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RESEARCH ON ELEVATED TEMPERATURE RESISTANT INORGANIC POLYMER ADHESIVES

HAROLD H. LEVINE

QUANTUM, INCORPORATED

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FOREWORD

This report was prepared by Quantum, Incorporated, Wallingford, Connecticut, under USAF Contract No. AF 33(616)-3824. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials," Task No. 73401, "Structural Adhesives". It was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. Floyd H. Bair acting as project engineer.

This report covers the period from August 1956 to August 1957.

ABSTRACT

Attempts to prepare heat stable materials for formulation with the ammeline-phosphorus pentoxide inorganic adhesive are described. The two approaches deemed as most promising were epoxysilicon and epoxy-s-triazine compounds.

The synthesis and preliminary evaluation of 2,4-bis(glycidyl)-6-methoxy-s-triazine is described. With certain formulations a tensile shear value of about 2100 psi was obtained from room temperature up to and including 400°F.

An unexpected degree of reactivity was found in 2,4-bis(glycidyl)-6-methoxy-s-triazine and materials such as diphenylsilanediol and commercial silicone polymers could be used as true curing agents.

The inorganic adhesive prepared from ammeline and phosphorus pentoxide cures the 2,4-bis(glycidyl)-6-methoxy-s-triazine. Further work is necessary on this particular system.

Synthesis of trimethylsilylpropylene oxide, as a model compound, was shown by infra-red analysis but could not be isolated.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

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

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I. Introduction

The purpose of this work is to investigate inorganic polymer systems which might function as metal-to-metal structural adhesives at temperatures up to 1000°F.

During the past two years, under AF 33(616)-2555, an investigation was carried out on new inorganic systems aimed at the preparation of a suitable adhesive.(9) A scanning program constituted the first year's work. This resulted in six promising reaction systems based on two criteria; thermal stability and reactivity. A description of this research was reported in WADC TR 55-271.

The second year's work examined these six systems by investigating the behavior of the reaction products under various parameters. The ammeline-phosphorus pentoxide reaction product was found to have adhesive properties which were increased from 65 lb/sq. in. to 285 lb/sq. in. by use of polar extraction solvents and titanium dioxide priming of the stainless steel. Furthermore, this inorganic system can withstand temperatures up to 900°F before decomposition results.(10)

To take full advantage of this inorganic material it is necessary to incorporate a thermally stable reactive medium that will convert the powdered adhesive into a liquid or semi-liquid system. Such chemical modification can result in improved adhesion by (1) reaction of the reactive medium with the inorganic adhesive, and (2) by reaction of the reactive medium with the substrate.

Epoxy compounds offer an excellent basis for chemical modification because they can react with the substrate or the adhesive system. However, new epoxy compounds are needed because known epoxy resins do not have sufficient thermal stability.

The work for this year's program is based upon this chemical approach. Studies on priming agents and fillers can result in marginal increases in adhesion. It is anticipated that chemical modification will result in a significant increase in adhesive strength.

II. Silicon Compounds

A. Discussion

It was decided to attempt the synthesis of (a) epoxy silanes and (b) epoxy s-triazine compounds.

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(a) Epoxy silanes can be approached by two methods, condensation of halosilanes with epichlorohydrin and epoxidation of unsaturated silanes.

$$Me_3SiCl + CH_2\!\!\diagdown\!\!\diagup\!\!O\!\!-\!\!CHCH_2Cl \xrightarrow{2Na} Me_3SiCH_2CH\!\!\diagdown\!\!\diagup\!\!O\!\!-\!\!CH_2 + 2NaCl$$

$$Me_3SiCH_2CH{:}CH_2 \xrightarrow{MeCO_3H} Me_3SiCH_2CH\!\!\diagdown\!\!\diagup\!\!O\!\!-\!\!CH_2 + MeCO_2H$$

The Wurtz synthesis has been carried out successfully on Me_3SiCl and $ClCH_2SiMe_2OEt$.[3]

Epoxidation of allyl silanes should proceed satisfactorily because of the relatively electropositive Si atom. It has been demonstrated that electronegative groups decrease the epoxidation reaction rate and can even inhibit it completely.[7]

Epoxidation of vinylsubstituted silanes presents another problem. The large size of the Si atom may prevent epoxidation because of steric factors despite the electropositive nature of the Si atom. The objective of this program is to obtain suitable, heat stable reactive media for incorporation into an adhesive system based on the ammeline-phosphorus pentoxide product. One proposed reactive medium is based on bis(epoxy)silanes such as $\overbrace{OCH_2CHCH_2}SiR_2CH_2\overbrace{CHCH_2}O$. Since such compounds are new, it is necessary to synthesize the monoepoxysilane, as a model compound, to gain familiarity with the reaction and the physical characteristics of such a compound. This is a double-pronged approach because a polymer from the bis(epoxy)silane may by itself function as a suitable thermally stable adhesive in which the ammeline-phosphorus pentoxide product could be added as a reactive filler.

(b) The s-triazine nucleus has been demonstrated to have excellent heat resistance. Attempts will be made to epoxidize unsaturated triazines such as triallylcyanurate. Another approach is by interaction of cyanuric chloride with glycidol.

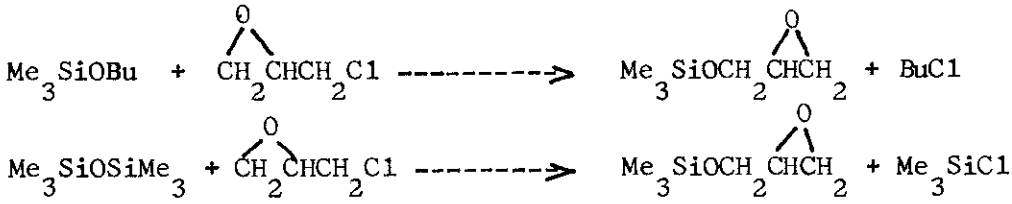
B. Experimental

All boiling points and melting points are uncorrected. All commercial silicon compounds were redistilled or recrystallized prior to use.

1. Preliminary Reactions

(a) Trimethylsiloxypropylene oxide $Me_3SiOCH_2\overline{CHCH_2O}$

The following reactions were based on the idea that the reaction of epichlorohydrin with a silane ether would result in elimination of an alkyl chloride.



A 100ml 3-neck flask fitted with a reflux condenser, dropping funnel and a glass helice packed column connected to a distillation condenser was charged with 16.2g (0.1 mole) hexamethyldisiloxane. The mixture was brought to reflux and 9.3g (0.1 mole) epichlorohydrin added during 20 minutes. By closing off the distillation condenser the mixture could be refluxed, and by closing the reflux condenser and opening the distillation condenser, distillation could be affected.

After 90 minutes reflux, distillation showed no material corresponding to chlorotrimethylsilane. The mixture was refluxed overnight. Distillation gave 10g of distillate b.p. 90-2°C/764mm, N_D^{20} 1.3900.

The distillate was completely soluble in cetane; hexamethyldisiloxane is soluble while epichlorohydrin is insoluble in cetane.

The distillation residue was transferred to a 20 ml flask and fractionated to give 4.0g of distillate b.p. 91-2°C, N_D^{20} 1.3902, 0.5g of intermediate, 2.0g of distillate b.p. 111-2°C, $N_D^{23.5}$ 1.4357 and a 1.0g residue.

The materials boiling at 90-2°C were combined and redistilled and collected at 90°C/764mm, N_D^{21} 1.3892. Sodium fusion indicated the presence of chlorine.

It appears that no reaction occurred and that two azeotropes were obtained. The first was rich in hexamethyldisiloxane and the second was rich in epichlorohydrin.

(b) $Me_3SiOBu + CH_2\overset{O}{\diagup\diagdown}CHCH_2Cl \longrightarrow Me_3SiOCH_2\overset{O}{\diagup\diagdown}CHCH_2 + BuCl$

A mixture consisting of 14.6g (0.1 mole) butoxytrimethylsilane and 9.3g (0.1 mole) epichlorohydrin were reacted as in the

previous example. Distillation through a semi-micro Vigreaux column gave a material boiling at 106-8°C/759 mm. A heart cut boiling at 108°C had a N_D^{20} 1.4120.

This reaction should give the same reaction product as the previous experiment. The distillates obtained had boiling points of 92°C and 108°C, respectively. It seems fairly certain that a reaction failed to take place and that azeotropes were obtained.

(c) Reaction (a) was repeated with the addition of 2.9g (0.1g-atom) of magnesium turnings added to the 16.2g (0.1 mole) of hexamethyldisiloxane. Slow addition of 9.2g (0.1 mole) of epichlorohydrin failed to show any signs of reaction on the surface of the magnesium. The mixture was refluxed overnight. Distillation yielded 14.5g of distillate b.p. 90-2°C/759mm, N_D^{20} 1.3901 (on a heart cut at 92°C). This is identical to the material obtained from this reaction without the use of magnesium.

The epichlorohydrin was used as taken from the bottle. Distillation of this compound, prior to use for a Wurtz reaction, disclosed the presence of moisture. This could prevent reaction with magnesium.

These reactions were not pursued further because Dr. C. Tamborski of the Polymers Section of Materials, Laboratory WADC, suggested that the Si-O-C bond would not be as hydrolytically stable as the Si-C bond. As a result of this information, emphasis was shifted to the synthesis of epoxy silanes.

2. Wurtz Reaction

(a) Trimethylsilylpropylene oxide $Me_3SiCH_2\overline{CHCH_2O}$

(1) The apparatus consisted of a 100ml flask fitted with an inner thermometer, dropping funnel, Tru-bore stirrer and reflux condenser protected by a drying tube. The flask was charged with 60 ml of dry toluene and 2.3g (0.1g-atom) of thin sodium slices. When reflux temperature was attained, vigorous stirring was started to produce small droplets of molten sodium. A mixture consisting of 10 ml toluene, 5.43g (0.05 mole) trimethylchlorosilane and 4.73g (0.05 mole) epichlorohydrin was added dropwise during 45 minutes. The reaction was instantaneous and exothermic and a temperature of 109-110°C could be maintained without external application of heat. No signs of the chlorosilane (b.p. 57°C) were seen by refluxing in the condenser. The mixture was refluxed an extra 15 minutes, allowed to stand until the solid separated to give a yellow supernatant liquid.

