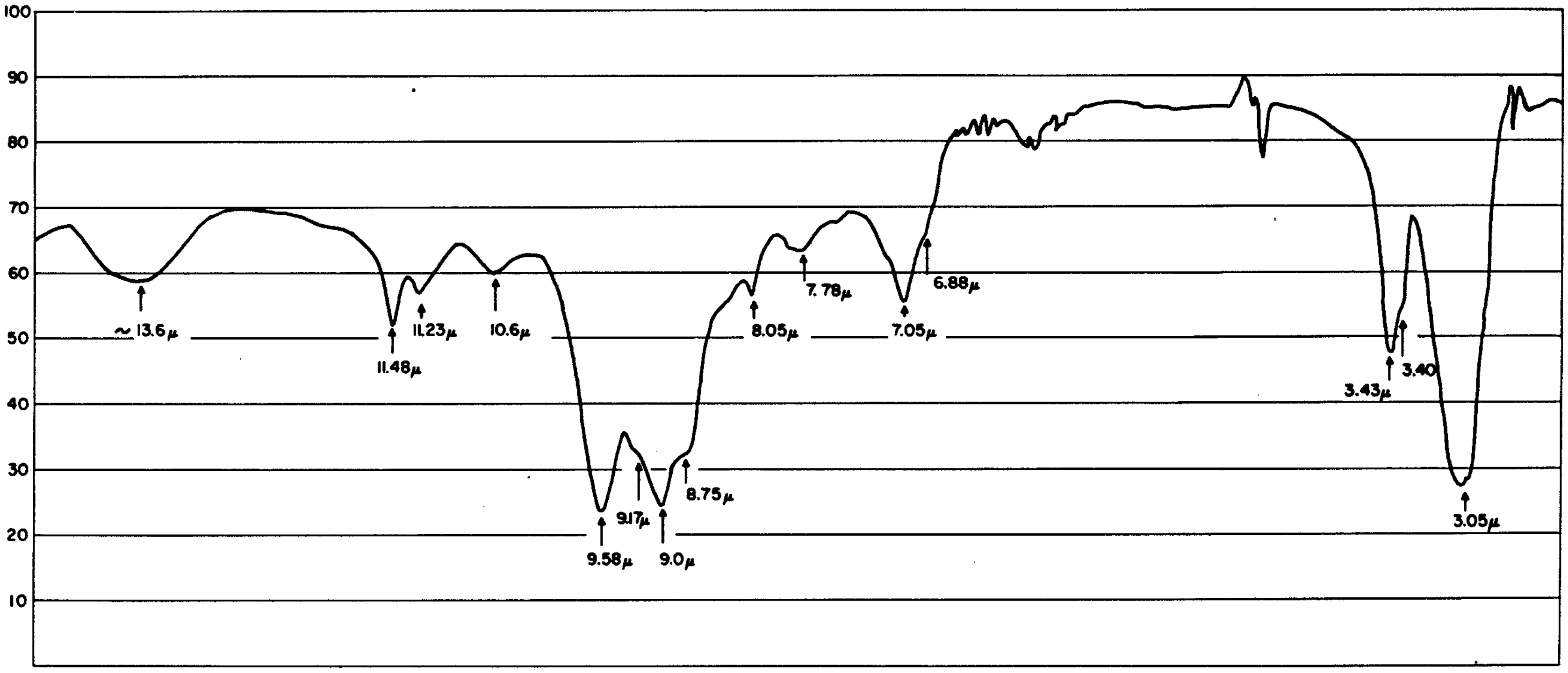


Figure 34. Infrared Spectra of Experiment K-98 Residue After Dioxane Extraction (thin film)

