

DEVELOPMENT OF IMPROVED ADHESIVES
FOR USE AT CRYOGENIC TEMPERATURES TO -423° F.

Final Summary Report
For The Period
July 11, 1963 - August 31, 1965

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

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Submitted by: The Borden Chemical Company
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In conclusion, several adhesives have been made which meet all the temperature requirements but do not have the proper T-peel strength when cured at 73° F. The adhesives which meet the tensile shear strength requirements are the epoxy esters which are cured at 100° C. for two hours. Standard bisphenol A epoxy adhesives can be greatly improved in tensile shear strength by curing with cyclopentane tetracarboxylic acid dianhydride.

As the adhesives become more flexible to meet the T-peel requirements the tensile shear strengths at 250° and 400° F. begin to decrease. Consequently it was not feasible to prepare adhesives meeting the tensile shear requirements and having a T-peel in excess of 10 lbs./in. It appears that curing at room temperature is sufficient for some epoxies and polyurethanes where tensile shear strength at 400° F. is not required. Using an elevated cure temperature produces a more cross-linked adhesive showing more rigidity, lower T-peel, but good elevated temperature tensile shear strength.

SUMMARY

During the Contract period a large part of our effort was placed on evaluating polyurethanes and epoxy resins as cryogenic adhesives showing good tensile shear and T-peel properties over the temperature range of -423° F. to 400° F. In addition, several other chemical structures were investigated.

Our first objective in the polyurethane investigation was to devise methods for the successful preparation of model systems in order to study their structure-property relationships in regard to good cryogenic adhesive properties.

It soon became apparent that the polyethers gave the highest tensile shear strength and T-peel on aluminum but that they had poor properties at 250° and 400° F. Modification of the polyol, diisocyanate, or amine curing agents did not alleviate the problem. Curing at 100° C. for 2 hours gave satisfactory values from -320° to 250° F. for some systems but on lowering the cure temperature most of these systems showed a decrease in strength over the entire temperature range..

Copolymerizing epoxy resins with good high temperature tensile shear properties with polyurethanes which lacked these properties gave only a small increase over the latter's results for the homopolymer. It was discovered in the course of this work that the structure of the copolymers were poly-2-oxazolidones, a new polymer system.

Trimerization of isocyanate-terminated polyurethane prepolymers at 165° F. converted them to polyisocyanurates showing tensile shear strengths of about 1000 psi at 400° F. Attempts to lower the temperature proved unsuccessful.

The investigation of several bisphenol epoxy adhesives indicated that the substituents in the aromatic ring had no effect on adhesive performance but that the epoxy content was the major factor.

The use of epoxy esters (polyglycidyl esters of polycarboxylic acid) yielded some adhesives that showed much higher tensile shear strengths than bisphenol A epoxies at 400° F. when cured with 4,4'-diaminodiphenylmethane (MDA) at 100° C. The increase became much less apparent when cyclopentane tetracarboxylic acid (CPDA) dianhydride was used as the curing agent in place of MDA at 100° C. In other words, bisphenol A epoxies also showed high tensile shear strengths at 400° F. when cured with CPDA.

Attempts to improve the T-peel strength of the epoxy resins by the addition of some polyether structures led to a decrease in the elevated temperature properties. Several flexibilized epoxy resins were produced from epoxy polyether dianhydrides or diisocyanates.

FOREWORD

This Final Report was prepared by The Borden Chemical Company, a Division of The Borden Company, under contract NAS 8-11518, "Development of Improved Adhesives for Use at Cryogenic Temperatures to -423° F." for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with Dr. William E. Hill acting as Project Manager.

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I. EPOXY ESTER ADHESIVES

A. The Synthesis of Aromatic Glycidyl Esters

Glycidyl esters of aromatic acids appear to have been relatively unexplored as compared to the aliphatic acids ^{1/} except for their descriptions in some patents. ^{2-11/} The patents have described the preparation of these materials rather crudely except for one case where carbon and hydrogen analyses have been reported for crystalline diglycidyl terephthalate. ^{2,11/} The object of this investigation was to synthesize pure glycidyl esters of aromatic acids in order to be able to explore their use for adhesives.

Diglycidyl phthalate and diglycidyl terephthalate are described in detail in a procedure ^{2,11/} which recommends addition of the acid chloride to a mixture of glycidol in the presence of triethylamine at 0-5° C. in benzene or toluene solution. This procedure suffers from the disadvantage that glycidol itself polymerizes ^{12/} exothermically in the presence of basic materials and thus contaminates the products which are subsequently isolated in low yields. The products are easily polymerized by the application of heat in the presence of basic catalysts such as triethylamine. Some investigators ^{2,11/} have neglected this fact and procedures are given wherein the products are heated to 160° at 10 mm. pressure in vessels which originally had basic catalysts. Therefore, in order to prepare purer products with acceptable analyses a modified procedure was developed which utilized low temperatures and separate addition of triethylamine. Many of the crystalline products obtained in this investigation have been reported by earlier investigators as resins. The physical constants and analyses for the glycidyl ester appear in Table I. The general procedure is illustrated below utilizing the preparation of diglycidyl isophthalate as an example.

-
- ^{1/} E. B. Kester and M. E. Lazar, J. Org. Chem., 8, 550 (1948).
 - ^{2/} Brit. Pat. 735,001, Aug. 10, 1955 to Henkel & Cie.
 - ^{3/} French Pat. 1,086,934, Feb. 17, 1955 to Henkel & Cie.
 - ^{4/} G. B. Payne and C. W. Smith, U. S. Patent 2,761,870, Sept. 4, 1956 to Shell Dev. Co.
 - ^{5/} I. H. Updegraff, U. S. Pat. 2,781,333, Feb. 12, 1957 to Am. Cyanamid.
 - ^{6/} T. J. Suen and G. Hewlett, U.S. Pat. 2,801,232, July 30, 1957 to Am. Cyanamid.
 - ^{7/} B. Raecke, R. Kohler and A. Pietsch, U. S. Pat. 2,865,897, Dec. 23, 1958 to Henkel & Cie.
 - ^{8/} E. C. Shokal and A. C. Mueller, U.S. Pat. 2,895,945, July 21, 1959 to Shell Dev. Co.
 - ^{9/} British Pat. 862,588 March 15, 1961 to Canadian Industries, Ltd.
 - ^{10/} W.H.M. Nieuwenhuis and P. Bruin, Neth. Pat. 96,753, Jan. 16, 1961 to N. V. De Bataafsche Petroleum Maatschappij.
 - ^{11/} B. Raecke and R. Kohler, U. S. Pat. 3,073,804, Jan. 15, 1963 to Henkel & Cie.
 - ^{12/} S. R. Sandler and F. Berg, J. Polymer Sci. to be published 1965.

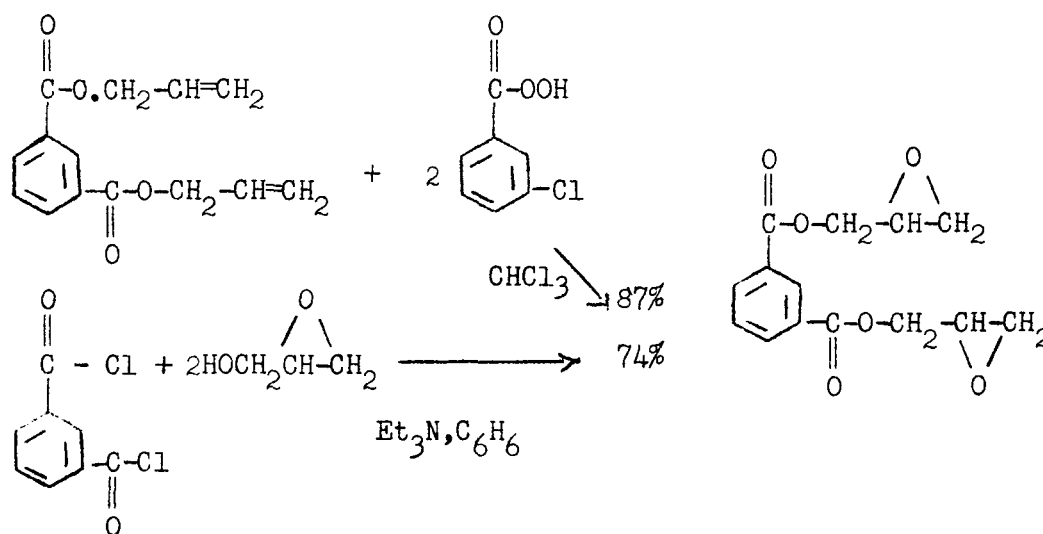
Table I. - Preparation of Polyglycidyl Esters of Polycarboxylic Acids

Product	% Yield	Physical Properties ^{13/}				M. P. ° C. liq.
		Calc'd.		Found		
		% C	% H	% C	% H	
Diglycidyl Isophthalate	78	60.43	5.07	60.42	5.13	60-63°
Diglycidyl Terephthalate	67	60.43	5.07	60.37	5.19	94-96°
Diglycidyl Hexahydroterephthalate ^{14/}	25	59.14	7.09	58.67	6.86	88-90°
Diglycidyl Phthalate	94	60.43	5.07	60.04	5.39	liq.
Diglycidyl 2,5-Dichloroterephthalate	53	48.44	3.45	48.66	3.68	113-114°
Diglycidyl Diphenate	85	67.80	5.08	68.04	5.10	liq.
Triglycidyl Trimesoate	46	57.14	4.80	57.59	5.38	liq.
Triglycidyl Trimesoate	58	57.14	4.80	57.18	4.86	58-63°
Triglycidyl Trimellitate	52	57.14	4.80	57.98	5.35	liq.
Triglycidyl Trimellitate	63	57.14	4.80	58.16	5.09	liq.
Tetraglycidyl Pyromellitate	30	55.23	4.64	55.18	4.81	113-123°

^{13/} The carbon-hydrogen analyses were determined by Dr. Stephen M. Nagy, Microchemical Laboratory, 78 Oliver Road, Cambridge, Mass.

^{14/} The properties of diglycidyl hexahydroterephthalate are shown for comparison although this is not an aromatic system.

An additional method that is useful for the preparation of glycidyl esters is the reaction of the diallyl esters of aromatic acids with *m*-chloroperbenzoic acid. Although peracetic ^{9/} acid has been reported to peroxidize diallyl esters it was found to suffer from the disadvantage that the epoxy esters decomposed in the presence of acetic acid. Meta-chloroperbenzoic acid gave a clear reaction and separation from the by-product *m*-chlorobenzoic acid was effected by washing the organic layer with dilute sodium carbonate or sodium hydroxide. Recently other investigators ^{15/} have also found *m*-chlorobenzoic acid to be useful for preparing volatile epoxides. The procedure for preparing diglycidyl terephthalate from diallyl terephthalate is given below. Table II describes other examples.



^{15/} D. J. Pasto and C. C. Cumbo, J. Org. Chem., 30, 1271 (1965).

Experimental

Diglycidyl isophthalate (471-21) - A one-liter resin kettle was fitted with a stirrer, thermometer, condenser with drying tube, and two 300 ml. dropping funnels. All the equipment was carefully dried and flushed with nitrogen for ten minutes. Glycidol (74.1 g., 1.0 m.) and 200 ml. benzene were placed in the flask and cooled, with stirring, to 0° C. in an ice-water-methanol bath. A solution of isophthaloyl chloride (101.5 g., 0.5 m.) in 150 ml. benzene was placed in one dropping funnel and a solution of triethylamine (101 g., 1.0 m.) in 150 ml. benzene was placed in the second dropping funnel. The dropwise addition of the acid chloride was begun first, then the dropwise addition of the triethylamine solution. The rates were controlled so that the pot temperature did not exceed 5° C. and so that the acid chloride addition was slightly faster than that of the triethylamine. Complete addition required three hours. Stirring was continued for three hours longer while the pot reached room temperature. The solids (triethylamine hydrochloride) were filtered, rinsed with 50 ml. benzene, and dried. The weight of triethylamine hydrochloride was 123 g. (theoretical weight = 137.5 g.).

The filtrate and benzene rinsing were washed in a separatory funnel with 200 ml. saturated aqueous sodium chloride, twice with 200 ml. portions of distilled water, and dried over anhydrous calcium chloride. The salt was removed by gravity filtration and the benzene was stripped from the filtrate by vacuum pump and a warm water (40-45° C.) bath. The residue, a white solid, was mixed with petroleum ether and filtered. The crude product weighed 111 g. (theoretical yield = 139 g.) and melted at 48-53° C. The product was dissolved in 700 ml. petroleum ether-benzene (1:1) solution, stirred with about 5 g. activated charcoal, filtered and cooled. About 25 ml. petroleum ether was added. The recrystallized material was filtered and dried in a vacuum oven at room temperature. Final yield: 36 g., m.p. 60-63° C.

Analysis calc'd. $C_{14}H_{14}O_6$: % C, 60.43; % H, 5.07

Found: 13/ % C, 60.42; % H, 5.13.

Peroxidation of Diallyl Esters with m-Chloroperbenzoic Acid to Yield Glycidyl Esters - The reaction of diallyl terephthalate with m-chloroperbenzoic acid to prepare 450-127 consisted of cooling to 0-3° C. a solution of the acid (0.4 m.) in chloroform (700 ml.) and adding the diester (0.2 m.) in small portions with gentle agitation over a period of four hours. The stoppered reaction flask was stored at 3-5° C. for three days and then brought to room temperature. The solids were removed by filtration and the filtrate was washed with a solution of Na₂CO₃ (0.2 m.) in 250 ml. water, then several times with water, and finally dried over CaSO₄. The washings were acidified and the solids collected. The weight of the combined recovered solids was equal to the theoretical weight of m-chlorobenzoic acid (62.6 g.). The dried filtrate was concentrated by water suction, then residual chloroform was removed by the vacuum pump. The product was a pale yellow liquid from which some solids separated. Several preparations are summarized in Table II.

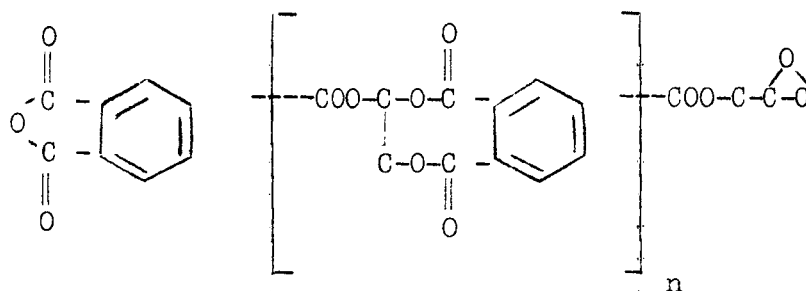
Table II. - Preparation of Epoxy Esters Using Meta-Chloroperbenzoic Acid and Allyl Esters

Allyl Ester	% Yield (a) of Corresponding Diglycidyl Ester
Diallyl isophthalate	87
Diallyl terephthalate	28
Diallyl phthalate	100

(a) The infrared spectra of the above products were identical to the epoxy esters prepared using glycidol and the acid chlorides.

B. Mono Glycidyl Esters

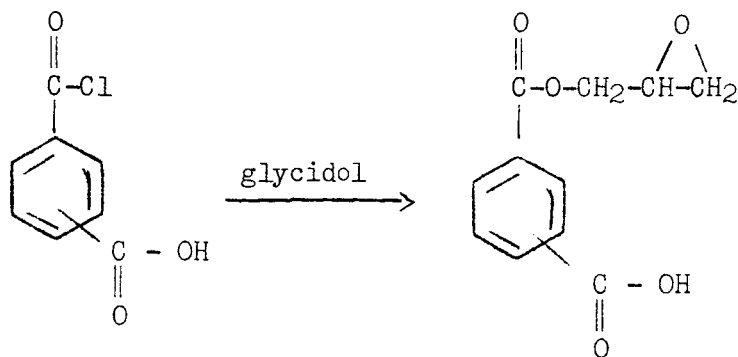
Some of these compounds were prepared by the technique used for diglycidyl esters except half the amount of glycidol was reacted. The remaining acid chloride group was reacted with water to form the carboxylic acid group. This procedure yielded resinous materials of high melting points. For example the monoepoxy ester of trimellitic anhydride was made several times and appeared to undergo polymerization before adequate testing could be performed. About half the product was isolated as an amber, viscous liquid which on standing became a brittle solid ($T_s = 73^\circ \text{C.}$) and half was obtained as a white solid which darkened at 230°C. and did not melt at 340°C. Curing of the epoxide group by the anhydride would give the polymer shown below:



Monoglycidyl esters of phthalic (461-79) and isophthalic acids (471-8, 450-141), (all prepared by the reaction of the acid dichloride first with glycidol and then water in the presence of triethylamine), which had solidified exhibited similar properties on heating. During heating, the evolution of gas (H_2O) indicated polymerization.

Sample	T_s	T_p (appeared to melt, then polymerized)
461-79	50	115
471-8	63	95
450-141	50	160

An alternate method for making the compounds described above is the reaction of glycidol and the monochloride of a dicarboxylic acid.



A

The literature^{1/} reports the preparation of the para isomer of compound A in 72% yields (decomposed ca. 200° C.) and the meta isomer in 39% yield (m.p. 130°) by refluxing the dichloride with water in ether for 45 hours. Under the same conditions, the ortho compound formed the anhydride.

^{1/}_m-Chloroformyl benzoic acid was prepared by the method of Marvel and Kraiman^{1/} in which isophthaloyl chloride (90 g.) and water (8.5 g.) in diethyl ether (1 l.) were refluxed for 40 hours. The solids were filtered out and combined with the solid residue obtained when the ether was evaporated. The product was extracted with benzene and precipitated by cooling. The analyses are shown in Table III.