The purple solid was collected on a sintered glass funnel and washed with toluene which was added to the filtrate. Washing with

chloroform formed a yellow solid which became white on air drying and weighing 4.8g. This solid was completely soluble in water except for 0.1g of brown solid and the solution had a pH of about 6, indicating that this was sodium chloride.

Fractional distillation at 758mm gave no trimethylchlorosilane.

Fraction (1)	b.p. 104°C	N_D^{20}	1.4772
(2)	b.p. 106-8°C	N_D^{20}	1.4995
(3)	residue		4.3g

The possible compounds obtainable from this reaction mixture were toluene b.p. 110°C, N_D^{24} 1.4893; epichlorohydrin b.p. 116°C, N_D^{16} 1.4397; hexamethyldisilane (not very likely) b.p. 113°C and diepoxyhexane b.p. 86-8°C/18mm, N_D^{15} 1.4445.

Using toluene was a poor choice because its boiling point is too close to epichlorohydrin, hexamethyldisilane and possibly the desired product to permit separation in the available column. Another possible reason for the poor materials balance is azeotrope formation.

Redistillation of fractions (1) and (2) through a semi-micro column packed with glass helices and a variable reflux-ratio take-off head failed to show any low boiling materials. The residue was carefully distilled to give:

Fraction (1)	b.p. 48°C/85mm	N_D^{19}	1.4950	Weight 3.5g
(2)	taken over by lowering the pressure	$N_D^{18.5}$	1.4948	
(3)	residue			Weight 0.8g

Nothing could be found having any definite signs of a different material. The reaction had to be re-run using a higher boiling solvent.

(2) The above reaction was repeated, using anhydrous xylene. Addition of the reagents required 40 minutes during which time the temperature was kept 115-20°C. The exothermic reaction gave a dark brown precipitate. Filtration of the mixture was very slow and gave a brown-purple solid and a pale yellow filtrate. The solid was slurried with fresh xylene, filtered and the washings added to the main filtrate. After slurrying the solid with ether and filtering, the solid was dried at 60°C for 6 hours at 2mm to give 5.6g of brown material. Burning on a spatula indicated organic material. Incomplete solution in water resulted (pH of 8), leaving a yellow, translucent precipitate that weighed 1.0g after drying. Ignition did not leave a white residue indicating silicon. This could be a polymer formed from condensation of epichlorohydrin.

Fractional distillation through a vacuum jacket column, packed with glass helices and a variable reflux ratio take-off head, gave the following fractions at 762mm:

Fraction (1)	b.p. room temperature - 96-99°C	1.6g	N_D^{21}	1.3943
(2)	b.p. 99-102°C	0.9g	N_D^{21}	1.4034
(3)	b.p. 102-116°C	0.3g		
(4)	b.p. 116°C	0.2g	N_D^{21}	1.4410

The above fractions were recombined and distilled from a 10 ml flask to give:

Fraction (1)	b.p. up to 96°C	N_D^{20}	1.3954
(2)	b.p. 96-98°C	N_D^{20}	1.3968
(3)	b.p. 98°C	N_D^{20}	1.3982
(4)	b.p. 98°C	N_D^{20}	1.3996
(5)	residue		

Fraction (4) gave a positive test for chlorine after sodium fusion. No definite product was found. However, it seems that a slight excess of sodium should be used in subsequent reactions.

(3) The following was a repeat run of the above reaction except that excess sodium was used and the entire reaction was run in an atmosphere of nitrogen.

A 1 liter 3-neck flask was fitted with a Claisen adapter in each of the two side arms, a mercury-sealed stirrer, inner thermometer, pressure-equalized dropping funnel, reflux condenser, and gas inlet tube which in turn was connected to a trap and a bubbler containing sulfuric acid. The system was purged with nitrogen for 1 hour and charged with 250 ml of anhydrous xylene and 13.0g (0.564g-atom) of sodium. With a slow stream of gas entering, the solvent was heated to 110°C and vigorous stirring was begun to form small droplets of molten sodium. A mixture was prepared containing 50 ml of xylene, 27.15g (0.25 mole) trimethylchlorosilane, and 23.63g (0.25 mole) of epichlorohydrin (redistilled and kept over "Drierite" for 48 hours). This mixture was added dropwise to the stirred suspension at such a rate as to maintain a temperature of 110-20°C. Because of the highly exothermic reaction, addition required 90 minutes. After the addition was completed, a heating mantle was used to keep the mixture at 115°C for almost 2 hours. The mixture was cooled to 90°C to allow the excess sodium to freeze, and the stirrer was shut off.

The reaction mixture was cooled and the apparatus modified to permit distillation in a nitrogen atmosphere. A total of 10.5g of distillate, boiling at 74-103°C/773mm, was obtained and refractionated through a Vigreaux column and a variable reflux ratio take-off head. This gave:

Fraction (1)	b.p. 97.5-9.0°C	N_D^{20}	1.3870	
(2)	b.p. 99-100°C	N_D^{20}	1.3864)	
			)	3.5g
(3)	b.p. 100-2°C	N_D^{20}	1.3864)	
(4)	residue			

The slurry, containing excess sodium, the brown solid, and xylene, was diluted with ethanol to remove the sodium. This was washed with water to remove the NaOEt. Acidification of the water washing gave a small amount of sticky solid. Distillation of the organic layer gave only xylene and 5 drops of liquid, b.p. 50-2°C/1mm, N_D^{20} 1.4730.

Fractions (2) and (3) were combined and sodium fusion gave a negative test for chlorine. Three drops of this material were placed on a watch glass and ignited. Very vigorous burning occurred with a bright yellow, sooty flame and left a white residue (silica?).

Calculated for $Me_3SiCH_2\overbrace{CHCH_2O}$, $C_6H_{14}OSi$: C 55.45%, H 10.76%, Si 21.56%. Found: C 50.80%, H 11.76%, Si 26.95%. This corresponds to an empirical formula of $C_{6.4}H_{17.7}Si_{1.45}O$, indicating a mixture containing a material richer in silicon.

In all these experiments considerable darkening in color occurred. It was assumed to be caused by the elevated temperature of the reaction and as a likely cause for the poor yields. The following reaction was carried out in refluxing ether to modify the severity.

(4) A 1 liter 3-neck flask was equipped with a sealed stirrer, nitrogen inlet, and reflux condenser protected by a drying tube, and charged with 13.0g (0.564g-atom) sodium and 250 ml of anhydrous toluene. The system was purged with nitrogen for 30 minutes. When the solvent was vigorously refluxing, vigorous stirring was maintained for 15 minutes. The contents of the flask were allowed to cool, with vigorous stirring, to 75°C so that a coarse sodium sand was obtained. The solvent was removed by a siphon and the sodium washed twice with anhydrous ether. Finally, 250 ml of anhydrous ether was added and the apparatus modified so that a pressure-equalizing dropping funnel could be used. A mixture consisting of 0.25 mole each of trimethylchlorosilane and epichlorohydrin in 50 ml of ether was added dropwise during 1 hour. An immediate

reaction occurred as shown by the formation of a white precipitate and the refluxing of the solvent. A dry-ice condenser was added to the top of the reflux condenser to prevent any material loss. During the reaction no dark purple-brown color or chocolate brown precipitate was formed. The mixture was stirred and refluxed an additional 2 1/2 hours. The heat was shut off at this time because a tan color was developing. After cooling, the mixture was filtered to give a colorless filtrate.

The ether was stripped off through a Vigreaux column until a pot temperature of 80°C was reached. The residue was transferred to a semi-micro distillation set up containing a Vigreaux modified Claisen head. Distillation gave:

Fraction (1)	b.p. 34.5-35.0°C		
(2)	b.p. 35-94°C	0.5g	
(3)	b.p. 94-6°C	1.6g	
(4)	b.p. 96-100°C	23.4g	

Fraction (4) represents a 73% yield based on the desired trimethylsilyl propylene oxide. A heart cut taken at 100°C had N_D^{20} 1.3980.

Fractions (3) and (4) were combined and fractionated through a vacuum jacketed semi-micro column packed with glass helices and a variable reflux ratio take-off head. This gave:

Fraction	pot temp.	b.p.	wt.	N_D^{20}	reflux ratio
A	102°C	to 96°C	0.3g	1.3940	
B	102.0-2.5°C	96-8°C	1.7g	1.3968	20: 1
C	102.5-3.0°C	98.0-8.5°C	2.1g	1.3970	20: 1
D	103°C	98.5-9.0°C	2.0g	1.3970	10: 1
E	103°C	99.0-9.2°C	6.9g	1.3971	10: 1
F	103-5°C	99.2-9.0°C	5.1g	1.3971	10: 1

Fraction E was used for analytical purposes; d_{20}^{20} 0.8086, M_D = 39.84 (calculated = 38.49).

The calculated value differs too much from the value obtained by the Lorentz and Lorenz formula.

A 3 gram sample of the reaction product was refluxed for 45 minutes with 50 ml of the oxirane reagent and the products distilled directly from the mixture. The distillate was washed 3 times with water in a 10 ml separatory funnel, dried over calcium chloride and fractionally distilled. This gave 2 products:

(1) b.p. 44-6°C N_D^{19} 1.4146

(2) b.p. 97-8°C N_D^{19} 1.3802 major product

Fraction (1) corresponds to allyl chloride b.p. 44-5°C, N_D^{20} 1.4154.

Fraction (2) corresponds to hexamethyldisiloxane b.p. 99°C, N_D^{20} 1.3788.

These reaction products came, most probably, from allyloxytrimethylsilane, $Me_3SiOCH_2CH{:}CH_2$ which is isomeric with the desired epoxysilane. The allyloxy compound has a calculated M_D of 38.84.

$$Me_3SiOCH_2CH{:}CH_2 \xrightarrow{HCl,H_2O} (Me_3SiOH) + CH_2{:}CHCH_2Cl$$

$$(Me_3SiOH) \rightarrow Me_3SiOSiMe_3 + H_2O$$

The formation of allyloxytrimethylsilane was predicted by Dr. H. H. Wasserman in a private communication on the basis of unpublished work involving the reaction of Zn with bromomethylstyrene oxide.

$$PhCH\underset{\diagdown O \diagup}{CH}CH_2Br + Zn \longrightarrow PhCH(OH)CH{:}CH_2$$

Oxirane content

Analyses were run according to the method of Kerchov[4] as described by Siggia.[6]

The oxirane reagent was prepared by adding 95 ml of concentrated hydrochloric acid to a solution of 810g calcium chloride dihydrate in 600 ml of water.

