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FUEL CELL SEALANT COMPOUNDS

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FOREWORD

This report was prepared by the Thiokol Chemical Corporation, under USAF Contract No. AF-33(038)-30523. The contract was initiated under Research and Development Order No. 617-12 (C-J), "Compounding of Elastomers," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. Norman T. Lendzian acting as project engineer.

ABSTRACT

This work was undertaken by the Thiokol Chemical Corporation to develop integral fuel tank sealant compounds with improved properties.

The hexamethylene terpolymer sealant compound, prepared and submitted to Wright Field at the end of the first year's work on this contract showed better heat resistance coupled with greatly improved low temperature properties than a comparable IP-2 compound. The 0.5 mole % of TCP and 2 mole % of TCP cross-linked pentamethylene formal copolymers showed better heat and aromatic fuel resistance than the 2 mole % of TCP cross-linked copolymer previously submitted.

Compounding studies showed that IP-32 should be more suitable than IP-2 compounds since lower moduli and higher ultimate elongation before and after heat aging and after immersion in aromatic fuel were attained.

Five two-package mix experimental translucent sealant compounds prepared from the liquid polysulfide/epoxy resin system and submitted to Wright Field were tough and resistant to jet fuel but did not pass all of the Air Force specifications. However, the compounds displayed promising potentialities.

The IP-2 base experimental translucent sealant compound submitted to Wright Field for evaluation showed good potentialities as an improved sealant and was more transparent during and after application and cure than an IP-2 base commercial sealant compound.

Many of the materials tested in this investigation were not developed or intended by the manufacturer for the conditions to which they have been subjected. Any failure or poor performance of the material is therefore not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. Whitmore

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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SUMMARY

I. DEVELOPMENT OF NEW LIQUID POLYSULFIDE POLYMERS FOR IMPROVED PROPERTIES

A. COPOLYMERS OF PENTAMETHYLENE DICHLORIDE IN COMBINATION WITH VARIOUS MONOMERS

Three different series of pentamethylene dichloride copolymers were prepared and evaluated to study the effects of structure on polymer properties. The primary objective was to develop a pentamethylene dichloride copolymer possessing the excellent low temperature properties of the pentamethylene/formal copolymer, but with better aromatic fuel and heat aging resistance and toughness characteristics. All of these copolymers had a rank of 2.25 and were crosslinked with 2 mole % trichloropropane.

1. 60/38 mole % pentamethylene dichloride/triglycol dichloride.
2. 60/38 mole % pentamethylene dichloride/glycerol dichlorohydrin.
3. 60/38 mole % pentamethylene dichloride/N-methyl dichlorodiethylamine.

The first two copolymers did not show merit for use in integral fuel cell sealant compounds. These copolymers were inferior to the pentamethylene dichloride/formal control copolymer in low temperature torsional stiffness and toughness properties before and after immersion in aromatic fuel. Attempts to prepare the pentamethylene dichloride/N-methyl dichlorodiethylamine copolymer were unsuccessful.

A series of pentamethylene dichloride/formal copolymers of rank 2.25 were prepared with two different amounts and types of crosslinking agents and evaluated to determine the effect on the polymer properties with particular attention to resistance to volume swell, heat aging and "shortness" after immersion in aromatic fuel. The crosslinkings investigated were:

1. 0.5 and 2 mole % trichloropropane (TCP)
2. 0.5 and 2 mole % tetrachloropropyl formal (TCF)

The copolymer crosslinked with 0.5 mole % of TCP gave a tougher and more heat and aromatic fuel resistant rubber than the one with 2 mole % of TCP. However, the 2 mole % of TCF crosslinked copolymer appeared better than the 0.5 mole % TCP crosslinked copolymer in resistance to heat aging and physical properties after immersion in aromatic fuel and should make a more suitable integral fuel cell sealant compound than the 0.5 mole % TCP crosslinked copolymer. In a properly compounded sealant, the low crosslinked copolymer should be equivalent in toughness, somewhat less resistant to aromatic fuel and much better in low temperature properties than "Thiokol" LP-32. Also, its resistance to aging at 212°F should be good.

B. COPOLYMERS CONTAINING FORMAL AND VARIOUS MONOMERS

Copolymers containing 10/88/2 and 30/68/2 mole % of ethylene dichloride/formal/TCP were prepared and evaluated as possible substitutes for

for IP-2 in integral fuel cell sealant compounds. With the proportion of ethylene dichloride necessary to effect a significant reduction in cost (30 mole % or higher), the toughness and low temperature properties of the formal polymer would be deleteriously affected. Therefore, ethylene dichloride/formal copolymer was not considered further for this purpose.

Studies conducted on another project showed that bis (4-chlorobutyl) formal/formal crude rubbers possessed good toughness and resistance to heat aging and excellent low temperature properties. Since hexamethylene glycol, which is used for the preparation of hexamethylene dichloride for the hexamethylene/triglycol/formal terpolymer, became unavailable, bis (4-chlorobutyl)formal/formal copolymer was considered as a substitute for this terpolymer. Bis (4-chlorobutyl)formal monomer was prepared in the pilot plant for the preparation of 100 mole % latex which was to be used for synthesizing a series of copolymers for investigation. However, time did not permit the completion of this work.

C. TERPOLYMERS OF PENTAMETHYLENE DICHLORIDE IN COMBINATION WITH VARIOUS MONOMERS

The following terpolymers, all of which had a rank of 2.25 and contained 2 mole % of trichloropropane as a crosslinking agent, were prepared and evaluated to compare their properties, specifically resistance to volume swell and "shortness" after immersion in aromatic fuel, with those of the 60/38/2 mole % pentamethylene dichloride/formal/TCP copolymer:

1. 50/25/23 mole % pentamethylene dichloride/triglycol dichloride/formal
2. 50/25/23 mole % pentamethylene dichloride/glycerol dichlorohydrin/formal

These terpolymers were inferior to the pentamethylene dichloride/formal copolymer in low temperature properties and toughness characteristics before and after immersion in aromatic fuel and did not show promise for compounding integral fuel cell sealant compounds.

D. HEXAMETHYLENE DICHLORIDE/TRIGLYCOL DICHLORIDE/FORMAL TERPOLYMER

Attempts were made to prepare a liquid terpolymer containing 50/25/24.5/0.5 mole % of hexamethylene dichloride/triglycol dichloride/formal/TCP to determine whether 0.5 mole % of TCP crosslinking would give a more aromatic fuel resistant polymer than 2 mole % of crosslinking, but these experiments were unsuccessful.