Table III. - Analyses of Mono Acid Chlorides^{a/}

Sample No.	Isomer	% Yield	% Chlorine	
			Calc.	Found
471-75	Meta	66	19.2	19.65
471-76	Para	86	19.2	18.05

^{a/} Benzoic acid monoformyl chloride.

^{1/} C. S. Marvel and Eugene A. Kraiman, J. Org. Chem., 18, 1664-9 (1953).

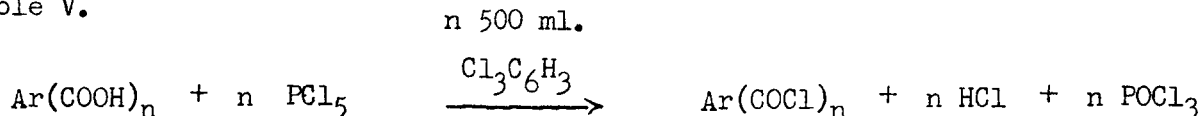
Monoglycidyl esters of terephthalic acid (461-97, 461-103), isophthalic acid (461-83, 461-109), and trimellitic anhydride (461-101) were prepared and are shown in Table IV. The shelf-life of these self-curing esters is significantly prolonged on storing at low temperatures (-10° C.)

Table IV. - Monoglycidyl Esters

Sample No.	Reactants	Product M.P.	Yield %	% C		% H	
				Calc.	Fd.	Calc.	Fd.
461-97	Terephthaloyl monochloride (461-76) Glycidol and Et ₃ N	88-95	10	59.46	61.14	4.54	5.54
461-103	Terephthaloyl Chloride Glycidol, Water and Et ₃ N	liq.	31				
461-109	Isophthaloyl Monochloride (461-75) Glycidol and Et ₃ N	gum	6				
461-143-1 ()							
471-8 ()	Isophthaloyl chloride, Glycidol, water and Et ₃ N	gum	70	59.46	61.59	4.54	6.58
461-101-1	Trimellitic Anhydride Acid Chloride, Glycidol and Et ₃ N	liq.	17	58.07	61.48	3.25	1.96
450-14-2	Monoglycidyl Trimellitic Acid polymer			54.0	53.95	3.76	4.55
461-79-2 () 450-148)	Phthaloyl chloride, Glycidol Water and Et ₃ N	gum	71-86	59.46	60.68	4.54	5.67

C. Acid Chlorides

Although acid chlorides were readily obtained by the reaction of thionyl chloride on trimesic acid and terephthalic acid, difficulty was encountered in preparing pyromellitoyl chloride and trimellitoyl chloride.^{a/} These have now been prepared by the use of phosphorus pentachloride^{b/} and are described in Table V.



One-third of the required amounts of the reactants were stirred to a slurry in 2/3 the required amount of 1,2,4-trichlorobenzene at room temperature. After the exotherm subsided, one third of the reactants were added and the resulting exotherm was again allowed to subside. The remaining portions of the reactants and solvent were added and stirring at room temperature was continued for 45 minutes. Finally, heat was applied gradually to a maximum of 130° C. or until a clear solution was obtained (1-3 hours). POCl₃ was removed by atmospheric distillation, then trichlorobenzene and the product were distilled under vacuum.

The acids used were obtained by hydrolysis of the anhydrides, which were commercial materials.

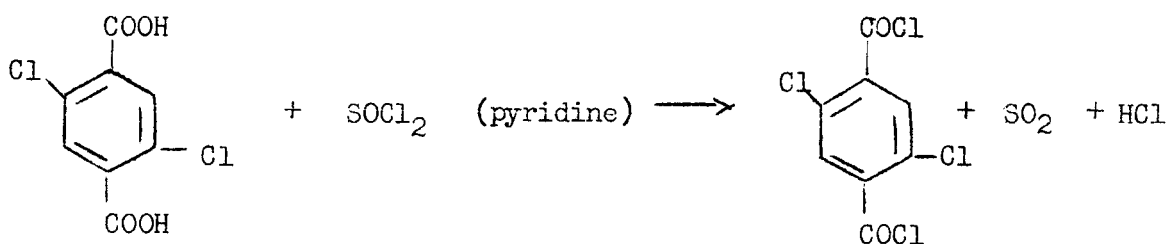
Table V. - Preparation of Pyromellitoyl and Trimellitoyl Chlorides

Sample No.	Starting Material	Yield	% Cl	
			Calc.	Fd.
450-90	Trimellitic Anhydride	93.	40.1	36.7
450-110	Pyromellitic Acid (c)	85.	43.3	42.4
461-22	Trimellitic Acid (d)	83.	40.1	37.1
461-43	Pyromellitic Acid (c)	75.	43.3	
(c)	Anal. Calc'd. for C ₁₀ H ₂ Cl ₄ O ₄	% C, 36.6;	% H, 0.61	
	Found:	% C, 37.67;	% H, 0.28	
(d)	Anal. Calc'd. for C ₉ H ₃ Cl ₃ O ₃	% C, 40.72;	% H, 1.14	
	Found:	% C, 41.23;	% H, 0.93	

^{a/} Heating 0.2M trimellitic anhydride (38 g.) with 100 ml. SOCl₂ and 3 drops DMF for 120 hours yielded 92.5% of trimellitoyl chloride of identical infrared spectra for the product prepared from PCl₅ and trimellitic acid.

^{b/} Du Pont Information Bulletin, Nov. 1955.

The Synthesis of 2,5-Dichloroterephthaloyl Chloride



To a round bottom flask equipped with a stirrer, dropping funnel and condenser with drying tube was added 231.8 g. (0.99 M) 2,5-dichloroterephthalic acid and 2 ml. of pyridine. Then 800 g. (6.72 M) thionyl chloride was added dropwise. When all the material had been added, the mixture was refluxed for 24 hours while hydrochloric acid and sulfur dioxide were being given off. On standing overnight crystals separated which were filtered and washed with n-hexane. The weight of the crystals was 78.8 g., m.p. 68° C.

Anal.	Calc'd.	% Cl,	26.2	(acid chloride chlorine)
	Found	% Cl,	25.9	

The remaining thionyl chloride was distilled off to give a solid which upon recrystallization from n-hexane yielded 37.1 g. m.p. 65-67° C. The total yield was 115.9 g. (43.1%).

Anal.	Calc'd.	% C,	35.2;	% H,	0.735
	Found.	% C,	35.1;	% H,	0.86.

D. Evaluation of Glycidyl Esters as Adhesives

As a result of the availability of pure glycidyl esters of mono- and polybasic aromatic acids from our synthesis program the compounds were evaluated as adhesives by reacting them with amines and anhydrides in order to polymerize them to high molecular weight materials. Initially it was felt that glycidyl esters would offer greater advantages than glycidyl ethers since the ester group, being more polar, would enhance adhesion. The physical testing procedure is given below in detail and is representative of the method used to test all the types of compounds described in this investigation.

General Procedure for the Physical Testing of Adhesives - The physical testing data are presented in Tables VI-XII. In most cases the adhesives were tested at 400°, 73°, -60° and -320° F. using 0.064 inch thick Alclad aluminum 2014-T6, Federal Specification QQ-A-255. Some adhesives were tested on #321 stainless steel 0.064 inch thick, Federal Specification QQ-S-766. The aluminum was etched with sulfuric acid-dichromate according to procedure B described in the data sheet for Borden's Epiphen 825A. The samples were cured at 100° C. for 2 hours, unless otherwise specified, and equilibrated before testing for 7 days at room temperature (73° F.) in a constant temperature-humidity room. The tensile shear strength was determined using a Tinius Olsen Electromatic Universal Testing Machine. The cryostat was obtained from Hofman Laboratories, Inc., Newark, New Jersey. It is a stainless steel Dewar flask having the dimensions 20-3/4" height, 7-1/4" outside diameter, 18" inside depth, and 6" inside diameter. It is constructed with a copper heat radiation shield between the inner and outer walls. The Dewar is evacuated to about 2×10^{-6} mm. Hg by connecting it to the high vacuum system of a Kinney Evaporator, Model KSE-2. All internal surfaces facing the vacuum are gold plated. The liquid nitrogen is added to the cryostat which is used in conjunction with the Tinius Olsen Electromatic Universal Testing Machine.

T-Peel Testing of Adhesives - The T-peel results appear in Table I where data were obtained on 0.032 inch thick aluminum without wire spacers and cured for 2 hours in a heated press at approximately 25 psi.

Table VI. - Adhesive Properties of Epoxy Esters Cured With
4,4'-Diaminodiphenylmethane

Sample No.	Composition	Tensile Shear Strength (a)					T-Peel lbs./in.
		psi, °F. on Aluminum					
		-453°	-320°	73°	250°	400°	
432-144-5 432-72-3	Diglycidyl terephthalate + MDA (2.1:0.5)	2270	3350	2740	2220	428	< 1
462-50-5	Diglycidyl Hexahydroterephthalate + MDA (1.4:0.5)	-	3390	-	-	282	
462-27-1 (c)	Diglycidyl isophthalate + MDA (2.8:1.0) (b)	-	4200	3780	2660	385	< 2
432-21-1	Diglycidyl phthalate + MDA (2.5:0.9)	-	5037	4057	1166	-	< 2
432-113-1	Triglycidyl trimesoate + MDA (3.0:0.6)	2920	2700	2700	2410	1700	
462-10-3	Triglycidyl trimellitate + MDA (3.6:1.0)			1370			
462-150-9	Tetraglycidyl pyromellitate + MDA (2.4:1.0)		1810	2220	2960	1098(d)	
432-150-5	Diglycidyl 2,5-Dichloroterephthalate + MDA (2.1:0.3)		2930	2700		1120	
462-48-1	" (1.7:0.5)		3540			240	
432-129-3	Diglycidyl diphenate + MDA (3.0:0.6)		1030	1540	92	-	

a. Average of 3 determinations. The samples were cured at 100° C. for 2 hr. and equilibrated 7 days prior to testing.

b. T-peel strength on aluminum was less than 2 psi at 73° F.

c. Diglycidyl isophthalate prepared from epoxidation of diallyl isophthalate used in place of the material above prepared from glycidol and isophthaloyl chloride gave tensile shear strength on aluminum of 3720 psi at -320° F. and 180 psi at 400° F.

d. Values as high as 1190 have been obtained.

Table VII. - Adhesive Properties of Epoxy Esters Cured with 1,2,3,4-
Cyclopentane Tetracarboxylic Acid Dianhydride (CPDA) ^{a/}

Sample No.	Composition	Tensile Shear Strength(b)				T-Peel lbs./in.
		psi, °F. on aluminum				
		-320°	73°	250°	400°	
462-27-4	Diglycidyl isophthalate + CPDA + BDA (Benzyl dimethylamine) (2.8/2.1/0.06 ml)	1650	1560	1730	1210	< 2
432-142-7	Diglycidyl Terephthalate + CPDA + BDA (1.7/1.0/0.03 ml)	1746	3150	3390	1535	< 2
462-50-6	Diglycidyl Hexahydroterephthalate + CPDA + BDA (0.7/1.1/0.04 ml)	2150	-	-	579	< 2
462-45-2	Tetraglycidyl pyromellitate + CPDA + BDA (1.2/1.0/0.03 ml)	888			862	< 2
462-29-5	Diglycidyl phthalate + CPDA + BDA (1.4/2.1/0.06 ml)	1280	2120	2530	1030	< 2
462-30-1	Triglycidyl trimellitate + CPDA + BDA (1.3/2.1/0.06 ml)	901	1920	1970	1040	< 2
462-31-1	Triglycidyl trimesoate + CPDA + BDA (1.3/2.1/0.06 ml)	1270	1830	1810	1100	< 2
462-48-3	Diglycidyl 2,5-dichloroterephthalate + CPDA + BDA (1.2/1.0/0.03 ml)	1350	-	-	1500	< 2

^{a/} The samples were cured at 100° C. for 2 hrs. and equilibrated 7 days prior to testing.

^{b/} An average of 3 determinations.

Table VIII. - Results of NASA Tests on Diglycidyl Isophthalate Adhesives

Sample No. 462-	Composition	Tensile Shear Strength (a) psi at ° F.			
		-320°	73°	250°	400°
27-1 (Borden)	471-21-1 (diglycidyl isophthalate) + Methylene dianiline (2.8/1.0) cured 2 hours at 100° C.	4710	3250	1600	350
NASA	" " "	-	4120 (b)	3740 (c)	-
27-4 (Borden)	471-21-1 (diglycidyl isophthalate) + Cyclopentane tetracarboxylic acid dianhydride + Benzyl dimethylamine (2.8/2.1/0.06 ml) cured 2 hrs. at 100° C.	1650	1560	1730	1210
NASA	" " "	-	2450 (b)	3200 (c)	

- (a) An average of three determinations.
- (b) Determined by NASA at room temperature.
- (c) Determined by NASA at 200° F.

Table IX. - Comparison of Anhydrides as Curing Agents for Diglycidyl Terephthalate (450-26-2a, 428-109-3)

Sample No.	Composition (a)	Tensile Shear Strength (b) psi, ° F. on Aluminum			
		-320°	73°	250°	400°
432-142-5	450-26-2a (diglycidyl terephthalate) + PMDA + BDA (1.7/1.1/0.03 ml)	2000	2620	2410	1286
432-142-7	450-26-2a (diglycidyl terephthalate) + CPDA + BDA (1.7/1.0/0.03 ml)	1746	3150	3390	1535
432-141-3	428-109-3 (diglycidyl terephthalate) + Phthalic Anhydride + BDA (2/1/0.04 ml).	2060	2194	2450	127
432-142-3	450-26-2a (diglycidyl terephthalate) + TMA + BDA (1.7/1.3/0.03 ml)	1440	2420	1823	139

(a) Definition of Abbreviations

PMDA	Pyromellitic dianhydride
CPDA	Cyclopentane tetracarboxylic dianhydride
TMA	Trimellitic anhydride
BDA	Benzyl dimethylamine

(b) Average of 3 determinations. The samples were cured at 100° C. for 2 hours and equilibrated 7 days prior to testing.

Table X. - Evaluation of Several Amines as Curing Agents for
Diglycidyl Terephthalate (450-26-2a)

Sample No.	Composition	Tensile Shear Strength (a)				
		psi at ° F.				
462-		-450°	-320°	73°	250°	400°
3-1	450-26-2a (diglycidyl terephthalate) + N,N'-(2-aminoethyl)oxydibenzylamine (2:1.0)		1840	1940	501	
3-2	Same as 1 except cured at 165° C. for 2 hrs.		1220	1610	617	
3-3	450-26-2a (diglycidyl terephthalate) + (N,N,N',N'-tetramethyloxydibenzyl- amine)(2.1:0.03)		2890	2460	1280	189
3-4	Same as 3 except cured at 165° C. for 2 hrs.		2940	2800	872	-
3-5	450-26-2a (diglycidyl terephthalate) + Versamid 115 (0.8:1.1)		1070	2160	178	-
3-6	Same as 5 except cured at 165° C. for 2 hrs.		615	2600	213	-
3-7	450-26-2a (diglycidyl terephthalate) + o-chloroaniline (0.85:1.05:0.6)		1930	2380	141	
3-8	Same as 7 except cured at 165° C. for 2 hrs.					
428-422	450-26-2a (diglycidyl terephthalate) + 3,3',4,4'-Tetraaminobiphenyl (1.0/0.5)	2480	-	-	-	-

(a) Cure: 2 hrs. at 100° C.

Table XI. - Evaluation of Room Temperature Curing Epoxy Esters

Sample No.	Composition	Pot Life Min.	Tensile Shear Strength psi, at ° F.		
			73°	250°	400°
40-3	461-95 (tetraglycidyl pyromellitate) + Tri-ethylenetetramine (1.2/0.13 ml.)	-	1100	-	-
37-9	461-89 (diglycidyl phthalate) + Triethyl-enetetramine (TETA) (1.7/0.13 ml.)	>60	1410	240	-
40-1	461-91 (triglycidyl trimellitate) + Tri-ethylenetetramine (1.8/0.13 ml.)	>60	1000	-	-
40-2	461-93 (triglycidyl trimesoate) + Tri-ethylenetetramine (1.3/0.13 ml.)	30	2230	156	-
37-2	461-89 (diglycidyl phthalate) + Diethyl-enetriamine (DETA) (1.4/0.15 ml.)	>60	1740	239	-
37-3	461-91 (triglycidyl trimellitate) + Di-ethylenetriamine (1.3/0.15 ml.)	>60	1560	403	-
37-5	461-95 (tetraglycidyl pyromellitate) + Diethylenetriamine (1.2/0.15 ml.)	10	2110	657	-
24-3	461-72-3 (Diglycidyl terephthalate) + DETA (2.0/0.17 ml.)		499	-	-
24-4	467-55 (Triglycidyl trimesoate) + DETA (2.4/0.17 ml.)		1920	-	-
24-5	467-57 (Diglycidyl phthalate) + DETA (2.2/0.17 ml.)		407	-	-
24-8	461-72-3 (Diglycidyl terephthalate) + TETA (2.0/0.28 ml.)		223	-	-
25-1	467-55 (Triglycidyl trimesoate) + TETA (2.4/0.14 ml.)		1700	157	-
25-2	467-57 (Triglycidyl trimesoate) + TETA (2.2/0.10 ml.)		587	-	-

Table XII. - Adhesive Properties of Monoepoxy Esters Using Various Curing Agents

Sample No.	Composition	Tensile Shear Strength, psi °F. on Aluminum ^{a/}		
		-320°	73°	250°
462-13-1	Monoglycidyl phthalate (60% soln. in MEK) - open time 10 min.		2430	198
462-15-1	Monoglycidyl phthalate (no solvent)		2210	247
432-147-5	Monoglycidyl terephthalate + BDA (benzyl dimethylamine) (1.0/0.02 ml.)	1130	2530	83
432-147-6	Same as 432-147-5 except cured 2 hours at 165° C.	2420	2940	302
462-10-1	Monoglycidyl isophthalate + BDA (2.0/0.03 ml.)		2540	166
462-10-2	Same as 462-10-1 except cured 2 hrs. at 165°		2270	501

^{a/} The samples were cured at 100° C. for 2 hrs. and equilibrated 7 days prior to testing. An average of 3 determinations is shown.

