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QUICK-CURING FOAM SYSTEMS

L. W. Hartzel, L. E. Brown, J. D. Nutter and E. G. Thomas

AEC Research and Development REPORT

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MONSANTO RESEARCH CORPORATION

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S U M M A R Y

Many formulations prepared from commercially available materials were briefly scanned in order to develop a rapid-curing foam system which would yield a satisfactory product at room temperature. The most promising of these systems were evaluated for reactivity over the temperature range -60 to 80°C , foaming ability, and solvent resistance of the end product. Simultaneously, studies were made on the stability of components of these formulations when subjected to storage at 110°C . The effect of this aging on viscosity, refractive index, heat of reaction, and foaming ability was determined. On the basis of the above-mentioned tests, formulations were continually modified to improve their properties. The effect of the incorporation of flexible modifiers and silicone surfactants into epoxy foam formulations was investigated. The effect of increased catalyst concentration on the foaming ability of an epoxide-trimethoxyboroxine formulation at -60°C was determined; similarly, the effect of the incorporation of various solvents into this formulation was studied. The effect of inhibitors on the polymerization of furfuryl alcohol at 110°C , the effect of aging on the foaming ability of silicone surfactant SF-1079, and the efficiency of some non-silicone foam control agents in some foam systems were briefly investigated.

INTRODUCTION

This report covers research, conducted by Monsanto Research Corporation at Mound Laboratory and funded under Lawrence Radiation Laboratory Purchase Order SANL 211-040, to develop a rapid-curing polymeric foam material. The goal of the 6-month project was to develop a two-component foam-in-place system which would react rapidly over the temperature range -60° to 80°C to yield a rigid or semi-rigid foam within 1 min. The foam was to show a thirty to forty-fold volume increase, be resistant to solvents, and have good strength. In addition, the components of the system were to endure storage for 4 years at 80°C without appreciable loss of reactivity. The surface temperature of the completed foam, due to the heat of reaction of the components, was not to exceed 180°C .

The program was terminated after six months with the development of a foam system which met most, but not all, of the original specifications. This report summarizes the results obtained and recommends the course of any further research on rapid-curing foam systems.

EXPERIMENTAL

SAMPLE PREPARATION

All formulating was done on a "parts by weight" basis. All materials were commercially available and used directly with no purification. Samples were prepared by hand mixing the reactants in small (4 to 5 oz), untreated paper cups.

PRELIMINARY FORMULATION EVALUATION

The preliminary evaluation of a formulation consisted of observing the elapsed time from mixing of the reactants to visible evidence of reaction (fuming, boiling, gelation, or foaming of the reaction mixture). This time is referred to as "reaction time". The peak exotherm generated during reaction was measured with an iron-constantan thermocouple placed in the approximate center of the sample attached to either an API Temp-print recorder or an L & N potentiometer. The product of the reaction was always given a cursory examination for evidence of incomplete reaction, friability, flexibility, strength, and uniformity. The product was also examined for decomposition which may have resulted from either excessive heat of reaction or from strong acids, bases or redox agents which were initially present or formed during the reaction. If the product was a foam, the foam rise (i.e., the ratio of the foam volume to the volume of the unreacted components) was also noted.

FINAL FORMULATION EVALUATION

If the formulation appeared promising (on the basis of reaction time and appearance of the product) the solvent resistance and performance of the formulation at -60° , 0° , 24° , and 80°C were determined. The solvent resistance was based on the ability of the reaction product to endure immersion in a solvent without dissolution or loss of cohesiveness. The usual solvents were acetic acid, acetone, chloroform, ethanol, dimethyl sulfoxide, dimethyl formamide, dioxane, methyl ethyl ketone, phenylglycidyl ether, pyridine, N-methyl pyrrolidone, tetrahydrofuran, and toluene. Nitric acid was included in the study of products of systems E-3 and PB-1. Small samples (approximately 1 in. X 0.25 in. X 0.25 in.) of the product were placed in 2-dram glass vials containing the solvent. The samples were examined periodically for evidence of solution or loss of cohesive strength. The solvent resistance of the products of systems E-3 and PB-1 was determined by preparing the foams in 8-oz glass jars, boring a hole in the foam, and introducing the solvent.

The performance of a formulation at various temperatures was based on reaction time, peak exotherm, foam rise, and appearance of the reaction product. The reactions at -60°C were run in dry ice snow, an ethanol-dry ice bath, or an environmental chamber, while those at 0°C were run in an ice bath or the environmental chamber. The reactions at 80°C were run in an oil bath or the environmental chamber. For running reactions in a bath, the components were placed in separate containers (glass vials, glass or polypropylene beakers) and were allowed to attain the test temperature¹ or to come to thermal equilibrium with the bath. One of the components was then poured into the other and the materials were mixed by hand. Many of the reactions, especially those at -60°C , were run in an environmental chamber (Cincinnati Sub-Zero Products, Inc.).

One of the components was weighed into an 8-oz glass jar. The second component was weighed into a 10-ml ampoule; the ampoule was sealed and also placed in the jar. The jar was then clamped in position in the chamber. When a thermocouple indicated that the test temperature was reached, the ampoule was broken with a glass rod controlled from outside the chamber. Figure 1 shows the chamber with a sample jar in place.

In addition to the tests listed above, aging studies were carried out on components of promising systems. Changes in viscosity caused by aging were determined on individual components and mixtures of components. A precise determination of the effect of aging on the more promising systems was determined by measuring their heats of reaction before and after aging by means of a calorimeter. A description of the apparatus and procedures used is found in a subsequent section of this report.

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¹The temperature of the ethanol-dry ice bath was about -77°C . The reaction was started when the sample temperature reached -60°C (as measured by means of a thermocouple).

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Figure 1

APPARATUS FOR MIXING FOAM SYSTEMS IN THE ENVIRONMENTAL CHAMBER

Accelerated aging was accomplished by storing the sample at 110°C for a given period of time. The sample containers were 4-oz glass jars in which the paper cap liner was replaced with a 1/16-in.-thick Teflon disk.

The viscosity of the polyol component of formulation PF-3 was determined using a Gardner bubble viscosimeter. All other viscosity measurements were determined with a Cannon-Fenske viscosimeter (size 200) in a water bath at 30°C. The results were reported as efflux time--the time required for the sample to flow between two marks on the viscosimeter. The refractive index was determined at 24°C using a Bausch and Lomb Abbé refractometer.

CALORIMETRIC DETERMINATION OF THE HEAT OF REACTION

The aluminum block calorimeter described below was used in the determination of the heats of reaction. Earlier versions and modifications of the calorimeter were described in previous reports of this project.

The assembled calorimeter is shown in Figure 2. The outer vessel, surrounded by an isothermal bath, was a stainless steel Dewar flask with a 6.0-in. I.D. and a 11.5-in. inside depth. The aluminum block centered in the Dewar flask was 5.0 in. in diameter and 6.0 in. high.

Figure 2

ALUMINUM BLOCK CALORIMETER

The outer surfaces of the aluminum cylinder were plated with nickel on copper to give polished surfaces. Lucite spacer rings at the top and bottom of the aluminum cylinder maintained a 5/16-in. air gap on all surfaces of the cylinder. This cylinder was bored to accept a 4.0-in.-O.D. by 5.25-in.-long inner aluminum cylinder. The inner solid cylinder was bored to accept a 2.13-in.-diameter by 3.31-in.-high 4-oz

soft glass reaction vessel. A 2.4-in.-diameter by 0.25-in.-thick Teflon disk served as the lid for the glass reaction vessel. A 0.5-in.-O.D., 3/16-in.-I.D. polyvinyl chloride tube threaded in the center of the Teflon extended to the top of the Dewar flask and served as a guide for the stirrer.

The four-bladed stirrer was constructed entirely of 8-mm Pyrex rod. This stirrer was used to break the 10-ml thin-walled Pyrex bulb containing the curing agent. A 3.5-in.-diameter by 0.25-in.-thick nickel-plated brass ring with four 0.25-in. nickel-plated brass screws (1.5 in. long) which extend into the aluminum block was used to compress the Teflon lid on the glass jar to seal the top of the jar.

The styrofoam plug which was spaced 5/16-in. away from the top of the aluminum cylinder by the Lucite rings served as an insulating medium from room temperature fluctuations. The heater was manganin wire with a nominal resistance of 200 ohms (Dale RH-25, 200 Ω). Items T_1 and T_2 were 10,000-ohm thermistors. To insure good thermal contact with the block, the thermistors were placed in 0.5 ml of Dow Corning 704 Fluid.

The thermistors T_1 and T_2 were connected in parallel in one arm of a Wheatstone bridge. Two 1.35-v mercury dry cells connected in parallel served as the power supply for the bridge. The null of the bridge was detected by a L & N 9835-B D.C. microvolt amplifier. The output of the amplifier was recorded on a 10-mv L & N Speedomax W Recorder.

The thermistors were calibrated by comparing their resistance with that obtained from a platinum resistance thermometer at a known temperature. A G-1 Mueller Bridge was used to measure the resistance of the platinum thermometer. The platinum thermometer was placed in a hole in the aluminum block and 0.5 ml of Dow Corning 704 Fluid was added to insure good thermal contact. Sufficient time (~30 min) was allowed for the system to reach temperature equilibrium before readings were taken. The temperature of the block was adjusted to a new value and the same procedure of equilibration and reading of resistances was followed. The temperature range of calibration was from 23°C to 30°C. The temperature equation for the thermistors was found to be:

$$\theta = \theta^{\circ} + A \log (R^{\circ}/R)$$

where: θ = observed temperature in °C
 θ° = 25.00000°C (assigned temperature)
 R° = thermistor resistance at 25.00000°C = 5126.296 ohms
 R = observed resistance in ohms
 A = constant

The constant A was determined by a plot of θ for the platinum thermometer versus $\log (R^{\circ}/R)$ over the temperature range. The slope of the resulting line is equal to A .

Procedure for Determination of the Heat of Reaction An empty 10-ml Pyrex glass bulb was tared on an analytical balance and the desired quantity of curing agent was added using a hypodermic syringe. The tip of the bulb was then sealed with an epoxy resin.² The desired quantity of resin component was added to the 4-oz glass jar and the 10-ml sealed glass bulb was placed in the bottom of the jar. The calorimeter was assembled after the inner aluminum cylinder was pre-cooled to about 23°C.

All reactions were initiated at $25.0 \pm 0.1^\circ\text{C}$. The energy equivalent was run on the products of the reaction over the same temperature interval as the reaction. The energy equivalent of the calorimeter is 965 cal/deg.

The temperature of the isothermal bath was set so that the final temperature of the calorimeter after reaction would be equal to the bath temperature. The use of this procedure minimizes heat losses during the long (~50 min) after-period of reaction.

The reaction was initiated by manually breaking the glass bulb and mixing the components for about 10 sec or less. The mixing time depended on the reactants being used

The sensitivity of the calorimeter during the fore-period of reaction and electrical heating was 7×10^{-4} deg/0.1 in. of recorder chart; the sensitivity during the after-period of reaction and electrical heating was 6×10^{-4} deg/0.1 inch of recorder chart.

The electrical energy input, Q_c , was calculated from the equation:

$$Q_c = K \cdot E_s \cdot E_v \cdot Dt$$

where K is a constant determined from lead resistances, the voltage divider used in the heater circuit and the defined calorie of 4.1840 absolute joules; E_s is the potential across a standard resistor; E_v is the potential across the heater inside the calorimeter; and Dt is the duration of heating in seconds.

The heat of reaction was evaluated from the equation:

$$Q_x = Q_c \frac{D\theta_x}{D\theta_c}$$

²Mereco Adhesive H-305, Mereco Products Division, Metachem Resins Corporation, Cranston, R. I.

where Q_x is the heat of reaction, Q_c is the electric energy input, $D\theta_x$ is the corrected temperature change³ produced by the reaction, and $D\theta_c$ is the corrected temperature change produced by the electrical energy input.