The 50/25/23/2 mole % of hexamethylene dichloride/triglycol dichloride/formal/TCP experimental sealant compound previously developed on this contract (see p 99 WADC Technical Report 52-230) was evaluated further for heat aging resistance. It out-classed a comparable IP-2 sealant in resistance to heat aging at 212°, 250°, and 300°F.

II. EVALUATION AND COMPOUNDING STUDIES

A. EVALUATION OF "THIOKOL" LP-32

Development studies were conducted with "Thiokol" LP-32. The results of this work showed that LP-32 should be more suitable than LP-2 for integral fuel cell sealant compounds because lower moduli and considerably higher ultimate elongation before and after heat aging at 212°F and after immersion in aromatic fuel were attained.

The results also indicated that the ultimate elongation of the pentamethylene dichloride/formal and hexamethylene dichloride/triglycol dichloride/formal experimental polymers before and after immersion in aromatic fuel should be improved with 0.5 mole % in lieu of 2 mole % of TCP for crosslinking.

B. ADHESION ADDITIVE AND CURE STUDIES WITH "THIOKOL" LP-2 AND LP-32 BASE SEALANT COMPOUNDS

A number of studies were made with adhesion additives and combinations of additives with "Thiokol" LP-2 and LP-32 to develop a sealant formulation with satisfactory working life and good curing and adhesion properties that could be adapted to the pentamethylene/formal, hexamethylene/triglycol/formal and other experimental polymers developed on this contract.

Two formulations which should be satisfactory for this purpose were developed. In the LP-2 compounds, phenolic resin BR-6741 was not generally as good an adhesion additive as a 25% solution of maleic anhydride in cyclohexanone. However, the LP-32 compound containing maleic anhydride was extremely slow curing at room temperature after aging for 30 days at 80°F.

Polymer additive studies with an oil modified phenolic resin, BK-3962, and LP-2 disclosed that this resin did not improve the sealant compound. Compositions containing only LP-2 and BK-3962 might be of value as protective coatings for LP-2 base sealants subjected to jet fuels.

C. INCORPORATION OF "THIOKOL" WD-6/SARAN F-120 BASE REVERSE PHASE IN EXPERIMENTAL POLYMER SEALANT COMPOUND

Incorporation of ten parts (solid basis) of a WD-6/Saran Base Reverse Phase per 100 parts of the hexamethylene/triglycol/formal terpolymer experimental sealant compound was of no value for improving the aromatic fuel resistance of the compound.

D. INVESTIGATION OF NEW TYPES OF FILLERS

Very fine particle size silicon dioxides, Aerosil and Ex. Silica 54-EP-88, were evaluated as fillers in a "Thiokol" LP-32 formulation cured with a lead peroxide/lead stearate/sulfur system. They proved to be excellent reinforcing agents for the liquid polymer. Better physical properties were obtained with 15 parts (by weight) of these fillers than with the same amount of Pelletex SRF-3. Studies conducted with LP-2, Aerosil and cumene hydroperoxide curing systems showed the possibilities of obtaining a translucent sealant compound.

E. ORGANIC CURING SYSTEMS

Adhesion and cure studies were made with an integral fuel cell sealant based on "Thiokol" LP-32 to develop a satisfactory cure and adhesion with organic curing systems. Previous studies (see p 65 of WADC Technical Report 52-230) showed organic curing systems, such as p-quinonedioxime/amine, to give superior resistance to heat aging than the lead peroxide curing system. Some of the p-quinonedioxime/amine and trinitrobenzene/amine curing systems showed good potentialities with respect to cure and adhesion characteristics.

III. TRANSLUCENT SEALANT COMPOUND DEVELOPMENT

The major portion of the program was devoted to the development of a translucent integral fuel cell sealant compound which would possess generally improved properties and permit visual inspection during and after application and cure.

A. GENERAL COMPOUNDING STUDIES WITH VARIOUS COMMERCIAL EPOXY RESINS AND "THIOKOL" LIQUID POLYSULFIDE POLYMERS

A clear, liquid polysulfide polymer/epoxy resin composition possessing all of the properties considered necessary for integral fuel cell sealant application was not obtained. However, some formulations were developed which possessed potentialities for this use.

A number of elastomeric compositions with physical properties approaching the requirements considered necessary for the present "Thiokol" LP-2 base sealant compounds were prepared. Some of these compounds possessed tensile strengths of 500 to 600 lb/sq in., elongations of 100 to 160% and tear strengths of 75 lb/in. and a Shore A hardness of about 70. Their relatively high aromatic fuel extraction signified that the reaction between the polysulfide liquid polymer and epoxy resins was not complete. The low temperature properties of some of these compositions were quite good. If the apparently unreacted "Thiokol" liquid polymer in these compositions could have been cured without destroying the elasticity, they would have possessed good potentialities for an improved integral fuel cell sealant compound.

Formulations were developed which gave relatively hard compositions of high modulus, high tensile and tear strengths and low ultimate elongation. One of these had over 3,000 lb/sq in. tensile strength and more than 400 lb/in. tear strength. The majority of these materials had low aromatic fuel extraction values, indicating that the reaction between the epoxy resin and polysulfide liquid polymers was almost complete.

SUMMARY (Contd.)

All of these compositions possessed the following inherent defects which may make them unsatisfactory for this application: (a) low peel bond adhesive strength to aluminum (b) loss of strength at elevated temperature. These materials, however, were not attacked by JP-3A fuel after immersion for one month at 80°F.

B. ADHESION ADDITIVE STUDIES

Adhesion studies conducted with additives such as maleic anhydride and urea-formaldehyde polymer to improve the peel adhesive bond strength of the liquid polysulfide polymer/epoxy polymer compositions to aluminum were unsuccessful.

C. REGULATION AND STABILIZATION OF CURE TO OBTAIN BALANCED PHYSICAL PROPERTIES

Since the test data obtained on the "Thiokol" liquid polymer/epoxy resin compositions indicated that their structures were too highly crosslinked to possess a proper balance of physical properties over a temperature range, studies were conducted in an effort to circumvent this excessive crosslinking. Studies using reagents such as benzyl mercaptan, allyl glycidyl ether, tris (a-methylbenzyl) phenol and phenolic polymers, in liquid polymer/epoxy resin systems in order to reduce the functionality of the epoxy resin and hence, to regulate and stabilize the cure were unsuccessful.