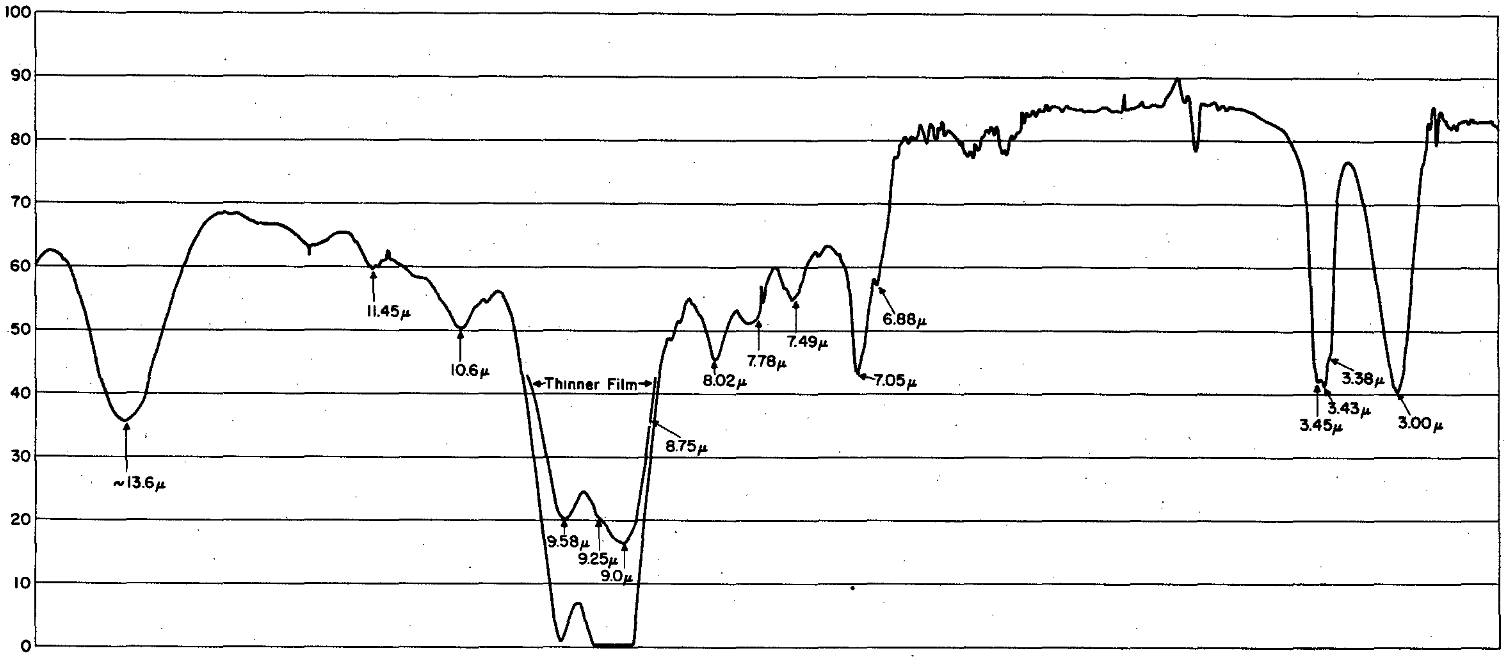


Figure 35. Infrared Spectra of Experiment K-98 Residue After Tetrahydrofuran and CCl_4 Extraction (thin film)

In any case, the following comments are made concerning spectral changes expected in this region of the spectrum. If the primary alcohol group of THPO is destroyed, the 9.58 microns band should decrease or disappear. However, the ether and secondary alcohol groups present in the molecule could possible give rise to absorption bands at this approximate wavelength. Therefore, this frequency range offers no conclusive evidence for structural assignments, although indications of the presence of ether and secondary alcohol groups are observed.

(4) If the phosphoryl absorption at 8.85 microns is due to both intermolecular and intramolecular bonded $P = O$, then this frequency would shift only slightly for intermediate products in the reaction indicated above. However, if the final reaction product with a free phosphoryl group were formed, then the phosphoryl absorption frequency sould shift considerably to the unbound phosphoryl range, namely, 7 to 8.5 microns.

In summary, the above comments have been presented in order to indicate how the spectral data in other sections of this report have been evaluated. The remaining comments are of a general nature and examine the technique used to obtain the various spectra discussed in the report. Since the samples, in general, were not soluble in any of the usual spectroscopic solvents, it was necessary in most instances to obtain the spectra by placing a thin film of the samples on a rock salt plate. This technique often leads to strong absorbance with poor resolution, particularly if the film is too thick, as is often the case with viscous materials.

In addition to film thickness, impure samples will often result in poorly-resolved spectra with broad bands. In several cases, the poor resolution has been attributed to additive absorption due to several components of an impure sample.