D A T A   A N D   D I S C U S S I O N

FORMULATION DEVELOPMENT AND EVALUATION

The initial research was directed toward demonstrating the feasibility of a rapid-curing polymeric foam. Subsequent research involved the refinement of formulations which appeared most feasible, investigation of new formulations, and aging studies which included determination of heats of reaction by means of a calorimeter. The cursory investigation of many formulations was dictated by both the short-term nature of the research contract and the multitude of materials which in various combinations and proportions may yield polymeric products. Tables A to F in the Appendix list the formulations which were briefly scanned but discarded because of no reaction, long reaction time, or unsatisfactory product. The formulations which received more intensive investigation are discussed in the following sections.

Investigation of Polyurethane Formulations Polyurethanes are perhaps the most versatile of polymeric foam materials. By proper formulation, foams with a wide range of density, reaction time, rigidity, chain length, and degree of cross-linking are easily obtained. Basically, a polyurethane may be formed by the reaction of an isocyanate with an alcohol:

Polymers are obtained when difunctional isocyanates are allowed to react with di-, tri- or polyfunctional hydroxyl compounds.

The rigidity and chain length of the polymer is largely determined by the hydroxyl compound (polyol) used. The degree of cross-linking is determined by the functionality of the polyol. The reaction time may be varied according to the type and quantity of catalyst used. In the case of a foam, the density may be adjusted by the type and quantity of blowing agent used.

³J. Coops, et al., Experimental Thermochemistry, F. D. Rossini (ed.), New York, Interscience Publishers, 1956, p. 28-30.

The chemistry and technology of polyurethane foams has been well documented^{4,5} and the references cited may be consulted for a more complete discussion.

The first formulation (PF-1) developed at Mound appears in Table 1. This formulation exhibited a short reaction time and produced a

Table 1

POLYURETHANE FORMULATIONS

<u>Formulation</u>	<u>Component A</u>	<u>Component B</u>
PF-1	Mondur MR ^a : 25.4 parts ^b Polycin U-63 ^c : 50.7 parts	1,4-butanediol ^d : 9 parts Glycerine ^e : 9 parts Dabco 33-LV ^f : 5.8 parts
PF-2	Mondur MR: 47.7 parts	Niax LG-168 ^g : 31.6 parts Niax LA-700 ^h : 15.0 parts Dabco 33-LV: 5.6 parts
PF-3	Mondur TDS ⁱ : 24.7 parts	Niax LG-168: 65.8 parts Dabco 33-LV: 5.5 parts Y-4347 ^j : 2.6 parts Y-4499 ^j : 1.3 parts

^aCrude p, p'-diphenylmethane diisocyanate (Reference 5).

^bParts by weight based on total formulation weight.

^cIsocyanate terminated prepolymer (Reference 8).

^dMatheson, Coleman, and Bell.

^eMallinckrodt Chemical Co.

^fOne part by weight triethylene diamine in two parts dipropylene glycol (Reference 9).

^gPolyether triol (Reference 10).

^hPolyether pentol (Reference 10).

ⁱ2,4-tolylene diisocyanate (Reference 11).

^jTwo-part silicone surfactant system (Reference 7).

⁴J. H. Saunders and K. C. Frisch, Polyurethanes: Chemistry and Technology. Part I. Chemistry, New York, Interscience Publishers, 1962.

⁵T. H. Ferrigno, Rigid Plastic Foams, New York, Reinhold Publishing Corp., 1963.

⁶Methylene Chloride for Plastic Foam Systems, Stauffer Chemical Co. product bulletin, 1965.

⁷A One-Shot System for Manufacturing Semi-Rigid Urethane Foam, Union Carbide Corp., Silicones Division, customer service bulletin 45-8, 1964.

relatively high exotherm (Table 2). However, the solvent resistance of this system was very poor.

The unsatisfactory solvent resistance of formulation PF-1 was attributed to short chain lengths, the result of using low molecular weight glycols.^{1,2} Polyols with increasing functionality and higher molecular weight were used in formulation PF-2 (Table 1). Although this foam was not resistant to all of the test solvents, it showed marked improvement when compared with formulation PF-1 (Table 2).

The performance of formulation PF-2 at several temperatures was determined. The solidification temperature ranges of the two components of PF-1 were: component A, -29°C to -40°C; component B, -34° to -40°C.^{1,3} The solidification temperature of each component was depressed below -60°C by adding 25 parts by weight of toluene in 75 parts of the component; both modified components were quite viscous at -60°C, however. The toluene solutions were used only for the reactions at -60°C; the results appear in Table 2.

Several modifications of formulation PF-2 were attempted. Genetron G-113, trichlorotrifluoroethane, (Allied Chemical Co.) was evaluated as a freezing point depressant for Mondur MR. The solidification temperature of a mixture consisting of 75 parts by weight of Mondur MR and 25 parts by weight of G-113 (F.P.: -35°C)⁶ was -45°C. Further use of G-113 was discontinued.

The products obtained from formulation PF-2 were rather brittle. In an attempt to obtain a semi-rigid or flexible polyurethane, Mondur MR was allowed to react with several polyols of different molecular weight and functionality. The formulations (Reactions 147 - 205) appear in Table A of the Appendix. A semi-rigid foam was obtained when a mixture of 50 parts of Niax LG-168 and 10 parts of Niax-PPG-4025, a diol (Reference 10), was allowed to react with Mondur MR.

⁸Urethane Elastomers Based on Polycin Prepolymers and Polyols, Baker Castor Oil Co., technical bulletin No. 76, 1963.

⁹Dabco 33-LV Low Viscosity Solution, Houdry Process and Chemical Co. technical data, 1963.

¹⁰Niax Polyethers, Union Carbide Corp. technical bulletin.

¹¹Mondur TDS, Mobay Chemical Co. data sheet, 1964.

¹²The solvent resistance was determined for three formulations in which (1) Niax LG-168 was substituted for glycerine in PF-1, (2) a pentol (Niax LA-700) was added to the formulation, and (3) butanediol was omitted. The best solvent resistance was obtained when neither glycerine nor butanediol was present in the formulation (Appendix Table A, Reactions 188, 187 and 238, respectively).

¹³Determined by cooling the component in dry ice snow and observing the temperature (measured with an iron-constantan thermocouple) at which the sample became solid.

Table 2

EVALUATION OF POLYURETHANE FORMULATIONS

Formu- lation	Reaction Time (sec) at				Exotherm	Solvent Attack ^a
	-60°C	0°C	24°C	80°C		
PF-1	-	-	17-20	-	24°:155°C	A,B,C,D,E,F,G, H, <u>J</u> ,K, <u>L</u> (22 hr)
PF-2	No Reaction	35	10	5	0°:120°C 24°:146°C 80°:151°C	F, <u>K</u> (95 hr) ^b
PF-3	-	-	15	-	-	- -

^aThe letters refer to the solvents, listed below, which attacked the sample; the underlined letter indicates the solvents which were particularly destructive. The number in parenthesis indicates immersion time. Solvent tests were run at ambient temperature.

A - acetic acid	H - methyl ethyl ketone
B - acetone	I - phenyl glycidyl ether
C - chloroform	J - pyridine
D - ethanol	K - N-methyl pyrrolidone
E - dimethyl sulfoxide	L - tetrahydrofuran
F - dimethyl formamide	M - toluene
G - dioxane	

^bThe solvents used for testing this formulation were B,C,D,F,K, and L.

Formulation PF-3 (Table 1) produced a semi-rigid foam within 15 sec. This formulation resulted from modifications to a published formulation.⁷

Semi-rigid and flexible materials were obtained when Mondur MR was allowed to react with a thiol-terminated polysulfide (Thiokol Chemical Corporation) containing Dabco 33-LV. Formulations of this type exhibited immediate gelation at room temperature; the formulations (Reactions 238-242) appear in the Appendix in Table B.

Storage tests were carried out on the diisocyanate components of polyurethane foams. Mondur MR solidified after storage for 60 days in an Erlenmeyer flask immersed in an oil bath at 80°C. Samples of Mondur TD 80 (a 4:1 mixture of 2,4- and 2,6-tolylene diisocyanate, respectively) and Mondur TDS (2,4-tolylene diisocyanate) were placed in 4-oz glass jars and stored for 66 hr at 110°C. The TDS sample formed crystals upon cooling to room temperature, while the TD 80 sample showed crystal

formation 72 hr after cooling to room temperature. Because of the poor stability of these components, work with polyurethane foams was stopped and other systems were evaluated.

The effect of elevated temperature storage on component B of formulation PF-3 is discussed in a later section of this report.

Investigation of Vinyl Monomer Formulations It was reported that the reaction of boron trifluoride etherate with styrene proceeds instantaneously at -28°C .¹⁴ The reaction may be represented as a cationic polymerization:¹⁵

where $\phi = \text{C}_6\text{H}_5$

This work was repeated with divinyl benzene as a cross-linking agent (Table 3). It was necessary to add toluene to the vinyl monomer mixture (one part toluene in three parts vinyl monomer mixture) to depress the freezing point of the olefin mixture. Without toluene, crystals formed in the mixture at -41°C ; with toluene, crystals formed at -56°C . When the boron trifluoride etherate was added at -60°C , no reaction occurred until the solution was mixed; no mixing was necessary at 0°C .

Since polystyrene is soluble in aromatic and chlorinated hydrocarbons,¹⁶ solvents of this type were used for the solvent resistance study rather than the solvents normally employed which were listed in Table 2 (see Table 3). Investigation of this formulation was terminated because of the poor solvent resistance and the crystal formation observed at low temperature.

Several other vinyl monomers as well as various catalysts were evaluated; the formulations appear in the Appendix in Table C. The majority of these formulations yielded unsatisfactory reaction products.

¹⁴ Development and Field Production of Foamed-in-Place Plastic, Energy-Absorbing Materials, AD-426-294, 1961.

¹⁵ Y. Imanishi, et al., Makromol. Chem., **70**, 68 (1964).

¹⁶ "Plastics Properties Chart", Modern Plastics Encyclopedia, **41**, (1963).

Table 3

EVALUATION OF A VINYL MONOMER FORMULATION

<u>Formulation</u>	<u>Reaction Time</u>	<u>Solvent Attack^f</u>
Component A Boron trifluoride etherate ^a : 20 parts ^b	0°C:96°C <1 sec	Attacked by all solvents
Component B Styrene ^c : 60 parts Divinyl benzene ^d : 20 parts	-60°C: <1 sec ^e	

^aFisher Scientific Co.

^bParts by weight based on total formulation weight.

^cInhibited styrene, Fisher Scientific Co.

^dDow Chemical Co.

^eReaction was instantaneous upon mixing.

^fThe solvents used were: acetone; tetrachloroethane; carbon tetrachloride; chloroform; α,α,α -trichlorotoluene; toluene. Test was conducted at ambient temperature.

Investigation of Phospholeum and Phosphorofluoridic Acid Catalyzed Epoxy Foams Phosphoric acid was reported as a catalyst for the curing of epoxy resins.¹⁷ When commercial 85% phosphoric acid was allowed to react with several epoxy resins in this laboratory, hard solids were obtained in 10 to 15 sec. Due to the high freezing point (about 15°C) of this acid, the reaction was not suitable for low-temperature applications. Phospholeum, a complex mixture equivalent to 105% phosphoric acid, has a lower freezing point and was therefore substituted for 85% phosphoric acid as a catalyst. Many formulations were prepared; the best formulation obtained (PB-1) contained boron trifluoride etherate as a co-catalyst with phospholeum (Table 4). A foam rise of 20:1 was obtained in less than 1 sec at 25°C. At -60°C, however, no foam rise occurred. At -30°C a foam rise of about 8:1 occurred in 7 sec. Although this foam was weakened after standing for 100 hr at room temperature in the various test solvents, it did not deteriorate. Attempts to modify the formulation in order to obtain a foam at -60°C were unsuccessful.