Discussion

It has been shown in a related work on diglycidyl ethers of bisphenol A that the tensile shear strength varies with epoxy content. Consequently high purity glycidyl esters are required in order to get the maximum adhesive potential of each material.

Glycidyl esters have been prepared for this investigation (Table I) by reacting the acid chloride and triethylamine using separate additions at 0-5° C. with glycidol (2,3-epoxypropanol). The monoglycidyl esters (Table IV) are quite reactive and require low temperatures for prolonged storage. Monoglycidyl isophthalic acid is stable for more than one month at -10° C.

The physical testing results of Table VI indicates that as the epoxy or glycidyl groups/molecule increase so does the tensile shear strength of the adhesives at 400° F. The opposite trend appears to be indicated for the tensile shear strengths at -320° F. The latter may be true since the diglycidyl esters are probably more flexible when cured with MDA at -320° F. as a result of the lower degree of cross-linking. Satisfactory agreement of our testing results with those of NASA is shown in Table VIII.

Use of CPDA as the curing agent, Table VII, yielded stronger adhesives at 400° F. This is probably due to the greater rigidity and cross-linking of this dianhydride. The surprising fact is that CPDA is slightly better than PMDA as a curing agent to give high temperature adhesives (Table IX). CPDA is aliphatic whereas PMDA is aromatic and one would ordinarily expect that an aromatic system would be more stable at higher temperatures. A comparison of several anhydrides as curing agents is shown in Table IX. Benzyl dimethylamine has been found to accelerate the reaction of anhydrides with glycidyl groups and thus is used as a catalyst 0.03-0.6 ml. (see p. 42).

Substituting other amines for MDA and curing at room temperatures resulted in poor adhesives as is shown in Tables X-XI. This probably is a result of the lower degree of aromaticity and lower cross-linking.

A comparison of glycidyl ester adhesives with other commercial epoxy adhesives is shown in Fig. 1.

Monoepoxy esters (Table XI) offer the advantage of a one component adhesive system requiring no curing agent except a catalyst. The tensile shear strengths at 73° F. on aluminum vary from 2210 to 2940 psi with the strength being at the high end when cured 2 hrs. at 165. These adhesives show only fair strength at +250° F. and -320° F.

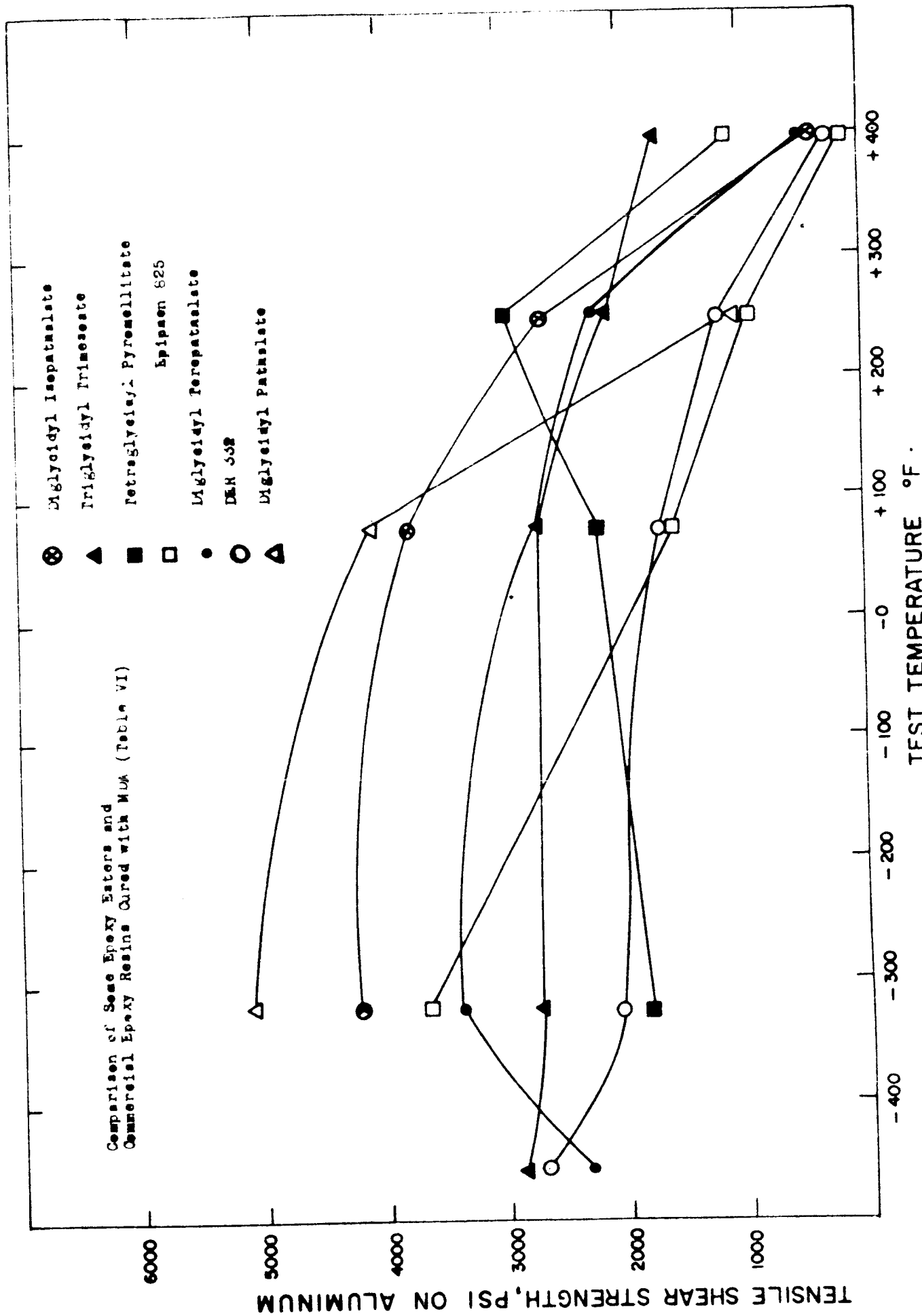


Figure 1.

II. BISPHENOL EPOXY ADHESIVES

The Effect of Polarity of Bisphenol A Epoxy Resins on Adhesion
at Cryogenic and Elevated Temperatures.

Introduction

During the course of investigating epoxy resins for their effectiveness as cryogenic adhesives which also show good elevated temperature properties, it was of interest to explore the use of substituted bisphenol epoxy resins for this purpose.

In the literature there appeared no systematic study using bisphenol epoxy resins as cryogenic adhesives. However, Erich and Bodnar^{1/} had reported a preliminary investigation of the effect of molecular structure on the mechanical properties of epoxy resins which left many questions unanswered. It was not clear from their work what the epoxy content of each material was. In addition the adhesives were tested only at 73.5° F. and 160° F.; nevertheless, Erich and Bodnar showed that a decrease in shear strength is obtained at 160° F. when the methyl groups in Bisphenol A are replaced by increasingly longer aliphatic chains. These correlations would have been more meaningful had they all been related in some way to their epoxy content.

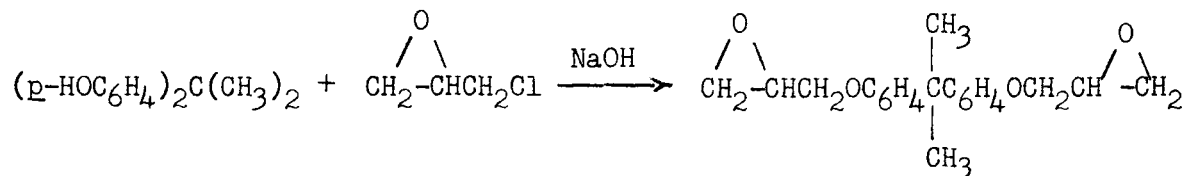
The object of this investigation was to compare the effect of polarity of substituted bisphenol epoxy resins with the epoxy content of these resins as factors affecting adhesion to aluminum over the temperature range from -320° F. to +400° F. The curing agent used was 4,4'-diaminodiphenylmethane.

^{1/} W. Erich and M. J. Bodnar, J. Applied Polymer Science 3 (9) 296 (1960).

Experimental

A. Synthesis

Epoxy resins were prepared by a procedure^{2/} known to produce compounds of low molecular weight and high epoxy content.



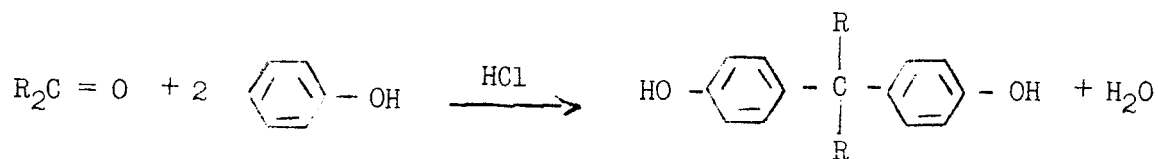
The Bisphenol compound (1.0 M), epichlorohydrin (10.0 M), and 5 ml. of water were mixed in a resin kettle fitted with a stirrer, condenser and thermometer. Solid NaOH (2.05 M) was added in 6 or 7 small portions. After the first addition, the flask was heated and cooled alternately as required, while the NaOH additions were made, maintaining the pot temperature between 95° and 100° C. After the final addition, no further cooling was applied. When the exotherm had subsided, the epichlorohydrin was distilled off under vacuum (50 mm.) until the temperature in the flask reached 150° C. To the residue, cooled to 70° C., was added 50 ml. of benzene. The precipitated salt was filtered out and washed with 50 ml. of benzene. The benzene solutions were distilled until the temperature in the flask reached 125° C. and then the distillation was continued at 5 mm. until the temperature reached 170° C. The results are summarized in Table I.

^{2/} W. R. Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry, Interscience Publishers, Inc., 1961, p. 309.

Table I. - Preparation of Epoxy Resins

Sample No.	Starting Material	Product	% Yield	Epoxy Content	
				Calcd.	Found
428-48	1,1,3-Tri(4-hydroxyphenyl)propane	Amber v.l.	86	0.613	0.439
428-86	1,1-bis-(4-hydroxyphenyl)cyclohexane	Tan soft solid	85	0.510	0.355
409-142	1,1-Di(4-hydroxyphenyl)-4-methyl-cyclohexane	Yellow v.l.	76	0.508	0.452
391-98	Tetrachlorobisphenol A	Amber liq.	93	0.418	0.361
391-139	Tetrabromobisphenol A	Brown syrup	71	0.305	0.302
391-141	2,2-Methylene-bis-(4-ethyl-6-t-butyl phenol)	Brown soft solid	39	0.417	0.162
409-11	2,2-Bis(4-hydroxy-3-methylphenyl)butane	Amber v.l.	91	0.524	0.427
409-59 (409-13)	2,2-Bis(4-hydroxy-3,5-dimethylphenyl)propane	Amber v.l.	100	0.505	0.422
409-53	2,2-Bis(4-hydroxy-3-methylphenyl)propane	Amber v.l.	100	0.543	0.485
409-70	Bisphenol A	Amber v.l.	89	0.588	0.518
409-110	Bis(4-hydroxyphenyl)sulfone	Brown solid	41	0.552	0.341
409-115	Bis(4-hydroxyphenyl)ether	Tan solid	100	0.641	0.532
409-117	2,2-Bis(4-hydroxy-3,5-dibromophenyl)-hexafluoropropane	solid, m.p. 28-9°	65	0.261	0.235
409-118	2,2-Bis(4-hydroxyphenyl)-sym-tetrafluorodichloropropane	Amber syrup	83	0.417	0.336
428-5	$(\text{HO} \text{C}_6\text{H}_4)_2 \overset{\text{CH}_3}{\text{C}} (\text{CH}_2)_8 \text{CH}_3$	Amber v.l.	64	0.372	0.361
428-7	$(\text{HO} \text{C}_6\text{H}_4)_2 \overset{\text{CH}_3}{\text{C}} (\text{CH}_2)_{14} \text{CH}_3$	Amber v.l.	74	0.441	0.200
428-29	$(\text{HO} \text{C}_6\text{H}_4)_2 \overset{\text{CH}_3}{\text{C}} (\text{CH}_2)_6 \text{CH}_3$	Amber v.l.	87	0.472	0.336

Bisphenols were prepared by the reaction of the ketone with phenol according to the procedure described by Erich and Bodnar¹ from aliphatic ketones.

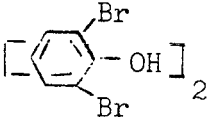
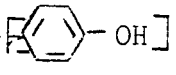


A typical preparation is the synthesis of 1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane starting with 1 mole of 4-methylcyclohexanone and 4 moles phenol in the presence of 40 g. calcium chloride, 4 g. hydrochloric acid and 3 ml. beta mercaptopropionic acid. The reactants were stirred at 110° for 4-1/2 hours and then allowed to stand overnight. The reaction mixture changed color going from yellow to red. The excess phenol was carefully distilled and the residue dissolved in hot toluene. The hot toluene was filtered, decolorized, concentrated and cooled to give 74 g. (25%) of a solid, m.p. 156-164. A sample on recrystallization melted at 166-170° C.

<u>Anal.</u>	Calc'd. for	C ₁₉ H ₂₃ O ₂	% C,	80.8;	% H,	7.85
	Found		% C,	81.09;	% H,	7.88

The analysis of some new bisphenol A compounds are listed in Table II.

Table II. - Analysis of Bisphenol Derivatives (a)

Sample No.	Bisphenol	% C		% H	
		Calcd.	Found	Calcd.	Found
409-117	(F ₃ C) ₂ C-  -OH]₂	27.64	28.13	0.93	0.99
409-118	(F ₂ ClC) ₂ C-  -OH]₂	48.83	49.03	2.74	2.83

(a) These compounds were provided to us by the courtesy of Mr. Strickling of the General Chemical Research Laboratory, Allied Chemical Corporation, Morris Township, New Jersey. 07960.

B. Physical Testing

The physical testing data are presented in Table III. In most cases the adhesives were tested at 73°, 250°, 400° and -320° F. using 0.064 inch thick Alclad aluminum 2014-T6, Federal Specification QQ-A-255. Some adhesives were tested on #321 stainless steel, 0.064 inch thick, Federal Specification QQ-S-766. The stainless steel and aluminum were etched according to the procedure described below.

Preparation of Metal Surfaces for Bonding (1" x 3" x 0.064" Panels)

I. Scrubbing

All visible dirt and markings were removed by rubbing the metal with a cloth dipped in acetone. The panels were handled with clean rubber gloves or forceps.

II. Degreasing

The scrubbed panels were suspended by small clips from a rod which was mounted about two inches above the surface of gently boiling trichloroethylene. The panels were kept in the vapor bath for ten minutes (minimum) and stored in a wide-mouth container of distilled trichloroethylene.

III. Etching

The degreased panels were removed individually with forceps from trichloroethylene and laid on paper towels to air-dry. When the surfaces appeared dry, the panel was turned over and placed on a fresh towel.

A. Aluminum

1. Etching Solution

10 gms.	Potassium or Sodium Dichromate
300 mls.	Distilled Water
100 gms. (54.5 ml.)	Concentrated Sulfuric Acid

The dichromate was added to the water and stirred until most of the salt was dissolved. The acid was added very slowly with stirring. Stirring was continued until all the solid was dissolved. The solution was poured into a pyrex dish approximately six inches in diameter and three inches high and warmed on a hot plate to 70° C.

2. Procedure

The dry panels were placed in the bath by leaning them at a small angle against the wall of the dish so that at least three quarters of an inch of the metal was immersed in the bath. The temperature, which usually dropped a few degrees when the metal was placed in the bath, was maintained at 66-68° C. The dish described accommodated 14 to 20 panels. After ten minutes, the panels were removed with forceps and dropped into a beaker of water. The panels were rinsed at least 5 times with tap water, then rinsed individually with distilled water and laid on clean paper towels to air dry. After most of the water had been absorbed, the panels were turned over onto clean towels and used as soon as they appeared dry. They were used within three hours. The etching bath was used for no more than sixty panels.

B. Stainless

1. Etching Solution

262.0 ml.	Concentrated Hydrochloric Acid
27.5 ml.	Ortho Phosphoric Acid
13.2 ml.	Hydrofluoric acid

The phosphoric acid was added to the hydrochloric acid with stirring, then the hydrofluoric acid was stirred in and the solution was transferred to a pyrex dish, approximately six inches in diameter, and three inches high. The dish was heated on a hot plate to 82° C. Boiling occurred and subsided before this temperature was reached.

2. Procedure

The dried panels were placed in the bath so that at least three quarters of an inch was immersed in the solution. (See procedure for aluminum.) At the end of two minutes, the panels were removed and rinsed as described in the procedure for aluminum. If a carbon residue was visible on the etched portion of the stainless steel panels after rinsing, they were immersed for 10-15 seconds in a 10% nitric acid bath and rinsed thoroughly with distilled water.