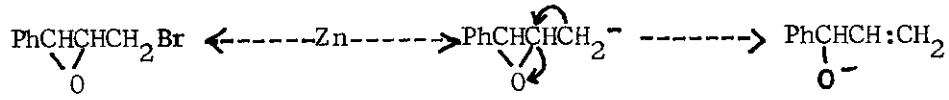
	Blank	No. 1	No. 2
Sample	--	1.753g	2.210g
ml reagent	50.00	50.00	50.00
ml N NaOH	55.10	53.50	53.10
% $Me_3SiCH_2\overline{CHCH_2O}$		11.9	11.8

To check this method an analysis of epichlorohydrin was made. A sample weighing 2.289g required 30.20 ml of N NaOH for a value of 98.0% purity.

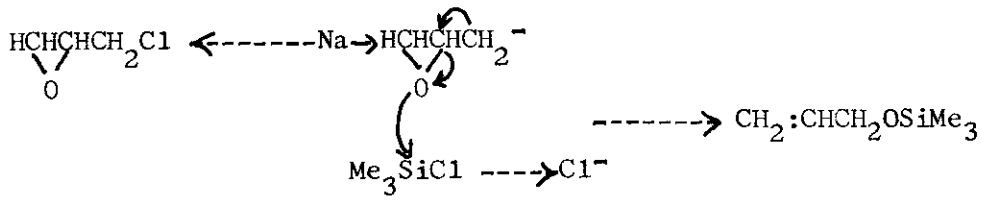
The above data indicate that the product was a mixture. This was substantiated by infrared analyses. Figure IV is a spectrum of the reaction product. The peak at 10.83μ corresponds exactly to the peak found in epichlorohydrin. The epoxy group has been placed at 10.92μ.(2) This indicates that the mixture contained some of the desired product. Peaks at 7.0-7.1μ and at 7.9-8.0μ are due to C-H stretch of Si-CH_3 and methyl rocking of Si-CH_3. These could be from the epoxy compound and/or the contaiminants.

Two very broad peaks at 9.15-9.7μ and at 11.35-12.05μ are due to Si-O stretch and Si-C stretch of Me_3SiO, respectively, which are found at 9.5μ and 11.88μ.(1) The reaction product also shows a peak at 6.03μ that is characteristic of the allyl group which has been assigned to 6.02-6.11μ.(5)

The tentatively assigned mechanism is:



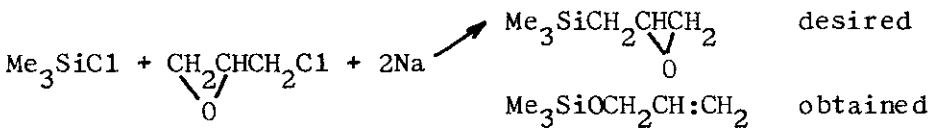
Thus, in an analagous manner,



It would seem that at least one more compound is present. Since the allyloxysilane and epoxysilane are isomeric, the high silicon and low carbon analyses bear this out. This could be from a compound containing a Si-Si linkage. A peak at 14.5μ could be due to this linkage, although it has been shown that Me_3SiCl does not undergo a Wurtz reaction with sodium. The spectrum of $Me_3SiSiMe_3$ contains a peak at 14.5μ.(1)

3. Zinc as the Condensing Agent

Attempts to prepare epoxysilanes by interaction of a halosilane with epichlorohydrin, via a Wurtz reaction, gave an isomer of the desired product.



This reaction in the presence of sodium yielded allyloxytrimethylsilane instead of the desired trimethylsilylpropylene oxide. The postulated mechanism proposes attack by sodium on epichlorohydrin. It was decided to replace the sodium by less vigorous metals, zinc and magnesium.

Therefore, the use of sodium was abandoned but repeated with zinc and magnesium.

Another possible route would be interaction of glycidol with a halosilane to give a siloxy epoxy compound.

$$Me_3SiCl + HOCH_2\underset{O}{\overset{\diagup\!\diagdown}{CH}}CH_2 \xrightarrow{Et_3N} Me_3SiOCH_2\underset{O}{\overset{\diagup\!\diagdown}{CH}}CH_2 + Et_3N\cdot HCl$$

However, the hydrolytic instability of the Si-O-C bond at elevated temperatures does cast some doubt on this approach.

A 500 ml 3-neck flask was fitted with a mercury sealed stirrer, a nitrogen inlet connected to the cylinder via a sulfuric acid bubbler and trap, a dropping funnel and a reflux condenser which in turn was connected to a dry ice trap whose opening was protected by a drying tube.

The flask was flushed with nitrogen and flamed dry. Nitrogen was admitted during the entire reaction period. After cooling, the flask was charged with 100 ml anhydrous ether and 16.35g (0.25g-atom) of zinc dust. With good stirring a solution consisting of 35 ml ether, 27.15g (0.25 mole) chlorotrimethylsilane and 23.6g (0.25 mole) epichlorohydrin was added during 1.5 hours. No exothermic reaction occurred. The mixture was stirred and refluxed for 6.5 hours. After cooling, the reaction mixture was filtered and the colorless filtrate was distilled through a 3-foot packed column to remove the ether. The pale straw colored residue, with a pungent camphoraceous odor, was transferred to a semi-micro distillation apparatus equipped with a variable reflux take-off head. No distillate was obtained up to a pot temperature of 125°C. The reaction with sodium gave a product boiling at 98°C.

The product was distilled in vacuo.

Fraction	pot temp.	b.p.	pressure	yield	N_D^{22}
1	90°-2°C	37°C	34mm	0.08g	-
2	92°-3°C	37-86°C	34mm	0.5g	-
3	93°C	86-91-92°C	34mm	43.53g	1.4426

Fraction 3 corresponded closely to the b.p. and refractive idex of diepoxyhexane. However, the yield was greatly in excess of the theoretical yield, 28.5g. The theoretical yield of the desired product was 32.5g. Therefore, the product must have a higher molecular weight and the only possibility available is either a complex with ether or a substance containing chlorine. Sodium fusion gave a strong test for chlorine.

Fraction 3 was redistilled with severe foaming.

Fraction	pot temp.	b.p.	pressure	yield	N_D^{20}
1	78°C	to 75°C	18mm	2.29g	1.4469
2	78-9°C	75-7°C	18mm	3.27g	1.4460
3	79°C	77-77.5°C	18mm	3.83g	1.4449
4	79-79.5°C	77.5-78.0°C	18mm	5.96g	1.4443
5	79.5°C	78°C	18mm	22.33g	1.4429
6	residue	-	-	2.32g	1.4412
				40.00g	

Fraction 5 was taken for analysis; d_{20}^{20} = 1.072 and oxirane titration showed that no epoxy compound was present.

From the refractive indices of the fractions it would seem that the product consisted of several materials. Fractions 4 and 5 appear to be identical.

The reaction product is completely different from that obtained, using the same reactants but substituting zinc for sodium.

	N_d^{20}	b.p.	d_{20}^{20}
Sodium product	1.3970	99-99.2°C	0.8086
Zinc product	1.4429	78°C/18mm	1.072

To elucidate the structure, 16.0g of the reaction product was refluxed for 4 hours with 40 ml of oxirane reagent. After cooling the mixture was poured into a separatory funnel and formed 3 layers. The lowest layer was discarded. The middle layer (A) weighed 9.3g and the upper layer (B) weighed 5.5g. Redistillation of (B) gave hexamethyldisiloxane b.p. 97°C, N_D^{20} 1.3785. Redistillation of (A)

gave a viscous oil b.p. 73°C/17mm, N_D^{20} 1.4836, d^{20} 1.359. This corresponds closely to 1,3-dichloro-2-propanol b.p. 69-75°C/12mm, N_D^{20} 1.4837, d_4^{25} 1.359. Thus, it is possible that the reaction product was:

$$ClCH_2CHCH_2Cl$$
$$\quad\quad|$$
$$\quad OSiMe_3$$

4. Magnesium as the Condensing Agent

The apparatus was identical to that used in the previously described experiment. In place of zinc, 12.16g (0.5g-atom) of Grignard grade magnesium was used.

No signs of reaction were noticed either exothermically or by etching of the magnesium. The mixture was stirred and refluxed for an additional 2.5 hours.

Distillation of the filtrate gave a mixture consisting of ether and chlorotrimethylsilane followed by pure chlorotrimethylsilane b.p. 54°C up to a pot temperature of 110°C. The residue was transferred to a semi-micro distillation apparatus and fractionated.

Fraction	pot temp.	b.p.	yield	N_D^{20}
1	40-70°C	36°C/28mm) 26-8°C/18mm)	5.5g	-
2	40-86°C	28-73°C/18mm	0.3g	-
3	86-88°C	73-6°C/18mm	1.5g	
4	88-100°C	76-80°C/18mm	18.5g	1.4431

Fraction 4 is identical to the product obtained in the experiment using Zn dust. The lower yield could be due to the decreased reflux time and/or the much smaller surface area of the magnesium as compared to zinc dust.

These reactions give entirely different products than those desired and do not merit further work for the contract. Nevertheless, the reactions are extremely interesting chemically.

5. Epoxidation of Allyltrimethylsilane

Still another approach is direct epoxidation of an allylsilane with a per-acid. Since silicon is electropositive, epoxidation should be possible because of a greater electron density at the double bond.

Further, with the allyl group, the bulky silicon atom should not sterically impede the reaction as it might do with a vinyl group. This was a trial run to determine the feasibility of this approach to an epoxy silane.

A 50 ml 3-neck flask was equipped with a stirrer, dropping funnel and inner thermometer and charged with 19.0g (0.1 mole) of 40% peracetic acid. To this was added, dropwise, 11.4g (0.1 mole) of redistilled allyltrimethylsilane. The exothermic reaction was controlled at 15-20°C by the addition rate and cooling in an ice bath. Addition of the silane required 45 minutes. The system was heterogeneous and this could be the cause for the reaction evolving heat for an additional 2.5 hours. When the exothermic reaction stopped, the mixture was vigorously stirred and warmed for an extra 2 hours at 32-3°C.