The use of trinitrobenzene and cumene hydroperoxide as co-curing agents in a very elastomeric liquid polysulfide polymer/epoxy resin composition did not improve the physical properties of the material at room or elevated temperatures.

Studies conducted with reduced 2,4,6-tri(dimethylaminomethyl) phenol catalyst (DMP-30) concentrations in liquid polymer/epoxy resin systems did not result in compositions with better properties for integral fuel tank sealants. Triethylenetetramine and tetraethylenepentamine were inferior to DMP-30 for catalyzing the cure of liquid polymer/epoxy resin systems at room temperature.

D. INVESTIGATION OF POLYESTERS AND POLYAMIDES IN LIQUID POLYSULFIDE POLYMER SYSTEMS

Polysulfide liquid polymer/polyester systems with and without epoxy resins were investigated. Although very resilient reaction products were obtained in most cases, the physical properties at room and elevated temperatures were not encouraging for integral fuel cell sealants. The polyamide polymers appeared to be too incompatible in liquid polymer/epoxy resin systems to be of value.

E. EFFECT OF POST CURE AND PLASTICIZATION OF POLYSULFIDE LIQUID POLYMER/EPOXY RESIN COMPOSITIONS

The post curing of liquid polymer/epoxy resin compositions at elevated temperature and the plasticization of such systems with WD-2 polymer did not improve the over-all physical properties of the compounds at either room or elevated temperatures.

F. COMPOSITIONS PREPARED WITH HIGH VISCOSITY LIQUID POLYSULFIDE POLYMER AND EPOXY RESINS

A WD-2 type crude containing some thiol terminals was redistributed with LP-33 to obtain a high viscosity (1500 poises) thiol-terminated polymer. Systems prepared with this polymer and epoxy polymers were rubber-like and possessed encouraging physical and adhesion properties for an integral fuel cell sealant compound. They were equivalent to an LP-2 base sealant in low temperature torsional stiffness, but were not sufficiently resistant to aromatic fuel and were quite weak at elevated temperatures.

IV. PROPERTIES OF EXPERIMENTAL SEALANT COMPOUNDS

Five two-package mix sealant compounds were prepared with liquid polysulfide polymer/epoxy resin compositions for integral fuel cell application and submitted to the Wright Air Development Center. These compositions were of a "buttery" consistency and exhibited no appreciable run-down during application. They were sufficiently transparent to permit visual inspection during and after application. None of these compounds passed all of the Mil-S-5043A (Aer) requirement tests and were deficient in working life, heat resistance, resistance to salt water and hydrocarbons and low temperature flexibility requirements. However, they did possess properties such as toughness and jet fuel resistance, over present "Thiokol" LP-2 base sealant compounds for this use. These materials are of a different structure and consequently have properties which are not analogous to those of LP-2 base sealants. Therefore, the Mil-S-5043A(Aer) requirements for an integral fuel cell sealant material may not be entirely applicable for these compositions.

It was intended to submit samples of experimental sealant compounds prepared with the 60/38/2 mole % pentamethylene dichloride/formal/tetrachloropropyl formal and 60/39.5/0.5 mole % pentamethylene dichloride/formal/trichloropropane copolymers. However, it was not possible to do this since the copolymers were unsatisfactory and time did not permit preparation of additional samples.

A two-package mix, "Thiokol" LP-2 base translucent integral fuel cell sealant compound was developed which possessed considerably better resistance to heat aging and aromatic fuel than a commercial LP-2 base sealant. The over-all physical properties of this experimental sealant before and after heat aging are considered to be more suitable for this application than those of the commercial sealant compound.

This sealant compound possessed good cure characteristics and adhesion to aluminum. It was sufficiently transparent for visual inspection during and after application and cure, which should give it an advantage over present commercial paste sealants for improved sealing, ready detection of leaks and lower maintenance costs. A sample was submitted to the Wright Air Development Center.

INTRODUCTION

This report covers the work performed by the Thiokol Chemical Corporation from 13 July, 1952 to 13 July, 1953 under Contract No. AF-33(038)-30523. The investigations conducted on this contract from 13 July, 1951 to 13 July, 1952 were discussed in WADC Technical Report 52-230.

During this period the primary objectives of the program were as follows:

1. Development of Experimental Liquid Polysulfide Polymers Possessing Optimum Properties for Integral Fuel Cell Sealant Compound Application

    a. Improvement of the aromatic fuel resistance and toughness of the pentamethylene dichloride/formal and hexamethylene dichloride/triglycol dichloride/formal polymers which were developed during the period from 13 July, 1951 to 13 July, 1952 for compounding an improved integral fuel cell sealant compound.

    b. Development of new copolymers and terpolymers containing pentamethylene dichloride and relatively polar comonomers for improved toughness and aromatic fuel and heat resistance over the pentamethylene dichloride/formal copolymer.

    c. Preparation and evaluation of new experimental liquid polysulfide copolymers containing bis(4-chlorobutyl) formal.

2. General Evaluation and Compounding Studies

    a. Evaluation of "Thiokol" liquid polysulfide polymer LP-32 to determine its merits for the preparation of integral fuel cell sealant compounds.

    b. Compounding studies with "Thiokol" LP-2 and LP-32 utilizing various curing systems and adhesion additives to develop a practical sealant formulation possessing optimum properties which could be adapted to the new experimental polymers.

    c. Evaluation of new types of fillers.

    d. Development of organic curing systems for liquid polysulfide polymers.

3. Translucent Sealant Compound Development

    a. Investigation of liquid polysulfide polymer/epoxy resin systems for the development of a translucent sealant compound which would permit visual inspection during and after application and cure and possess improved properties in general.

b. Development of a translucent sealant compound with "Thiokol" LP-2 utilizing a soluble organic curing system and a re-enforcing material with a refractive index comparable to that of the liquid polymer.

The preparation and evaluation of the new experimental polymers is presented in this report. Also, the compounding and curing studies which were conducted are described. The results obtained in the evaluation of five translucent liquid polysulfide polymer/epoxy resin and one translucent "Thiokol" LP-2 sealant compounds, which were submitted to the Wright Air Development Center, are included.