The adhesive was prepared by adding the melted curing agent to the resin, (solid resins were first liquified), and stirring the mixture thoroughly. Generally, 5.0 g. resin was treated with the theoretical equivalent of curing agent, calculating one epoxide group equivalent to one active (amine) hydrogen. The adhesive was applied with a spatula to both etched surfaces to be bonded. One panel was placed on a jig designed to allow 0.50 inch overlap of 1" x 3" panels. The second panel was put in place and the 0.50 inch bonded area was clamped at each edge with a small spring clip.

The samples were cured at 100° C. for 2 hours, unless otherwise specified, and equilibrated before testing for 7 days at room temperature (73° F.) in a constant temperature-humidity room. The tensile shear strength was determined using a Tinius Olsen Electomatic Universal Testing Machine. The cryostat was obtained from Hofman Laboratories, Inc., Newark, New Jersey. It is a stainless steel Dewar flask having the dimensions 20-3/4" height, 7-1/4" outside diameter, 18" inside depth, and 6" inside diameter. It is constructed with a copper heat radiation shield between the inner and outer walls. The Dewar is evacuated to about 2×10^{-6} mm. Hg by connecting it to the high vacuum system of a Kinney Evaporator, Model KSE-2. All internal surfaces facing the vacuum are gold plated. The liquid nitrogen was added to the cryostat which was used in conjunction with the Tinius Olsen Electomatic Universal Testing Machine.

Results and Discussion

The bisphenols listed in Table I were converted to diglycidyl ethers by means of epichlorohydrin and sodium hydroxide as described in the Experimental Section. The resulting products are shown in Table I along with their epoxy contents, calculated and analytically found. In some cases the experimentally obtained epoxy contents are close to those calculated. The discrepancy in values is probably due to the nature of the synthesis such that some polycondensation takes place via the glycidyl group to give higher molecular weight resins.

The physical testing results are listed in Table III where tensile shear strengths on aluminum are reported from -320° to $+250^{\circ}$ F. in most cases with some results also listed at -453° F.

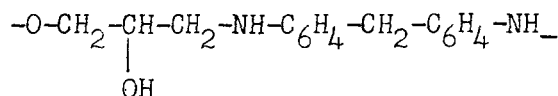
Examination of these results indicates that the tensile shear strength at -320° F. increases with epoxy content of the starting resins regardless of the nature of the polar groups as in the halogenated resins numbered 5, 9, 10 and tetramethyl bisphenol A resin number 8. The results are plotted in Fig. 1A and D as tensile shear strength, psi at -320° F. versus epoxy content for aluminum and stainless steel test specimens. The results at 73° and 250° F. for aluminum are shown in Fig. 1B and C. For stainless steel the results at -320° , 73° and 250° F. are shown in Fig. 1D, 1E and 1F. From Fig. 1A it is seen that polarity of the molecule is not as important as epoxy content. It was expected that compound 9 would deviate greatly.

In Fig. 2 the plot of theoretical epoxy content against the theoretical tensile shear strengths obtained by extrapolation indicates that even compound 9 does not deviate. The correlations for all the epoxy compounds does not give straight lines for stainless steel, the values are more scattered.

The presence of alkyl groups appears also not to have a significant effect on increasing the tensile shear strength values other than giving values expected from their epoxy contents. Removing the alkyl bridge from the bisphenols as in compound number 7 (4,4'-dihydroxydiphenyl ether) gives no marked change.

The preparation of bisphenol epoxy resins with long chain aliphatic groups (428-7 in Table III) gave a drastic reduction in the adhesive strength at 73° F. It was hoped that the long hydrocarbon chain would flexibilize the adhesive and increase its adhesive strength at -320° F. It is possible that a more polar chain (polyether type) would be more effective in giving adhesion to aluminum. The adhesive strength of DER 332 was decreased by the use of 20% 428-5 in it. However, replacing the propane bridge in the bisphenols by a cyclohexyl group (compound number 12) appeared to increase the tensile shear strength at all temperatures.

It does not appear that the tensile shear strength of the diglycidyl ethers of the substituted bisphenols shows a Hammett substituent effect since no correlation of polarity appears to exist other than that of the epoxy content as described above. Since these epoxy compounds are cured with 4,4'-diaminodiphenylmethane they all have the common polymer backbone group



and other related forms of it crosslinked via the OH and NH groups. This structure may be more important in its effect on adhesion to aluminum and stainless steel than the effect of substituents on the aromatic ring of the bisphenol.

Table III. - Epoxy Resins Cured with an Equivalent of 4,4'-Diaminodiphenylmethane (MDA)

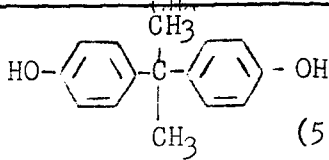
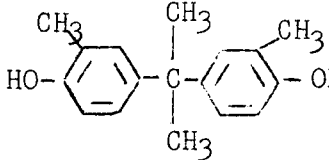
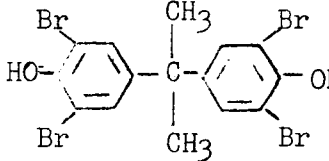
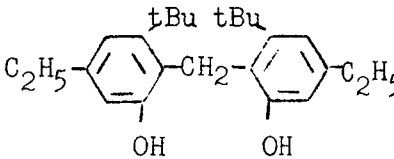
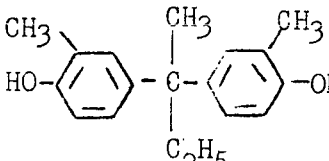
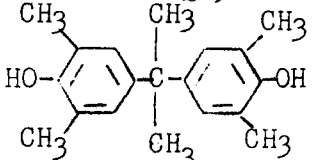
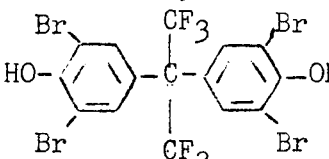
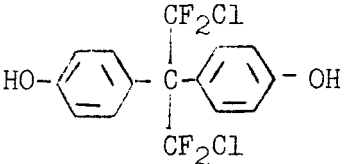
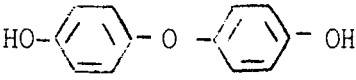
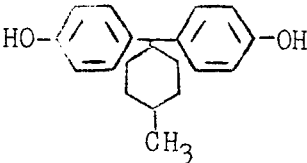
Com- pound No.	Sample No. of Epoxy Resin	Structure of Starting Bisphenol	Epoxy Content Found	Tensile Shear Strength ^a / psi, ° F.						
				On Aluminum			Stainless Steel			
				-453°	-320°	73°	250°	-320°	73°	250°
(1)	Epon 826	 (5:1.4)	0.542	2795	3630	2170	1754	4300	2850	2052
(2)	Epon 828 or DER 332 (b)	Same as above	0.518	4200	2610	1804	4070	2690	1931	
(3)	Epon 830	Same as above	0.500	4270	2310	1685	3160	2420	1258	
(4)	409-53		0.485	3570	1478	351	3000	1757	1549	
(5)	391-139		0.302	680	1391	557	864	1005	~0	
(6)	391-141		0.162	0	0	0	0	0	0	
(7)	409-11		0.427	3510	2890	850	2200	1800	1660	
(8)	409-13		0.422	2680	2240	943	462	645	227	
(9)	409-117	 (10:1.2)	0.235	1143	1330	1799	1325	1577	1605	

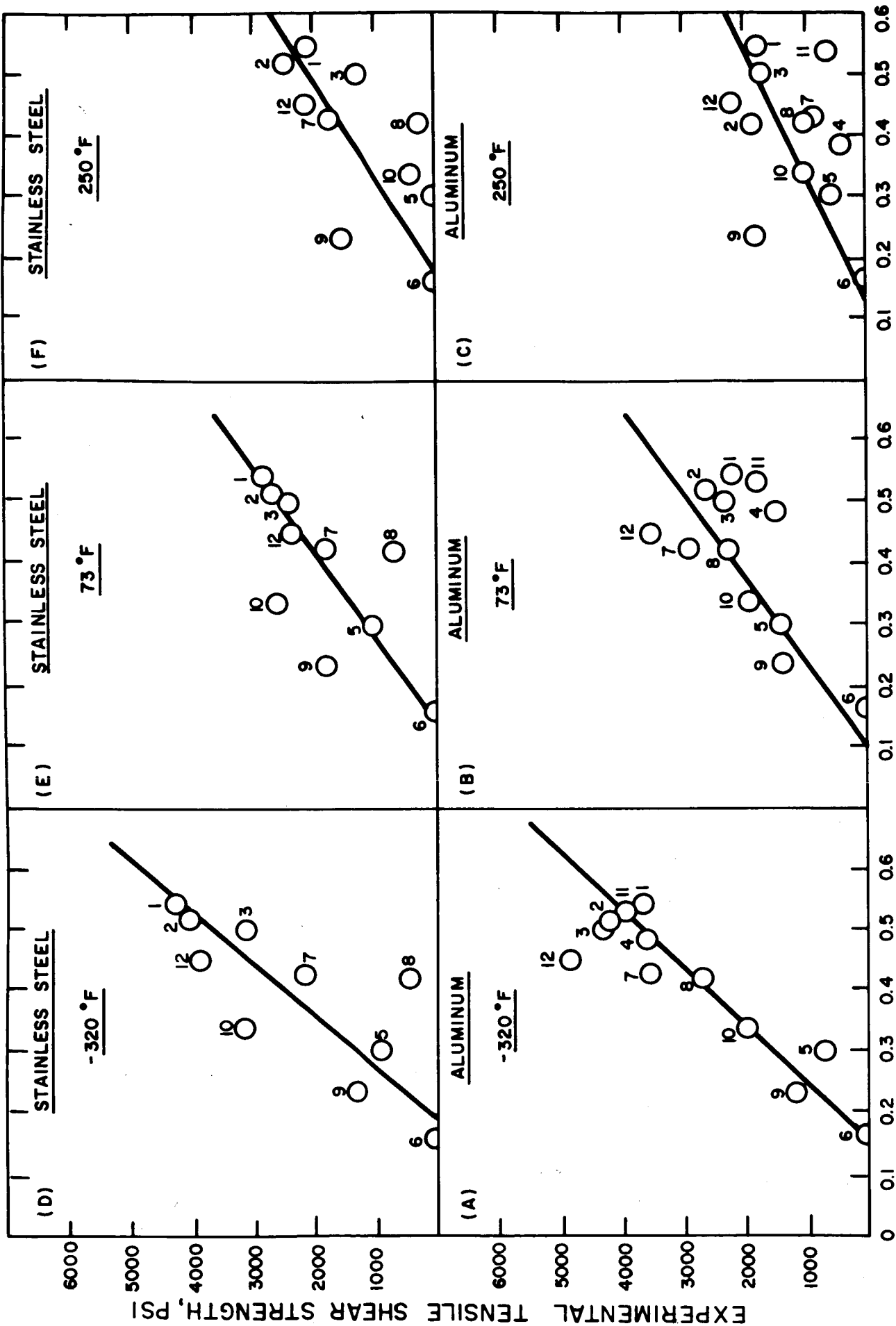
TABLE CONTINUED ON FOLLOWING SHEET

Table III. - Epoxy Resins Cured with an Equivalent of 4,4'-Diaminodiphenylmethane (MDA) - CONTINUED

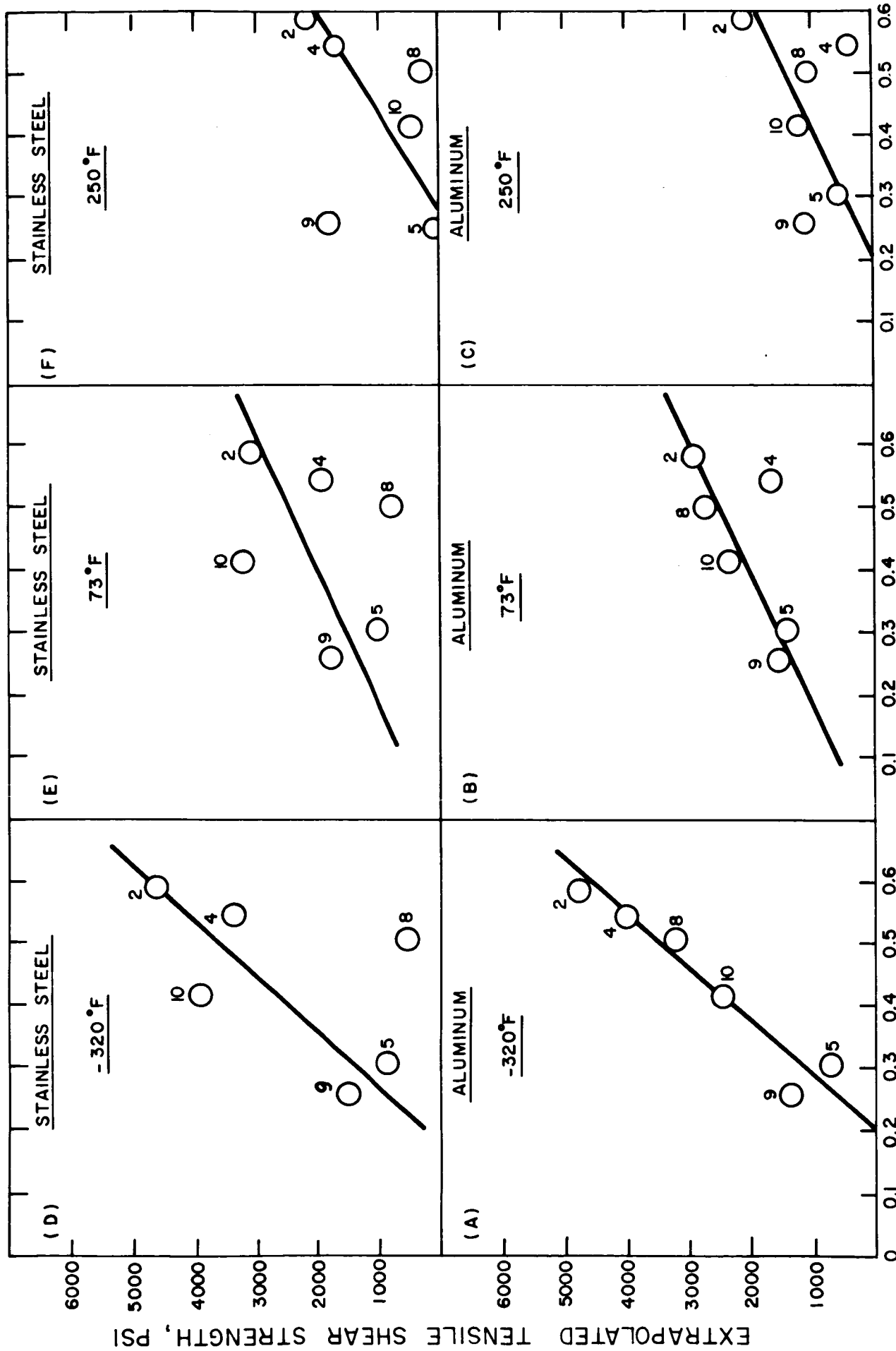
Com- pound No.	Sample No. of Epoxy Resin	Structure of Starting Bisphenol	Epoxy Content Found	Tensile Shear Strength ^a / psi, °F.					
				On Aluminum			Stainless Steel		
				-320°	73°	250°	-320°	73°	250°
(10)	409-118		0.336	1950	1867	959	3120	2580	352
(11)	409-115		0.532	3910	1736	564	-	-	-
(12)	409-142		0.452	4800	3490	2079	3870	2350	2095

(a) The epoxy resins were cured with the calculated equivalent of 4,4'-diaminodiphenylmethane (methylenedianiline) at 100° C. for 2 hours and the results shown are the average of three determinations.

(b) Tensile shear strength on aluminum at 400° F. is 556 psi and on stainless steel 547 psi.



EPOXY CONTENT
Figure 1.



THEORETICAL EPOXY CONTENT
Figure 2.

Figure Captions

Figure 1: Tensile Shear Strength versus Epoxy Content for Substituted Bisphenol A Epoxy Resins Evaluated on Aluminum and Stainless Steel. (See Table III for the definition of the numbered compounds).

Figure 2: Extrapolated Theoretical Tensile Shear Strengths versus the Theoretical Epoxy Contents for Substituted Bisphenol Epoxy Resins Evaluated on Aluminum and Stainless Steel at -320° , 73° and 250° F. (See Table III for the definition of the numbered compounds).

C. Evaluation of Miscellaneous Epoxy Resins with Several Curing Agents

In this phase of the investigation several epoxy resins were screened for their adhesive strength from -320° F. to 400° F. with several curing agents as shown in Table IV. Most of the epoxy resins had T-peel strengths less than 1-2 lbs./in. on aluminum even though they had satisfactory strength at the Contract-specified temperatures.

In order to flexibilize the epoxy resins to give them good T-peel as shown in Table V it was necessary to use polyether anhydrides as co-curing agents. However, as shown in Tables V and VIII the tensile shear strength at 250° and 400° F. was drastically lowered. The T-peel of Dow DER-332 was increased from 1 to 6 as seen from 462-27. However, the strength at 400° dropped to 183 psi.

The results in Table VII show that free acid lowers the strength of a CPDA cured epoxy resin (EPIPHEM 825).

Several miscellaneous systems are shown in Table IV along with experiments indicating that an excess of tertiary amine catalyst (BDA) for the anhydride cure lowered the tensile shear strength.