In all cases, the recording conditions and sampling techniques were varied to obtain maximum resolution. The spectra of THPC, THPO, Tilac, Bisphenol A, Epichlorohydrin, Glycidol, and Shell Epon 834 were recorded for comparison purposes, in addition to other organophosphorous compounds obtained commercially.

The spectra of all the various materials were obtained with a Model 13U Perkin Elmer double beam infra-red spectrophotometer.

2.3.6.2 Methods of Analysis for Phosphorous, Chloride, Epoxide Equivalents, Carbon, Hydrogen and Oxygen. The organophosphorous compound was decomposed in accordance with the method described by Wreath[1]. In this method the organophosphorous compound is decomposed with concentrated nitric and perchloric acids. The resultant phosphate was then determined by the alkalimetric method described by Bachofer and Wagner[2].

Using the technique described by Beamish[3] and Parr Bomb Manual 121[4], the chloride content of the various reaction products was determined. A 22 ml Parr bomb with an electrical ignition system was used to decompose the organic compound. The resultant chloride formed was determined by the Volhard Method[5].

The epoxide equivalents of the various reaction products were determined using the pyridine-pyridinium hydrochloride method[6]. In certain instances, were the phenophthalein end point was not clearly visible, the method described by Durbetaki was used [7,8]. In this procedure the compounds are titrated directly with HBr is backtitrated with standard silver nitrate solution.

Since the isolation of the various reaction products in a pure state has proven to be very difficult, no attempt has been made to determine the carbon, hydrogen and oxygen content of the samples on a micro-analytical scale. It is expected, of course, that in the future such analysis will be conducted.

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3. Beamish, F. E., "Determination of Organic Halides," Ind. Eng. Chem., Anal. Ed., 6, 352 (1943).

4. Peroxide Bomb Apparatus and Method, Parr Manual No. 121 (1950).

5. Pierce and Haenisch, "Quantitative Analysis," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 300.

6. Weissberger, A., "Organic Analysis," Vol. I., Interscience Publishers, Inc., New York, N. Y., (1953), pp. 136.

7. Durbetaki, A. J., "Direct Titration of Oxirane Oxygen with Hydrogen Bromide in Acetic Acid," Becco Chemical Division, Food Mach. and Chemical Corp., Station B., Buffalo 7, N. Y.

8. Durbetaki, A. J., "Determination of Oxirane Oxygen In Salts of Epoxy Acids and in Presence of Amines," Anal. Chem., 30, 2024 (1958).

2.4 Curing of Reaction Products

The curing of selected reaction products obtained during the period of the contract was conducted. Although the exact structure of these reaction products had not been determined, it was felt that useful products might be obtained by catalytic and crosslinking curing agents. In addition, attempts were made to cure commercial epoxide resins with some organo-phosphorus and organo-titanium compounds: (See Table XI)

TABLE XI

CURING OF REACTION PRODUCTS

REACTION PRODUCT	CURING AGENT		CURE SCHEDULE	CONDITION OF FINAL SAMPLE	SOLUBILITY	TYPE OF STRUCTURE
P-1A	BF-3-400[1] (Shell	2PHR[2]	20 hrs. at 150°C	Hardened	Water soluble	Flexible foam
P-1A	Nadic Anhydride (National Aniline	200 PHR	20 Hrs. at 120°C 17 Hrs. at 170°C	Hardened	Water soluble	Foam
P-1A	PMDA[3] MA[4]	34 PHR 46 PHR	17 Hrs. at 170°C	Hardened	Water insoluble	Foam
P-1B	Pyridine PMDA MA	0.5 PHR 34 PHR 46 PHR	$19\frac{1}{4}$ Hrs. at 150°C	Hardened	Absorbed water but did not dissolve	Foam
P-1C	BF 3-400	2 PHR	20 Hrs. at 150°C	Hardened	Water soluble	Flexible foam
P-1C	Nadic Anhydride	200 PHR	20 Hrs. at 120°C 17 Hrs. at 170°C	Hardened	Water insoluble	Foam
P-1C	PMDA MA	34 PHR 46 PHR	17 Hrs. at 170°C	Hardened	Water insoluble	Foam
P-3	DDS[5] BF 3-400		15.5 Hrs. at 127°C	Thermo-plastic	---------	-----
P-11	Too Viscous to mix with DDS at 132°.		----------------	-------	---------	-----
P-4	DDS BF 3-400		14.5 Hrs. at 127°C	Thermo-plastic	---------	-----
P-11	BF3-400		7.5 Hrs. at 150°C	Tacky on surface; hard beneath surface	Water soluble	-----