The preparation methods used for the polymers synthesized in this report are described in Appendix A; evaluation procedures are presented in Appendix B; a glossary of terms is given in Appendix C.

I. DEVELOPMENT OF POLYMERS TO YIELD THE MOST DESIRABLE PROPERTIES

A. INTRODUCTION

During the first year of work on this contract, experimental sealant compounds were prepared with the 60/38/2 mole % of pentamethylene dichloride/formal/TCP copolymer and the 50/25/23/2 mole % of hexamethylene dichloride/triglycol dichloride/formal/TCP terpolymer developed on this contract. In comparison to an LP-2 sealant compound, these experimental polymer sealants possessed a marked improvement in low temperature properties, equivalent toughness, adhesion and resistance to heat aging at 212°F and somewhat less resistance to volume change in aromatic fuel. Both of the experimental polymer sealants were very "short" after immersion in aromatic fuel. Therefore, this phase of the program was chiefly concerned with the preparation and evaluation of liquid polysulfide polymers containing pentamethylene dichloride and polymers containing hexamethylene dichloride monomer with the primary objectives of maintaining good low temperature properties and improving the aromatic fuel resistance and toughness.

The following general types of polymer systems were studied:

1. Copolymers of pentamethylene dichloride and various monomers with structures which were conducive to improved resistance to volume swell and "shortness" after immersion in aromatic fuel. The effect of type and extent of cross-linking on the properties of the pentamethylene dichloride/formal copolymer was investigated.

2. Copolymers of ethylene dichloride and formal as possible substitutes for formal polymer and copolymer of bis(4-chlorobutyl) formal and formal to obtain a substitute for the hexamethylene dichloride/triglycol dichloride/formal terpolymer.

3. Terpolymers of pentamethylene dichloride with more polar monomers to achieve a desirable balance of properties.

4. Terpolymer of hexamethylene dichloride/triglycol dichloride/formal cross-linked with 0.5 mole % trichloropropane.

These liquid polymers were prepared on a laboratory scale by previously developed techniques described in Appendix B. Therefore, in some cases, the quantity of polymer available for evaluation limited the extent to which they could be tested.

The polymers were subjected to screening tests to determine if the structures yielded improvement in the desired properties. The test methods employed in the evaluation of these polymers are described in Appendix B. Either ASTM or military specification tests were used when applicable.

B. COPOLYMERS OF PENTAMETHYLENE DICHLORIDE IN COMBINATION WITH VARIOUS MONOMERS

1. Introduction

Various comonomers, which were relatively polar, were copolymerized with pentamethylene dichloride to obtain a polymer structure possessing improved toughness and resistance to aromatic fuel and heat aging over the pentamethylene dichloride/formal copolymer. The comonomers employed were as follows:

a. Triglycol dichloride

b. Glycerol dichlorohydrin

c. N-Methyl dichlorodiethylamine

d. Copolymers of pentamethylene dichloride and formal were prepared with different types and amounts of cross-linking agents for this same purpose. The cross-linking agents studied were:

   1. 0.5 and 2 mole % trichloropropane (TCP)

   2. 0.5 and 2 mole % tetrachloropropyl formal (TCF)

2. Copolymers of Pentamethylene Dichloride with Triglycol Dichloride and Glycerol Dichlorohydrin

Copolymers containing 60/38/2 mole % of pentamethylene dichloride/triglycol dichloride/TCP and pentamethylene dichloride/glycerol dichlorohydrin/TCP were prepared and evaluated to compare their properties, specifically resistance to volume swell and "shortness" after immersion in aromatic fuel, with those of the control, 60/38/2 mole % of pentamethylene dichloride/formal/TCP copolymer. Glycerol dichlorohydrin (triglycol) is quite polar and would be expected to improve aromatic fuel resistance.

Neither of the copolymers showed merit for the preparation of integral fuel cell sealant compounds with satisfactory toughness and resistance to the action of aromatic fuel. The data in Table 1 reveal that these copolymers were inferior to the control in toughness properties before and after immersion in SR-6 fuel and in low temperature torsional stiffness, but possessed better resistance to heat aging than the control copolymer. However, the toughness properties of the two copolymers were too poor for their use in a primary integral fuel cell sealant. The pentamethylene dichloride/triglycol/TCP copolymer was of interest because it was not attacked appreciably by JP-3A fuel after one month of immersion.

3. Pentamethylene Dichloride/N-Methyl Dichlorodiethylamine Copolymer

Several attempts were made to prepare a 60/38/2 mole % of pentamethylene dichloride/N-methyl dichlorodiethylamine/TCP copolymer. The N-methyl dichlorodiethylamine monomer was prepared and used in the form of the hydrochloride salt, dissolved in water and added to the reaction after the formal/TCP mixture had been added. The objective was to obtain a polymer with better toughness and heat-aging properties than the pentamethylene dichloride/formal/TCP copolymer and with equivalent low temperature characteristics; these properties were shown in previous studies (see p. 11 of WADC Technical Report 52-230). However, the number of toughenings required to obtain a copolymer of satisfactory hardness with N-methyl dichlorodiethylamine made it unsuitable for splitting to a liquid polymer. It was planned to prepare a liquid copolymer of this composition by redistributing the N-methyl dichlorodiethylamine latex with the pentamethylene dichloride latex, toughening and then splitting, but time did not permit it.

4. Copolymers of Pentamethylene Dichloride with Formal

Previous studies showed that formal polymers cross-linked with 0.5 mole % of TCP such as "Thiokol" LP-32 possessed considerably better tensile strength and elongation, both before and after heat aging at 212°F, and equivalent low temperature torsional stiffness properties compared to polymers cross-linked with 2 mole % of TCP (see p. 3 of WADC Technical Report 52-230). Additional work with "Thiokol" LP-32 showed that it gave integral fuel cell sealant compounds of lower moduli and considerably higher ultimate elongations before and after heat aging at 212°F and after immersion in aromatic fuel.

Copolymers containing 60/38/2 and 60/39.5/0.5 mole % of pentamethylene dichloride/formal/TCP and pentamethylene dichloride/formal/TCF were prepared and evaluated to compare the effects of 0.5 mole % with 2 mole % TCP and TCF cross-linking on polymer properties, especially resistance to heat aging and "shortness" after immersion in aromatic fuel. The physical properties of the 0.5 mole % cross-linked copolymer before and after heat aging were also compared to those of LP-32 (see Table 2).