Considerable work was also carried out with phosphorofluoridic acid as a catalyst. This acid was selected because its low freezing point made it useful as a low-temperature catalyst. The best system obtained,

¹⁷EpoxyLite Research Report RR-63-611, June 11, 1963.

Table 4

COMPONENTS OF EXPERIMENTAL FOAMS PB-1 AND PA-1

<u>Parameter</u>	<u>Foam PB-1</u>		<u>Foam PA-1</u>	
Component A	Boron trifluoride etherate	4 pbw ^a	Phosphorofluoridic acid	5 pbw
	Phospholeum	2	Diisopropyl ether	1
	Diisopropyl ether	3		
Component B	Epon 812	8 pbw	Epon 812	8 pbw
	Vinylcyclohexene dioxide	2	Vinylcyclohexene dioxide	2
	Tetrahydrofuran	3	Tetrahydrofuran	3
	SF-1079	0.6	SF-1079	0.6
Ratio of A to B in foam	4.5:13.6		6.0:13.6	

^aParts by weight

PA-1 (Table 4), initially showed some promise. At room temperature and at 80°C a foam rise of about 12:1 was obtained; at -40°C, the foam rise was about 10:1. Unfortunately this system would not foam at -60°C. Several modifications of this formulation were prepared and evaluated, but no satisfactory system was developed.

The effect of storage at elevated temperature on individual components and mixtures of components of this system is discussed in a subsequent section of this report.

Investigation of Polyol-Trichlorosilane Foam Systems Since trichlorosilanes react readily with alcohols and amines, liberating hydrogen chloride as a by-product,¹⁸ the reactions of several trichlorosilanes with various polyols and amines were investigated. Although the reactions of amines with trichlorosilane were too exothermic to produce suitable foams, reactions of the silane with various polyols gave foams with satisfactory cell structure and flexibility.

Unfortunately, all of the foams prepared by these reactions were very soluble in all test solvents. Attempts to build solvent resistance into these formulations were unsuccessful. A list of these formulations appears in the Appendix, Table A.

Investigation of Epoxide-Trimethoxyboroxine Formulations The use of trimethoxyboroxine (TMB) as a room-temperature curing agent for epoxy resins was described by Lee and Neville.¹⁹ Later, Chen and Nixon^{20,21} reported the development of a rapid-curing foam-in-place system using an epoxy resin, a primary aromatic diamine, and trimethoxyboroxine. Although the curing mechanism of TMB has not been unequivocally proved, evidence^{21,22} indicates that TMB acts as both a Lewis acid-type catalyst (Reaction 1) and a curing agent (Reaction 2). The following mechanism is proposed for the reaction of TMB with an epoxy compound:

¹⁸ Silanes, Union Carbide Corp., bulletin SF-1160A, October, 1962.

¹⁹ H. Lee and K. Neville, "New Curing Agents for Epoxy Resin", SPE Journal, 16, 315-18 (1960).

²⁰ H. H. Chen, Foamed Resin Obtained by the Reaction of a Polyepoxide, Trimethoxyboroxine, and an Amine, U. S. Patent 3,025,249, March 13, 1962.

²¹ H. H. Chen and A. C. Nixon, "Heat-Resistant Epoxy-Boroxine Foams", Papers Presented at the Los Angeles Meeting, March-April 1963. The A.C.S., 1963, p. 221-43.

²² L. E. Brown and J. B. Harshman, Jr., Epoxy Foams Resistant to High Temperatures, MLM-CF-64-8-1 (August 10, 1964).

As can be seen from the reactions above, the use of difunctional epoxy compounds would yield a highly cross-linked polymer.

Vinylcyclohexene dioxide²⁴ (VCD) is a difunctional epoxy compound:

This material was unique in that it was extremely reactive when used with TMB. Other low-molecular-weight epoxide compounds were evaluated (Appendix, Table D, Reactions 145-150), but none equalled the performance of VCD.

The first formulation developed, E-1, appears in Table 5. The results of evaluation tests appear in Table 6. It was necessary²⁵ to add toluene as a freezing point depressant to the formulation before attempting a reaction at -60°C; 25% toluene solutions of each component were viscous liquids at -60°C.

The foam rise obtained at several temperatures is shown in Table 6. The addition of a silicone surfactant to the formulation (1 wt %) greatly improved the foam rise. At 24°C, a foam rise of 15:1 was obtained with XF-1066 (General Electric); however, the foam collapsed upon cooling to room temperature. At the same temperature, an 8:1 foam, with no collapse, was obtained with a two-part surfactant system (Y-4347 and Y-4499, Union Carbide Silicones Division).

The foams obtained from E-1 were very brittle and friable. An attempt was made to reduce this brittleness by introducing flexibilizing modifiers into the formulation (Appendix Table D, Reactions 113-124). Unfortunately, the incorporation of the modifiers yielded foams which exhibited poor foam rise or collapsed upon cooling.

²⁴ Vinylcyclohexene dioxide is sold by Union Carbide Chemical Corp. as Unox Epoxide 206 or Bakelite ERL 4206.

²⁵ The solidification temperature range of component B was -42° to -48°C, while that of TMB was -34° to -44°C.

Table 5

EPOXY-TRIMETHOXYBOROXINE FORMULATIONS

<u>Formulation</u>	<u>Component A</u>	<u>Component B</u>
E-1 (without toluene)	Trimethoxyboroxine ^a : 10 parts ^b	Epon 828 ^c : 50 parts VCD ^d : 50 parts
E-1 (with toluene)	Trimethoxyboroxine: 10 parts Toluene: 3.3 parts	Epon 828: 50 parts VCD: 50 parts Toluene: 33 parts
E-1A	Trimethoxyboroxine: 10 parts	Oxiron 2002 ^e : 50 parts VCD: 50 parts
E-2	Trimethoxyboroxine: 10 parts Toluene: 3.3 parts	Epon 871 ^c : 50 parts VCD: 50 parts Toluene: 33 parts SF-1079 ^f : 1 part
E-3	Trimethoxyboroxine: 15 parts Toluene: 5 parts	VCD: 100 parts SF-1079: 1 part
E-3A	Trimethoxyboroxine: 15 parts Toluene: 10 parts	VCD: 100 parts SF-1079: 1 part
E-4	Trimethoxyboroxine: 50 parts Methylene dichloride: 50 parts	VCD: 100 parts SF-1079: 1 part

^aAnderson Chemical Division, Stauffer Chemical Co.

^bParts by weight

^cShell Chemical Co.

^dVinylcyclohexene dioxide, ERL 4206 or Unox Epoxide 206, Union Carbide Chemical Corp.

^eFMC Corporation

^fSilicone surfactant, General Electric Co.

Table 6

EVALUATION OF EPOXY-TRIMETHOXYBOROXINE FORMULATIONS

<u>Formulation</u>	<u>Reaction Time (sec) at</u>				<u>Exotherm</u>	<u>Foam Rise</u>	<u>Solvent Attack^a</u>
	<u>-60°C</u>	<u>0°C</u>	<u>24°C</u>	<u>80°C</u>			
E-1 (without toluene)	-	10	5	-	0°: >260°C 24°: >260°C	24°C: ~2/1	F, G (20 hr) A, C, D, <u>F</u> , <u>G</u> , J, K, (119 hr)
E-1 (with toluene)	640	45	75	-	-60°: 97°C 0°: 129°C 24°: 150°C	-60°C: 1.25/1 0°C: 5/1 24°C: 3/1	Not determined
E-1A	-	80	17	10	0°: 100°C 24°: 134°C 80°: 190°C	24°C: ~1.25/1	B, <u>C</u> , <u>F</u> , <u>G</u> , <u>J</u> , <u>K</u> (20 hr)
E-2	No reaction (-16°C: 72 -23°C: 85 -40°C: 145)	21	8	<1	-40°: - -23°: 149°C -16°: 207°C 0°: 200°C 24°: 242°C 80°: 231°C	-40°C: 1/1 -23°C: 1/1 -16°C: 2/1 0°C: 4/1 24°C: 5/1 80°C: 5/1	A, <u>C</u> , <u>D</u> , <u>E</u> , G, J, <u>K</u> , L, M, N, (24 hr)
E-3	75	4	<1	<1	Not determined	-60°C: 7/1 0°C: 7/1 24°C: 10/1 80°C: 10/1	D (168 hr) Nitric acid also dissolves the foam
E-3A	17.5	4	<1	<1	Not determined	-60°C: -	Not determined

Table 6
(Continued)

^aThe letters refer to the solvents, listed below, which attacked the sample; the underlined letters denote solvents which were particularly destructive. The number in parenthesis is the immersion time. Tests were carried out at ambient temperature.

A - acetic acid	H - methyl ethyl ketone
B - acetone	I - phenyl glycidyl ether
C - chloroform	J - pyridine
D - ethanol	K - N-methyl pyrrolidone
E - dimethyl sulfoxide	L - tetrahydrofuran
F - dimethyl formamide	M - toluene
G - dioxane	N - water (used only for E-2 and E-3)

A second epoxide-TMB formulation (E-1A) was developed simultaneously in which epoxy resin Epon 828 was replaced by Oxiron 2002 (Table 5). This formulation was less exothermic than was formulation E-1. The solvent resistance of this foam was unsatisfactory, and its reaction time at 0°C was too long (Table 6). Thus, further work with this formulation was discontinued.

Attempts to reduce the brittleness of E-1 foams resulted in the development of formulation E-2 (Table 5). Several so-called "flexible" epoxy resins were evaluated as a co-reactant with VCD. The materials used appear in the Appendix in Table D, Reactions 128-141. The formulation which yielded the strongest and least friable foam was given the designation E-2. The results of evaluation tests appear in Table 6. No reaction was observed at -60°C. Boron trifluoride etherate was substituted for trimethoxyboroxine in an attempt to obtain a reaction at -60°C (Table 7). The lowest temperature at which reaction could be initiated was -49°C. In addition to a lack of low-temperature reactivity, E-2 foams had poor solvent resistance.

Although the reaction of TMB with VCD alone was briefly evaluated in earlier work, it was thought to be too exothermic. After the failure of E-2 to initiate at -60°C, the system was re-evaluated and a modified formulation (E-3) was developed (Table 6). The results of evaluation tests (Table 6) showed that formulation E-3 was a satisfactory system; reaction occurred at -60°C, and foam rise and solvent resistance were good. However, the foams were friable and the reaction at -60°C appeared to be rather slow. Several attempts to rectify these deficiencies were made. Addition of flexibilizing modifiers (Appendix Table D, Reactions 128-141) did not improve the quality of the foam. Amine curing agents (Appendix Table D, Reactions 80, 152, 164-165)

Table 7

REACTION OF BORON TRIFLUORIDE ETHERATE WITH
COMPONENT B,^a FORMULATION E-2, AT LOW TEMPERATURES

<u>Component B</u>	<u>BF₃ Etherate (g)</u>	<u>Reaction Temperature (°C)</u>	<u>Reaction Time (sec)</u>
20 g	0.5	-50	No reaction
20 g	1.0	-57	No reaction
20 g + 2 g toluene	1.0	-49	60
20 g + 2 g toluene	1.0	-54	No reaction
20 g + 4 g toluene	1.0	-59	No reaction
20 g + 3 g of 1:3 mixture of styrene and toluene	1.0	-56	No reaction

^aReactive ingredients only (i.e., 1:1 mixture of Epon 871 and VCD).

were substituted for the trimethoxyboroxine in an effort to obtain a more rapid reaction, but no reaction was observed when these compounds were used.

It was found that incorporation into the formulation of silicone surfactants of the type used in polyurethane foam formulations greatly improved the uniformity and foam rise of epoxy foams. Table 8 lists the surfactants evaluated. The most efficient surfactants were DC-201, SF-1079, and XF-1066. There was little difference between foams whether 1 or 8 parts of surfactant were used in the formulations.