TABLE XI (CON'T)

CURING OF REACTION PRODUCTS

REACTION PRODUCTS	CURING AGENT		CURING SCHEDULE	CONDITION OF FINAL SAMPLE	SOLUBILITY	TYPE OF STRUCTURE
P-13	Pyridine PMDA MA	0.5 PHR 34 PHR 46 PHR	22 3/4 Hrs. at 150°C	Hardened	Absorbed water but did not dissolve	Foam
P-14	Pyridine PMDA MA	0.5 PHR 34 PHR 46 PHR	$22\frac{1}{4}$ Hrs. at 150°C	Hardened	Foam structure destroyed Water insoluble	Foam
P-24	Pyridine PMDA MA	0.5 PHR 34 PHR 46 PHR	Cured immediately at 100°C	--------	Water soluble	----
T-2	BF 3-400		6.5 Hrs. at 150°C	Failed to harden	------------	----
Epon 828 (Shell)	TAT-21[6] (Dupont)	8.3 PHR	144 Hrs. at 60°C	Hardened	------------	----
Epon 828	(TAT-21)	16.6 PHR	49 Hrs. at 60°C	Hardened	------------	----
K-13	DETA[7]		12 Hrs. at Room Temp.	Failed to Harden	------------	----
K-13	PA[8]	20 PHR	12 Hrs. at 120°C	Failed to Harden	------------	----

TABLE XI (CON'T)

CURING OF REACTION PRODUCTS

REACTION PRODUCT	CURING AGENT CURE SCHEDULE	CONDITION OF FINAL SAMPLE	SOLUBILITY	TYPE OF STRUCTURE
Epon 828	Tris (2 diphenyl phosphite ethyl) Amine 15 PHR 55 Hrs. at Room Temp. 4 Hrs. at 100°C	Failed to harden	Water soluble	Foam
Epon 828 (75%) Diethyl 2, 3 epoxy propane phosphonate K-104[9] (25%)	Diethylene Triamine 10 PHR 24 Hrs. at Room Temp. 2 Hrs. at 100°C	Hardened[10]	Insoluble	Solid Plastic

Notes:

1. Boron trifluride amine complex
2. Parts per hundred resin
3. Pyromellitic Anhydride
4. Maleic anhydride
5. Diaminodiphenyl sulfone
6. Triethanol amine titanate and 20.5 percent isopropyl alcohol
7. Diethylene triamine
8. Phthalic Anhydride
9. This compound is an epoxy resin modifier.
10. Heat distortion temperature was disappointing 155°C compared to 255°C for Epon 828 without modifier.

2.5 Toxicity of Organo Phosphorus Compounds

Although phosphorus and phosphines have been known to be toxic for many years, only recently have the toxic properties of a great number of organic derivatives of phosphorus been appreciated. Esters of pyrophosphoric acid, fluorophosphates, some of the allylaryl phosphates and thionophosphates, and probably other classes have a profound influence on living organism, shown mostly by a powerful anticholinesterase activity. The effects of such compounds upon the nervous system make it definitely advisable to take adequate precautions before taking liberties with exposures to substances with unknown physiological action.

As a surveillance mechanism of the personnel involved in phosphorus chemistry concerning this contract, a bimonthly check on the red blood cell and plasma cholinesterase activity in the blood has been run. These checks will indicate the absorption of materials* that affect regular enzyme activity.

The basic principle behind this enzyme activity is the production of acid from the reaction of Cholinesterase on acetylcholine to produce acetic acid and choline. The acid production is measured in terms of the change in pH produced by enzymatic activity in a standard buffer solution over a definite period of time.

2.5.1 Analytical Method

The method chosen is the same as is used by the Army Chemical Center in the surveillance of their personnel involved in the chemistry of toxic materials.

The method developed by Harry O. Miche, Ph.D., of the Army Chemical Center is entitled "An Electrometric Method For The Determination of Red Blood Cell and Plasma Cholinesterase Activity."

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* Phosphorus compounds or their derivatives.