After cooling to room temperature, the product was poured into a separatory funnel and the upper oil layer retained, washed thrice with small portions of cold water and distilled.

Fraction	pot temp.	b.p.	P	yield	N_D^{22}
1	114-25°C	24-26-60°C	761mm	0.6g	-
2	125-30°C	60°C	761mm	0.5	1.3930
3	56-80°C	24-8°C	37	0.7	1.3846
4	52-68°C	35-8°C	6.4	1.1	1.3850
5	68-90°C	38-66°C	6.4	1.3	1.3893

Cuts 3 and 4 were combined and submitted for infra-red analysis along with cut 5. The results showed that these 3 cuts were virtually identical. Extremely broad peaks in the Si-O region of the spectra indicated a silicone polymer of some sort. This approach was dropped and emphasis placed on the synthesis of epoxytriazine compounds.

III. s-Triazine Compounds

A. Discussion

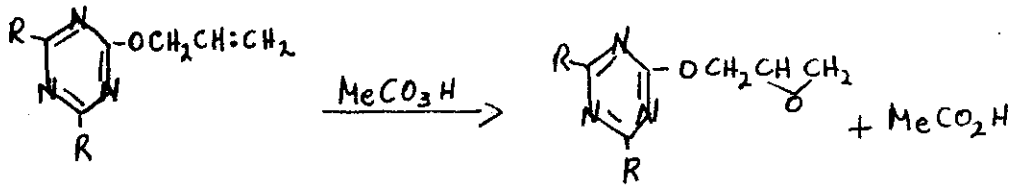
Another type of epoxy compound that seemed desirable is a s-triazine compound. Such an approach is of interest because of:

1. The heat stability of the s-triazine ring system.
2. The greater electronegativity of the ring nitrogen atom should increase reactivity of the oxirane group.

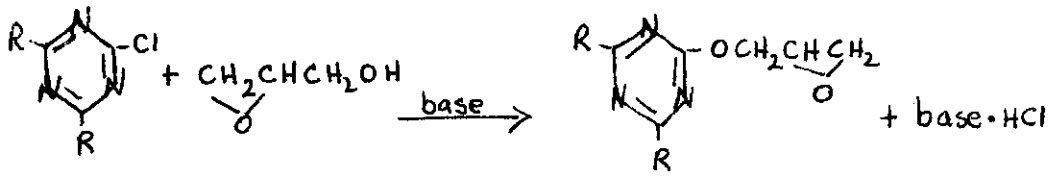
3. The higher percentage of oxirane content as compared to bis-phenol A derived epoxies.

Two ways are available for synthesis of epoxy s-triazines.

1. Epoxidation of unsaturated s-triazine compounds.



2. Interaction of chlorotriazines with glycidol.



Initially the synthesis of a monoepoxide will be carried out as a model preparation, then the difunctional epoxy compound will be prepared and evaluated.

B. Experimental

1. Preliminary Syntheses

(a) A 500 ml 3-neck flask was equipped with a sealed stirrer, dropping funnel, inner thermometer and reflux condenser protected by a drying tube. The flask was charged with 18.5g (0.1 mole) of cyanuric chloride dissolved in 100 ml of acetone and 75 ml of dioxane. With stirring and cooling, 19.8g (0.25 mole) of pyridine was added. A strong exothermic reaction occurred to give a red-brown ppt. while the temperature was kept at 20-2°C. When the addition was completed, a solution containing 14.8g (0.2 mole) of glycidol dissolved in 20 ml of acetone was added at such a rate as to keep the exothermic reaction at 25°C.

The reaction mixture was filtered to give a tan solid and a blood red filtrate. The solid was washed with cold water (slightly soluble) and dried in the oven at 82-5°C. However, the solid decomposed to a carbonaceous mass. Such behavior does not augur well for the program.

Further, the presence of highly reactive chlorine atoms should be avoided. It was also learned that pyridine can react with cyanuric chloride despite the fact it is a tertiary amine. Because of this, it will be necessary to use another tertiary amine such as triethylamine in all future work with chlorotriazines.

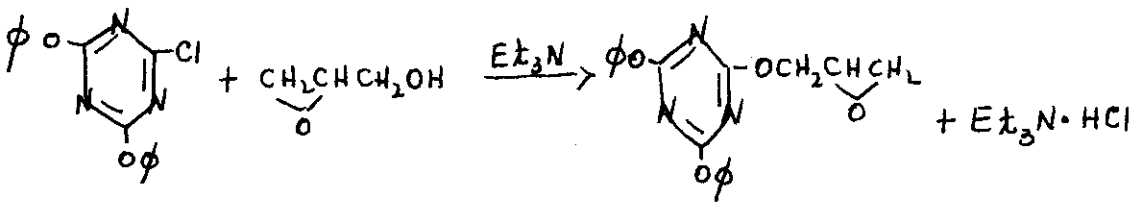
(b) The above reaction was made with the trifunctional cyanuric chloride. This run was made with the difunctional triazine.

A 500 ml 3-neck flask was fitted with a stirrer, inner thermometer and dropping funnel. This was charged with 13.8g (77 m moles) methoxy-dichloro-s-triazine dissolved in 200 ml of dry dioxane. To this was added 24.2g (240 m moles) triethylamine in 50 ml of dioxane during 15 minutes so as to keep the temperature at 10-15°C. This gave a pale yellow precipitate. A solution containing 17.8g (240 m moles) of glycidol in 25 ml of dioxane was added dropwise at 10°C. After 4-5 ml had been added, the mixture became very doughy and caused the stirrer to stop. The cooling bath was removed and after remaining at room temperature for about 3 hours, stirring became possible. The remaining glycidol was then added and the mixture stirred 3 hours longer at room temperature.

The mixture was filtered to give an extremely water soluble solid. This solution was treated with Nuchar, filtered and left standing. After about 2 weeks small needles appeared and crystallization was proceeding very slowly.

The dioxane filtrate was distilled at reduced pressure until about 50 ml remained. This residue was poured into water and yielded a slight amount of an oily liquid. This was taken up in Et_2O and evaporated to leave a viscous oil. After standing 2 weeks some crystallization started. After 5 weeks about half of the oil had solidified.

2. 2-glycidyl-4,6-diphenoxy-s-triazine



The use of a monochlorotriazine should give a monoepoxy compound that would be easier to identify and would serve as the model reaction for the preparation of polymers.

A 100 ml 3-neck flask was fitted with a sealed stirrer, dropping funnel and reflux condenser. The flask was charged with 13.0g (43.4 m moles) of chlorodiphenoxy-s-triazine and 35 ml of dioxane. To this was added dropwise 4.38g (43.4 m moles) of triethylamine in 10 ml of dioxane. An exothermic reaction occurred and formed a thick slurry of what probably is the triethylamine salt. The mixture was cooled to room temperature and 3.56g (48.1 m moles) of glycidol was added during 5 minutes. The precipitate suddenly dissolved at the end of the addition to give an almost clear solution. In about 1-2 minutes a new precipitate formed during the slightly exothermic reaction that set in. After stirring an extra hour, the reaction mixture was filtered, sucked dry, washed with a small amount of fresh dioxane and dried in an oven to give 7.0g of a white solid. A portion was re-crystallized from acetone, m.p. 237.5-238.0°C, (459-460°F). Samples of the reaction product and starting material were submitted for infra-red analysis and the reaction product alone for elemental analysis.

Calculated for $C_{18}H_{15}N_3O_4$:C=64.09;H=4.48;N=12.46;0=18.97 (difference)

Found :C=66.67;H=6.40;N=11.50;0=15.43 (difference)

Analysis indicated an empirical structure of $C_7H_8NO_{1.17}$. For N atoms in the ring, the formula would then be $C_{21}H_{24}N_3O_{3.5}$. This is by 3 x CH_3 or C_3H_9. The sharp melting point would indicate a pure meterial but it is possible to have a eutectic mixture.

Infra-red analysis was made as a mull in Nujol. The following were observed:

1. It seems almost certain that the product contains an epoxy group because of the 2 characteristic absorption peaks at 8.28μ and 10.93μ .

2. Characteristic peaks for the s-triazine nucleus appear at 6.35μ, 7.25μ and 13.10μ . The appearance of a strong peak at 13.64μ may be due to the isotriazine structure but this is not certain.

3. The aromatic C-H peak was found at 3.30μ.

4. Peaks at 5.15μ, 5.34μ, 5.58μ and 5.75μ indicate the presence of monosubstituted phenyl groups.

5. New peaks at 3.86μ, and 4.03μ cannot be interpreted as yet other than a possibility of a salt type material such as a hydrochloride.

6. Disappearance of peaks at 7.75 μ, 7.99 μ and 10.53 μ are also unexplainable.

7. The presence of phenyl groups in the starting and final materials has caused considerable difficulty in the interpretation. It is necessary to repeat the reaction with dimethoxychloro-s-triazine.

3. 2,4-bis(glycidyl)-6-methoxy-s-triazine

A 300 ml 3-neck flask was equipped with a sealed stirrer, inner thermometer and dropping funnel. To the flask was added 100 ml of chloroform, 18.0g (0.1 mole) of dichloromethoxy-s-triazine and 22.9g (0.309 mole) glycidol. The mixture was stirred and cooled to 3°C. A solution of 8.4g (0.21 mole) of sodium hydroxide in 11 ml of water was added dropwise during 50 minutes. The temperature was kept below 10°C by use of an ice-salt bath because of the very exothermic reaction. After completing the addition, the mixture was stirred an extra hour and 100 ml of water was added. After stirring a short time, the mixture was filtered. The colorless organic layer was washed with four 50 ml portions of water and filtered.

Most of the chloroform was removed on a steam bath and the residue slowly heated to 120°C at 1mm pressure. This gave a colorless, slightly opalescent, viscous residue weighing 22.5g (87.8% yield).

Oxirane analysis: To 100 ml of purified dioxane was added 1.5 ml of concentrated hydrochloric acid and the mixture swirled gently for 10 minutes. This, 20 ml, was added to 0.1000-0.2000g of product, swirled until dissolved and allowed to stand 10 minutes. A blank was run simultaneously. Neutralized isopropanol, 20 ml, was added and the solutions titrated with 0.1N sodium hydroxide to a phenolphthalein end point.

$$\frac{\text{Blank-titration x N x equivalent weight x 100}}{\text{sample x 1000}} = \% \text{ oxirane}$$

The dioxane was purified by standing three days over potassium hydroxide pellets and distilling through a short column.