Component A (TMB mixed with 25% toluene) was rather viscous at -60°C. In order to determine whether a reduction in the viscosity of the component would result in a shorter reaction time at -60°C, several different solvents were evaluated as freezing point depressants for TMB (Table 9). The diisopropyl ether - TMB solution appeared to be more fluid than the normal toluene - TMB component. Further investigation of this approach for increasing reactivity at low temperature is discussed in a subsequent section.

A significant decrease in the reaction time was observed when the toluene content of component A was increased from 5 parts to 10 parts (formulation E-3A, Table 5). The reaction time appears in Table 6. No other evaluation tests were performed on E-3A foams.

Table 8

EVALUATION OF SILICONE SURFACTANTS
IN FORMULATION E-3 AT AMBIENT TEMPERATURE

<u>Sample</u>	<u>Surfactant</u>	<u>Percent Surfactant^a</u>	<u>Foam Rise (Estimated)</u>
1	None	0	2:1
2	DC-201 ^b	1	10:1
3	DC-201	8	7:1
4	XF-1066 ^c	1	11:1
5	XF-1066	8	10:1
6	SF-1079	1	8:1
7	SF-1079	8	8:1
8	DC-113 ^b	1	3:1
9	Y-4347 ^d	4	25:1
	Y-4499	2	
10	L-5320 ^d	1	7:1
11	L-5320	8	7:1

^aPercent by weight

^bDow-Corning Corp.

^cGeneral Electric Co.

^dUnion Carbide Corp., Silicone Division

Table 9

MISCIBILITY OF TRIMETHOXYBOROXINE
AND SELECTED SOLVENTS AT AMBIENT TEMPERATURE

<u>Solvent</u> ^a	<u>Result</u>
Stoddard solvent	Not miscible
Methyl cyclohexane	Not miscible
Diisopropyl ether	Miscible
Tetrahydrofuran	Miscible
Acetone	Miscible
Dimethyl sulfoxide	Miscible, but mixture was more viscous than pure TMB
Ethanol	White precipitate formed
Butyl cellosolve acetate	Miscible

^aThree grams of the solvent was added to 10 g of TMB in a 25-ml Erlenmeyer flask.

A sample of formulation E-3A was evaluated at Union Carbide's Y-12 facility at Oak Ridge, Tennessee. The evaluation consisted of noting the foam rise of the formulation at several temperatures when mixed and injected into a special mold using a special apparatus. Although satisfactory foams were obtained at room temperature, no foaming was observed at -60°C. This was contrary to results obtained at Mound (see Table 6, E-3A reaction time and foam rise). A possible explanation was that the experiments at Y-12 deposited the reactants in a thin layer, thus reducing the exotherm produced, while in the Mound experiments the reactions were run in a small container, where the initial heat of reaction was not quickly dissipated. These results led to a series of experiments designed to improve the foaming of E-3A at -60°C. The modifications and the results appear in Tables 10 and 11.

An increase in the catalyst concentrations did not improve the foaming. The measured exotherm of the initial runs indicated that the boiling point of toluene (110.6°C) was not being attained. Therefore, several

Table 10

REACTION OF SYSTEM E-3 AT -60°C, MODIFIED COMPONENT A

Run	TMB ^a (%)	Solvent ^b	Solvent ^c (%)	Reaction Time (sec)	Foam Rise	Exotherm (°C)
1	15.2	Toluene	40	15	1:1	81
2	22.1	Toluene	40	15	1:1	69
3	32.8	Toluene	40	10	1:1	-
4	42.6	Toluene	40	11	1:1	138
5	58.3	Toluene	40	20	1:1	-
6 ^d	53.3	Toluene	40	43	4:1	74
7	14.9	Acetone	40	>180	-	-
8	29.7	Acetone	40	72	2:1	-
9	44.7	Acetone	40	122	5:1	-
10	15.1	Trichloro- ethylene	40	10	2:1	-
11	29.6	Trichloro- ethylene	40	7	2:1	-
12	49.7	Trichloro- ethylene	40	15	2:1	-
13	20.4	Trichloro- ethylene	51 ^e	19	2:1	109
14	61.3	Trichloro- ethylene	51 ^e	8	2:1	94
15	15.0	Methylene dichloride	51 ^e	12	3:1	-
16	29.8	Methylene dichloride	51 ^e	10	3:1	-
17	51.8	Methylene dichloride	51 ^e	11	4:1	-
18	15.9	Diisopropyl ether	36	~10	3:1	175
19	32.5	Diisopropyl ether	36	7	2:1	48
20	57.3	Diisopropyl ether	36	7	3:1	97
21	45.7	Acetone	40	64	5:1	66

^aThe weight of trimethoxyboroxine is calculated as:

$$\frac{\text{weight of component B} \times \text{wt \% solvent} - 100}{\text{weight of component A}}$$

^bSolvent used in component B.

^cPercent solvent based on total weight of component B.

^dComponent A contained 20% acetone.

^eQuantity needed to give volume equivalent to that obtained with 40 wt % toluene.

Table 11

REACTION OF SYSTEM E-3 AT -60°C, MODIFIED COMPONENT B

<u>Run</u>	<u>TMB^a</u> <u>(%)</u>	<u>Solvent^b</u>	<u>Reaction Time</u> <u>(sec)</u>	<u>Foam Rise</u>	<u>Exotherm</u> <u>(°C)</u>
1	18.7	Toluene	32	2:1	59
2	18.7	Acetone	183	4:1	103
3	18.8	Trichloro- ethylene	30	2:1	89
4	18.5	Methylene dichloride	50	1.5:1	50
5	18.7	Diisopropyl ether	53	1.5:1	75
6	18.8	Genetron G-113	39	3:1	80
7	18.7	Glycidol	122	2:1	67
8	18.6	Methanol	>300	-	-

^aSee note "a" in Table 10.

^bSolvent used in component A according to the formula:

VCD - 100 parts
SF-1079 - 1 part
Solvent - 10 parts

solvents with lower boiling points (Table 10) were substituted for the toluene in component A. The best foam rise was obtained with acetone but the long period before reaction began was considered to be unsatisfactory. The best system observed contained methylene dichloride (Table 10). The other modifications resulted in foams which were no better than normal E-3A foams obtained at -60°C. Table 11 shows the results obtained when Component B was modified. No improvement was observed.

Formulation E-3A was modified according to the results discussed above (i.e., methylene dichloride was substituted for toluene and the TMB concentration was increased; Table 5, formulation E-4). The new formulation was evaluated in the Y-12 apparatus; the results are shown in Table 12.

Table 12

PERFORMANCE OF E-4 FORMULATION IN THE Y-12 APPARATUS

<u>Reaction Temperature (°C)</u>	<u>Foam Rise</u>	<u>Exotherm (°C)</u>	<u>Maximum Pressure (psig)</u>	<u>Condition of Product</u>
-60	8:1-9:1	96	70	Solid foam
25	8:1-9:1	132	80	Solid foam
80	None	180	105	Liquid

The effects of storage at elevated temperatures on the components of several of the formulations discussed above are reported in the next section of this report.

Investigation of Miscellaneous Foam Systems Many reactions not covered elsewhere in this section were carried out in an effort to prepare satisfactory foam materials. These reactions were not investigated fully, but appeared to be less likely to produce satisfactory material than those listed above. In many cases, only one or two experiments were carried out with each system. A list of these reactions is found in the Appendix, Tables A to F.

EFFECTS OF STORAGE AT 110°C ON SELECTED PROPERTIES OF SEVERAL FORMULATIONS - CALORIMETRIC STUDIES

Measurement of the heats of reaction of rapid-curing foam formulations has a two-fold purpose: first, to determine if the system meets specifications as far as the heat of reaction is concerned; second, to use the heats of reaction as a criterion for determining the effect of accelerated aging on materials used in formulating the system.

The maximum temperature rise which the foam and surrounding reactor vessel might attain during the course of the reaction can be calculated by use of the heats of reaction data and heat capacity of the reaction vessel.

Comparison of the heat of reaction of fresh materials with that of aged materials gives an estimate of the stability of the materials during storage at 110°C. For example, assume that the heat of reaction for fresh materials yielded 1 kcal per 10g of product. For an identical weight of sample of aged materials which had prepolymerized 10%, the heat of reaction should exhibit a corresponding change in value to 900 calories, or 100 calories less than fresh materials.

Using the heats of reaction as a criterion for aging studies, one may observe the following:

1. A decrease in the heat of reaction
2. An increase in the heat of reaction
3. No change in the heat of reaction

A decrease in the heat of reaction indicates one or more of the following: prepolymerization of material; destruction of reactive groups through decomposition (epoxide to hydroxyl group); destruction of curing agent; and incomplete reaction or poor mixing of materials.

An increase in the heat of reaction indicates one or more of the following: breakdown of resin or curing agent into more reactive chemical entities; poor mixing leading to inhibited foam formation, and/or charring in the product.

No change in the heat of reaction indicates one of the following: all materials are stable and aging has no effect; breakdown of materials resulted in some chemical species which are exothermic in reaction and some which are endothermic with an overall heat of reaction equal to that of fresh materials.

Using viscosity and refractive index measurements, one can eliminate many of the causes for changes in the heat of reaction.

Measurement of the heats of reaction of rapid-curing foam systems presents some difficulties experimentally. Incomplete mixing of reactants in the calorimeter may lead to incorrect values, as described previously. Due to the nature of the product formed in the reaction, one may encounter incomplete reaction or a decrease in the rate as the reaction becomes diffusion controlled. The rate becomes diffusion controlled and falls off abruptly in the region of 95% conversion.²⁶ In some cases, the equilibrium constant between the starting monomer and the polymer may be rather large.

The most direct method of measuring energy changes produced by a chemical reaction is to carry out the reaction in a calorimeter and to observe the temperature change produced by it. Inasmuch as many of these reactions are difficult to reproduce, a calorimeter capable of measuring heat quantities to $\pm 1\%$ will suffice. An additional requirement is a relatively short period of time (~ 4 hr) to make each determination.

Measurement of temperature changes produced by these reactions in a metal block appeared to be the most promising for the time requirement and the desired accuracy in the energy measurement.

²⁶F. S. Dainton and K. J. Ivin, in Experimental Thermochemistry, H. A. Skinner (ed.), Vol. II, New York, Interscience Publishers, 1962, p. 256.

A silver or copper²⁷ block would be the most suitable for this system; however, aluminum is readily available and was used as a substitute.

The precision of the heats of reaction is better than $\pm 3\%$ and the energy equivalent determinations could be reproduced to $\pm 0.15\%$. The accuracy of the results can only be estimated inasmuch as the reactions became diffusion controlled at about 95% completion. The heats of reaction were estimated to be 3 to 6% low. However, this does not affect the results of the aging comparison study, because of the substitutional nature of the procedure used in making comparisons.

Aged formulations have the same composition as do fresh formulations. All calorimetric determinations were carried out using the same procedures.

Effect of Storage at 110°C, Formulation PF-3 The heat of reaction for formulation PF-3 was found, over five runs, to be 49.12 ± 0.76 cal/g of product. The approximate weights of materials used in the reaction were 3.0 g of component A and 10.4 g of component B.

Table 13 lists the heats of reaction for components of this formulation which were aged in an oven at 110°C for 3 weeks. The heats of reaction of the aged components are compared to those for fresh components.

The following set of equations was used to determine which components had decomposed.

The heats of reaction for equations 2, 3, and 4 were less than the heat of reaction for equation 1; the amount of decomposition was 2%, 2% and 5%, respectively. Equation 2 appears to have some reaction occurring which does not take place in the other equations, but yields a higher heat of reaction than would be predicted by combination of the other equations.

The viscosity of unaged component B was 2.25 - 2.50 stokes, while that of an aged sample was 1.40 - 1.65 stokes. The decrease in viscosity indicated that some degradation had occurred and, therefore, could explain the decreased reactivity.