Table IV. - Evaluation of Epoxy Resins with Several Curing Agents

No.	Resin (R)	Curing Agent (C)	Ratio E/C	Cure		Tensile Shear (psi) ° F. on Aluminum				
				Hrs.	°C.	-453°	-320°	73°	250°	400°
432- 18-4	(a) DER 332	MDA	5.0/1.4	2	100		3540	2430	1177	556
18-5	"	"	" "	2	100		3750	2610	1217	
131-8	"	"	" "	2	165		4330	3390	2790	
145-3	"	CPDA, BDA	3.4/2.1/0.06	2	100	1950		1512		869
145-4	"	" "	" " "	2	165			1717		776
131-6	"	" "	3.4/2.1/0.05	2	165		1765	1910	1880	1374
62-4	"	PMDA	1.7/1.1	1	180		1740	1640	1350	880
145-1	"	" , BDA	3.4/2.0/0.06	2	100			1857		
145-2	"	" "	" " "	2	165			1407		
138-5	"	" "	3.4/2.2/0.06	4	165		1699	1830	2242	546
138-6	"	" "	" " "	8	"		1689	1940	2441	656
62-5	"	BTA	1.7/1.6	1	180		1310	1460	1340	867
141-2	"	" , BDA	3.4/3.2/0.05	2	100			1324	777	
131-4	"	" "	" " "	2	165		910	1190	782	
135-3	"	PA, BDA	1.7/1.5/0.10	2	100		1600	1945	1885	46
135-4	"	" "	" " "	2	165		1340	1790	1055	
145-5	"	TMA, BDA	1.7/1.9/0.08	2	100			1523		143
145-6	"	" "	" " "	2	165			1103		
138-7	"	Het, BDA	1.7/2.6/0.03	4	165		2295	1585	1418	
462- 24-2	"	DETA	5.0/0.42	168	73			692		
432- 131-5	"	NMA, BDA	5.0/4.4/0.08	2	165		1975	2310	1220	280
131-1	DEN 438	NMA, BDA	5.4/4.0/0.08	2	165		1945	1480	1135	368
462- 20-2	EPIPHEN 825	CPDA, BDA	3.6/2.1/0.06	2	100		1560	1596 (b)	2610	950 (b)

CONTINUED

Table IV. - Evaluation of Epoxy Resins with Several Curing Agents (CONTINUED)

No.	Resin (R)	Curing Agent (C)	Ratio R/C	Cure		Tensile Shear (psi) ° F. on Aluminum			
				Hrs.	°C.	-320°	73°	250°	400°
431- 148-10	EPIPHEN 825	CPDA, BDA	3.6/2.1/0.06	2	165		1463		683
432- 145-8	"	PMDA, BDA	3.6/2.0/0.06	2	100	1260	1911 (c)	745	888 (c)
145-8	"	" "	" " "	2	165		1526		
138-1	"	" "	3.6/2.0/0.06	4	165	1670	2010	2520	458
138-2	"	" "	" " "	8	165	1690	2000	2330	486
138-3	"	Het, BDA	1.8/2.6/0.03	4	165	1724	1490	2057	356
138-4	"	" "	" " "	8	165	1359	1540	1800	
462- 24-1	EPIPHEN 825-A	DETA	5.0/0.64	168	73	1870	2030	982	501
24-3	"	PMDA, BDA	3.6/2.2/0.06	2	100	1640		851	
31-7	"	CPDA, BDA	1.8/2.1/0.06	2	100	1590	2580	2540	1190

(a) This composition had T.S. on stainless steel of 2610 psi at -453° F.

Table V. - Evaluation of Flexible Epoxy Resins

Sample No. 462-	Composition	T-Peel on Aluminum at 73°F.	Tensile Shear Strength ^{a/} psi, at °F., on Aluminum		
			-320°	73°	400°
38	495-17 (Polyetherester anhydride ^{c/} of Dow P-1000 - Polyoxypropylene glycol, M.W. 1000) + Cyclopentane tetracarboxylic acid dianhydride + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (2/1/2.7/0.04 ml.)	1.5	2030	1300	178
35	495-16 (Polyether ester anhydride of Dow P-710 - Polyoxypropylene glycol, M.W. 756) + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (11/3.4/0.06 ml.)	2.8	4450 ^{b/}	-	150
36	495-16-2 (Fraction 495-16 above heated before using as a resin) + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (11/3.4/0.06 ml.)	3.3	2910	-	213
37	495-17 (Polyetherester anhydride ^{c/} of Dow P-1000 - Polyoxypropylene glycol, M.W. 1000) + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (11/3.4/0.06 ml.)	1.5	600	-	25
52	495-19 (Polyetherester anhydride of Pluracol TP-740 - Polyoxypropylene triol, M.W. 711, Wyandotte) + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (4.1/1.7/0.03 ml.)	1	2990	3720	-
27	495-12 (Polyetherester anhydride of Pluracol P-410 - Polyoxypropylene glycol M.W. 426, Wyandotte) + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (3.9/1.7/0.03 ml.)	6	3430	3130	183
28	495-12 (Polyetherester anhydride of Pluracol P-410 - Polyoxypropylene glycol, M.W. 426, Wyandotte) + 461-139-1 (Diglycidyl isophthalate) + Benzyl dimethylamine (3.9/1.4/0.03 ml.)	1.8	4520	2900	183
29	495-11 (Polyetherester anhydride of di-propylene glycol) + DER 332 (Dow Epoxy Resin) + Benzyl dimethylamine (2.4/1.7/0.03 ml.)	<1	2270	2150	363
30	495-11 (Polyetherester anhydride of di-propylene glycol) + 461-139-1 (Diglycidyl isophthalate) + Benzyl dimethylamine (2.4/1.4/0.03 ml.)	0.25	1290	1520	152

^{a/} Average of 3 determinations.

^{b/} One sample gave 6220 psi.

^{c/} Trimellitic anhydride polyesters.

Table VI. - Evaluation of A Polyether Epoxy Anhydride (461-59)^{a/}
For Curing Epoxy Resins

Sample No.	Composition				Cure	Tensile Shear Strength psi at ° F.			
	DER 332	461-59 (a)	MDA	BDA (mL.)		-320°	73°	250°	400°
22-1	1.0	3.4	-	0.04	100	-	1160	-	-
22-2	1.0	3.4	-	0.04	165	-	668	-	-
22-3	5.1	0.4	1.4	-	100	2290	2130	1041	355
22-4	5.1	0.4	1.4	-	165	3110	2480	1220	422
22-5	5.5	1.7	1.4	-	100	-	2980	588	-
22-6	5.5	1.7	1.4	-	165	-	3050	598	-
22-7	6.0	3.3	1.4	-	100	-	2470	234	-
22-8	6.0	3.3	1.4	-	165	-	3500	207	-
23-1	5.1	0.4	1.6	-	100	-	2920	896	-
23-2	5.1	0.4	1.6	-	165	2920	2490	1550	265
23-3	5.5	1.7	1.8	-	100	2670	3060	1520	300
23-4	5.5	1.7	1.8	-	165	2350	2850	1020	387
23-5	6.0	3.3	2.3	-	100	-	2090	494	-
23-6	6.0	3.3	2.3	-	165	-	2850	863	-

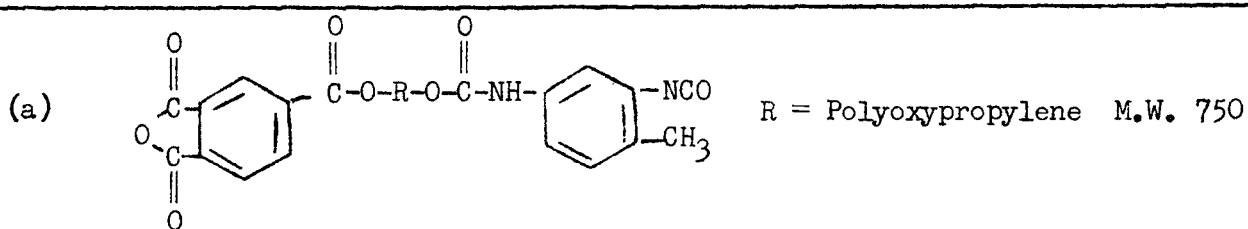


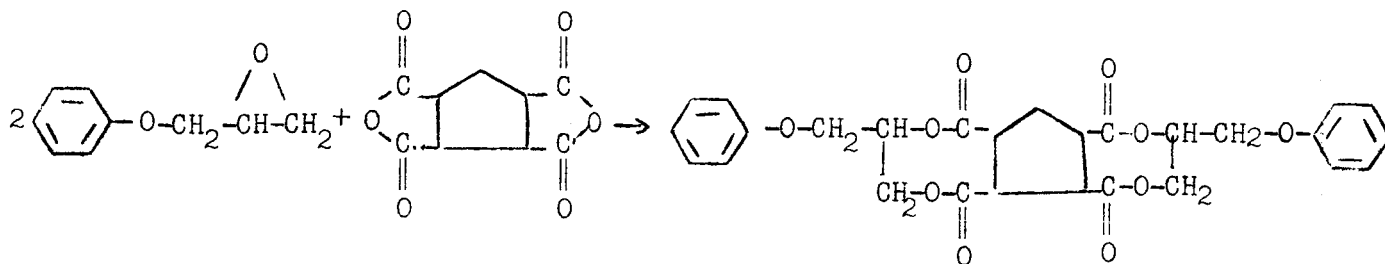
Table VII. - The Effect of Added Cyclopentane Tetracarboxylic Acid
on Adhesive Strength of the Anhydride Cure

Sample No.	Epiphen 825 (Borden Epoxy Resin)	Cyclopentane Tetracarboxylic acid Dianhydride	Cyclopentane Tetracarboxylic acid	Benzyl Dimethyl-amine	Tensile Shear Strength psi, on Aluminum, at °F.	
					-320°	+400°
46-1	1.8	1.05	0	0.06	1500	918
46-2	1.8	0.945	0.123	0.06	1230	889
46-3	1.8	0.840	0.246	0.06	1080	799
46-4	1.8	0.735	0.369	0.06	1060	708
46-5	1.8	0.630	0.492	0.06	1050	603
46-6	1.8	0.525	0.615	0.06	1100	448

Table VIII. - Evaluation of Modified Epoxy Adhesives

Sample No. 462-	Composition	T-Peel on Aluminum at 73°	Tensile Shear Strength psi, at °F., on Aluminum		
			-320°	73°	400°
31	488-96 (Epoxidized Diphenyl ether modified Novolac resin) + 4,4'-Methylene dianiline (2.6/0.5)	1	1780	2290	170
32	488-96 (Epoxidized Diphenyl ether modified Novolac resin) + 4,4'-Diaminodiphenylsulfone (2.6/0.5)	0	-	264	-
33	488-96 (Epoxidized Diphenyl ether modified Novolac resin) + Cyclopentane tetracarboxylic acid dianhydride + Benzyl dimethylamine (2.5/1.1/0.03 ml.)	-	1040	1950	217
60-1	4.5 g. (7.2 g. Epiphen 825A - Borden Epoxy Resin + 4.2 g. Cyclopentane tetracarboxylic acid dianhydride + 0.12 g. Benzyl dimethylamine) + 0.5 g. (10.0 g. Adiprene L-167 - Du Pont Polyurethane Elastomer + 2 g. 4,4'-Methylene bis(ortho-chloroaniline))	<2	1550		721
60-2	4.0 g. (7.2 g. Epiphen 825A - Borden Epoxy Resin + 4.2 g. Cyclopentane tetracarboxylic acid dianhydride + 0.12 g. Benzyl dimethylamine) + 1.0 g. (10 g. Adiprene L-167 - Du Pont Polyurethane elastomer + 2 g. 4,4'-Methylene bis(ortho-chloroaniline))	2.5-3	1850		566
60-3	3.5 g. (7.2 g. Epiphen 825A - Borden Epoxy Resin + 4.2 g. Cyclopentane tetracarboxylic acid dianhydride + 0.12 g. 4,4'-Methylene bis(ortho-chloroaniline) + 1.5 g. (10 g. Adiprene L-167 - Du Pont Polyurethane Elastomer + 2 g. 4,4'-Methylene bis(ortho-chloroaniline))	4-5	2620		242
57-1	3.4 g. DER 332 (Dow Epoxy Resin) + 2.1 g. Cyclopentane tetracarboxylic acid dianhydride		306		561
57-3	57-1 + 0.05 ml. Benzyl dimethylamine		1320		1050
57-5	57-1 + 0.10 ml. Benzyl dimethylamine		969		770
57-7	57-1 + 0.20 ml. Benzyl dimethylamine		849		1110
57-9	57-1 + 0.40 ml. Benzyl dimethylamine		774		948
57-11	57-1 + 0.60 ml. Benzyl dimethylamine		817		582

D. Catalysis of the Reaction Between Epoxide and Anhydride Compounds



Dilatometric measurements were made on solutions in dimethyl formamide (DMF) of phenyl glycidyl ether (PGE) and cyclopentane tetracarboxylic acid dianhydride (CPDA) treated with varying amounts of benzyldimethyl amine (BDA). Table IX lists the solutions that were studied:

Table IX. - Catalysis of Epoxide Reactions Using Phenyl Glycidyl Ether

Sample No.	ml. 0.1 N soln. meq. PGE	ml. 0.1 N soln. meq. CPDA	ml. 5.0 N BDA	ml. DMF	meq. BDA	Total Volume	Symbols in Fig. 3
471-							
64-1	5.00	5.00	0.00	1.00	0.00	11.00	○
-2	5.00	5.00	0.02	0.98	0.10	11.00	□
-3	5.00	5.00	0.10	0.90	0.50	11.00	●
-4	5.00	5.00	0.20	0.80	1.00	11.00	■
-5	5.00	5.00	1.00	0.00	5.00	11.00	△

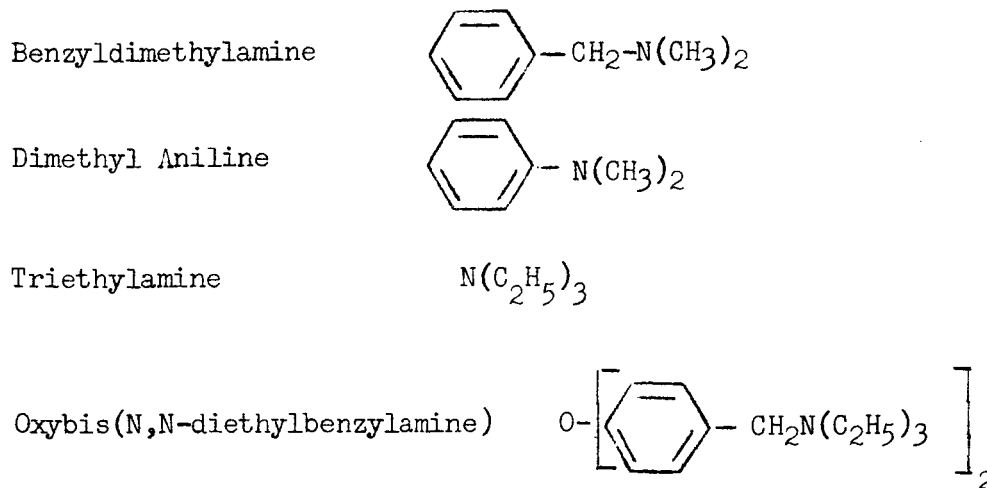
The sample was thoroughly mixed and about 8 ml. was transferred to a dilatometer (approximate capacity 8 ml.) in a water bath at 50° C. The decreasing column height was recorded at 30 minute intervals and the change in height (Δh) was plotted against time in seconds. (See Figure 3).

In a similarly conducted experiment a study was made of the effect of different catalysts on the reaction between 5 meq. diglycidyl isophthalate (DGI) and 5 meq. CPDA. The results obtained for the systems are listed below in Table X and are plotted in Figure 4.

Table X. - Catalysis of the Epoxide Reaction Using Diglycidyl Isophthalate

Sample No.	Catalyst	meq. Catalyst	Symbols in Fig. 4
471-76-			
1	None		○
2	Benzyldimethylamine	0.50	●
3	"	0.75	□
4	"	1.00	■
5	"	5.00	△
6	Triethylamine	1.00	▲
7	Dimethyl aniline	1.00	▽
8	Oxybis(N,N-diethylbenzylamine)	1.00	◇
9	Boron trifluoride n-butyl etherate	1.00	◇
10	"	3.00	◇

The data indicate that benzyldimethylamine and boron trifluoride n-butyl etherate are the most effective among the catalysts used, the former being superior to such related amines as those tested.



Increasing the amount of BDA in the adhesive made from epoxy resins and CPDA did affect the bond strength when samples were cured for two hours at 165° C. as seen in Table IV.