By the above method the product was found to have a purity of 82.2%.

Elemental analysis: Calculated for $C_{10}H_{13}N_3O_5$, molecular weight 255; C = 47.0%; H = 5.1%; N = 16.5%. Found molecular weight 230 (ebullioscopic in butanone) C = 30.8%; H = 4.2%; N = 13.1%. The elemental analyses were extremely poor and the molecular weight agreed fairly well. This suggested the possibility of impurities with about the same molecular weight but with very different elemental composition.

Infra-red analysis showed a strong peak for epoxide but also peaks in the region assigned to ionized carboxyl groups. These could result for partial reaction of the dichloromethoxytriazine with water to give a salt of the cyanuric acid species. The methoxy group remained untouched. The presence of contaminants containing one or two ONa groups in place of the $OCH_2\overbrace{CH_2CH_2}O$ would cause a slight decrease in molecular weight but a significant decrease in C value. The other possible contaminant could be chlorine containing materials as represented by unreacted or partially reacted dichloromethoxytriazine. A chlorine analysis showed 7.2% chlorine.

Since this product was a new epoxy material, testing was initiated to determine its value as an adhesive. This was done despite the presence of chlorine. It has been shown that chlorine has a detrimental influence upon the desirable properties of epoxy resins.

Simultaneously with the evaluation program, attempts were made to prepare a purer bis(glycidyl)methoxy-s-triazine. The use of purified starting materials was tried first.

Glycidol (Caribou Chemical Company) was fractionally distilled through a 400 x 12mm vacuum jacketed column packed with Podbielniak random packing. After a slight forerun, containing some water, the product was collected at 46-7°C/5mm.

The 2,4-dichloro-6-methoxy-s-triazine was recrystallized from n-heptane and dried in a vacuum oven over paraffin flakes and concentrated sulfuric acid. m.p. 90.0-90.2°C.

The reaction was repeated under identical conditions to give essentially the same yield of reaction product. Oxirane analysis indicated a purity of 88.0%. Based on $C_{10}H_{13}N_3O_5$; C = 47.0%; H = 5.1%; N = 16.5%. Found C = 44.6%; H = 4.5%; N = 16.5% but chlorine was still present.

a. Curing Agents

The first step in evaluating the bis(glycidyl)methoxy triazine was to find curing agents. The extreme reactivity of this compound was indicated in the very first test. Piperidine, 6 PHR (parts per hundred parts), was added to the bis(glycicyl)methoxy triazine. An immediate, violent reaction occurred and the exotherm was so great, for a 10g sample, that the end of the wooden splint, used to stir the mixture, was completely burned off. Dicyandiamide was found to bring about a cure at temperatures that would result in no curing of commercial epoxide resins.

Because of this reactivity, semi-inorganic and inorganic materials were tried as curing agents. The remarkable reactivity of

the bis(glycidyl)methoxy triazine permitted curing with such weakly acidic compounds as diphenylsilanediol and cyanuric acid.

(1) Usual Curing Agents

Curing Agent	Concentration	Epon 828	bis(glycidyl)methoxy triazine
piperidine	6 PHR	180 mins./176°F	immediate, violent @ RT
dicyandiamide	6 PHR	30 mins./329°F	16 hrs./140°F(1)(2)
DDS(3)	30 PHR	5 hrs./260°F 1 hr./390°F(4)	2 1/2 hrs./140°F
PMDA(5)	30 PHR	2 hrs./150°F	30 mins./RT

(1) Dicyandiamide will not cure commercial epoxy resins at this temperature.

(2) Not completely soluble and settles out.

(3) Diaminodiphenyl sulfone (Merck & Co.).

(4) This includes addition of an accelerator, 1% of boron trifluoride-triethylamine complex. Time is the pot life.

(5) Pyromelliticdianhydride (E. I. duPont de Nemours & Co.)

(2) Unusual Curing Agents

The following compounds are called unusual curing agents because they have not been used to cure the commercial epoxy resins such as the Epons and Araldites.

Curing Agent	Concentration	Epon 828	bis(glycidyl)methoxy triazine
diphenylsilanediol	17 PHR	No cure	16 hrs./140°F or 30 mins./190°F(1)
tetraisopropylorthotitanate	20 PHR	-	violent after 1 hr./140°F
cyanuric acid	10 PHR	-	weekend/140°F(2)
dimethylhydrogen phosphite	10 PHR	-	16 hrs./140°F
ammeline-P_2O_5 product	100 PHR	-	16 hrs./140°F then 2 hrs./300°F
Dow-Corning 2106	-	-	16 hrs./140°F

(1) On the heating block, the polymer began to soften at 520°F, began to darken slightly at 545-550°F and was incompletely softened with no bubbling at 575°F.

(2) Not examined over the weekend. Polymerization probably occurred before examination.

b. Tensile Tests

(1) Preliminary Tensile Shear Tests at Room Temperature

Curing Agent	Concentration	Curing Time and Temp.	Filler	Support	Average Shear
diphenylsilanediol[7]	17 PHR	2 hrs./190°F	-	-	500 lb/sq.in.
"	17 PHR	16 hrs./190°F	-	-	884 lb/sq.in.
"	6 PHR	2 hrs./190°F	-	-	uncured
"	6 PHR	16 hrs./190°F	-	-	780 lb/sq.in.
diphenylsilanediol	17 PHR	16 hrs./190°F	Zn dust[3]	-	553 lb/sq.in.
"	17 PHR	2 hrs./190°F	-	Fiber-glass[3]	1000 lb/sq.in.
"	17 PHR	16 hrs./190°F	-	"	1150 lb/sq.in.
"	17 PHR	16 hrs./300°F	Al[4]	-	1170 lb/sq.in.[5]
ammeline-P_2O_5 product	100 PHR	16 hrs./300°F	-	-	450 lb/sq.in.[6]
dicyandiamide	6 PHR	16 hrs./190°F	-	-	193 lb/sq.in.[1]

(1) Dicyandiamide was not completely soluble. Crystals remained dispersed throughout and served to weaken bond.

(2) Used 100 PHR of bisepoxytriazine.

(3) 120 Fiberglass cloth with Volan A treatment.

(4) Metals Disintegrating Co. Al powder MD 201 (Grease-Free), 100 PHR of bis(glycidyl)methoxy triazine.

(5) Examination of the lap joints after pulling indicated a starved bond. During the heating, before curing set in, the viscosity decreased and much of the bis(glycidyl)methoxy triazine flowed out of the joint. It was decided to use a pre-cured system.

(6) The ammeline-P_2O_5 product could not be ground down to a very fine particle size with a mortar and pestle. This caused premature rupture and was evident from examination of the lap joint. The solid product was then placed in a micro ball mill and tumbled for varying periods up to 48 hours. There was breakdown to a finer particle size

but this was still too coarse. On continued grinding the finer particles agglomerated into small, hard balls and were useless for formulation.

Some improved technique is required to reduce the ammeline-phosphorus pentoxide adhesive to a fine powder. One method that was not tried, because of lack of time, was to pulverize the solid in liquid nitrogen.

(7) Pot life over about 2 weeks at room temperature.

(2) Pre-curing Tests

Curing Agent	Concentration	Temperature	Remarks
Pyromelliticdianhydride (PMDA)	5 PHR	115°F	Thickening after 45 mins.
"	10 PHR	115°F	Extremely viscous after 15 mins.
diphenylsilanediol	5 PHR	115°F	Very slow
"	10 PHR	115°F	Very slow
diaminodiphenyl sulfone (DDS)	5 PHR	115°F	Very tacky after 4 hrs.
"	10 PHR	115°F	almost solid after 4 hrs.

(3) Tensile Shear Tests at Room Temperature

These tests were made on pre-cured adhesive systems so that starved joints would not result. By this approach a large increase in tensile shear values was found. Thus the diphenylsilanediol-bis(glycidyl)-methoxy triazine system cured at 190°F for 2 hours gave an average value of 500 psi. Under identical conditions but using the above system in a pre-cured stage gave an average value of 1380 psi.

Based on the pre-cure tests, the use of PMDA was examined because the adhesive made with diphenylsilanediol was too brittle. The highest average tensile shear value, 2115 psi, was obtained with this system when used with Al powder as a filler and Volan A treated fiberglass cloth.

Two most encouraging results were found in these tensile shear values on systems using PMDA as curing agent:

(1) Very good reproducibility was obtained in any set of tests to determine the average shear value.

(2) All the breaks were completely adhesive. The phrase "completely adhesive" requires some comment at this point. Definitions for adhesive and cohesive failure are necessary.

The adhesive industry commonly refers to cohesive failure as occurring in the adhesive proper (in the glue line); adhesive failure occurs cleanly at the interface between the metal substrate and the adhesive (along the very edge of the glue line).

Such concepts are acceptable on a macro scale but are erroneous on a micro or molecular scale. In AF 33(616)-3882, Quantum, Inc. has shown that it is virtually impossible to break the bond so that bare metal remains without a monomolecular layer of adhesive remaining on the surface. Since this is a proven experimental datum, all breaks are truly cohesive on a molecular scale. Examination of a "bare" metal surface always finds a monomolecular film present. The use of complete or 100% adhesive failure in this report is based on the macro scale common to the adhesive industry.

Curing agent	Concentration	Pre-cure	Cure	Filler	Support	Average Shear Value
diphenylsilanediol	17 PHR	3 wks./RT	2 hrs./190°F	-	-	1380 psi
"	17 PHR	none	2 hrs./190°F	-	-	500 psi
pyromellitic-dianhydride(PMDA)	10 PHR	1 hr./100°F	2 hrs./300°F	Al(1)	Fiberglas(2)	2115 psi
"	10 PHR	1 hr./100°F	6 hrs./300°F	"	"	1900 psi
"	10 PHR	1 hr./100°F	2 hrs./300°F	Al(3)	"	1850 psi
"	10 PHR	1 hr./100°F	16 hrs./300°F	"	"	985 psi
"	20 PHR	1/2 hr./100°F	2 hrs./300°F	Al(1)	-	1900 psi
"	20 PHR	1/2 hr./100°F	16 hrs./300°F	"	-	1825 psi
"	20 PHR	1/2 hr./100°F	2 hrs./300°F	"	Fiberglass(2)	1900 psi
"	20 PHR	1/2 hr./100°F	16 hrs./300°F	"	"	1900 psi

(1) 100 PHR based on bis(glycidyl)methoxy triazine.