From the data in Table 3, it is apparent that the 2 and 0.5 mole % of TCF cross-linked rubbers were equivalent in physical properties before heat aging. After heat aging for 72 hours at 212°F and after 24 hours immersion in aromatic fuel, the 2 mole % cross-linked rubber possessed lower moduli and considerably higher ultimate elongation. Compared to "Thiokol" LP-32, it could be compounded with more filler to give a rubber with physical properties which should be at least equivalent to those of LP-32.

The 2 mole % of TCF copolymer should make a sealant compound with better physical properties after immersion in aromatic fuel than the 0.5 mole % TCP cross-linked copolymer.

Over one pound batches of 60/39.5/0.5 mole % pentamethylene dichloride/formal/TCP and 60/38/2 mole % of pentamethylene dichloride/formal/TCF were prepared. These copolymers were to be compounded in a two-package mix sealant formulation and submitted to the Wright Air Development Center but were not of satisfactory quality.

C. COPOLYMERS CONTAINING ETHYLENE DICHLORIDE/FORMAL AND BIS(4-CHLOROBUTYL) FORMAL/FORMAL WITH VARIOUS MONOMERS

1. Ethylene Dichloride/Formal Copolymers

On the basis of previous work (see Tables 11 and 12 in WADC Technical Report 52-230) and because of the lower cost of ethylene dichloride, the ethylene dichloride/formal copolymer was considered as a possible substitute for LP-2 in integral fuel cell sealant compounds. Therefore, additional quantities of ethylene dichloride/formal copolymers containing 10 and 30 mole % of ethylene dichloride and 2 mole % of TCP were prepared and evaluated.

The data in Table 4 show that with the proportion of ethylene dichloride (over 30 mole %) required for a significant reduction in cost, the physical and low temperature properties of the formal polymer would be deleteriously affected. The physical properties of the 10 mole % of ethylene dichloride copolymer were in the same range as the LP-2 control both before and after immersion in SR-6 fuel. Also, this copolymer was comparable to the control in low temperature torsional stiffness and tension-retraction characteristics. The stress-strain properties, the low temperature torsional stiffness and tension-retraction properties, of the 30 mole % copolymer were somewhat poorer than those of the 10 mole % copolymer; and both copolymers were inferior to LP-2 in resistance to compression set at 158°F.

2. Copolymers of Bis(4-Chlorobutyl) Formal and Formal

A pilot plant batch of the bis(4-chlorobutyl) formal monomer was prepared and tested. From the results of the polymerization of this monomer to a polymer on a laboratory scale, it appeared that the 100 mole % of bis(4-chlorobutyl) latex could be prepared on a pilot plant scale for the preparation of a series of copolymers for evaluation of integral fuel cell sealant compounds.

D. TERPOLYMERS OF PENTAMETHYLENE DICHLORIDE IN COMBINATION WITH VARIOUS MONOMERS

1. Introduction

The purpose of preparing terpolymers with pentamethylene dichloride and more polar monomers was to obtain a polymer structure with excellent low temperature properties coupled with better toughness characteristics and resistance to aromatic fuel and heat aging than the pentamethylene dichloride/formal copolymer. The comonomers used were triglycol dichloride, glycerol dichlorohydrin and formal.

2. Terpolymers of Pentamethylene Dichloride with Triglycol Dichloride and Glycerol Dichlorohydrin

Two terpolymers containing 50/25/23/2 mole % of pentamethylene dichloride/glycerol dichlorohydrin/formal/TCP and pentamethylene dichloride/triglycol dichloride/formal/TCP were prepared and investigated.

From the data in Table 5, it is apparent that these terpolymers did not show promise for use in integral fuel cell sealant compounds with the required toughness and resistance to aromatic fuel. Both of the terpolymers had poorer stress-strain properties than the pentamethylene dichloride/formal/TCP control polymer both before and after immersion in aromatic fuel and were also poorer in low temperature torsional stiffness. The resistance of these terpolymers to aging at 212°F was quite good but they lacked sufficient toughness characteristics. Their resistance to volume swell in SR-6 fuel was not improved over that of the pentamethylene/formal copolymer but was superior to that of the copolymer in SR-10 fuel. It was observed that the glycerol dichlorohydrin terpolymer was not attacked appreciably after immersion for one month in JP-3A fuel.

E. TERPOLYMER OF HEXAMETHYLENE DICHLORIDE/TRIGLYCOL DICHLORIDE/FORMAL

1. Introduction

Improved over-all physical properties and resistance to heat aging and aromatic fuel were obtained with formal polymer and pentamethylene dichloride/formal copolymer cross-linked with 0.5 mole % of TCP in lieu of 2 mole % TCP. Therefore, the effect of 0.5 mole % of TCP cross-linking on the properties of this terpolymer was investigated.

2. Hexamethylene Dichloride/Triglycol Dichloride/Formal Terpolymer

A 50/25/24.5/0.5 mole % of hexamethylene dichloride/triglycol dichloride/formal/TCP terpolymer was prepared, but it could not be toughened to a satisfactory hardness. The terpolymer was prepared a second time with hexamethylene dibromide since hexamethylene dichloride was unavailable. This polymer required five toughenings and did not split to a suitable liquid polymer. Because of the unavailability of the monomer, no further work could be done with this terpolymer.

3. Heat Aging Resistance of Experimental Sealant Compound Prepared from Hexamethylene Dichloride/Triglycol Dichloride/Formal Terpolymer

Cured samples of the 50/25/23/2 mole % hexamethylene dichloride/triglycol dichloride/formal/TCP cross-linked terpolymer and the LP-2 experimental sealant compounds, which were previously submitted to the Wright Air Development Center, were further evaluated for heat aging characteristics.

From the data in Table 6, it is apparent that the terpolymer sealant compound was far superior to a comparable sealant prepared with LP-2 in respect to decrease in weight and volume and increase in hardness after seven days aging at 212°, 250°, and 300°F. After seven days aging at 300°F, the weight loss and decrease in volume of the LP-2 sealant compound was 2.5 and 3 times that of the terpolymer sealant material.