Equipment

1. pH Meter with miniature electrodes of the Silver Chloride type.
2. Constant temperature bath.
3. 5 ml beakers - 4 per individual
4. Sakli pipettes - 4 per individual
5. Blood Capillary tubes 6 inches long - 2 per individual
6. Centrifuge
7. Blood Lancit
8. Cotton
9. Alcohol

Reagents

1. Buffer (for Red Cells)
   a) 2.0168 grams Sodium Barbitol
   b) 0.2723 grams KH_2PO_4
   c) 22.365 grams KCl

Mix above and dilute with 3x distilled water to 250 ml. Check pH and adjust as necessary to a pH of 8.10 ± .02 with 0.1N NaOH or 0.1N HCl. After adjustment dilute to 500 ml.

2. Buffer (Plasma)
   a) 0.6185 grams Sodium Barbitol (Veronal)
   b) 0.0680 grams KH_2PO_4
   c) 8.780 grams NaCl

Proceed same as for red cell buffer but adjust pH to 9.02 ± .01 prior to diluting to 500 ml.

Procedure

1. Remove heparin solution and buffer solution from refrigerator to permit ambient temperature equilibrium.

2. Rinse capillary tubes (6 inches long) (2 for each subject) with heparin solution; drain out excess heparin.

3. Have subject soak finger tips in beaker of hot water for about 5 minutes to insure capillary dilatation for adequate blood supply; dry hand.

4. Cleanse finger tip with an alcohol sponge. Dry with clean dry sponge.

5. Puncture finger tip with individual, disposable lancet. Ear lobe may also be used for puncture.

6. Fill capillary tube with blood by holding it slightly downward, allowing the blood to flow by gravity and capillarity to within 1 inch of end.

7. Seal in a micro burner the unfilled end of the capillary tube. Place in a horizontal position to cool. Then place each sealed capillary in its corresponding numbered or named test tube (4 x ½ inch).

8. Balance all centrifuge cups and centrifuge at 2000 rpm for 20 minutes. Gauge speed with techometer. After 20 minutes remove capillaries from centrifuge and proceed as follows:

9. Set up beakers (5.0 ml) for each subject; 2 beakers for RB cell determination and 2 for plasma (4 for each blood sample).

10. Number the beakers in the numberical order of the blood samples. Place in each beaker 1.0 ml of distilled water.

11. Starting in numberical order, take the first capillary tube, score sealed end just above the closure with an ampule file and break off the end with a forcep. Score the tube again just below and above the white cell layer and break tube at these points, discarding the white cell layer.

12. RBC: With a Sahli Pipette and suction tubing, take up 0.02 ml red cells measured accurately to the mark, wipe off any excess blood from tip of Sahli pipette and expel gently into the beaker of distilled water keeping the tip of the pipette below the surface of water. Do not mix at this time. Rinse Sahli pipette with supernatant distilled water 3X to remove all of the blood; then mix thoroughly with small stirring rod. To insure complete hemolysis, let stand 10 - 15 minutes.

13. Plasma-Repeat procedure as for red cells. Duplicate samples.

14. Standardize pH meter with 7.0 standard buffer. Verify pH of buffer solutions before adding to the blood and plasma mixtures in the beakers. Adjust pH if necessary. Don't use buffers more than 2 weeks old, even if pH is stable - buffering capacity is lost due to instability of Veronal (Sodium Barbitol) in aqueous solution.

15. Add 1.0 ml of red cell buffer to beakers containing red cells in solution. Add 1.0 ml of plasma buffer to the beakers containing plasma. Mix contents of each beaker thoroughly with small stirring rod.

16. Incubate all beakers in trays on water bath at 25. ± .5°C. for 10 - 15 minutes. Then mix sample well with small stirring rods and:

17. Take an initial pH (pH_1) on all samples, rinsing with distilled water the electrodes and drying same with gause wipette between each reading. Record all readings.

18. Acetylcholine chloride sol. is made up at this point as follows:
For RBC ChE use 0.11M (2%)
1 amp (100 mg) to 5 ml dist H_2O
For plasma ChE-0.165 M (3%)
3 amps (100 mg ea) to 10 ml dist H_2O
Acetylocholine chloride is unstable and must be made up just before use. It deteriorates at a rate of 10% perday and at the end of 4-5 days a stock solution is only 50% ± active. It is made up fresh for each days work and any remaining solution is discarded.