(2) Volan A treated #121.

(3) 50 PHR based on bis(glycidyl)methoxy triazine.

(4) All breaks were 100% adhesive on a macro scale.

(4) Tensile Shear Tests at Room Temperature after Exposure to High Temperatures

Specimens were cured at 190°F for 2 hours, then 16 hours at 300°F, and finally 1 hour at 500°F and 700°F. Formulation consisted of equal weights of Al powder and bis(glycidyl)methoxy triazine with 17 PHR of diphenylsilanediol.

Temperature	Average Shear
300°F	1380 psi
500°F	750 psi
700°F	425 psi

(5) Elevated Temperature Tensile Shear Tests

The formulation consisted of 2.00g bis(glycidyl)methoxy triazine, 2.00g Al powder, and 0.50g PMDA. After application to the steel the coupons were pre-cured in the jig for one hour at room temperature until it had set beyond the flow stage and finally for 2 hours at 300°F. The specimens were brought to temperature and pulled.

Temperature	Average Tensile Shear
Room temperature	2150 psi
150°F	2075 psi
300°F	2100 psi
400°F	2100 psi
500°F	400 psi

c. Formulations with Other Resins

The following formulations using the epoxytriazine were made with other adhesives known to have high heat stability. These were made in an attempt to increase elevated temperature shear values.

No.	wt.epoxy	resin	wt resin	cure time	cure temp.	rt.tensile	500°F tensile
1	2.10g	Resinox RS-6537	0.63g	10 mins.	300°F	1625 psi	600 psi
2	2.10g	Resinox RS-6531	0.63g	2 hrs.	300°F	1870 psi	600 psi
3	2.00g	DC 5701	0.53g	4 hrs.	300°F	545 psi	--

Using Narmco's Experimental Phenolic[1]

No.	Wt. Epoxy	Wt. Resin	Wt. Curing Agent	100 PHR A1	Cure Time	Cure Temp.	R.T. Tensile	500°F Tensile
1	5.00g	2.45g	0.45g dicyandiamide	yes	16 hrs.	300°F	1450 psi[2]	100 psi
2	5.00g	2.45g	0.45g dicyandiamide	yes	16 hrs.	300°F	1400 psi[3]	150 psi
3	2.00g	0.70g	0.50g PMDA	yes	16 hrs.	300°F	1400 psi	
4	2.50g	1.23g	0.25g hexamine	yes	16 hrs.	300°F	1000 psi	
5	2.10g	0.63g	0.12g hexamine	yes	16 hrs.	300°F	600 psi	
			Control, using epoxytriazine only					
6	2.00g	-	0.50g PMDA	yes	16 hrs.	300°F	1850 psi[4]	425[5]

(1) The nature of this resin is not known.

(2) Unsupported.

(3) Supported with Fiberglas cloth 112/38 1/2, Volan treated.

(4) Formulations using only the epoxytriazine gave better tensile shear values at room temperature and 500°F than formulations using the experimental phenolic.

(5) The 500°F tensile shear is less than the formulations incorporating Resinox RS-6537 while room temperature shear values are identical. Further work should be done on Resinox RS-6537 formulations.

One experiment was carried out using Linde Y-1544 as a priming agent on the stainless steel. Cure was for 2 hours @ 300°F using the same batch of adhesive.

	Unprimed	Primed
R.T.	1850 psi	1590 psi
400°F	1875 psi	590 psi

In another series of test strips, the effect of sand blast cleaning of the steel was determined. The sand blast treatment was with dry, very fine sand and this gave a clean active surface. Again, the same formulation was used and cured for 2 hours at 300°F.

	WS-4 treatment	Sand blast
R.T.	1850 psi	1825 psi
500°F	425 psi	550 psi

Some improvement was found in the 500°F tensile shear value. If the steel were cleaned with WS-4 solution or any chromium solution, this might increase the tensile shear values, but these would most likely be marginal.

In an attempt to increase heat resistance, the use of triglycidylcyanurate was evaluated.

2.00g triglycidylcyanurate

0.67g PMDA

The following results were obtained: 1000 psi at room temperature, 1000 psi at 300°F and 700 psi at 400°F. Further work was discontinued because the adhesive was extremely brittle and the tensile shear values were dropping at 400°F as compared to no decrease at 400°F with the bis(glycidyl)methoxy triazine.

IV. Synthetic

a. Hexamethyldisiloxane

The preparation was based on the work of Sauer.[8]

To 360 ml of boiling water, in a 3-neck flask, fitted with a reflux condenser, was added 114g (1.045 moles) of freshly distilled chlorotrimethylsilane (b.p. 56.5-7.0°C) during a period of 1 1/4 hours.

No hydrogen chloride was evolved during the addition or during the extra hour of reflux. After cooling, the upper organic layer was separated, washed with water, dilute sodium bicarbonate, water and dried over potassium carbonate. Distillation through a 24-inch column packed with glass helices gave 80.6g of wet product. This was dried over potassium carbonate for 30 minutes in the refrigerator and distilled to give:

Fraction (1)	b.p. 66-99°C/763mm	4.2g		
(2)	b.p. 99°C	50.5g	N_D^{21}	1.3764
(3)	residue			

The residue was transferred to a semi-micro apparatus to give an additional 12.5g of product, N_D^{22} 1.3762 and a residue of 2.6g. The total yield of product was 63.0g or 77.8%.

b. Butoxytrimethylsilane

Butanol was distilled and the azeotrope and fore-cuts removed. Pure n-butanol was collected at 116-7°C.

The procedure of Sauer[8] was followed for this preparation.

A distillation flask connected to Vigreaux modified Claisen head that lead to a distillation assembly was charged with 62.6g (0.574 mole) of chlorotrimethylsilane and 44g (0.594 mole) n-butanol was added. The mixture was slowly heated and distilled, collecting a distillate at 42-3°C/759mm. This probably was chlorotrimethylsilane being swept out by the HCl. This was returned to the reaction flask and refluxed until the pot temperature reached 104°C after 1 1/2 hours. Evolution of HCl was still taking place but, after an additional 2 hour reflux period, the pot temperature did not increase. The mixture was slowly fractionated to give:

Fraction (1)	57-109°C			
(2)	110-2°C	47.0g		
(3)	112-121.5°C			
(4)	121.5-122.0°C	16.1g	$N_D^{20.5}$	1.3921
(5)	residue			

Fraction (2) was the 42:58 azeotrope of n-BuOH - Me_3SiOBu

2-chloro-4,6-diphenoxy-s-triazine

This preparation was reported by Thurston et al. JACS 73 2992 (1951).

A slurry of 92.2g (0.5 mole) of cyanuric chloride and 375 ml of acetone was prepared in a 1 liter 3-neck flask. To this was added 1.0 mole of sodium phenolate in 375 ml of water. After 1.5 hours at 15-20°C and 1 hour at 25°C, the product was collected on a Buchner funnel, sucked dry, and dried in a vacuum. Yield of crude product was 143g (97%) m.p. 110-5°C. Recrystallization from heptane raised the m.p. to 121-2°C.

2,4-dimethoxy-6-chloro-s-triazine

A 1 liter 3-neck flask was fitted with a sealed stirrer, reflux condenser and inner thermometer. The flask was charged with 225g (7.0 moles) of methanol, 25g of water, 84.0g (1.0 mole) of sodium bicarbonate, and 92.5g (0.5 mole) of cyanuric chloride. Evolution of CO_2 began almost immediately and the temperature increased to 49°C. The mixture was cooled to 40°C but by this time gas evolution ceased. The mixture was stirred and refluxed for 30 minutes, diluted with 500 ml of water and filtered. This operation was repeated and the solid dried in a vacuum oven overnight. A yield of 52.3g (59.6%) of crude product m.p. 75-6°C was obtained. Recrystallization from n-heptane raised the m.p. to 77-8°C.

2,4-dichloro-6-methoxy-s-triazine

A 3 liter 3-neck creased flask was equipped with a stirrer and inner thermometer and was charged with 1.2 liters (29.6 moles) of methanol, 150.5 ml of water, 205g (2.44 moles) of sodium bicarbonate and 224g (1.216 moles) of cyanuric chloride.

Reaction set in at 25°C with evolution of carbon dioxide and a gradual increase in temperature. The reaction temperature was maintained at 30-2°C for 30 minutes by use of an ice bath. The mixture was poured into 4 liters of water, stirred, filtered and sucked dry. The filter cake was slurried with ice water and filtered. This was repeated and then slurried once with water at 25°C, filtered and sucked dry. The filter cake was dried in a vacuum oven at 35°C/5mm. Yield 154g (70.4%) m.p. 88-90°C.

V. Conclusions

(1) The synthesis of a new, highly promising epoxy resin, 2,4-bis(glycidyl)-6-methoxy-s-triazine has been carried out.

(2) The above epoxy resin has been shown to be extremely reactive with the usual epoxy curing agents.

(3) The above epoxy resin can be cured with unusual materials such as silicone compounds and resins.

(4) Certain formulations of the above epoxy compound, maintain a constant tensile shear value up to 400°F.

(5) The ammeline-phosphorus pentoxide reaction product has the ability to cure the above epoxy resin. Further work is necessary on techniques to obtain a fine particle size for compounding with the epoxy resin.

(6) The 2,4-bis(glycidyl)-6-methoxy-s-triazine compound is also of interest as an ingredient in a room temperature curing adhesive system for use in the 500°F range.

VI. Recommendations

(1) Further work is necessary on formulations containing the ammeline-phosphorus pentoxide reaction product and the bis(glycidyl)methoxy-s-triazine. A technique has to be found to pulverize the inorganic constituent. One approach is comminution in liquid nitrogen.

(2) An evaluation of the bis(glycidyl)methoxy-s-triazine should be carried out, examining the parameters inherent in an adhesive system.

(3) Other new bis(glycidyl)-s-triazines should be synthesized and evaluated including those containing hetero atoms as substituents in the triazine side chain.

(4) Investigate polymeric Werner complexes based on the s-triazine ring system.