TABLE 1

PROPERTIES OF PENTAMETHYLENE DICHLORIDE/TRIGLYCOL DICHLORIDE AND PENTAMETHYLENE DICHLORIDE/GLYCEROL DICHLOROHYDRIN COPOLYMERS

Polymer No.	A19444R1 (Control)	A46142BI-1	A46142BI-2
Formal, mole %	60	--	--
Pentamethylene dichloride, mole %	38	60	60
Triglycol dichloride, mole %	--	38	--
Glycerol dichlorohydrin, mole %	--	--	38
Trichloropropane, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness (Shore A)	50	50	50
Brookfield viscosity, poises	200	600	530

Vulcanizate Properties (Cured 24 hr. at 77°F)[a]

Compound No.	25977-4 b / c / d	43253-1 b / c / d	43253-2 b / c / d
Shore A hardness	48/ 67/ --	50/ 57/ --	53/ 57/ --
100% Modulus, lb/sq in.	150/190/175	190/--/150	200/250/160
300% Modulus, lb/sq in.	275/-- /--	-- -- --	-- -- --
Tensile strength, lb/sq in.	425/190/300	250/300/150	275/350/160
Elongation, %	500/100/200	120/ 90/100	140/160/100
Tear Strength, lb/in.	54/ 34/ --	0/ 0/ --	22/ 20/ --
Compression Set, %			
At 1 hour			
158°F	97	61	31
-40°F	32	38	21
Torsional Test			
Relative modulus			
T_5, - °F	70	58	65
T_{10}	73	63	68
T_{50}	80	70	76
T_{100}	82	73	78
Absolute modulus			
G_{rt}, lb/sq in.	189	252	258
$G_{5,000}$, - °F	79	66	71
$G_{10,000}$	82	69	76
$G_{20,000}$	84	72	79
Swelling volume, %			
SR-6 1 day	31	26	33
1 month	5	26	35
SR-10 1 day	11	2	3
1 month	12	5	5
JP-3A 1 day	6	7	9
1 month	7[e]	13	19[e]

[a] Unless specified otherwise, the specimens were unaged and untreated.

[b] Unaged.

[c] Aged 72 hours at 212°F.

[d] Test specimens immersed in SR-6 at 80°F for 24 hours and tested while wet.

[e] Surface of test specimen attacked.

TABLE 2

PROPERTIES OF PENTAMETHYLENE DICHLORIDE/FORMAL COPOLYMERS

Polymer No.	LP-32	B41943 BJ	B43709 BI
Formal, mole %	99.5	38	39.5
Pentamethylene dichloride, mole %	—	60	60
Trichloropropane, mole %	0.5	2	0.5
Rank	2.25	2.25	2.25
Cake hardness (Shore A)	—	47	42
Brookfield viscosity, poises	400	300	270

Compounding Recipes

Compound No.	43266-3	43262-2	43262-1
LP-32	100	—	—
B41943 BJ	—	100	—
B43709 BI	—	—	100
Zinc sulfide (ZS-800)	50	50	50
Lead stearate	1.87	1.87	1.87
Lead peroxide	10	10	10
Sulfur	0.1	0.1	0.1

Vulcanizate Properties (Cured 24 hr. @ 77°F)

	a/ b/ c	a/ b/ c	a/ b/ c
Shore A hardness	45/50/—	50/56/—	43/ 47/—
100% Modulus, lb/sq in.	135/100/65	150/215/160	100/120/75
300% Modulus, lb/sq in.	235/200/145	350/370/--	175/190/140
Tensile strength, lb/sq in.	725/750/460	350/420/190	575/765/200
Elongation, %	865/1200/850	300/390/145	860/1220/455
Tear strength, lb/in.	86/87/52	25/45/0	90/100/20

a Unaged.
b Heat aged 72 hours at 212°F.
c Test specimens immersed in SR-6 at 80°F for 24 hours and tested while wet.

TABLE 3

PROPERTIES OF PENTAMETHYLENE DICHLORIDE/FORMAL COPOLYMERS

Polymer No.	LP-32	B44755 BJ-2	B46157 CL-1
Formal, mole %	99.5	38	39.5
Pentamethylene dichloride, mole %	--	60	60
Tetrachloropropyl formal, mole %	--	2	0.5
Trichloropropane, mole %	0.5	--	--
Rank	2.25	2.25	2.25
Cake hardness (Shore A)	--	43	42
Brookfield viscosity, poises	--	305	480

Compounding Recipes

Compound No.	43266-3	43266-2	43269-1
LP-32	100	--	--
B44755 BJ-2	--	100	--
B46157 CL-1	--	--	100
Zinc sulfide (ZS-800)	50	50	50
Lead stearate	1.87	1.87	1.87
Lead peroxide	10	10	10
Sulfur	0.1	0.1	0.1

Vulcanizate Properties (Cured 24 hr. @ 77°F)[a]

	b / c / d	b / c / d	b / c / d
Shore A hardness	45/50/--	45/ 49/ --	40/ 45/ --
100% Modulus, lb/sq in.	135/100/65	125/90/35	125/160/ 50
300% Modulus, lb/sq in.	235/200/145	155/125/50	125/200/100
Tensile strength, lb/sq in.	725/750/460	370/410/180	400/800/150
Elongation, %	865/1200/850	1120/1390/1190	1080/1000/600
Tear strength, lb/in.	86/ 87/ 52	70/ 61/ 30	70/104 / 17

Swelling volume, %				
SR-6	- 1 week	17	40	31
	- 1 month	11	28	--
SR-10	- 1 week	--	6	17
	- 1 month	--	4	23
JP-3A	- 1 day	--	13	19
	- 1 month	--	13	26

---

a Unless specified otherwise, the specimens were unaged and untreated.

b Unaged.

c Heat aged 72 hours at 212°F.

d Test specimens immersed in SR-6 fuel at 80°F for 24 hours and tested while wet.