19. After the initial pH readings are recorded, Acetyl Cholinechloride 0.2 ml is added to the first beaker with timing; to each successive beaker 0.2 ml Acetyl Cholinechloride is added allowing 1 minute (stopwatch) between each addition of Acetyl Colinechloride. Mix well and let remain in waterbath for 60 minutes.

20. At the end of 60 minutes remove beaker 1 from waterbath, mix contents with enclosed stirring rod, remove the latter and read in pH meter (pH_2). Continue in the numberical order of beakers until all readings are taken allowing 1 minute for reading pH of each beaker. Electrodes are rinsed with dist. H_2O and dried between each reading.

21. The pH_2 reading is subtracted from the pH_1 reading to obtain the delta pH (ΔpH) and the resulting figure is recorded. The ChE value is expressed as "ΔpH/hr".

22. Normal Average ChE values----RBC .81 pH/hr
Plasma .79 pH/hr

Range----RBC .60-1.00 JS
Plasma .61-1.50

23. Exposure Δ pH RBC .55 - recheck the ChE test on the following day, or lower - Important

24. Controls: RBC Variations

Consec. days
range
person

± .07 Δ pH
.10

Plasma

0.14 Δ pH units

25. Variations between .04, sample .02 - .06

3. CONCLUSIONS AND RECOMMENDATIONS

3.1 Literature Survey

Literature sources to date have not revealed any phosphorus epoxide polymers or any organo-phosphorus compounds containing more than one epoxide group. It is recommended that the current chemical and commercial literature be constantly searched for new developments in epoxide polymers and organophosphorus compounds containing epoxide groups.

3.2 Testing of Commercial Epoxy Resins

The characteristic thermal properties of commercial epoxy resins were obtained from Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Heat of Distortion values. Those resins tested included Dow Epoxy Novalac X2638.3, Eccomold L 266, Stycast 2662, Epoxylite 813, Maraset 617, Sealcast 506, Epon X1310 laminate, Epon 828/PMDA-MA, Epon 828-Epon X1310/Diaminodiphenylsulfone, Epon 828-Triethanol Amine Titanate, and Permacel ST 3994.

From these resins, Eccomold L 266 and Epon X1310 laminate exhibited the highest Heat of Distortion values (in excess of 350°C at 264 psi). Thermal Gravimetric Analysis indicated that Eccomold L 266 exhibited the highest degradation temperature. Differential Thermal Analysis indicated that Stycast 2662 exhibited highest degradation temperature (355°C) while Eccomold L 266 exhibited a degradation temperature of (340°C). DTA samples consisted of 90% Al_2O_3 and 10% of the test resin.

It was found that Thermal Gravimetric Analysis (TGA) as compared with Differential Thermal Analysis (DTA) had an inherent advantage for comparing the thermal stabilities of polymers. The (TGA) curves share a common, well defined "knee" in the temperature range wherein desruptive volatilization first becomes rapid, thus enabling clearer interpretation of degradation temperature.

3.3 Synthesis

A number of products resulting from the reaction of tetrakis (hydro-oxymethyl) phosphonium chloride and epichlorohydrin in the presence of aqueous sodium hydroxide yielded water insoluble foams when cured with anhydride type curing agents. Although positive identification of these products has been a formidable problem, the fact that polymers have been formed from the reaction of a quartenary phosphonium compound and epichlorohydrin is viewed as encouraging.

Even more promising results were observed in attempts to prepare a phosphorus containing epoxide by a two step reaction of tris (hydroxymethyl) phosphine oxide and epichlorohydrin. Conditions have been worked out for obtaining satisfactory yields in the first or acid catalyzed step, but more development work is required to define conditions for the second or ring closing step.

It is recommended that investigation of the two step reaction of THPO and epichlorohydrin be continued. In the first step, effort should be concentrated on improving the yield of completely reacted product. Thus far, it appears that mixtures have been obtained which result from the reaction of one, two and three moles of epichlorohydrin with THPO. It is suggested that by using a greater excess of epichlorohydrin, a higher temperature, and a longer reaction time all three of the hydroxyls of THPO might react with epichlorohydrin thus reducing the amount of, or eliminating the compounds in which only one or two moles of epichlorohydrin have reacted with a mole of THPO. In addition it is recommended that separation steps be more fully investigated.