VII. Bibliography

(1) C. C. Cerato, J. L. Lauer and H. C. Beachell, J. Chem. Phys. 22 1 (1954)

(2) H. Dannenberg and W. R. Harp, Jr., Anal. Chem. 28 86 (1956)

(3) J. T. Goodwin, Jr., W. E. Baldwin, and R. R. McGregor J. Am. Chem. Soc. 69 2247 (1947)

(4) Kerchov, Z. Anal. Chem. 108 249 (1937)

(5) Randall, Fowler, Fuson and Dangl, "Infra-red Determination of Organic Structures," Van Nostrand

(6) S. Siggia, "Quant. Analysis via Functional Groups," p. 108 John Wiley & Sons

(7) D. Swern, J. Am. Chem. Soc. 69 1692 (1947)

(8) R. O. Sauer ibid 66 1708 (1944)

(9) H. H. Levine, USAF TR 55-271

(10) H. H. Levine, USAF TR 55-271 Part II Astia Document AO110588

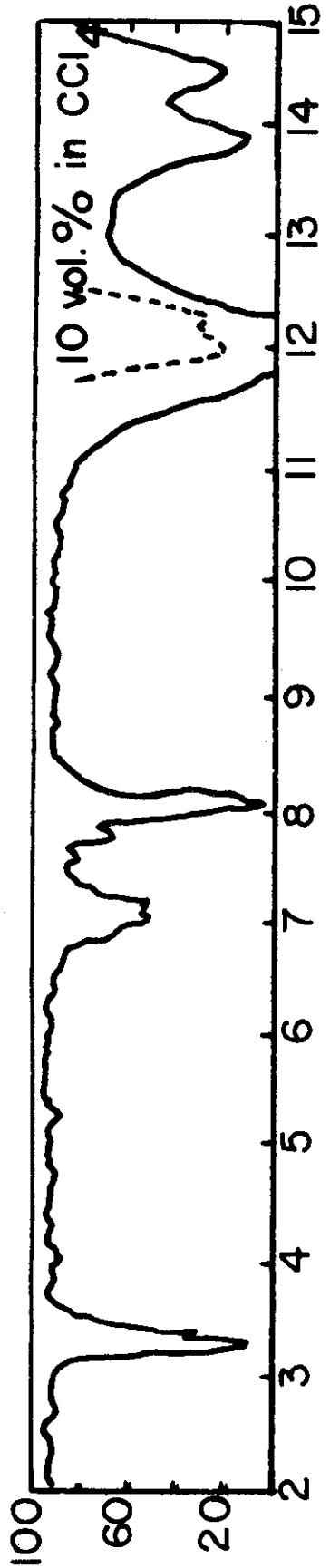


FIG. 1 Hexamethyldisilane

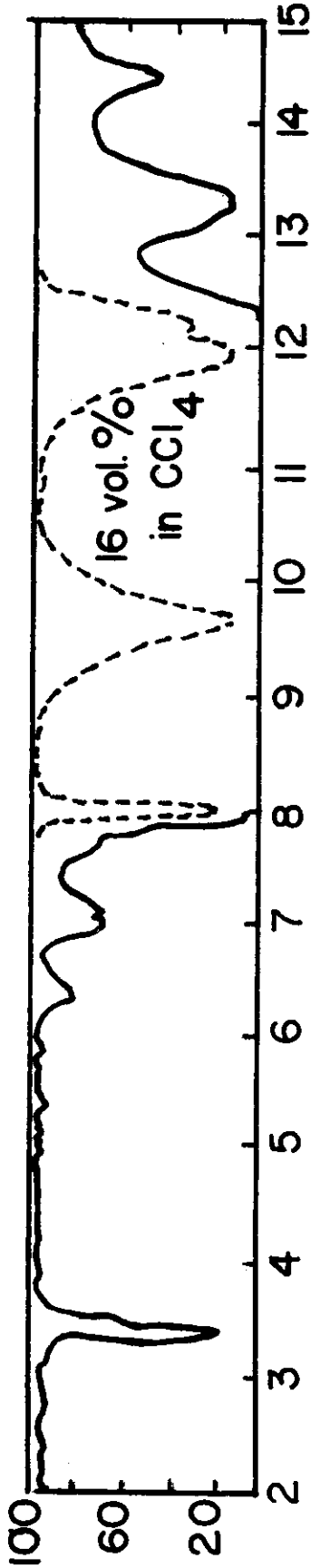


FIG. 2 Hexamethyldisiloxane

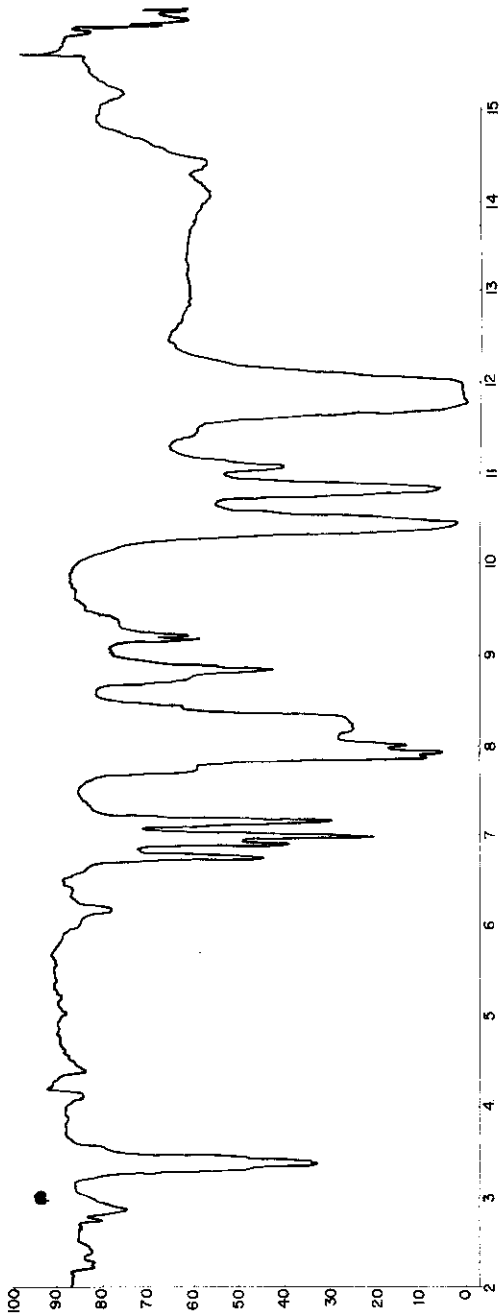