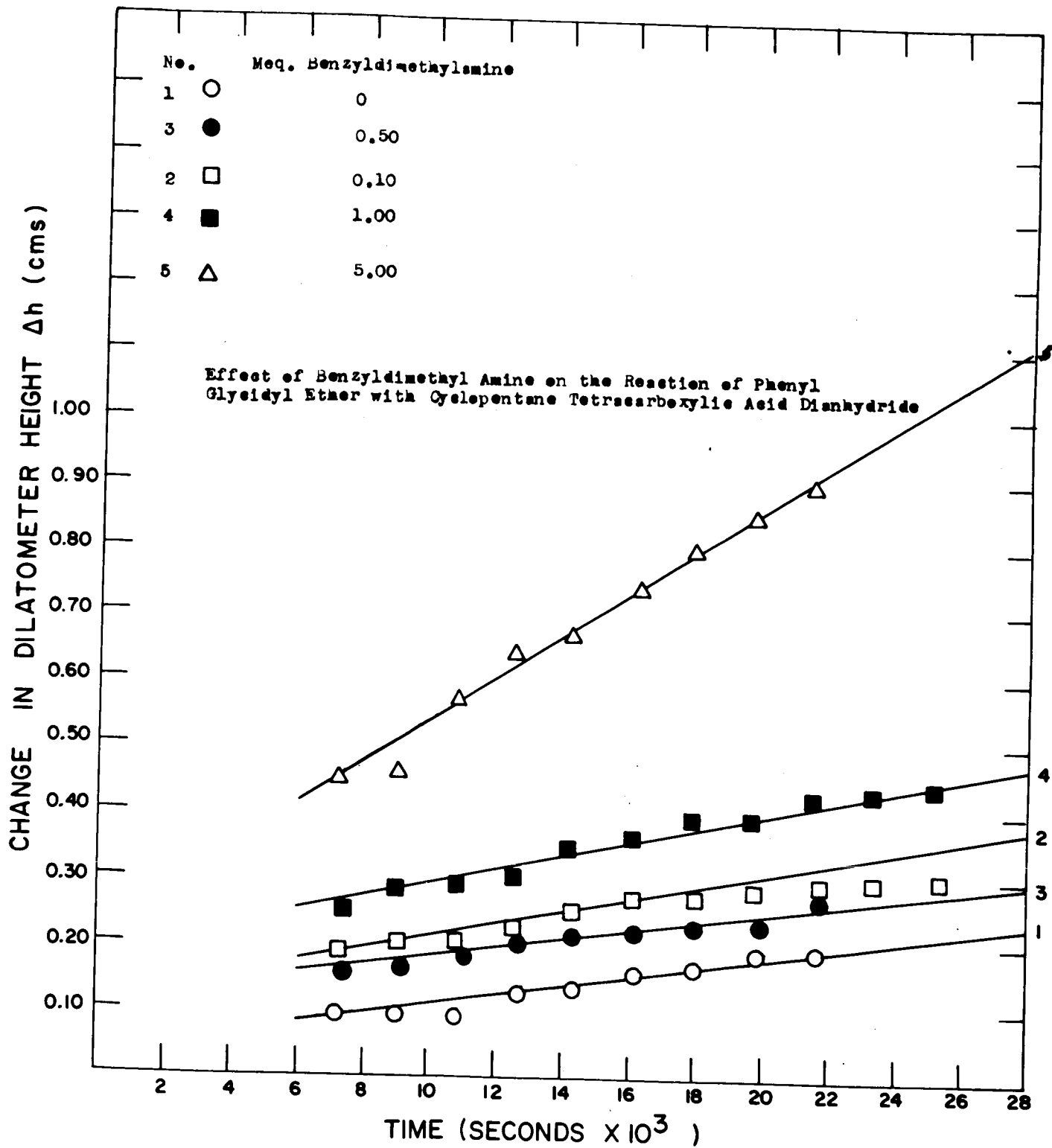


Figure 3.
-44-

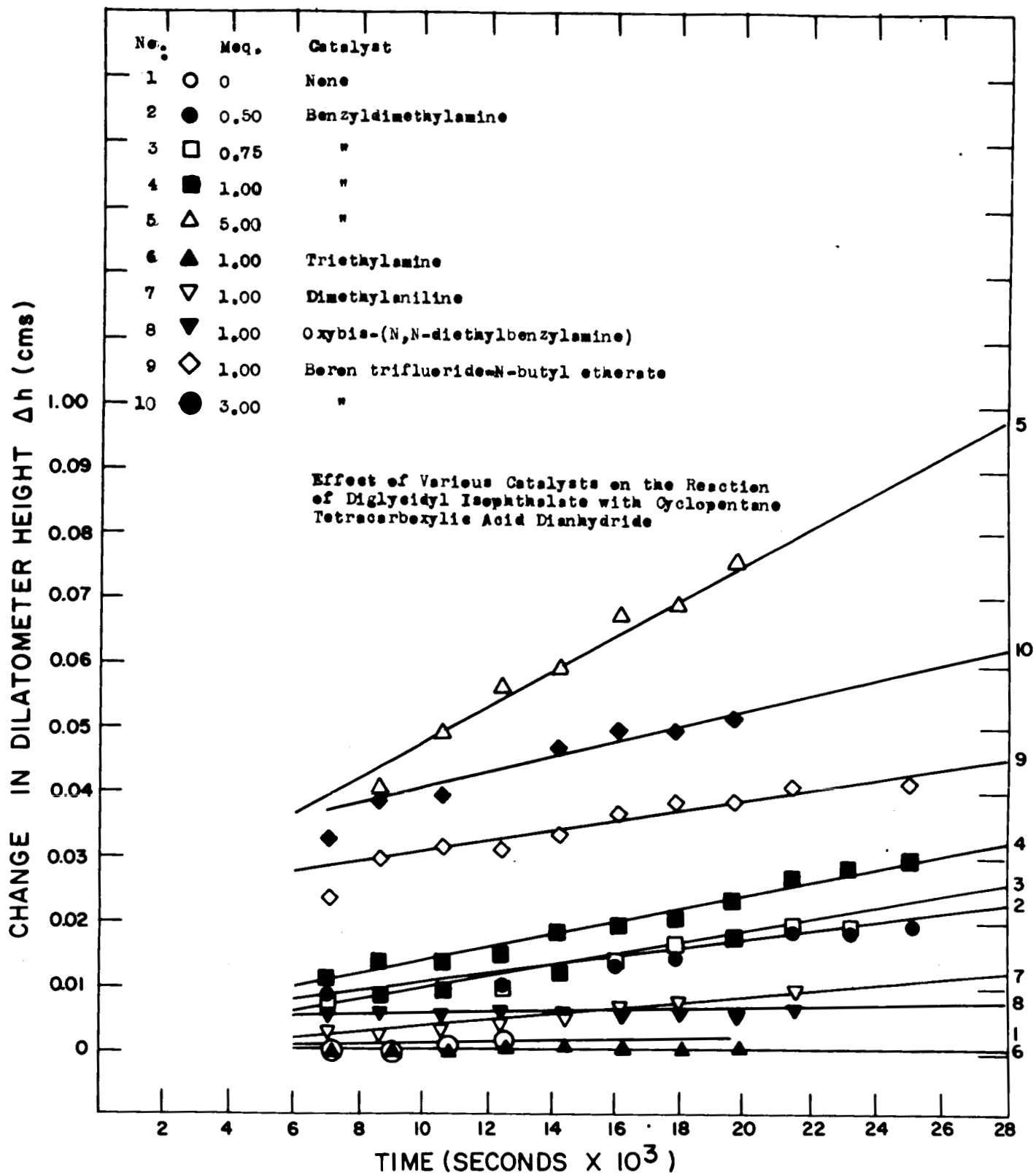


Figure 4.

III. POLYURETHANE ADHESIVES

POLYURETHANES AS CRYOGENIC ADHESIVES

INTRODUCTION

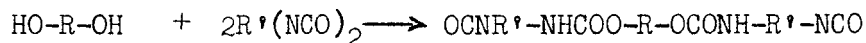
The object of this program was to develop a practical polyurethane adhesive showing good tensile shear strength over the temperature range of -423° F. to 400° F.

Earlier there appeared very little literature describing the chemical constitution of polyurethanes used for cryogenic applications.^{1-3/} However, Bodnar and Kelly^{4/} described an Adiprene L (Du Pont) resin as an adhesive formulation showing good strength at -65° F. (7470 psi). In this latter composition the chemical structure was disclosed to probably be a poly-1,4-butylene oxide polyglycol reacted with 2,4-toluene diisocyanate in the ratio of 2:3 respectively. More recently, a paper at the SPE Meeting May, 1964^{5/} described polyurethanes with tensile shear strengths of 5463 psi at -423° F. and 201 at 250° F. after room temperature curing.

RESULTS

In this program prepolymers were first prepared from aliphatic saturated diols or triols using 2,4-toluene diisocyanate; later, polyether polyols were shown to have superior cryogenic adhesive properties when used in the prepolymer synthesis. In addition, curing agents based on aromatic amines were superior to aliphatic amines or polyesters terminated with hydroxy groups. MOCA (Du Pont) (3,3'-dichloro-4,4'-diaminodiphenylmethane) was found to be the most useful curing agent.

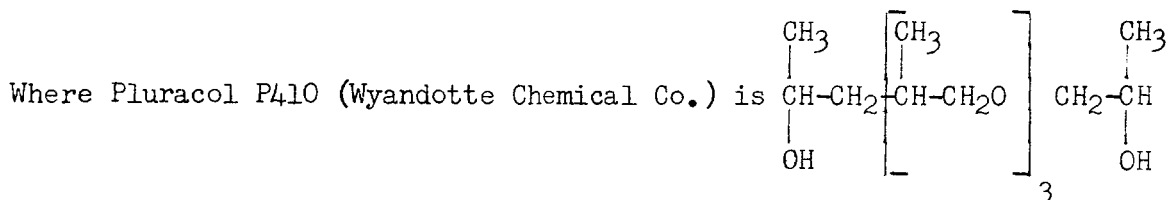
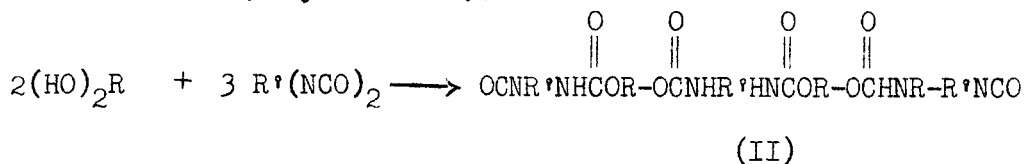
The reactions between diisocyanates and polyols were controlled to produce adducts containing NCO end groups and a varied number of carbamate linkages within the molecule. Di-adducts were prepared by the addition of a polyol to the diisocyanate according to the equation:



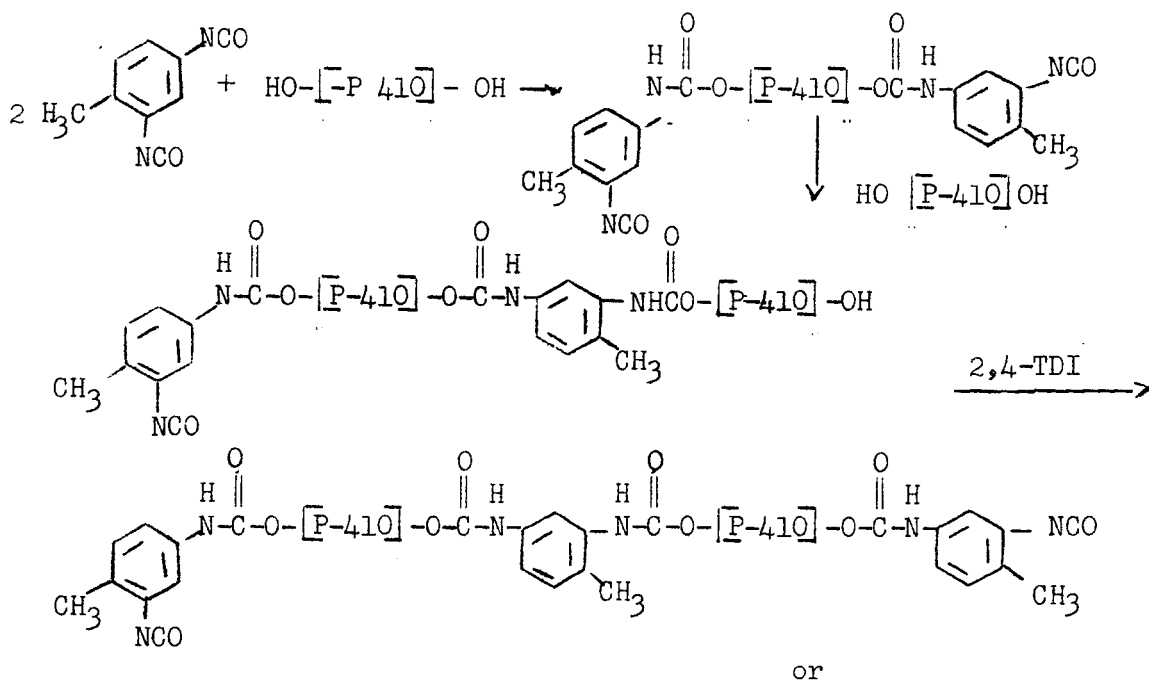
(I)

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- 1/ J. Hertz, *Advances in Cryogenic Engineering*, 7, 336 (1962).
 - 2/ M. B. Smith and S. E. Susman, *ibid.*, 8, 300 (1963).
 - 3/ R. C. Kausen, *Materials in Design Engineering*, Sept. 1964, p. 106.
 - 4/ M. J. Bodnar and E. R. Kelly, *Adhesives Age*, April, 1959, p. 29.
 - 5/ L. M. Roseland, *Seventh National Society of Aerospace Materials and Process Engineers Symposium on Adhesives and Elastomers for Environmental Extremes - May 20-22, 1964 at Los Angeles, California, Section 7.*

More complex adducts were prepared by the reaction of di- and trihydroxy polyethers with diisocyanates. As the di-adducts, these were made with or without solvent (ethyl acetate).



and abbreviated HO $\overline{\text{P-410}}$ - OH



Some examples of typical preparations are given below:

Preparation of a polyurethane prepolymer (409-39)

<u>Reactants</u>	<u>M. W.</u>	<u>Moles</u>	<u>Gms.</u>
2,4-Toluene diisocyanate (TDI)	174.2	0.1875	32.7
Polyoxypropylene glycol (Pluracol P-410)	400	0.1250	50.0

Apparatus

1 l. resin kettle, stirrer, thermometer, condenser with drying tube, dropping funnel, heating mantle.

Procedure

The apparatus was carefully dried and flushed with nitrogen. The TDI was placed in the kettle and heated to 50° C. The Pluracol P-410 was placed in the dropping funnel and added dropwise during two hours while the pot temperature was maintained at 65 ± 3° C. Stirring at that temperature was continued for two hours after final addition. The product was a very viscous, sticky syrup.

% NCO Calculated, 6.35; Found, 6.63.

Preparation of a polyurethane prepolymer (409-40)

<u>Reactants</u>	<u>M. W.</u>	<u>Moles</u>	<u>Gms.</u>
2,4-Toluene diisocyanate (TDI)	174.2	0.1875	32.7
Polyoxypropylene glycol (Pluracol P 710) (Wyandotte Chem. Co.)	700	0.1250	87.5

Apparatus

1 liter resin kettle, stirrer, thermometer, condenser with drying tube, dropping funnel, heating mantle.

Procedure

The apparatus was carefully dried and flushed with nitrogen. The TDI was placed in the kettle and heated to 50° C. with stirring. The Pluracol P 710 was placed in the funnel and added dropwise during two hours while the pot temperature was maintained at 65 ± 3° C. Stirring at that temperature was continued for an additional two hours after all the Pluracol P 710 was added. The product was a clear syrup.

% NCO Calculated, 4.37; Found, 5.56.

Preparation of a polyurethane prepolymer (428-104-2)

<u>Reactants</u>	<u>M.W.</u>	<u>Moles</u>	<u>Gms.</u>
2,4-Toluene diisocyanate (TDI)	174.2	0.2	34.8
Polyoxypropylene glycol (Dow P1000)	1000	0.1	100.0
o-Chlorobenzoyl chloride (CBC)			0.12

Apparatus

500 ml. resin kettle, stirrer, thermometer, condenser with drying tube, dropping funnel, heating mantle.

Procedure

The apparatus was carefully dried and flushed with nitrogen. The TDI and CBC were placed in the kettle and heated to 50° C. The Dow P1000 was placed in the funnel and added dropwise during two hours maintaining a pot temperature of 65 ± 3° C. Stirring at that temperature was continued for two hours after final addition. The product was a clear syrup (428-104-1).

% NCO Calculated, 6.23; Found, 6.27.

To 37.1 g. of 428-104-1 was added 2.9 g. TDI and the mixture was thoroughly stirred (428-104-2).

% NCO Calculated, 9.0; Found, 8.60.

POLYURETHANE ADHESIVES

Diisocyanate Prepolymers

Prepolymers were prepared from 2,4-toluene diisocyanate (TDI), or from a mixture of 65% of the 2,4-isomer and 35% of the 2,6-isomer (TDI-65, 35) or from diphenylmethane diisocyanate (DPMDI). Polypropylene glycols and polytetramethylene ether glycols were used. The NCO:OH ratio was either 2:1 or 1.6:1 and TDI was then added to these materials to increase the NCO content to the desired amount.^{6/} All the preparations were made at 50-60° C.

All the diisocyanate prepolymers contained o-chlorobenzoyl chloride equivalent to the % H₂O in the polyol plus 0.1% of the total weight of reactants.

^{6/} In order to increase the aromaticity of the adhesive more TDI and MOCA were added. It was felt that such an increase in aromaticity of the adhesive would favor better high temperature strength.