In the ring closing step, the products obtained thus far appeared to be cross-linked polymers which were completely infusible. It is recommended that additional ring closing experiments be attempted with: (1) dilute NaOH at room temperature or lower; and (2) sodium aluminate with dimethyl formamide as a solvent.

In addition to further study of the THPO-epichlorohydrin reaction, it is recommended that the preparation of certain other phosphorus containing epoxides be investigated.

The following program is recommended for the preparation of new phosphorus containing epoxides. In this outline, preparation of polyfunctional epoxides is described. In general, each synthesis problem should be approached in a stepwise manner by first considering the preparation of model monofunctional compounds which can be purified and identified. By this approach, a firm foundation for preparing the more complicated di- and trifunctional compounds could be established.

1. Epoxides From Polyhydric Phenols

A. Compound: Tris (4-hydroxyphenyl phosphine) $(4\text{-HO-}C_6H_4)_3P$
Reaction with Epichlorohydrin: Compound will be reacted with epichlorohydrin to yield epoxide resins analagous to those obtained commercially by the reaction of epichlorohydrin with Bis-phenol A.

Curing: Curing of the epoxide resin formed will be investigated with the usual anhydride and amine curing agents.

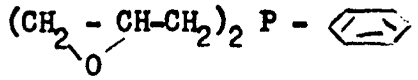
B. Compound: Tris-(3-hydroxyphenyl) phosphine oxide. $3\text{-}(HO\text{-}C_6H_4)_3$ P=O Reaction with epichlorohydrin and cure will use the same procedures as compound A.

C. Compound: Tris-(4-hydroxyphenyl) phosphate. $(4\text{-}HOC_6H_4O)_3$ P=O
Reaction with Epichlorohydrin: Some difficulty may be experienced in reacting with aqueous NaOH because of the likely hydrolytic cleavage of P=O bonds to give phosphoric acid. There is a possibility of reaction of epichlorohydrin with the compound by an acid catalyzed reaction under anhydrous conditions followed by dehydrohalogenation with base.

Curing: Curing of the epoxide formed will be investigated with the usual anhydride and amine curing agents.

2. Epoxidized Phosphorus Compounds

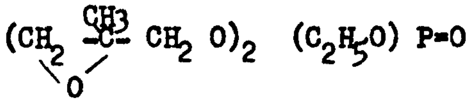
A. Compound: Bis (2,3 epoxypropane) phenyl phosphine



$(\underbrace{CH_2 - CH}_{O}-CH_2)_2\ P -$

Curing: Curing will be investigated with the usual amine and anhydride curing agents.

B. Compound: Bis (2-methyl 2,3 epoxy propane) ethyl phosphate



$(\underbrace{CH_2 - \overset{CH_3}{C}}_{O} - CH_2\ O)_2\ \ (C_2H_5O)\ P{=}O$

Curing: Curing will be investigated with the usual amine and anhydride curing agents.

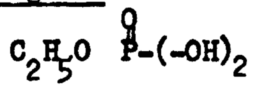
3. Phosphorus Diamines as Curing Agents

Compound: Bis (4-amino phenyl) phenyl phosphine

$(4\text{-}NH_2\text{-}C_6H_4)_2\ C_6H_5\text{-}P$

Use as curing agent: Compound will be tested as a curing agent (by crosslinking) with commercial epoxide resins.

4. Phosphoric Acid Derivatives as Curing Agents

Compound: Mono-ethyl Phosphate 

$C_2H_5O\ \overset{O}{\overset{\|}{P}}\text{-}(\text{-}OH)_2$

Use as curing agent: Compound will be tested as a curing agent (by crosslinking) with commercial epoxide resins.

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Unclassified report

Synthesis of phosphorous epoxide polymers or organo-phosphorous compounds containing more than one epoxide group were attempted. A number of products from the reaction of tetrakis (hydroxymethyl) phosphonium
(over)

(over)

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chloride and epichlorohydrin in aqueous caustic were produced but exact compositions could not be determined. Reaction was also attempted with tris(hydroxymethyl) phosphine oxide and epichlorohydrin. The characteristic thermal properties of commercial epoxy resins were obtained from Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Heat of Distortion values.

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