TABLE 4

PROPERTIES OF ETHYLENE DICHLORIDE/FORMAL COPOLYMERS

Polymer No.	LP-2 (Control)	B41351BE-1	B41351BE-2
Formal, mole %	98	88	68
Ethylene dichloride, mole %	--	10	30
Trichloropropane, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness (Shore A)	--	42	47
Brookfield viscosity, poises	350	375	590

Vulcanizate Properties (Cured 24 hr. at 77°F)[a]

Compound No.	43351-4 b/c	34396-1 b/c	34396-2 b/c
Shore A hardness	48/--	49/--	50/--
100% Modulus, lb/sq. in.	150/150	175/150	150/150
300% Modulus, lb/sq in	310/240	340/--	325/--
Tensile strength, lb/sq in.	490/290	460/250	410/220
Elongation, %	480/340	475/280	415/230
Tear strength, lb/in.	50/--	51/--	38/--
Compression Set, %			
At 1 hour			
158°F	67	100	94
-40°F	33	31	33
Torsional test			
Relative modulus			
T_5, - $^{\circ}$F	54	52	46
T_{10}	57	55	50
T_{50}	64	61	57
T_{100}	66	65	58
Absolute Modulus			
G_{rt}, lb/sq in.	152	172	154
$G_{5,000}$ - $^{\circ}$F	62	58	56
$G_{10,000}$	65	62	58
$G_{20,000}$	68	66	61
Tension-Retraction, %			
TR10, - $^{\circ}$F	60	60	56
TR30	55	55	51
TR50	47	47	44
TR70	33	32	33
TR10-TR70	27	28	23

(Table continued and footnotes on next page.)

TABLE 4 (Contd.)

PROPERTIES OF ETHYLENE DICHLORIDE/FORMAL COPOLYMERS

Compound No.		43351-4	34396-1	34396-2
		b/c	b/c	b/c
Swelling Volume, %				
SR-6	1 day	14	12	9
	1 month	16	13	10
SR-10	1 day	2	2	1
	1 month	2	2	0
JP-3A	1 day	4	4	2
	1 month	9[d]	8[d]	8[d]

a Unless specified otherwise, the specimens were unaged and untreated.

b Unaged.

c Test specimens immersed in SR-6 at 80°F for 24 hours and tested while wet.

d Surface of test specimen attacked.

TABLE 5

PROPERTIES OF TERPOLYMERS OF PENTAMETHYLENE DICHLORIDE WITH TRIGLYCOL DICHLORIDE AND GLYCEROL DICHLOROHYDRIN

Polymer No.	A19444R1 (Control)	A46139BI	A46140BI
Formal, mole %	60	23	23
Pentamethylene dichloride, mole %	38	50	50
Triglycol dichloride, mole %	--	25	--
Glycerol dichlorohydrin, mole %	--	--	25
Trichloropropane, mole %	2	2	2
Rank	2.25	2.25	2.25
Cake hardness (Shore A)	50	50	50
Brookfield viscosity, poises	200	535	275

Vulcanizate Properties (Cured 24 hr. at 77°F)[a]

Compound No.		25977-4	43252-1	43252-2
		b / c / d	b / c / d	b / c / d
Shore A hardness		48/ 67/ --	53/ 56/ --	53/ 58/ --
100% Modulus, lb/sq in.		150/190/175	160/210/150	200/300/ --
300% Modulus, lb/sq in.		275/ --/ --	-- /-- /--	--/ --/ --
Tensile strength, lb/sq in.		425/190/300	360/340/175	250/340/175
Elongation, %		500/100/200	275/210/200	130/120/ 80
Tear strength, lb/in.		54/ 34/ --	36/ 44/ --	6/ 0/ --
Compression Set, %				
At 1 hour				
158°F		97	66	43
-40°F		32	32	23
Torsional test				
Relative Modulus				
T_5, - °F		70	63	65
T_{10}		73	67	69
T_{50}		80	74	75
T_{100}		82	76	75
Absolute Modulus				
G_{rt}, lb/sq in.		189	174	191
$G_{5,000}$, - °F		79	72	73
$G_{10,000}$		82	75	76
$G_{20,000}$		84	78	81
Swelling volume, %				
SR-6	1 day	31	32	30
	1 month	5	18	27
SR-10	1 day	11	2	3
	1 month	12	1	4
JP-3A	1 day	6	1[e]	8
	1 month	7[e]	12[e]	12

[a] Unless specified otherwise, the specimens were unaged and untreated.
[b] Unaged.
[c] Aged 72 hours at 212°F.
[d] Test specimens immersed in SR-6 at 80°F for 24 hours and tested while wet.
[e] Surface of test specimen attacked.

TABLE 6

EFFECT OF HEAT AGING ON HEXAMETHYLENE DICHLORIDE/TRIGLYCOL DICHLORIDE/FORMAL TERPOLYMER

Compound No.	43259-1	43267-3
Hexamethylene dichloride/triglycol dichloride/formal terpolymer 50/25/23/2	100	--
LP-2	--	100
Pelletex SRF-3	30	30
Maleic anhydride	2	2
Epoxy Polymer C-8	0.5	0.5
C-11 Curing Agent[a]	12.6	12.6
Vulcanizate Properties (Cured 24 hr. @ 77°F)		
	b / c / d	b / c / d
Decrease in weight, %	3.5/6.5/24	11/27/57.5
Decrease in volume, %	2.5/5.5/28	12/31/84
Change in hardness, %	-11/ -7/29	8/17/63
Remarks after 7 days aging at 212°F	Very flexible, no cracking when flexed 180°	Very flexible, no cracking when flexed 180°
at 250°F	Very flexible, no cracking when flexed 180°	Flexible, no cracking when flexed 180°
at 300°F	Flexible but "short", broke when bent 180°	Hard and brittle

a 59.3% lead peroxide, 11.1% lead stearate and 29.6% dibutyl phthalate were used.
b Heat aged 7 days at 212°F.
c Heat aged 7 days at 250°F.
d Heat aged 7 days at 300°F.

II. EVALUATION AND COMPOUNDING STUDIES

A. INTRODUCTION

This phase of the program was devoted to the following studies:

1. Preliminary evaluation of the suitability of "Thiokol" LP-32 for integral fuel cell sealant compound application.
2. Adhesion additive and cure studies with "Thiokol" LP-2 and LP-32 base sealant compounds for the development of a satisfactory sealant formulation which would be adaptable to new experimental liquid polysulfide polymers.
3. Investigation of "Thiokol" LP-2 and LP-32 integral fuel cell sealant compounds.
4. Compounding WD-6/Saran F-120 Base Reverse Phase with the hexamethylene/triglycol/formal terpolymer sealant compound for improvement of its aromatic fuel resistance.
5. Evaluation of new types of fillers.
6. Investigation of organic curing systems.