Table I. - Polyurethane Cryogenic Adhesives

Sample No.	Composition	Tensile Shear Strength, psi, at °F. - on Aluminum		
		-320°	73°	250°
352-54-2	Polyglycol P 1000 (M.W. 1000)-2,4-TDI 2/1 adduct (428-104-2), % NCO = 8.6 cured with MOCA (5:1.4)	5930	2560	740
432-61-6	PTMEG 1103 (M.W. 1103)-2,4-TDI 2/1 adduct (428-117-3), % NCO = 8 cured with MOCA (5:1.6)	6650	2120	844
432-61-2	PTMEG 2005 (M.W. 2005)-2,4-TDI 2/1 adduct (439-42-2), % NCO = 6 cured with MOCA (5:1.0)	5580	1750	958
432-49-4	Witco ED-2000 (M.W. 2000)-2,4-TDI 2/1 adduct, (428-87-3), % NCO = 12.3 cured with MOCA (2:0.6)	2570	2370	964
432-63-2	Voranol 2700 (M.W. 2700)-2,4-TDI 2/1 adduct (428-85-3), % NCO = 12.2 cured with MOCA (2:0.8)	5830	1620	558
405-133-1	Pluracol P-710 (M.W. 775)-2,4-TDI 2/1 adduct (399-44), % NCO = 8.43 cured with MOCA (5:1.3)	1595	1563	56
405-121-3	Pluracol P 410 (M.W. 400)-4,4'- diphenylmethane diisocyanate - 2/1 adduct, (409-97), % NCO = 9.33 cured with MOCA (5:0.6)	4200	1940	301
405-137-5	Pluracol P 710 (M.W. 775)-2,4-TDI adduct 3/2, % NCO = 4.42 cured with MOCA (5:0.4)	6090	837	76

Polyglycol = Dow Chem Co., polyoxypropylene glycol

PTMEG - Quaker Chem. Co., polyoxybutylene glycol (polytetra-
methylene ether glycol = PTMEG)

Witco ED 2000 = Witco Chem. Co., polyoxypropylene glycol

Pluracol = Wyandotte = Polyoxypropylene glycols

Voranol = Dow polyglycol (polyoxypropylene glycol)

The molecular weights (M.W.) are given in parentheses near the appropriate polyol.

Table I. - Polyurethane Cryogenic Adhesives (CONTINUED)

Sample No.	Composition	Tensile Shear Strength, psi, at °F. - on Aluminum			T-Peel at 73°F. (e) psi
		-320°	73°	250°	
432-94-5	439-108-3 (a) + MOCA (5/1.4)	5390	2280	862	
450-28-4	450-28-4 (b) + MOCA (5/1.4)	4180	2090	640	
432-103-6	452-3-2 (an adduct from 0.15 M PTMEG-1103 + 0.06 M Dover 1000 + 0.04 M TDI, % NCO = 9%) + MOCA (5/1.0)	> 6950	3140	1104	16
432-103-8	452-5-2 (an adduct from 0.07 M PTMEG 1103, 0.03 M Dover 1000 and 0.20 DPMDI, % NCO = 9.0) + MOCA (5/1.4)	4025	2890	1255	
432-76-1	439-79-4 (c) + MOCA (5/1.9)	2660	2850	1240	
432-67-1	428-120-3 (d) + MOCA (5/1.4)	5920	2870	1070	

- (a) Prepolymer prepared from 0.14 moles Pluronic L 61 (Wyandotte) and 0.2 moles TDI (2,4 isomer) using 0.6 ml. orthochlorobenzoyl chloride. The % NCO was increased to 9% for the particular fraction for adhesive uses.
- (b) 450-28-4 - Prepolymer prepared from 0.2 moles of 4,4'-diphenylmethane diisocyanate and 0.1 mole PTMEG 2005 using 0.9 ml. orthochlorobenzoyl chloride. The % NCO was increased to 12% before using as an adhesive.
- (c) Prepolymer prepared from 0.40 moles TDI (65/35 2,4/2,6 isomer) and 0.25 moles Dow P 1000 using 0.6 ml. orthochlorobenzoyl chloride. The % NCO content was increased at the end to 12% for this particular adhesive.
- (d) 428-120-3 - Prepolymer prepared from 0.1 mole TDI (2,4 isomer) and 0.05 M PTMEG G 3196 using 0.15 ml. orthochlorobenzoyl chloride. The % NCO was increased to 9% before using as an adhesive.
- (e) ASTM Standard T-peel Test No. D1876-61T using a 10 mil thick nickel-chrome wire spacer for glue line thickness.

Table II. - Commercial Polyurethane Prepolymers Used as Cryogenic Adhesives

Sample No.	Composition	Tensile Shear Strength(a) psi, at °F., on aluminum				T-Peel at 73°F. psi
		-320°	73°	250°	400°	
405-41-2	Adiprene L-100 + MOCA (10/1.1)	2950	-	-	-	-
432-2	Adiprene L-213 + MOCA (5/2.5)	2450	-	-	-	-
405-97-1	Adiprene L-315 + MOCA (5/2)	6500	4085	1315	40(c)	
405-97-2	Adiprene L-315 + MOCA (5/1)	6430	4580	1365	25(d)	
432-60-4	Adiprene L-315 (5/1.5)	6520	2160	473	-	
405-97-3	Adiprene L-167 + MOCA (8/1)	7870(b)	1890	781		
432-54-4	Adiprene L-167 + MOCA (5/1)	7800(e)	1264	848		15
432-61-7	Polycin U56 + MOCA (5/1.6)	1950	1580	489		
405-109-A	Polycin U56 + Polycin 12 (7.4/2.7)	4380	1183	241		
432-44-2	Vibrathane 6005 + MOCA (10/0.95)	6850	990	166		
432-51-3	Vibrathane 6006 + MOCA (5/1)		1300	294		
432-44-3	Vibrathane 6006 + MOCA (5/1.0)	7070	1300	294		
432-51-4	Vibrathane 6008 + MOCA (10/1)	2760(f)	390			

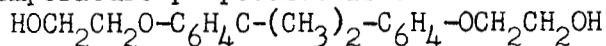
- (a) Average of 3 determinations.
(b) Metal failure at 8000 psi for two samples.
(c) Sample 432-66-1.
(d) Sample 432-66-2.
(e) Metal failure.
(f) Sample 432-44-4

Discussion

The purpose of this program was to develop polyurethane adhesives with good low temperature properties yet having a tensile shear strength at 400° F. of 800 psi on aluminum. Using the polyurethane adhesives and curing with MOCA gave adhesives which were useful for -453° to 250° F. At 400° F. the strengths dropped to values of the order of 20-100 psi. In a later report ^{7/} special catalysts were used to improve the 400° F. strength so that values in excess of 1000 psi were obtained. The only disadvantage with this latter modified system is that the cure temperature was 165° C. whereas temperatures close to room temperature were desired.

Polyethers derived from polyoxypropylene glycol or polytetramethylene glycol gave results similar to those as shown in Table I. The samples prepared from higher molecular weight polyols were more stable to sudden gelation. In addition, orthochlorobenzoyl chloride of 0.1% concentration was added above that necessary to react with the water content of the polyol. This material acted as an effective gelation inhibitor.

The isocyanate content appears to be critical since higher % NCO requires more MOCA to be effectively cured. This increases the aromaticity of the system and improves the tensile shear strength at 250° F. However, prepolymers with added TDI are more moisture sensitive and have short pot-lives. The use of 4,4'-diphenylmethane diisocyanate as in sample 405-121-3 did not give the expected increase in high temperature properties as seen in Table I. However, the use of Dcver 1000



(ethylene oxide adduct of bisphenol A) did cause some improvement in the tensile shear values at 250° F. as seen in samples 432-103-6 and 432-103-8.

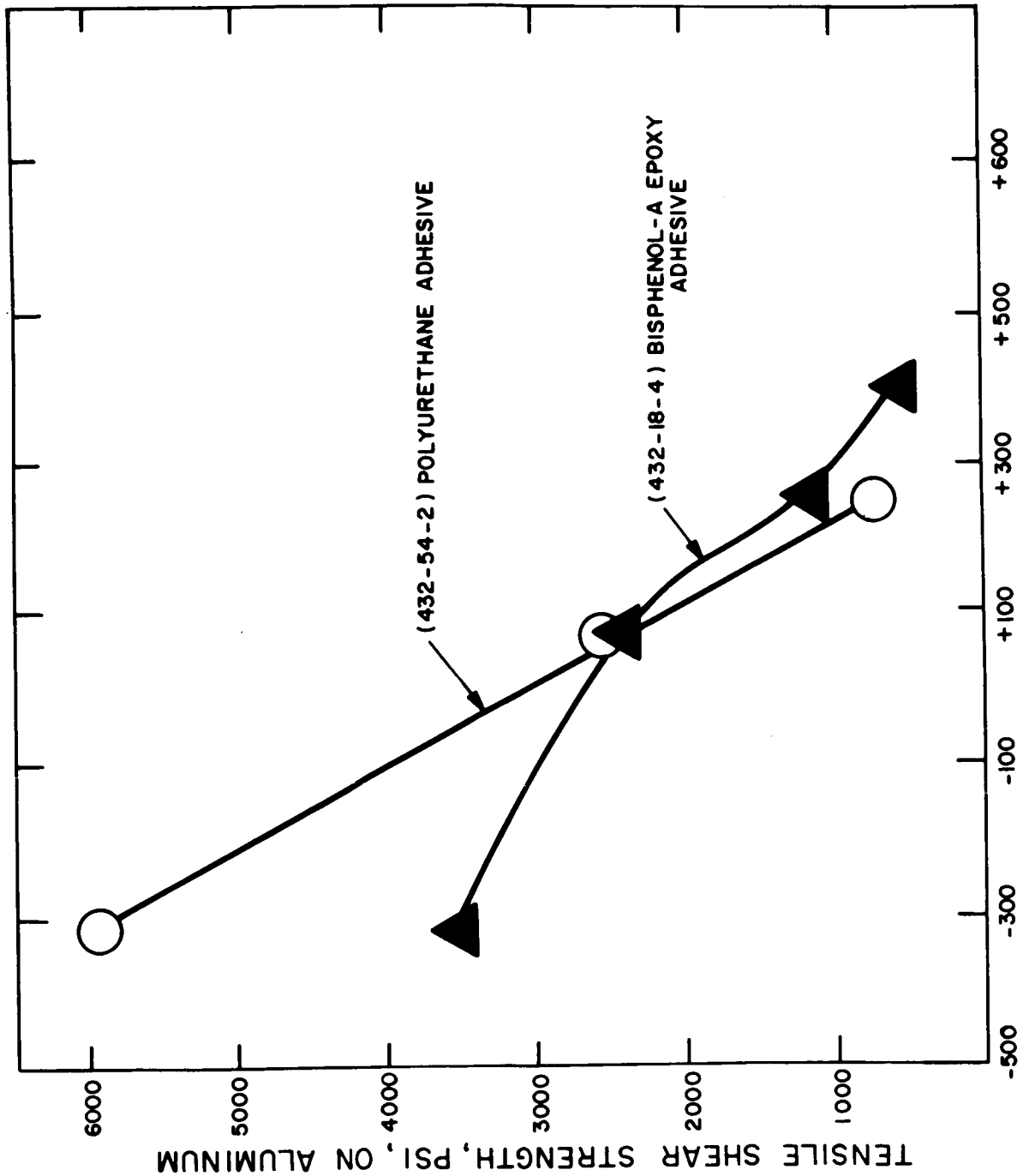
Several commercial polyurethane prepolymers were also evaluated and are shown in Table II. Among the latter samples the Adiprene systems gave the best results and compare favorably with our samples in Table I. It should be noted that the strength at 400° F. is 25 or 40 psi.

In conclusion, polyurethanes that were cured at 100° (or at room temperature) could not be modified to increase their high temperature (400° F.) strength. It is felt that the urethane linkage -NHCOO- is not stable at 400° F. and consequently the adhesives fail. In addition, the polyether backbone is too flexible at 400° F. Work in progress has shown that although more aromatic polyethers were substituted, failure at 400° F. still occurred.

Fig. 1 shows a comparison of one of our polyurethanes with an epoxy adhesive. It is noted that the epoxy resins are stronger at 400° F. but weaker than the polyurethanes at cryogenic temperatures. The latter results are due to the increased flexibility of the polyurethanes as they possess a polyether structural backbone.

^{7/}

This investigation involved the cyclization of polyisocyanates to polyisocyanurates and the results will form the subject of another paper.



TEMPERATURE °F
Figure 1.

IV. POLYISOCYANURATE ADHESIVES

POLYISOCYANURATES

INTRODUCTION

In an attempt to modify the polyurethane adhesives, based on polyether polyols, to give improved tensile shear strength at 400° F. it was found that poly-trimerization to polyisocyanurates was effective.

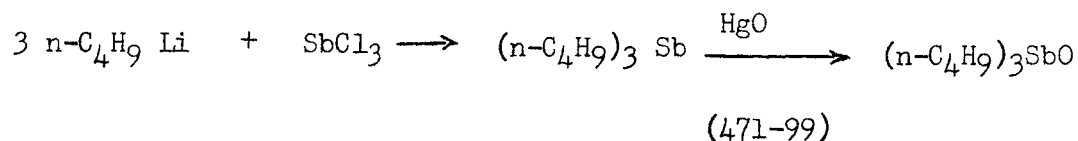
An earlier investigation of polyisocyanurate adhesives was reported by Kansens^{1/} mentioning the work of Gilman et al^{2/} under a government contract.

EXPERIMENTAL

The preparation of prepolymers is similar to that described for the polyurethanes in an earlier section. A few model preparations are given below.

The trimerization agent used in the initial phase of the investigation was calcium naphthenate solution obtained from Harshaw Chemical Co. and abbreviated as Ca-liq.

Tri-n-Butylstilbene Oxide



n-Butyllithium (15% in hexane, 0.3m) was added slowly to antimony trichloride (0.1m) in 100 ml tetrahydrofuran at 5° C. and stirred for an hour. The liquid was decanted and kept cold while mercuric oxide (0.1m) was added with stirring, then 200 ml. ethanol was added and the solids were removed by filtration. Solvents were removed by water suction on a hot water bath. The product (40% yield) was a viscous liquid. Trimerization occurred in about 15 minutes when phenylisocyanate (0.005m) was mixed with tri-n-butylantimony oxide (0.0001m). This was faster than any of the other compounds listed in Table III.

^{1/} R. C. Kansens, Society of Aerospace Materials and Process Engineers, Materials Symposium, 7th National SAMPE Symposium, Adhesives and Elastomers, For Environmental Extremes, May 20-22, 1964, Los Angeles, California. p.1-19.

^{2/} L. Gilman, et al, "High Temperature Laminating Resins Polyisocyanurates and Polymeric Chelates" Conference on Structural Plastics and Adhesives and Filament Wound Composites, p. 1 (Dec. 1962).

^{3/} Sheldon Herbstman, Trimerization of Isocyanates by Trialkylantimony and -Arsenic Compounds, J. Org. Chem., 30, 1259 (1965).

Preparation of Polyurethane Prepolymers (452-3-3)

A 500 ml. kettle equipped with stirrer, condenser, thermometer, and a 250 ml. dropping funnel was purged with nitrogen for 10 minutes. Toluene diisocyanate (Du Pont, Hylene T, 0.4 m, 69.6 g) and 0.7 ml. benzoyl chloride were placed in the kettle and heated to 45° C. Polytetramine ether glycol (Quaker Oats, PTMEG 1000, M.W. 1103, 0.14 m, 154.4 g) and polyester PR 1000 (Dover Chemical, M.W. 588, 0.06 m, 35.3 g) were mixed together while warm and the uniform mixture was placed in the funnel and added dropwise during two hours maintaining the pot temperature to 50-60° C. Stirring was continued for an hour after final addition while the pot reached room temperature. 80 g. of the product and 12.2 g. toluene diisocyanate were mixed together in an atmosphere of nitrogen for 15 minutes. % NCO calculated = 12.0.

Preparation of Polyurethane Prepolymer (452-5-3)

A 500 ml. kettle equipped with stirrer, condenser, thermometer, and a 250 ml. dropping funnel was purged with nitrogen for 10 minutes. Diphenylmethane diisocyanate (Nacconate 300, National Aniline, 0.20 m, 5.0 g) and 40 ml. benzoyl chloride were placed in the kettle and heated with stirring to 45° C. Polytetramethylene ether glycol (Quaker Oats PTMEG 1000, M.W. 1103, 0.07 m, 77.2 g.) and polyester PR 1000 (Dover Chemical, M.W. 588, 0.03 m, 17.6 g.) were mixed together while warm and the uniform mixture was placed in the funnel and added dropwise during two hours maintaining the pot temperature at 50-60° C. Stirring was continued for an hour after final addition while the pot reached room temperature. 40 gms. of the product and 11.5 g. diphenylmethane diisocyanate were mixed together at 45° C. in an atmosphere of nitrogen for 15 minutes. % NCO calculated = 12.0.

Preparation of Polyurethane Prepolymer (439-77-2)

A 500 ml. resin kettle equipped with stirrer, condenser, thermometer, and a 250 ml. dropping funnel was purged with nitrogen for ten minutes. Diphenylmethane diisocyanate (Nacconate 300, National Aniline, 0.24 m, 60 g.) and 0.6 ml o-chlorobenzoyl chloride were placed in the kettle and heated with stirring to 45° C. Polytetramethylene ether glycol (Quaker Oats PTMEG, M.W. 1103, 0.12 m, 132 g.) was placed in the funnel and added dropwise during two hours maintaining the pot temperature at 50-60° C. Stirring was continued for an hour after final addition while the pot reached room temperature. 50 gms. of the product and 2.1 gms. toluene diisocyanate (Du Pont, Hylene T) were mixed together in an atmosphere of nitrogen for 15 minutes. % NCO calculated = 7.0.