²⁷ J. M. Sturtevant, in Techniques of Organic Chemistry, A. Weissberger (ed.), Vol. 1, 3rd ed., New York, Interscience Publishers, 1959, p. 582.

Table 13

HEATS OF REACTION OF AGED FORMULATION PF-3

<u>Components</u>	<u>Equation No.</u>	<u>Heat of Reaction (cal/g of Component B)</u>
Fresh A and Fresh B	1	69.92 $\pm$ 0.07 (3 runs)
Aged A and Aged B	2	68.05
Aged A and Fresh B	3	66.35
Fresh A and Aged B	4	68.43
Fresh A and Fresh B; excess B		66.43
Aged A and Aged B; excess B		64.96

The last two values listed in the table are for reaction with an excess amount of component B. Tests²⁸ on the excess solution remaining in the reaction vessel indicated the solution to be excess component B. In this case, the heat of reaction for aged materials is 2% lower than that for fresh materials.

Effect of Storage at 110°C, Formulation E-3 Table 14 contains the results of the heats of reaction on fresh and aged samples of formulation E-3. The heats of reaction are given in cal/mole of VCD and cal/g of the reactive species (not inert materials such as SF-1079 and toluene) for comparison purposes. Fresh reactants are listed as zero time at 110°C.

Two aged samples demonstrated some decomposition in aging. The VCD aged in contact with copper apparently prepolymerized, since the heat of reaction is about 9% lower than for the fresh sample and the foam rise is about 50% smaller. Further evidence of some prepolymerization is given by an observed increase in viscosity (see Figure 3).

The VCD and SF-1079 aged in stainless steel had an increase in the heat of reaction. This is primarily a result of very little foam rise, causing spotted charring in the product. The change in viscosity of the E-3 sample is shown in Figure 3.

²⁸ Solution reacted with component A and not component B.

Table 14

EFFECT ON HEATS OF REACTION DUE TO STORAGE OF MATERIALS
AT ELEVATED TEMPERATURE FOR SYSTEM E-3

<u>No. of Runs</u>	<u>Aging Time at 110°C (days)</u>	<u>Heat of Reaction (kcal/mole of VCD)</u>	<u>Heat of Reaction (cal/g of reactive materials)</u>
<u>VCD in Contact with Copper - Fresh TMB</u>			
5	0	30.12 ± 0.18	185.7 ± 0.9
2	14	28.15 ± 0.13	172.6 ± 0.8
2	35	28.76 ± 0.01	178.4 ± 0.1
<u>VCD and SF-1079 in Contact with Copper - Fresh TMB</u>			
5	0	30.12 ± 0.18	185.7 ± 0.9
3	19	30.04 ± 0.36	186.4 ± 2.2
2	35	30.16 ± 0.09	187.1 ± 6.3
<u>VCD in Contact with Stainless Steel - Fresh TMB</u>			
5	0	30.12 ± 0.18	185.7 ± 0.9
2	14	30.78 ± 0.01	188.7 ± 0.1
2	35	29.49 ± 0.20	182.9 ± 1.7
<u>VCD and SF-1079 in Contact with Stainless Steel - Fresh TMB</u>			
5	0	30.12 ± 0.18	185.7 ± 0.9
2	19	29.72 ± 0.04	184.4 ± 0.3
2	35	32.46 ± 0.13	201.3 ± 0.9
<u>VCD and SF-1079 in Contact with Glass - Fresh TMB</u>			
2	0	31.14 ± 0.01	193.5 ± 0.4
5	10	31.47 ± 0.83	195.4 ± 6.4
2	21	30.66 ± 0.19	191.6 ± 1.6
<u>TMB - Fresh VCD</u>			
3	24	31.16 ± 0.24	192.8 ± 2.5
<u>Trichloroethylene-TMB Aged VCD and SF-1079 in Contact with Stainless Steel</u>			
2	19	30.83 ± 0.28	191.2 ± 1.7

Figure 3

EFFECT ON VISCOSITY OF STORAGE AT ELEVATED TEMPERATURES FOR SYSTEM E-3A EPOXY RESIN COMPONENTS

The last values in Table 14 are for a change in formulation. Toluene was replaced by an equivalent weight of trichloroethylene. The heat of reaction is about 3% higher for this reaction and the foam rise was about 10% higher, apparently due to better mixing of reactants.

Approximate weights of materials used in calorimetric determinations were 1.3 g of component A and 6.2 g of component B.

Heat of Reaction Determinations for Formulations E-1, E-1A, PB-1, and PA-1 Originally a complete aging study on formulations E-1, E-1A, PB-1 and PA-1 was to have been performed. However, either the formulation was superseded by another formulation or the components gelled during storage. Formulations E-1 and E-1A were supplemented by E-2 before completion of the aging study. The epoxy resin components of PB-1 and PA-1 gelled during storage at 110°C. Thus, only the heats of reaction of unaged components of these systems were determined.

Formulation E-1 and E-1A The only difference between these two formulations is that toluene was added to E-1A. The heats of reaction of these formulations were the first to be determined in the calorimeter. The large deviation in the heat of reaction of E-1 is due to the

difficulty in mixing the reactants to give a uniform mixture in the calorimeter. These runs were made with a two-bladed mixing device. Replacement of this device with a four-bladed propeller and addition of toluene (E-1A) to the reactants resolved this mixing problem and gave more consistent results.

Approximate weights of materials used in the calorimetric determinations were: without toluene, 2.0 g of component A and 20.0 g of component B; with toluene, 2.6 g of component A and 29.3 g of component B.

The heat of reaction of system E-1, in eight runs, was found to be 126.0 ± 14.0 cal/g of reactive materials; that of system E-1A, in eight runs, was found to be 124.7 ± 3.9 cal/g of reactive materials.

Formulation PB-1 Table 15 lists the heat of reaction for PB-1 and the composition of components A and B. The heat of reaction is given in calories per gram of product of reactive species. Listing the heats of reaction in this way eliminates all inert material in reactants and gives one a better value for comparison with other formulations.

The approximate weights of materials used in the calorimetric determination were: 1.1 g of component A and 3.3 g of component B.

Table 15

HEAT OF REACTION OF FORMULATION PB-1

<u>Q(cal/g of reactive materials)</u>	<u>Composition of Reactants</u>
141.4	Component A: 44.444% BF ₃ ether complex
136.6	22.222% Phospholeum
<u>143.9</u>	33.334% Diisopropyl ether
Ave. 140.6 ± 2.7	Component B: 58.824% Epon 812
	14.706% VCD
	22.058% Tetrahydrofuran
	4.412% SF-1079

Formulation PA-1 Tables 16 to 19 list the heats of reaction for formulation PA-1. Tables 17 to 19 give the results of the heats of reaction of the various chemical species used in the formulation of the resin component B reacting with phosphorofluoridic acid (PFA) solution. Toluene was added to the resin materials to aid in mixing reactants in the calorimeter vessel.

The heats of reaction listed in these tables were to be used as standards for aged materials of formulation PA-1; however, Epon 812 gelled on aging and every sample containing Epon 812 gelled. The study was terminated at this point.

The approximate weights of materials used in the calorimetric determinations were: 3.0 g of component A and 6.8 g of component B.

Table 16

HEAT OF REACTION OF FORMULATION PA-1

<u>Q(cal/g of reactive materials)</u>	<u>Composition of Reactants</u>
129.1	Component A: 83.333% PFA
128.8	16.667% Diisopropyl ether
<u>125.5</u>	
Ave. 127.8 $\pm$ 1.5	Component B: 58.824% Epon 812
	14.706% VCD
	22.058% THF
	4.412% SF-1079

Table 17

HEAT OF REACTION OF FRESH EPON 812 SOLUTION
WITH FRESH PFA SOLUTION IN FORMULATION PA-1

<u>Q(cal/g of reactive materials)</u>	<u>Composition of Reactants</u>
123.1	Component A: 33.333% PFA
125.3	66.667% Diisopropyl ether
126.2	
<u>127.5</u>	Component B: 79.350% Epon 812
	20.650% Toluene
Ave. 125.5 $\pm$ 1.3	

Table 18

HEAT OF REACTION OF FRESH EPON 812 AND SF-1079
WITH FRESH PFA SOLUTION IN FORMULATION PA-1

<u>Q(cal/g of reactive materials)</u>	<u>Composition of Reactants</u>
124.6	Component A: 33.333% PFA
124.2	66.667% Diisopropyl ether
<u>125.5</u>	
Ave. 124.8 $\pm$ 0.5	Component B: 75.479% Epon 812
	18.865% Toluene
	5.655% SF-1079

Table 19

HEAT OF REACTION OF FRESH EPON 812
AND VINYLCHYCLOHEXENE DIOXIDE (VCD)
WITH FRESH PHOSPHOROFUORIDIC ACID (PFA) SOLUTION

<u>Q(cal/g of reactive materials)</u>	<u>Composition of Reactants</u>
148.2	Component A: 33.333% PFA
152.8	66.666% Diisopropyl ether
<u>152.3</u>	
Ave. 151.1 $\pm$ 1.9	Component B: 63.858% Epon 812
	20.156% Toluene
	15.986% VCD

MISCELLANEOUS EXPERIMENTS

Inhibition of furfuryl alcohol polymerization at 110°C, the effect of elevated temperature storage on a silicone surfactant and the efficiency of some non-silicone type foam control agents in foam systems were studied briefly. While not directly related to the Mound effort, these subjects were of interest to other development groups.

At the request of Y-12, the effect of amines²⁹ on the inhibition of furfuryl alcohol polymerization at elevated temperatures was investigated. Five samples of furfuryl alcohol were stored for 1 month at 110°C. Four of the samples contained approximately 0.1 wt % of one of the following amines: N-cyclohexylpiperidine, diethylene triamine, triethylene tetramine, or triethylene diamine. All samples changed color from amber to a very dark brown during the storage period. The furfuryl alcohol containing no inhibitor gelled to a semi-rigid solid. The sample containing triethylene diamine appeared to be more viscous than before aging started. The other three samples showed no apparent change of viscosity. The refractive index of the sample containing N-cyclohexylpiperidine changed from 1.4845 (unaged) to 1.5164 (aged). The samples containing diethylene triamine or triethylene tetramine showed small increases of refractive index (i.e., 1.4859 to 1.4936 for the sample containing TETA). After aging, the sample containing triethylene diamine was too opaque to allow measurement of the refractive index.

Silicone surfactants may experience chain scission at the silicon atom when subjected to high temperatures.³⁰ In order to determine whether the silicone surfactant SF-1079, used in systems E-3, E-3A, E-4, and PB-1, would degrade and lose its effectiveness when stored at elevated temperatures, a sample of the surfactant was stored in a 2-oz glass jar at 90°C (immersed in an oil bath controlled at 90°C).

Samples were removed periodically and used to prepare E-3 foams. The foams thus obtained were compared with foams made using un-aged SF-1079. A 10 to 15% reduction in the foam rise was observed in samples prepared using aged SF-1079 aged for 37 days.

Subsequently, several non-silicone type foam control agents were evaluated as possible replacements for SF-1079. Lauric acid and Luperol RO-0 were ineffective. However, a good foam rise was obtained when Brulin 815 MX, a liquid detergent, was substituted for SF-1079 in an E-3 formulation. Although the cell structure was non-uniform and rather coarse, the foams appeared to be slightly stronger than those prepared with SF-1079.

C O N C L U S I O N S

An epoxy foam formulation (E-3) was developed which satisfied all of the specified requirements with the exception of low-temperature initiation. The foam was produced by allowing vinylcyclohexene dioxide, containing a silicone surfactant, to react with a toluene solution of trimethoxyboroxine.

²⁹A. P. Dunlop and F. N. Peters, Jr., Ind. Eng. Chem., **34**, 814 (1942).

³⁰M. A. Barnas, Jr., Union Carbide Corp., Silicones Division, private communication.