FIG. 3 EPICHLOROHYDRIN

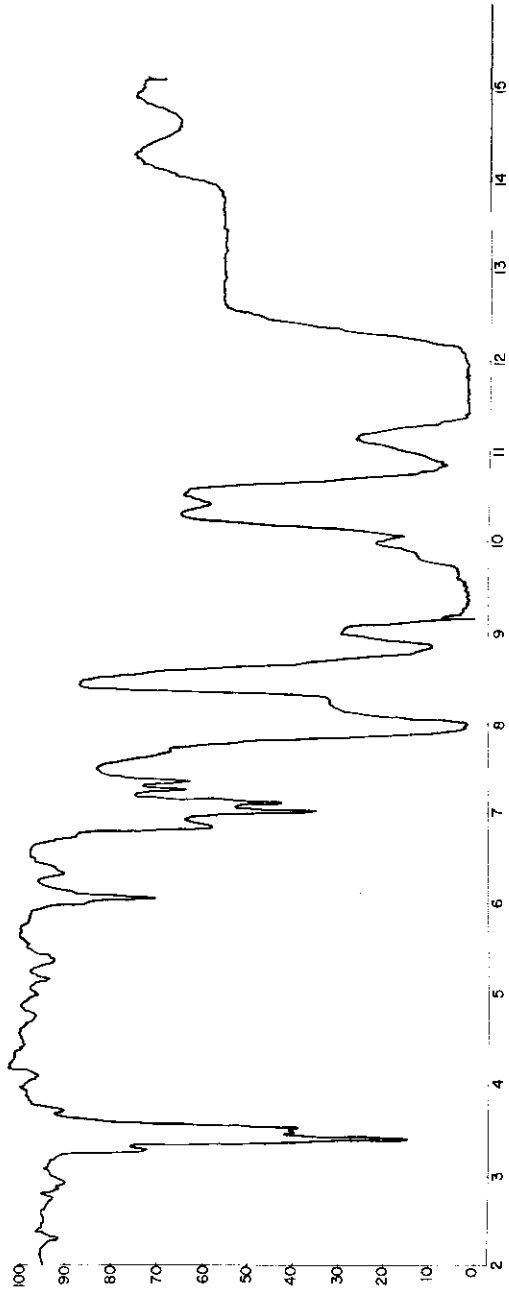


FIG. 4 REACTION PRODUCT

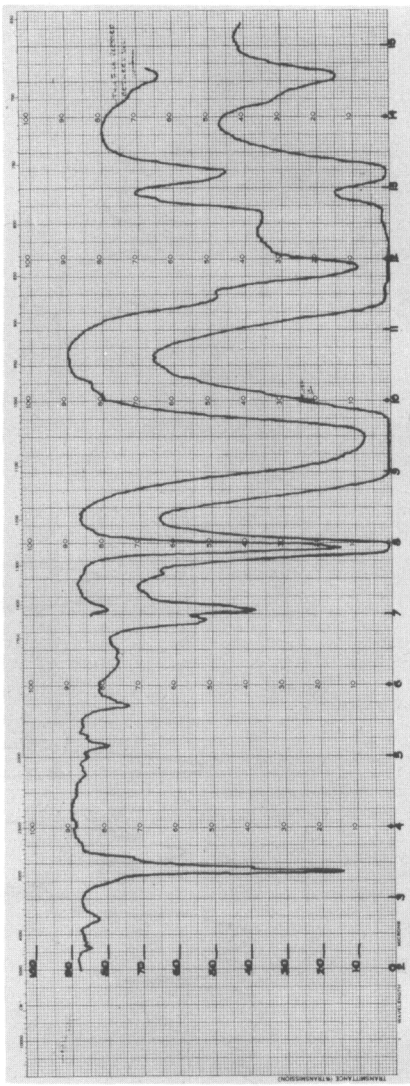


FIG. 5 Epoxidized product from Trimethylallylsilane

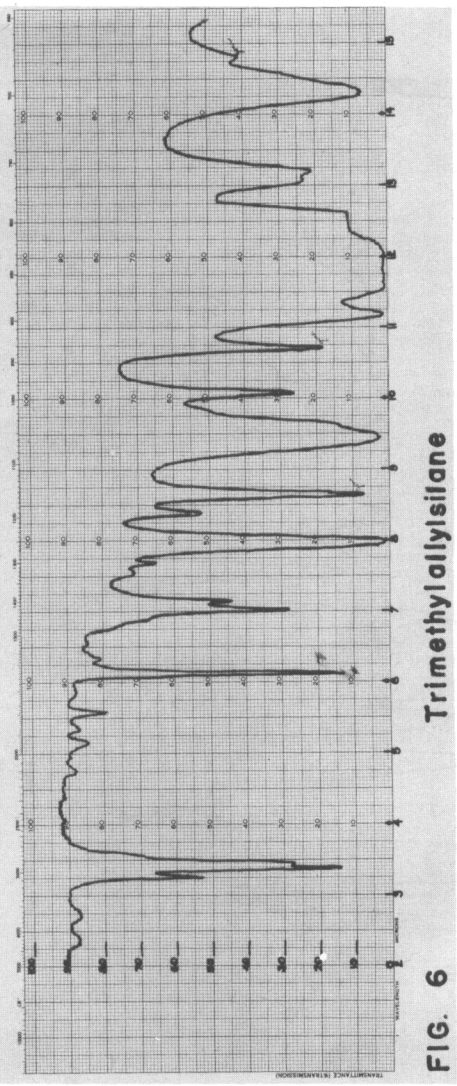


FIG. 6 Trimethylallylsilane

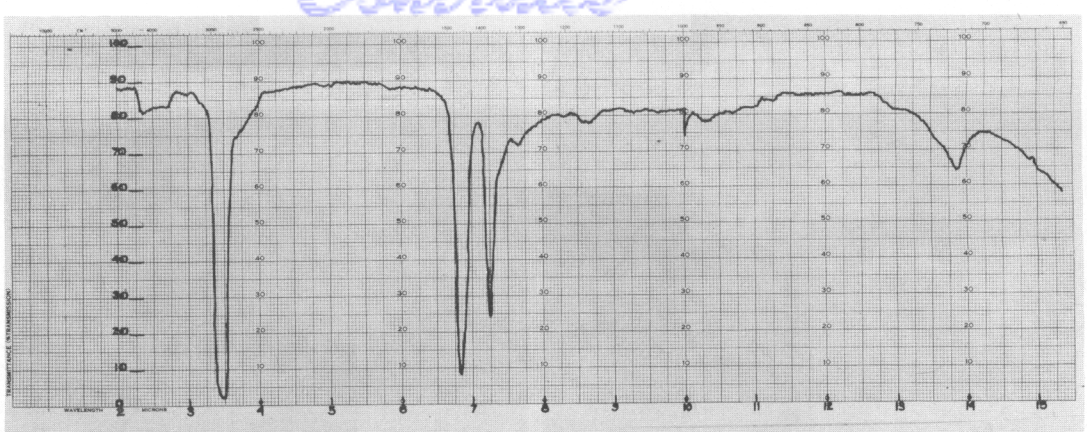


FIG. 7 Nujol

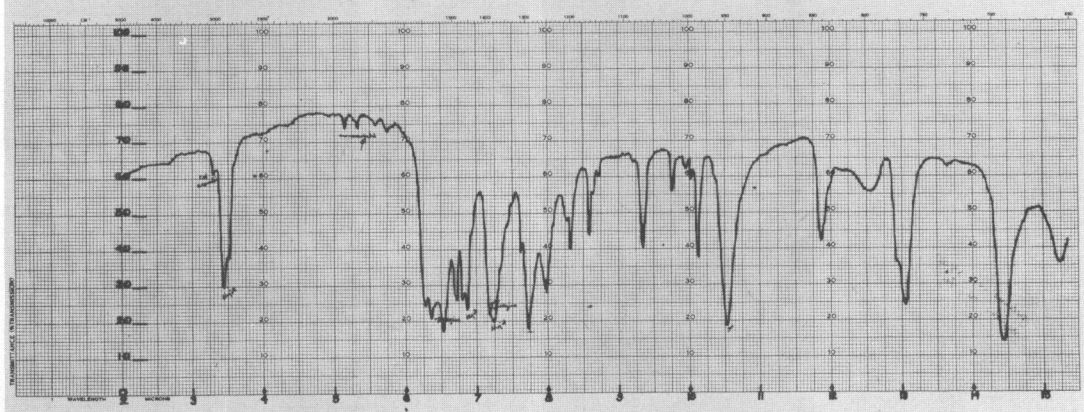


FIG. 8 2,4 - Diphenoxy - 6 - chloro - s - triazine

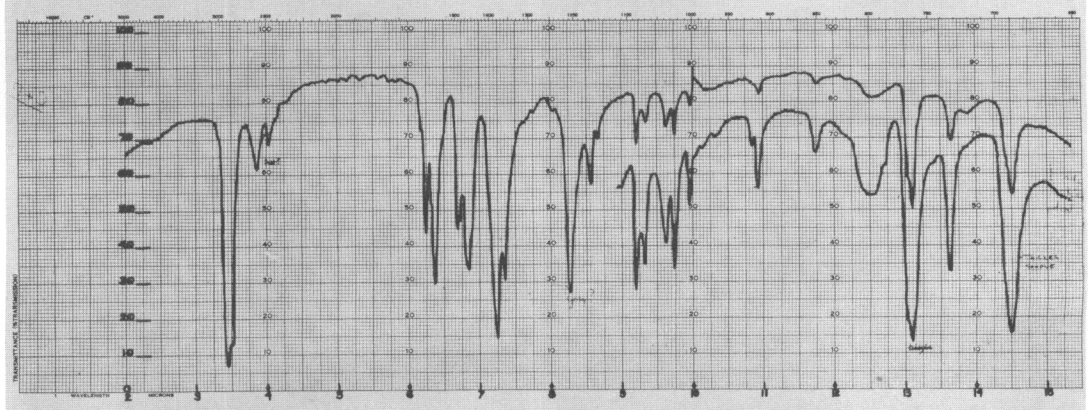


FIG. 9 2,4 - Diphenoxy - 6 - glycidyl - s - triazine

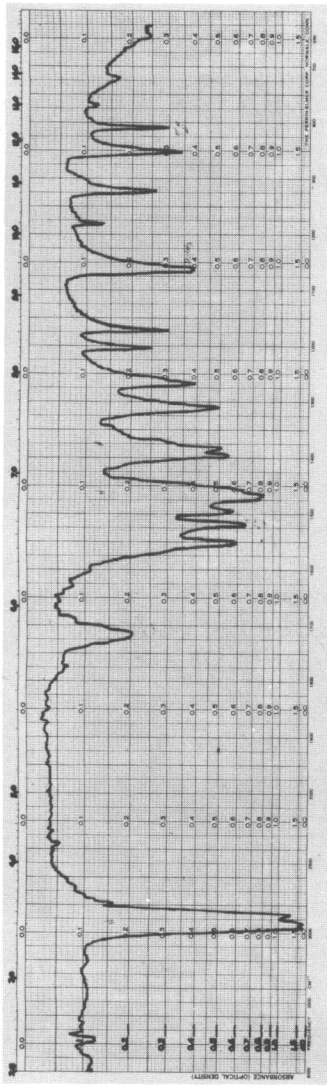


FIG. 10 Purer 2,4 - Bis(glycidyl) - 6 - methoxy - s - triazine

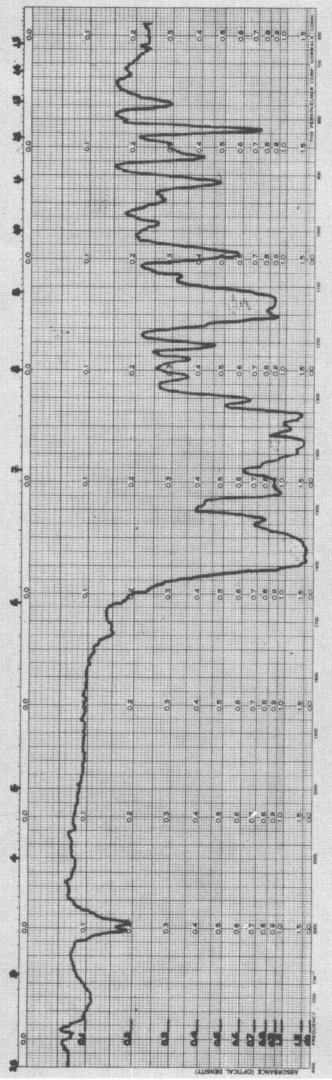


FIG. 11 2,4 - Bis (glycidyl) - 6 - methoxy - s - triazine

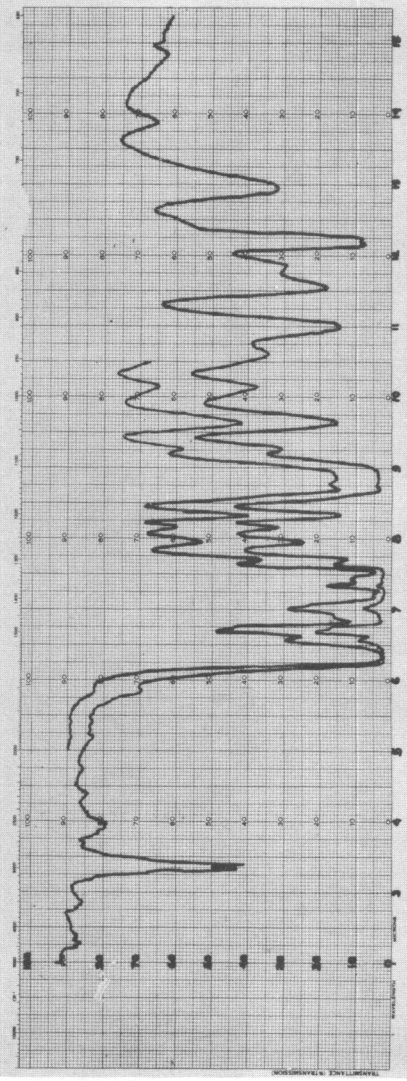


FIG. 12 2,4 - Dichloro - 6 - methoxy - s - triazine