Table I. - Physical Evaluation of Polyisocyanurates

Sample	Composition	Tensile Shear Strength, psi (a)				
		at ° F.		on Aluminum		
		-453°	-320°	73°	250°	400°
432-129-6	1.0 g Diphenylmethane diisocyanate (DPMDI) + 7 drops 0.5% soln. of calcium naphthenate in petroleum ether (Harshaw).	1230	1260	1165	1510	804
432-103-9	452-5-3 ^{b/} + 3,3'-dichloro-4,4'-diamino diphenylmethane (MOCA) (5/1.9)	-	776	2240	460	-
432-137-1	452-5-3 + DPMDI + Ca-liq. (0.3/2.7/3 drops)		1155	996	1030	812
432-137-2	452-5-3 + DPMDI + Ca-liq. (0.6/2.4 g/3 drops)		1650	1550	1380	1090
432-137-3	452-5-3 + DPMDI + Ca-liq. (0.9/2.1/3 drops)		1535	1330	971	833
432-137-4	452-5-3 + DPMDI + Ca-liq. (0.2/1.8/3 drops)		1935	857	871	624
432-137-5	452-5-3 + DPMDI + Ca-liq. (1.5/1.5/3 drops)		2490	1132	885	794
432-137-6	452-5-3 + MOCA + DMPDI + Ca-liq. (1.3/0.5/1.0/1 drop)		2800	4020	2289	188
462-12-3	452-3-3 ^{b/} + DPMDI + Ca-liq. (0.5/1.5/0.04 ml)		1630	1530	1410	1410
462-15-3	439-77-2 ^{b/} + DPMDI + Ca-liq. (0.5/2.5/0.05 ml)		1460	1630	1450	1300
462-78-280	Adiprene L-167 + Tri-n-butyl stibine oxide (6.0g/0.031 g)		-	147	-	-
462-78-286	Adiprene L-167 + MOCA (5.0/1.0)		-	1050	402	-

a. The samples were cured for 2 hours at 165° C. An average of three determinations is shown.

b. See experimental section for a description of this polyurethane prepolymer.

Table II. - Physical Evaluation of Polyisocyanurates

Sample No. 462-	Composition	Tensile Shear Strength (a) psi, at °F., on Aluminum	
		73° F.	250° F.
74-223 (a)	Adiprene L-167 + Bis tri-n-butyltin oxide (5.0/0.089)	320	0
74-224 (a)	439-146 (Polyurethane prepolymer from toluene diisocyanate and polyoxypropylene glycol M.W. 1000) + Bis tri-n-butyltin oxide (5.0/0.128)	646	115
74-225 (a)	452-50 (Polyurethane prepolymer from toluene diisocyanate, polytetramethylene glycol M.W. 1048, di(ethylene glycol) ether of bisphenol A) + Bis-tri-n-butyltin oxide (5.0/0.170)	499	26
74-237 (b)	452-4 (Polyurethane prepolymer from toluene diisocyanate and polytetramethylene glycol M.W. 1103) + Diphenylmethane diisocyanate + 5% calcium naphthenate (5.0/1.0/1.0)	329	82
74-238 (b)	Same as 74-237 (4.0/2.0/1.0)	211	36
74-239 (b)	" " " (3.0/1.0/1.0)	177	54
74-240 (b)	452-4 (see 74-237) + Diphenylmethane diisocyanate + Bis-tri-n-butyltin oxide (5.0/1.0/0.4)	397	54
76-241 (b)	Same as 74-240 (4.0/2.0/0.4)	825	204
76-242(b)	" " " (3.0/3.0/0.4)	1010	214
76-243(b)	452-50 (see 74-225) + Diphenylmethane diisocyanate + 5% Calcium Naphthenate (5.0/1.0/1.0)	508	70
76-244(b)	Same as 76-243 (4.0/2.0/1.0)	218	27
76-245(b)	" " " (3.0/3.0/1.0)	293	115
76-246(b)	452-50 (See 74-225) + Diphenylmethane diisocyanate + Bis-tri-n-butyltin oxide (5.0/1.0/0.4)	393	6
76-247(b)	Same as above (4.0/2.0/0.4)	814	93
76-248 (b)	" " " (3.0/3.0/0.4)	1060	176
76-249(b)	Adiprene L-167 + Diphenylmethane diisocyanate + 5% Calcium Naphthenate (5.0/1.0/1.0)	154	47
76-250(b)	Same as 76-249 (4.0/2.0/1.0)	132	41
76-251(b)	" " " (3.0/3.0/1.0)	204	70
76-252(b)	Adiprene L-167 + Diphenyldimethane diisocyanate + Bis-tri-n-butyltin oxide (5.0/1.0/0.4)	127	24
76-253 (b)	Same as 76-252 (4.0/2.0/0.4)	637	68
76-254(b)	" " " (3.0/3.0/0.4)	674	39

(a) Cure time: 16 hr. at 50° C.

(b) Cure time: 72 hr. at 23° C..

Table III. - Trimerization of Phenylisocyanate (0.005 M) by Various Catalysts (0.0001 M)

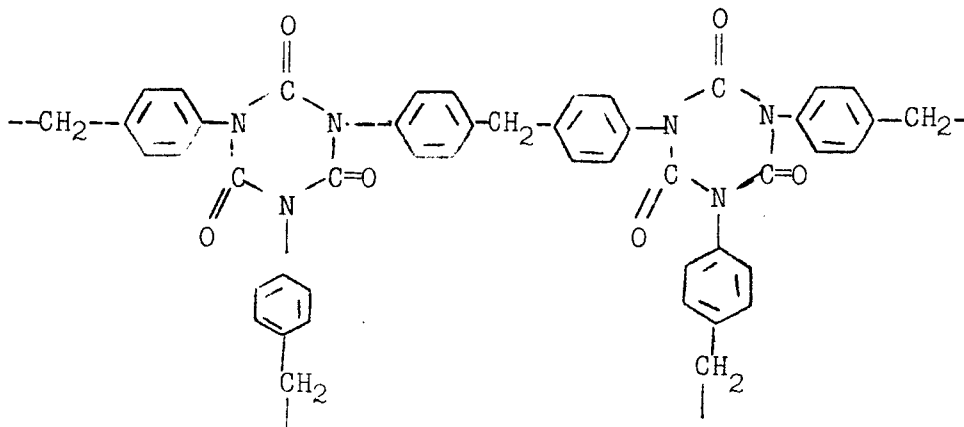
Catalyst	Trimer Observed ^(a)		M.P. °C. (c)
	23°C.	50°C.	
Triphenylarsine	N.R. (b)	N.R.	-
Bis(tri-n-butyltin)oxide	24 hours	7 hours	275-81°
Dibutyltin oxide	24 hours	-	-
Tricresyl phosphate	N.R.	N.R.	-
Antimony chloride	N.R.	N.R.	-
Bismuth trioxide	N.R.	N.R.	-
Bismuth oxychloride	N.R.	N.R.	-
Triphenyltin hydroxide	N.R.	N.R.	-
Tributyltin chloride	N.R.	N.R.	-
Triethylamine	N.R.	N.R.	-
Calcium naphthenate	N.R.	24 hours	270-75°
Dibutyltin dilaurate	N.R.	7 hours	-
Stannous octoate	24 hours	5 hours	275-81°
Aluminum isopropylate	N.R.	24 hours	275-81°
Sodium methoxide	48 hours	-	272-78°
Calcium oxide	N.R.	N.R.	-
Tri-n-butylantimony oxide	<u>15 minutes</u>	-	265-75°

- (a) The times listed are the times for complete solidification of the triphenylisocyanate.
- (b) No reaction.
- (c) Literature value for the m.p. of triphenylisocyanurate is 280-281°.

Discussion:

The polytrimerization of 4,4'-diphenylmethane-diisocyanate by means of calcium naphthenate has yielded a novel adhesive showing good strength over the range of -320° to +400° F.

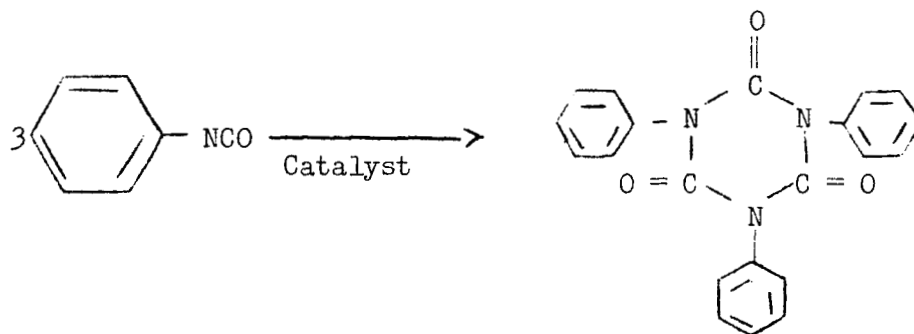
It was thought that incorporation of polyisocyanurate structures



with the polyether prepolymers may likewise cause an increase in tensile shear strength at 250 and 400° F. Brittleness can not be the main problem in the polyisocyanurates since they still exhibit tensile shear strength of 1260 psi at -320° F.

Infrared spectra of 432-137-5 (Table VI) has shown that the isocyanurate group is present as evidenced by the strong absorption band at 7.10 microns. The latter band is also found in triphenylisocyanurate.

Incorporation of the polyether group into the polyisocyanurates is shown in Table I and II where the polyether prepolymer 452-5-3 is added in 10% intervals until 50% concentration has been reached. The low temperature strength shows an increasing trend to 50% and the high temperature (400° F.) strength reaches 794 psi. The only disadvantage at present is that the systems are cured at 165° C. Experiments to reduce the cure temperature indicated that a temperature of 165° is necessary to obtain the maximum adhesion as shown in Table II using calcium naphthenate.



3/

In a recently published paper^{3/} it is reported that the trimerization of some isocyanates is effected at room temperature by organo-metallics such as tri-n-butylantimony and triisobutylarsenic oxides. The antimony compound was prepared and compared with other metal salts in their catalytic effect on phenylisocyanate trimerization shown above. Both tri-n-butylantimony oxide and stannous octoate produced a white, sticky, spongy material when added to a polyurethane prepolymer terminated with isocyanate groups; however, in the case of the faster catalyst, the pot-life of such a compound is too short for usefulness in adhesive applications. The variation of catalyst concentration may lead to longer pot lives.

V. POLY-2-OXAZOLIDONE ADHESIVES

V. POLY-2-OXAZOLIDONES

Introduction

In earlier reports we have shown that diglycidyl ethers react with diisocyanates in the presence of catalytic amounts of trimethylammonium iodide (TMAI) to give poly-2-oxazolidones.^{1,2/} The object of this investigation was to determine the usefulness of these polymers as adhesives at cryogenic and elevated temperatures for aluminum and stainless steel.

Experimental

The polyurethane prepolymers and epoxy resins have already been described in earlier sections.

Tetramethylammonium iodide was obtained from Eastman Organic Chemicals Co.

1/

S. R. Sandler, F. Berg and G. Kitazawa, Progress Report for the Period April 1- April 30, 1964 under contract NAS8-11518 to NASA, George C. Marshall Space Flight Center.

2/

S. R. Sandler, F. Berg and G. Kitazawa, "Poly-2-Oxazolidones," J. Applied Polymer Sci., 2, 1994 (1965).

Results:

Table I. - Physical Testing Results of Poly-2-Oxazolidone Adhesives^{a/}

Sample No.	Composition	Tensile Shear Strength, psi, °F			% Cohesive Failure at ° F.		
		-320°	73°	250°	-320°	73°	250°
423-109-2	Epiphen 825 + Adiprene L315 + MDA + TMAI (8.8:2.0:1.7:0.08)	1930	2980	1050	10	0	0
423-109-1	Epiphen 825 + Adiprene L315 + MDA (8.8:2.0:1.7)	2310	3080	757	0	10	0
423-103-1 423-94-2	Epiphen 825 + Adiprene L 315 + TMAI (3.2:7.8:0.08)	4466	1216	137	50	70	70
432-36-3	Epon 812 + 428-47 + TMAI (0.5:4.5:0.1)	5580	2870	135	0	50	0
432-36-4	Epon 812 + Adiprene L315 + MOCA + TMAI (0.5:4.5:1.4:0.1)	3000	3300	739	10	80	80
432-36-5	Epon 812 + Adiprene L315 + TMAI (0.5:4.5:0.1)	5640	1150	130	90	20	0
432-36-6	Epon 812 + Adiprene L315 + TMAI (1.0:3.0:0.08)	1740	198	-	0	80	-
423-75-5	DER332 + Adiprene L315 + MDA (5:2:1.8)	3640	3750	2580	10	10	10
432-29-1	DER332 + Adiprene L315 + MDA + Pyridine (5:2.0:1.8:1 drop)	2170	2193	1441	0	0	0
432-29-2	DER332 + Adiprene L315 + MDA + TMAI (5:2.0:1.8:0.08)	2250	2207	1407	0	0	0

Footnotes: a/ The samples were cured at 100° C. for 2 hr. and equilibrated 7 days prior to testing. An average of 3 determinations is shown.

Abbreviations:

Epiphen 825 = Borden epoxy resin (glycidyl ether type)
 Adiprene L315 = Du Pont polyurethane prepolymer with reactive isocyanate groups
 MDA = 4,4'-Diaminodiphenylmethane
 TMAI = Tetramethylammonium iodide
 Epon 812 = Glycerol triglycidyl ether (Shell)
 428-47 = TDI adduct of Pluracol P-410 TDI/P410 = 1.86/1 ratio
 MOCA* = 3,3'-Dichloro-4,4'-diaminodiphenylmethane

* Du Pont trade name.

a/

Table II. - Physical Evaluation of Poly-2-oxazolidone Adhesives on Stainless Steel

Sample No.	Composition	Tensile Shear Strength				% Cohesive Failure			
		psi.		° F.		° F.			
432-		-320°	73°	250°	400°	-320°	73°	250°	400°
50-2	DER 332 + Adiprene L315 + MDA + Pyridine (5:2:1.8:1 drop)	3270	3290	760	260	0	20	0	0
53-3	DER 332 + Adiprene L315 + MDA + TMAI (5:2.0:1.8:0.08)	2590	2250	1180	250	0	0	0	0
55-1	Adiprene L315 + 428-30 + TMAI (1.4:0.5:0.08)	3240	715	-	-	80	20	-	-
55-2	Adiprene L315 + 409-123 + TMAI (4.5:1.7:0.08)	3040	483	-	-	80	30	-	-
55-4	428-43 + 409-123 + TMAI (6.2:0.8:0.08)	2830	40	-	-	10	100	-	-
55-5	428-43 + 409-134 + TMAI (6.2:0.8:0.08)	7600	268	-	-	100	10	-	-
55-6	428-43 + Epiphen 825 + TMAI (10:1.8:0.08)	6700	343	-	-	90	20	-	-
55-7	428-53 + Epiphen 825 + TMAI (6.4:1.8:0.08)	5460	901	-	-	100	10	-	-
53-2	DER 332 + Adiprene L-315 + MDA + Pyridine (5:2:1.8:1 drop)	2740	2970	410	225	0	0	0	0

Footnotes:

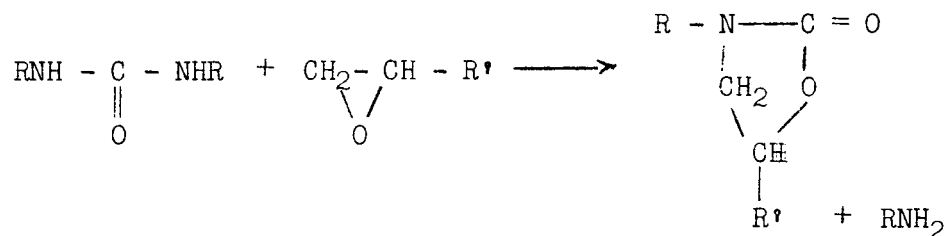
- DER 332 = Dow diglycidyl ether of bisphenol A
- Adiprene L315 = Du Pont polyurethane with reactive isocyanate groups
- MDA = 4,4'-Diaminodiphenylmethane
- TMAI = Tetramethylammonium iodide
- 428-43 = 3 moles TDI reacted with 2 moles Pluracol P710 to give a prepolymer with 4% NCO
- 409-123 = Diglycidyl phthalate
- 409-134 = Diglycidyl isophthalate
- Epiphen 825 = Borden glycidyl ether type epoxy resin
- 428-53 = 2 moles 3,3'-dimethyldiphenylmethane 4,4'-diisocyanate reacted with 1 mole of Pluracol P710 (1 drop ortho-chlorobenzoyl chloride) to give a prepolymer, % NCO = 7.20%.

a/ The samples were cured at 100° C. for 2 hr. and equilibrated 7 days prior to testing. An average of 3 determinations is shown.

Discussion:

The poly-2-oxazolidone adhesives produced with (TMAI) tetramethylammonium iodide catalyst alone do not appear to be as good at 250° F. as those containing MDA or MOCA as an additional curing agent. The adhesive system 423-75-5 (Table I) is superior to that of DER332 or Adiprene L315 alone. Thus, the poly-2-oxazolidone structure had produced added stability at 73° and 250° F. The beneficial effect of MDA or MOCA is probably due to the polymer structure and the added aromaticity because it is added in large amounts.

Recently Iwakura and Izawa^{3/} reported that ureas and epoxy groups react to produce oxazolidones.



Thus the addition of MDA to an isocyanate prepolymer and an epoxy resin may produce a polymer which may react with the epoxy groups to yield a poly-3,5-disubstituted-2-oxazolidone. The latter polymer is probably a mixture of polyurea, epoxy-amine, and poly-2-oxazolidone.

The results in Table II for stainless steel indicate that pyridine also can act as a catalyst for copolymerization.

It was of interest in the latter part of this investigation to establish that the poly-2-oxazolidones are more stable than the polyurethanes and to show by differential thermal analysis (D.T.A.) that the polymer characteristics were different than a mixture of two homopolymers, i.e., epoxy and polyurethanes or poly-2-oxazolidones up to 400° C. In addition all the samples lost weight but did not char.

^{3/} J. Iwakura and S. Izawa, *J. Org. Chem.*, 29, 379 (1964).

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