The reaction of phospholeum - boron trifluoride etherate mixture or phosphorofluoridic acid with a mixture of Epon 812 and vinylcyclohexene dioxide yielded room-temperature-curing flexible epoxy foams. Although foams prepared from these formulations had the best physical structure of any system investigated, their non-reactivity at -60°C rendered them unacceptable for the present application.

Polyurethane foams with the required reaction time and strength were readily formulated; also, the density and the rigidity of the foam were easily adjusted. However, the instability of the isocyanates used and the non-reactivity at -60°C rendered these formulations unacceptable.

Vinyl compounds were cured rapidly at -60°C with boron trifluoride etherate. No foams were obtained and the end products were not solvent-resistant.

The incorporation of silicone surfactants into epoxy formulations greatly improved their foaming ability.

Attempted modifications of the epoxy foam formulations to reduce brittleness or improve foaming at -60°C were unsuccessful.

Several amines (N-cyclohexylpiperidine, diethylene triamine, triethylene tetramine, or triethylene diamine) inhibited the polymerization of furfuryl alcohol stored for 30 days at 110°C .

Storage at 110°C for 35 days in the presence of copper or stainless steel did not adversely affect the heat of reaction, viscosity, or foaming ability of formulation E-3.

Epon 812 gelled when stored at 110°C for about one month.

Brulin 815 MX, a detergent, performed satisfactorily as a foam control agent in epoxy formulation E-3.

R E C O M M E N D A T I O N S   F O R   F U R T H E R   S T U D Y

The reaction of trimethoxyboroxine and vinylcyclohexene dioxide has not been fully investigated. A study of the reaction rates and mechanisms at -60° , 24° , and 80°C should be performed. The knowledge thus gained should prove most valuable in further formulation or modification of the system.

A complete aging study should be performed on the components of formulation E-3. This should include storage at several temperatures for long periods of time. The components should be thoroughly investigated periodically during the storage period.

Polyurethanes were the most versatile materials investigated; a lack of stability inherent in the isocyanates used prevented the use of polyurethane systems in the present application. An attempt to locate or synthesize stable isocyanates for use in polyurethane formulations should be undertaken.

Many of the listed formulations were briefly scanned. A re-evaluation with a more comprehensive test procedure might lead to the development of a satisfactory system.

The effects of solvents not previously tested on the heats of reaction of quick-rising foams should be determined.

A calorimeter capable of measuring heats of reaction with an excess amount of solvent should be designed and built. With this device, no solid formation at low temperature would take place. Thus, more precise values of the heats of reaction could be obtained.

APPENDIXES

T A B L E S   O F   F O R M U L A T I O N S

Table A
FORMULATIONS UTILIZING POLYOL COMPOUNDS

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
169	Egg albumin ¹ in water	Ethanol	-	Discarded because albumin coagulated at 80°C
170	Amyltrichlorosilane ²	LA-475 ³	Methyl methacrylate ¹	Immediate reaction
171	Amyltrichlorosilane	LA-475	Tetrahydrofuran	Immediate reaction, slight foam rise
172	Boron trifluoride etherate ⁴	Dipropylene glycol & triphenyl phosphite (Mod-Epox) ⁵	-	No immediate reaction
173	Ethyltrichlorosilane ²	LG-168 ³	-	Sets up in less than 1 minute; soft, rubbery
174	Ethyltrichlorosilane	Dow 166-450 ⁶	LG-168 ³	Rubbery material in 5 min
175	Ethyltrichlorosilane	LG-168 ³	166-450 ⁶ , XF-1066 ⁷	Foam rise 20 sec after mixing, collapses
176	Ethyltrichlorosilane	LG-168 ³	166-450, LA-475 Quadrol ⁸ XF-1066	Foams immediately; collapses

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
177	Ethyltrichlorosilane ²	LG-168 ³	166-450 ⁶ Quadrol ⁸ 1,4-butanediol ⁹ XF-1066 ⁷	Foaming immediate; collapses
178	Ethyltrichlorosilane	LG-168	166-450 Quadrol XF-1066	Foam rises in 30 sec, collapses
179	Ethyltrichlorosilane	LA-475	Methyl meth- acrylate	Reaction in less than 3 sec; some foaming
180	Ethyltrichlorosilane	LA-475	Tetrahydrofuran	Reaction in less than 3 sec; some foaming
181	Ethyltrichlorosilane	Triethanolamine ¹	-	Immediate reaction; tan powder
182	Ethyltrichlorosilane	Triethanolamine	Toluene	Immediate reaction; white powder
183	Methylvinylidichloro- silane ²	LG-168	166-450 XF-1066	No foam; reaction begins immediately
184	Methyltrichlorosilane ²	LA-475	Methyl meth- acrylate	Reaction in less than 2 sec
185	Mondur MR ¹⁰	1,4-butanediol	M & T T-9 ¹¹	Reaction time 20 sec

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
186	Mondur MR ¹⁰	1,4-butanediol	T-9 ¹¹ Cab-O-Sil ¹²	Reaction time 20 sec.
187	Mondur MR	1,4-butanediol	LG-168 LA-700 33-LV ¹³	Gelled in 9 sec; 158°C exotherm
188	Mondur MR	1,4-butanediol	LG-168 33-LV DC-210 ¹⁴	Gelled in 10 sec; 170°C exotherm
189	Mondur MR	1,4-butanediol	LK-380 ³ 33-LV	Gelled in 10 sec
190	Mondur MR	Glycerine ¹⁵	T-9	Reaction time 2 min
191	Mondur MR	1,4-butanediol	Glycerine 33-LV	Reaction time 25 sec
192	Mondur MR	1,4-butanediol	Glycerine T-9	Reaction time 45 sec
193	Mondur MR	1,4-butanediol	Glycerine T-9	Reaction time 35-45 sec
194	Mondur MR	Glycerine	33-LV ¹³	Reaction time 2-7 min

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
195	Mondur MR ^{1 0}	LG-168 ³	Y-4347 ² Y-4499 ² 33-LV ^{1 3} G-113 ^{1 6}	Reacted within 30 sec; very little foam rise
196	Mondur MR	LG-168	H ₂ O Y-4347 Y-4499 T-9	Reacted within 45 sec; partially cured
197	Mondur MR	LG-168	PPG-4025 ³ 33-LV	Gelled in 40 sec to semi-rigid state
198	Mondur MR	LG-168	33-LV	Reacted in 25 sec to a rigid material
199	Mondur MR	LG-168	M & T T-9	Reaction time 20 sec
200	Mondur MR	LHT-28 ³	33-LV	No reaction
201	Mondur MR	LK-380	33-LV	Reacted within 15 sec to yield a rigid solid
202	Mondur MR	PPG-425 ³	33-LV	Reacted in 20 sec; rigid
203	Mondur MR	PPG-1025 ³	33-LV	Reaction time 2-3 min; spongy, partially cured
204	Mondur MR	PPG-4025	33-LV	No reaction

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
205	Mondur MR	Atlas 2764 polyol ¹⁷	33-LV	Reacted within 15 sec
206	Mondur MR, Polycin U-63 ¹⁸	1,4-butanediol	T-9	Reaction time 30 sec
207	Mondur MR, Polycin U-63	1,4-butanediol	33-LV Glycerine	Reaction time 30 sec
208	Mondur MR, Polycin U-63	LG-168	Glycerine 33-LV DC-210	Reacted in 45 sec; slight foam rise
209	Mondur MR, Polycin U-63	LG-168	1,4-butanediol 33-LV DC-210	Reacted in 30-45 sec; no foam rise
210	Polycin U-63	1,4-butanediol	33-LV	Reacted within 50 sec
211	Polycin U-63	1,4-butanediol	T-9 ¹¹	Reacted within 60 sec
212	Sulfur dichloride ⁹	Glycerine	-	Reaction immediate; no gelation
213	Sulfur dichloride	LG-168	-	Reaction but no gel- ation
214	Sulfur dichloride	PPG-4025	-	Reaction but no gel- ation

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
215	Tolylene diisocyanate ¹⁰	LG-168	Y-4347 Y-4499 T-9 Water	A semi-rigid foam is produced within 30 sec
216	Tolylene diisocyanate	LG-168	Y-4347 Y-4499 T-9 G-113	A semi-rigid foam is produced within 30 sec
217	Tolylene diisocyanate	LG-168	Y-4347 Y-4499 33-LV G-113	A semi-rigid foam with good foam rise is produced within 15 sec
218	Borester #8 ²¹	LG-168	-	Gelation in 20 sec; soft, rubbery
219	Vinyltrichlorosilane ²	Thanol RS-500 ²²	-	Immediate reaction; solid formed
220	Vinyltrichlorosilane	Thanol RS-700 ²²	-	Immediate reaction and solidification
221	Vinyltrichlorosilane	Thanol RS-700	Tetrahydrofuran	Immediate reaction; slight foam rise
222	Vinyltrichlorosilane	LA-475	-	Rapid; reacted before thorough mixing

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
223	Vinyltrichlorosilane	LA-475	Methyl methacrylate	Immediate reaction
224	Vinyltrichlorosilane	LHT-67 ³	-	Gels in 12 min
225	Vinyltrichlorosilane	LHT-112 ³	-	Gels in 2 min
226	Vinyltrichlorosilane	LHT-240 ³	-	Gels in 10 sec
227	Vinyltrichlorosilane	LS-490 ³	Tetrahydrofuran	Starts foaming in 5 sec; only slight foam rise
228	Vinyltrichlorosilane	LA-475	LG-168 Tetrahydrofuran	Reaction immediate; slight foam rise
229	Vinyltrichlorosilane	LG-168	Tetrahydrofuran	Noticeable gelling after 3 min; sets up to crystal-clear solid in 4 min
230	Vinyltrichlorosilane	LG-168	PPG-425 Methyl ethyl ketone	Gels to soft material
231	Vinyltrichlorosilane	LG-168	166-450 XF-1066	Foam begins on mixing; collapses
232	Vinyltrichlorosilane	LG-168	166-450 Diethylamino-propylamine ²³ XF-1066	Foams immediately; collapses

Table A (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polyol Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
233	Vinyltrichlorosilane	LG-168	166-450 Triethylene tetramine ^{2,3} XF-1066	Foams immediately; collapses
234	Triphenyl phosphite (Mod-Epoxy)	Dipropylene glycol ⁶	-	No immediate reaction
235	Triphenyl phosphite	1,4-butanediol	-	No immediate reaction
236	Triphenyl phosphite	1,4-butanediol	33-LV	No immediate reaction
237	Triphenyl phosphite	1,4-butanediol	Sebacyl chloride ⁴	High exotherm developed but no gelation
238	Mondur MR	LG-168 LA-700	33-LV	Gelled in 10 sec; 146°C exotherm

Table B
FORMULATIONS UTILIZING POLYSULFIDE COMPOUNDS

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Polysulfide Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
238	Mondur MR	LP-3 ³¹	33-LV	Immediate gelation; semi-rigid, flexible
239	Mondur MR	LP-33 ³¹	33-LV	Immediate gelation; partially cured
240	Mondur MR	LP-8 ³¹	33-LV	No immediate reaction
241	Mondur MR	LP-8	33-LV	Immediate gelation to yield a semi-rigid solid
242	Mondur MR	LP-8	LA-700 (pento1) 33-LV	Immediate gelation; semi-rigid, flexible
243	Sebacyl chloride	LP-8	-	No reaction observed
244	Sulfur dichloride	LP-8	-	Exothermic reaction but no gelation
245	Tetraethylene pentamine ²³	LP-8	-	No immediate reaction
246	Trimethoxyboroxine ³⁷	LP-8	-	No immediate reaction

Table C
FORMULATIONS UTILIZING VINYL COMPOUNDS

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Vinyl Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
29	Aluminum chloride ^{1 6}	Vinyl acetate ⁴	-	Rapid reaction; black solid
30	Aluminum chloride	Vinyl triethoxy silane (A-151) ²	-	Turns orange-brown on mixing; slight heat; mostly liquid after 10 min
31	Aluminum chloride	Vinyl tris-(2-methoxy ethoxy) silane (A-172) ²	-	Rapid reaction; yellow solid
32	Boron trifluoride etherate	Buton MD-360 ^{2 4}	Furfural ⁹ Styrene	Brittle product; reaction in 10 sec
33	Boron trifluoride etherate	Buton MD-360	Furfural Vinyl acetate	Starts foaming in 20 sec to about twice the volume of the reactants
34	Boron trifluoride etherate	Styrene ⁴	Furfural Hexachloro-cyclopentadiene	Foam rise in 25 sec; brittle solid
35	Boron trifluoride etherate	Styrene	Furfural Hexachloro-cyclopentadiene ^{2 5}	Foam rise in 20 sec; brittle solid

Table C (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Vinyl Compounds</u>	<u>Other Component(s)</u>	<u>Comment</u>
36	Boron trifluoride etherate	Styrene	Furfural	Foams in 10 sec to about 10 times the volume of the reactants; collapses
37	Boron trifluoride etherate	Styrene	Furfural Trimethylolpropane-monoallyl ether ¹⁹	Immediate reaction
38	Boron trifluoride etherate	Styrene	Furfural Trimethylolpropane-diallyl ether ¹⁹	Foams in 10 sec to seven times the volume of the reactants; collapses somewhat
39	Boron trifluoride etherate	A-172 ²	Furfural Styrene	Gelling in 20 sec
40	Boron trifluoride etherate	Styrene	Furfural Ethyleneglycol-dimethacrylate	Foams in 50 sec
41	Boron trifluoride etherate	Styrene	Furfural Tetrallyloxyethane ²⁰	Foams in 10 sec
42	Boron trifluoride etherate	A-172 ²	-	No visible reaction in 10 min

Table C (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Vinyl Compounds</u>	<u>Other Component(s)</u>	<u>Comment</u>
43	Boron trifluoride etherate	A-172	-	No observed reaction in 2 days
44	Boron trifluoride etherate	A-151	-	No observed reaction in 2 days
45	Boron trifluoride etherate	Diallyl phthalate monomer	-	No reaction or gelation
46	Boron trifluoride etherate	Isoeugenol ⁴	-	Immediate reaction; solidifies on cooling
47	Boron trifluoride etherate	Isosafrole ⁴	-	Immediate reaction; solidifies on cooling
48	Boron trifluoride etherate	Divinyl benzene ⁶	-	Immediate reaction
49	Boron trifluoride etherate	Styrene Divinyl benzene	-	Immediate reaction
50	Boron trifluoride etherate	Styrene	-	Immediate reaction to yield a solid
51	Boron trifluoride etherate	Styrene	-	Immediate reaction
52	Boron trifluoride etherate	Styrene Divinyl benzene	Cab-O-Sil	Cured; no foaming

Table C (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Vinyl Compounds</u>	<u>Other Component(s)</u>	<u>Comment</u>
53	Boron trifluoride etherate	Tetraallyloxyethane	-	Reaction immediate; some foam rise
54	Boron trifluoride etherate	Vinyl acetate	-	Reaction proceeds slowly
55	Sulfuric acid (sp. gr. 1.84) ²⁶	Silane A-151	-	White precipitate first forms; turns to black solid; reaction begins immediately
56	Sulfuric acid (sp. gr. 1.84)	Tetraallyloxyethane	-	Immediate reaction; foam rise to black, brittle solid
57	Tributylborane ²⁷ in Stoddard solvent	Methyl methacrylate	-	No gelation
58	Tributylborane in Stoddard solvent	Styrene	-	No gelation
59	Titanium tetrachloride ¹	Diallyl phthalate monomer	-	Some evolution of heat; also appears to be an increase in viscosity
60	Trimethoxyboroxine	Indopol polybutene-100 ²⁹	-	No reaction

Table C (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Vinyl Compounds</u>	<u>Other Component(s)</u>	<u>Comment</u>
61	Vinyltrichlorosilane	Thanol RS-700	Epon 812 ²⁸ Methyl methacrylate	Foams in less than 3 sec
62	Vinyltrichlorosilane	Thanol RS-700	Epon 812 Methyl methacrylate Ethylene glycol dimethacrylate	Foams in less than 2 sec
63	Vinyltrichlorosilane	LA-475	RS-700 Epon 812 Methyl methacrylate	Reaction and foaming immediate

Table D

FORMULATIONS UTILIZING EPOXY COMPOUNDS

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
64	Chloromaleic anhydride	Epon 812	-	No reaction after 1 hr
65	Chloromaleic anhydride	Epon 812	-	No immediate reaction
66	Chloromaleic anhydride	Epon 812	-	No immediate reaction
67	Aluminum trichloride in chloroform	Epon 812	-	No reaction after 1 hr
68	Boron trifluoride etherate	VCD ^{2 3}	-	Immediate coagulation at point of contact
69	Boron trifluoride etherate	VCD	DER 732 ⁶	Gelation at point of contact
70	Boron trifluoride etherate	VCD	Epon 871	Reaction run at -57°C to -49°C; in general, no reaction
71	Boron trifluoride etherate	Epon 871 ²⁸	VCD Styrene Toluene	Reaction run at -56°C; no reaction

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
72	Boron trifluoride etherate Phospholeum/diisopropyl ether	Epon 812	Tetrahydrofuran VCD SF-1079 ⁷	Foam rise immediate to about 15 times the volume of the reactants
73	Boron trifluoride etherate	Epon 812	-	Resin coagulated at the point of contact with the BF ₃ etherate
74	Boron trifluoride etherate	Epon 828	Epon 812	Induction period, and then fast, exothermic reaction
75	Boron trifluoride etherate	Epon 828	-	No immediate reaction
76	Boron trifluoride etherate	Oxiron 2001 ³⁰	-	No immediate reaction
77	Boron trifluoride etherate	Oxiron 2002 ³⁰	-	Immediate gelation to a jelly-like material
78	Boron trifluoride etherate	Oxiron 2002	Epon 828 ²⁸	Immediate gelation to a jelly-like material
79	Boron trifluoride etherate	Y-4086 ²	-	Solid in 30 sec
80	Diethylene triamine ²³	VCD	SF-1079	No reaction

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
81	Diethylene triamine	Epon 812	Y-4086 Hexachlorocyclopentadiene ²⁵	Evolution of vapor about 7 min after addition of catalyst; same time foaming starts
82	Ethyltrichlorosilane	VCD	-	Exothermic; no gelation observed in 10 min
83	Ethyltrichlorosilane	VCD	Catalytic amount of water	Mixture starts warming rapidly; reaction visible in less than 1 min; foaming
84	Ethyltrichlorosilane	Dow 166-450	VCD	Viscous liquid in 10 min
85	Ferric chloride ¹⁶ Thionyl chloride ¹	Epoxide 201 ²³	-	Immediate reaction; black solid
86	Ferric chloride Thionyl chloride	Epoxide 201	Tetrahydrofuran	Immediate reaction; black solid
87	Mondur MR	Epon 812	-	No reaction
88	Mondur MR Triethanolamine	Epon 812	-	Exotherm developed, but no gelation
89	Sebacyl chloride	Epon 828	Phenylene diamine ⁴ Triethylene tetramine	Immediate gelation; jelly-like product

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
90	Sebacyl chloride	Epon 828	Triethylene tetramine	Immediate gelation; jelly-like product
91	Phosphoric acid ¹⁶	VCD	Furfuryl alcohol ⁹ Toluene	Reaction in less than 5 sec; hardens on cooling
92	Phosphoric acid	VCD	Furfuryl alcohol Chloroform	Reaction in less than 5 sec; soft, tar-like material
93	Phosphoric acid	VCD	Furfuryl alcohol Tetrahydrofuran	Reaction in less than 5 sec; black solid on cooling
94	Phosphoric acid	VCD	Epon 871	Highly exothermic but material cured into lumps
95	Phosphoric acid	Epon 828	-	Cured in less than 30 sec
96	Phosphoric acid Trimethoxyboroxine	Epon 871	VCD	TMB and H ₃ PO ₄ formed precipitate when mixed
97	Phosphorofluoridic acid ⁹	Epon 828	-	Reaction immediate

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
98	Phosphorofluoridic acid/Diisopropyl ether	Epon 812	VCD Tetrahydrofuran SF-1079	Foam rise almost immediate to about 12 times the volume of the reactants
99	Silicon tetra-chloride	Epon 812	-	Immediate reaction; white granular solid
100	Titanium tetra-chloride	VCD	-	Immediate reaction; solid material
101	Titanium tetra-chloride	Epon 812	-	Immediate reaction; paste-like material
102	Trimethoxyboroxine	Epon 828	-	No immediate reaction
103	Trimethoxyboroxine	Epon 828	Triethylene tetramine G-113	No immediate reaction
104	Trimethoxyboroxine	Epon 828	Y-4086	Gels in 15 sec
105	Trimethoxyboroxine	Oxiron 2002	Epon 828	Gelled in 5 sec; hardened in 40 sec; brittle
106	Trimethoxyboroxine	Epon 828	Oxiron 2002 G-113	Slowly foamed, but material cracked as it foamed

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
107	Trimethoxyboroxine	VCD	Epon 828	Cured in 5 sec; exothermic reaction
108	Trimethoxyboroxine	Epon 828	VCD	Reacted in 10 sec, with charring
109	Trimethoxyboroxine	Epon 828	VCD G-113	Foamed in 7 sec
110	Trimethoxyboroxine	Epon 828	VCD Toluene	A brittle foam was produced in 5-10 sec; exotherm 150°C
111	Trimethoxyboroxine	Epon 828	VCD Toluene plus a number of silicone surfactants	Two-part surfactant (Y-4347 Y-4499) system gave best foam rise with least collapse
112	Trimethoxyboroxine	Epon 828	VCD Y-4347 Y-4499 Toluene	Reaction time 30 sec; poor foam rise
113	Trimethoxyboroxine	VCD	DER 732 Epon 828	Reaction time 20 sec; very weak material
114	Trimethoxyboroxine Toluene	Epon 828	VCD Toluene DER 732	Reaction time 20 sec, but poor foam rise

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
115	Trimethoxyboroxine	Epon 828	VCD LG-56 ³	Reaction within 10 sec; less brittle than E-1 foams
116	Trimethoxyboroxine	Epon 828	VCD LG-168	Reacted within 20 sec
117	Trimethoxyboroxine	Epon 828	VCD Niax LHT-67 ³	Reacted within 10 sec
118	Trimethoxyboroxine	Epon 828	VCD Niax LHT-112 ³	Reacted within 10 sec; brittle
119	Trimethoxyboroxine	Epon 828	VCD LHT-240 ³ Y-4347 Y-4499 Toluene	Reaction time 60 sec; poor foam rise
120	Trimethoxyboroxine	Epon 828	VCD PPG-4025	Reaction time 30 sec; slightly less brittle than E-1 foams
121	Trimethoxyboroxine Toluene	Epon 828	VCD Y-4347 Y-4499 Toluene PPG-4025	Reaction time 40 sec; poor foam rise

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
122	Trimethoxyboroxine	Epon 828	VCD LP-8 ³¹	Reacted within 10 sec; less brittle than E-1 foams
123	Trimethoxyboroxine	Epon 828	VCD Toluene Y-4347 Y-4499 LP-8	Reaction time 40 sec; poor foam rise
124	Trimethoxyboroxine	Epon 828	VCD Duomeen L-11 ³²	No immediate reaction
125	Trimethoxyboroxine	VCD	-	Immediate gelation; highly exothermic
126	Trimethoxyboroxine	VCD	Silicone surfactants	Approximately 20:1 foam rise with DC-201, XF-1066, SF-1079
127	Trimethoxyboroxine	VCD	SF-1079	10:1 foam rise at 75°C 7:1 foam rise at 0°C 10:1 foam rise at 24°C Friable foam
128	Trimethoxyboroxine	VCD	SF-1079 Versamid 125 ³³	No foam rise
129	Trimethoxyboroxine	VCD	1,4-butanediol Diglycidyl ether ³⁴	Reaction times 35-80 sec, but weak, semi- rigid foams

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
130	Trimethoxyboroxine	VCD	Surfactants 1,4-butanediol Diglycidyl ether	Reaction time 20 sec; but foams collapsed- on cooling
131	Trimethoxyboroxine Toluene	VCD	SF-1079 1,4-butanediol Diglycidyl ether	Good foam rise but no apparent reduction of brittleness
132	Trimethoxyboroxine Toluene	VCD	SF-1079 Cardolite NC-513 ³⁵	Small foam rise
133	Trimethoxyboroxine	VCD	DER 732	Reaction time 5 sec; small foam rise with collapse
134	Trimethoxyboroxine	VCD	DER 732	Immediate reaction
135	Trimethoxyboroxine	VCD	DER 732 XF-1066	Reacted within 20 sec; foamed but material was very weak
136	Trimethoxyboroxine Toluene	VCD	SF-1079 DER 732	Somewhat stronger than E-3, but less foam rise
137	Trimethoxyboroxine Toluene	VCD	SF-1079 DER 736 ⁶	Some reduction of friability
138	Trimethoxyboroxine Boron trifluoride etherate	VCD	Epon 871	No reaction

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
139	Trimethoxyboroxine Toluene	VCD	Epon 871 SF-1079	Some reduction of friability but small foam rise
140	Trimethoxyboroxine	VCD	Epon 812 Epon 871	Foamed in 7 sec; 3:1 foam rise
141	Trimethoxyboroxine	VCD	Epon 871	Reaction time of 5 sec; foam was relatively strong; collapsed on cooling
142	Trimethoxyboroxine	Y-4086 ³	-	Foam rise in 40 sec
143	Trimethoxyboroxine	DER 732	-	No immediate reaction
144	Trimethoxyboroxine	Oxiron 2002	-	Gelled in 5-10 sec; very brittle
145	Trimethoxyboroxine	Epoxide 201	-	Gelled in 15 sec; hardened in 1 min
146	Trimethoxyboroxine	Epoxide 269 (dipentene dioxide) ²³	-	Exothermic reaction but no gelation
147	Trimethoxyboroxine	Limonene dioxide ³⁰	-	Exothermic reaction but no gelation
148	Trimethoxyboroxine	Phenyl glycidyl ether ⁴	-	No reaction

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
149	Trimethoxyboroxine	Octylene oxide ³⁰	-	No reaction
150	Trimethoxyboroxine	VCD	-	No gelation
151	Trimethoxyboroxine	VCD	SF-1079	No reaction
152	33-LV	Epon 812	-	No immediate reaction
153	Trimethoxyboroxine	Epon 812	-	No immediate reaction
154	Trimethoxyboroxine	VCD	SF-1079	No reaction
155	Trimethoxyboroxine	Epon 812	-	No immediate reaction
156	Tri-m,p-cresyl borate ²¹	Epoxide 201	-	No immediate reaction
157	Tri-m,p-cresyl borate	VCD	-	Reaction time 7 sec
158	Tri-m,p-cresyl borate	Epoxide 269	-	Exothermic reaction, but no gelation
159	Tri-m,p-cresyl borate	Epon 812	33-LV	Exotherm developed but no gelation
160	Tri-m,p-cresyl borate	Epon 812	-	No immediate reaction

Table D (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Epoxy Compound</u>	<u>Other Component(s)</u>	<u>Comment</u>
161	Tri-m,p-cresyl borate	Epon 828	-	No immediate reaction
162	Tri-m,p-cresyl borate	VCD	Epon 828	Reaction time 7 sec
163	Vinyltrichlorosilane	VCD	-	Some exotherm; no visible reaction
164	Curing Agent U ²⁸	VCD	SF-1079	No reaction
165	Curing Agent Z ²⁸	VCD	SF-1079	No reaction
166	EpoxyLite C-323 ³⁶ (curing agent in methyl ethyl ketone)	Epon 812	Methyl ethyl ketone	First sign of gelling 1.5 min after mixing; no foam
167	EpoxyLite C-323 ³⁶ (curing agent in methyl ethyl ketone)	Epon 812	Y-4086 Methyl ethyl ketone	Immediate reaction; some foaming
168	Curing Agent RTH with accelerator ²⁸	Epon 871	VCD	No immediate reaction

Table E

FORMULATIONS UTILIZING AMINES OR NITROGEN-CONTAINING COMPOUNDS

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Amine or Nitrogen Compounds</u>	<u>Other Component(s)</u>	<u>Comment</u>
1	Ethyltrichlorosilane	Aniline ¹	-	Immediate reaction; powder
2	Ethyltrichlorosilane	Duomeen L-11	-	No gelation
3	Ethyltrichlorosilane	Triethylene tetramine	-	Solid in less than 3 min
4	Sebacyl chloride 1:1	Triethylene tetramine	-	Immediate gelation; semi-rigid with entrapped liquid; jelly-like product
5	Sebacyl chloride 1:2	Triethylene tetramine	-	As in No. 4
6	Sebacyl chloride 1:3	Triethylene tetramine	-	As in No. 4
7	Sebacyl chloride	Triethylene tetramine	G-113	Rapid gelation; exothermic decomposition noted; little foam rise
8	Sebacyl chloride	Triethylene tetramine	5% Cab-O-Sil	Immediate gelation; jelly-like product
9	Sebacyl chloride	Triethylene tetramine	33-LV	Immediate gelation; semi-rigid with entrapped liquid; jelly-like product

Table E (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Amine or Nitrogen Compounds</u>	<u>Component(s)</u>	<u>Comment</u>
10	Sebacyl chloride	Tetraethylene pentamine	-	As in No. 9
11	Sebacyl chloride	Tetraethylene pentamine	-	As in No. 9
12	Sebacyl chloride	50% mixture of phenylene diamine and triethylene tetramine	-	Immediate gelation; jelly-like product
13	Sulfur dichloride	Duomeen L-11	-	Rapid; product solidifies on cooling
14	Sulfur dichloride	Triethylene tetramine	-	Immediate reaction, but product was viscous liquid
15	Sulfur dichloride	Tetraethylene triamine	-	Immediate reaction but no gelation
16	Sulfur dichloride	Curing Agent U	Tetraethylene triamine	Immediate reaction but no gelation
17	Sulfur dichloride	Curing Agent U	-	Immediate exothermic reaction but product was very viscous liquid
18	Sulfur dichloride	Versamid 140 ³³	-	Immediate reaction; partially gelled

Table E (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Amine or Nitrogen Compounds</u>	<u>Component(s)</u>	<u>Comment</u>
19	Sulfur dichloride	Genamid 250 ³³	-	Immediate reaction; partially gelled
20	Sulfur dichloride	Genamid 310 ³³	-	Immediate reaction; partially gelled
21	Trimethoxyboroxine	Duomeen L-11	-	Gelation in less than 1 min
22	Trimethoxyboroxine	Duomeen L-15 ³²	-	Gelation in less than 1 min
23	Trimethoxyboroxine	Triethylene tetramine	-	Gelation in less than 1 min
24	Trimethoxyboroxine	Tetraethylene pentamine	-	Gelation in less than 1 min
25	Trimethoxyboroxine	Versamid 140	-	Gelation in less than 1 min
26	Borester #8	Diethylene triamine ²³	-	Reaction with no gelation
27	Borester #8	Triethylene tetramine	-	Solid in a few minutes
28	Borester #8	Versamid 140	-	Gelled but did not appear fully cured

Table F
FORMULATIONS UTILIZING MISCELLANEOUS COMPOUNDS

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Co-Reactant</u>	<u>Other Component(s)</u>	<u>Comment</u>
247	Aluminum chloride	p-Dioxane ⁹	-	No observed reaction after 10 min
248	Aluminum chloride	Thiophene ⁴	-	Orange-brown color on mixing; not much heat; mostly liquid after 15 min
249	Aluminum chloride	Tetrahydrofuran	-	Reaction immediate; black liquid
250	Aluminum chloride	Benzyl chloride ¹	-	Rapid reaction; solid granular product
251	Boron trifluoride etherate	Furfural	-	No observed reaction in 1.5 hr
252	Boron trifluoride etherate	A-151	Furfural	Gelling in 20 sec
253	Boron trifluoride etherate	Furfural	Thiophene	Reaction in 2 min; foams
254	Boron trifluoride etherate	A-172	Furfural	Gelling in 10 sec
255	Boron trifluoride etherate	Thiophene	-	No observed reaction in 1.5 hr

Table F (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Co-Reactant</u>	<u>Other Component(s)</u>	<u>Comment</u>
256	Boron trifluoride etherate	p-Dioxane	-	No observed reaction in 10 min
257	Boron trifluoride etherate	LTV-602 ⁷	-	Rubbery material in 7 min
258	Ethyltrichlorosilane	USB-110 ²¹	-	Solid in less than 3 min
259	Phosphoric acid	Trimethoxyboroxine	-	Immediate formation of white precipitate
260	Phosphorofluoridic acid	Trimethoxyboroxine	-	Gelation; immediate reaction
261	Silicon tetrachloride	p-Dioxane	-	No observed reaction in 10 min
262	Silicon tetrachloride	Tetrahydrofuran	-	No observed reaction in 10 min
263	Sulfur dichloride	Borester #8	-	Reaction rapid; rubbery material
264	Sulfur dichloride	Dow 11-80 ⁶	-	Reaction but no gelling
265	Titanium tetrachloride	p-Dioxane	-	Immediate reaction; solid formed

Table F (Continued)

<u>Reaction No.</u>	<u>Catalyst or Curing Agent</u>	<u>Co-Reactant</u>	<u>Other Component(s)</u>	<u>Comment</u>
266	Titanium tetra-chloride	Thiophene	-	Slight heat of reaction; turns orange-brown on mixing; some solid after 5 min
267	Titanium tetra-chloride	Tetrahydrofuran	-	Immediate reaction; not solid after 2 min
268	Trimethoxyboroxine	Boron trifluoride etherate	-	Immediate formation of polymer on end of stirring rod
269	Trimethoxyboroxine	Polycin U-63	G-113	No immediate reaction

APPENDIX REFERENCES

1. Fisher Scientific Co.
2. Union Carbide Corp., Silicones Division
3. Niox Polyether, Union Carbide Chemical Co.
4. Eastman Organic Chemicals, Distillation Products Industries
5. Monsanto Co.
6. Dow Chemical Co.
7. General Electric Co., Silicone Product Department
8. Wyandotte Chemicals Corp.
9. Matheson, Coleman, and Bell
10. Mobay Chemical Co.
11. Metal and Thermit Corp.
12. Cabot Corp.
13. Houdry Process and Chemical Co.
14. Dow-Corning Corp.
15. Mallinckrodt Chemical Works
16. Allied Chemical, General Chemical Division
17. Atlas Chemical Industries, Inc.
18. Baker Castor Oil Co.
19. Celanese Chemical Corp.
20. Dr. F. Jonas Corp.
21. U. S. Borax Research
22. Jefferson Chemical Co.
23. Union Carbide Chemical Co.

24. Enjay Chemical Co.
25. Hooker Electrochemical Co.
26. E.I. duPont deNemours and Co.
27. Callery Chemical Co.
28. Shell Chemical Co.
29. Amoco Chemicals Corp.
30. FMC Corp., Chemicals and Plastics Division
31. Thiokol Chemical Corp.
32. General Mills, Chemical Div.
34. Ciba Products Corp.
35. 3M Company, Chemical Division
36. Epoxylite Corp.
37. Stauffer Chemical Co., Anderson Chemical Division