B. EVALUATION OF "THIOKOL" LP-32

On the basis of previous studies (see Table 2, p. 16 of WADC Technical Report 52-230 for test data) with formal liquid polymers, LP-32, (ZL-158) was investigated to obtain additional data on the merits of 0.5 mole % crosslinking in polysulfide liquid polymers for fuel cell sealant compounds. Higher ultimate elongation before and after heat aging and after immersion in aromatic fuel would be highly desirable in the pentamethylene dichloride/formal and hexamethylene dichloride/triglycol/formal experimental polymers and in the LP-2 formal polymer for use in integral fuel cell applications.

"Thiokol" LP-32 was evaluated in the standard test formulation with 0.1 and 0.25 parts of sulfur per 100 parts of polymer and without sulfur. According to the results in Table 7, the three LP-32 rubbers possessed lower 100 and 300% moduli, much better ultimate elongation than the "Thiokol" LP-2 rubber both before and after heat aging at 212°F and after 24 hours of immersion in SR-6 fuel. The rubbers prepared from the LP-32 compounds containing 0.1 and 0.25 part sulfur were equivalent to the LP-2 control in tensile strength before aging and after immersion in SR-6 fuel and possessed somewhat higher tensile strength after heat aging. In addition, the tear strengths of these compounds were considerably higher than those of the control.

Without sulfur, the LP-32 rubber "cold-flowed" somewhat at room temperature and flowed considerably at 212°F. The tensile strength was slightly lower than that of the LP-2 control before and after heat aging and after immersion in aromatic fuel.

C. ADHESION ADDITIVE AND CURE STUDIES WITH "THIOKOL" LP-2 AND LP-32

BASE SEALANT COMPOUNDS

1. Introduction

Preliminary studies were conducted with several adhesion additives and combinations of additives to determine the best type and concentration for use in an integral fuel cell sealant compound. The objective was to develop a sealant formulation with satisfactory working life and good curing and adhesion characteristics for application to new experimental liquid polymers. The effects of aging the base sealant compound and accelerator on adhesion characteristics were determined. In some studies, the effect of aging these sealant compounds on the working life and cure was also investigated.

2. Effect of One Part of Maleic Anhydride Per 100 Parts of LP-2

In this study, the four base sealant compounds listed in Table 8 were prepared and evaluated. These compounds were cured at room temperature with C-11 paste accelerator. The results indicated that 1 part of maleic anhydride per 100 parts of LP-2 imparted good adhesion to the unaged base compound after the 24 hour cure and after subsequent immersion for two days in SR-6 at 80°F. Also, a good cure, as indicated by Shore A hardness, was obtained after 24 hours. However, after the 24 hour cure plus seven days of immersion in SR-6 at 80°F, poor adhesion developed. Normal aging of the base compound for 30 days at 80°F produced a change which was harmful to the curing properties.

One part of maleic anhydride and 0.5 part of epoxide polymer (C-8 resin) per 100 parts of LP-2 gave good adhesion after the 24 hour cure at room temperature with freshly prepared base compound and also after aging for 30 days at 80°F. This combination of additives did not maintain satisfactory adhesion to aluminum after immersion for two days in SR-6 fuel. As indicated by Shore A hardness, a good cure was obtained after 24 hours at room temperature.

Incorporation of 20 parts of Paraplex 5B or G20 into the base sealant compound containing one part of maleic anhydride adversely affected the cure and adhesion properties. The compound containing Paraplex 5B did not cure properly on the aluminum test panels and was not evaluated.

3. Effect of Two Parts of Maleic Anhydride per 100 Parts of LP-2

The results in Table 9, show that the unaged sealant compounds containing 2 parts of maleic anhydride alone or 2 parts of maleic anhydride plus 0.5 part of C-8 resin per 100 parts of LP-2 cured to a good hardness, possessed fairly good working life and had good adhesion after either 24 hours or seven days of cure. The compound with the maleic anhydride and C-8 resin also gave good adhesion after seven days of immersion in SR-6 fuel. The compound with maleic anhydride alone was rated as fair to good in this property after immersion in the aromatic fuel.

After aging these base compounds for 30 days at 80°F, the compound containing both maleic anhydride and C-8 resin possessed good adhesion after 24 hours or seven days of cure and after seven days of immersion in SR-6, but possessed virtually no working life and was very "short" after immersion in SR-6 when aged for 30 days. Therefore, additives composed of maleic anhydride and C-8 resin were considered unsatisfactory for fuel cell sealant compounds. It was also noted that the base compound with maleic anhydride alone did not cure after aging for 30 days.

Formulations containing 2 parts of maleic anhydride plus 5 or 10 parts of Paraplex 5B, Paraplex G20 or Bakelite resin BR-6741 were of no value for integral fuel cell sealant compounds. The unaged compounds containing the Paraplex resins had satisfactory working life, cured to a good hardness after 24 hours, but possessed poor adhesion. After aging for 30 days at 80°F, these compounds would not cure at room temperature. The unaged BR-6741 compounds did not cure after 48 hours at room temperature.

4. Effect of Bakelite Phenolic Resin BR-6741

Six formulations containing Bakelite phenolic resin BR-6741 alone and in combination with maleic anhydride were prepared and evaluated. The compositions containing both BR-6741 and maleic anhydride were of no value since they did not cure within five days.

From the data in Table 10, it is apparent that only the compound containing 5 parts of BR-6741 without maleic anhydride was of value. This compound possessed good working life, cured to a satisfactory hardness in 24 hours and had good adhesion before and after seven days of immersion in SR-6 as well as after aging the base compound for 30 days at 80°F. Compared to a commercial LP-2 base sealant compound, it possessed somewhat better working life, greater hardness and comparable adhesion characteristics.

5. Effect of Solutions of Maleic Anhydride in Cyclohexanone

Solutions of maleic anhydride in cyclohexanone were investigated as adhesion additives in the base LP-2 sealant compound with the objectives of eliminating the toxicity hazard encountered during paint milling the maleic anhydride into the compound as well as to determine the effect on working life, cure and adhesion characteristics. Better dispersion of the maleic anhydride was obtained by incorporating it into the compound as a solution in a solvent compatible with the liquid polymer.

Base sealant compounds containing LP-32 and LP-2 were prepared with 4 parts of a 50% solution of maleic anhydride in cyclohexanone and with 4 and 8 parts of a 25% solution of maleic anhydride in cyclohexanone per 100 parts of polymer. One-tenth part of sulfur per 100 parts of polymer was incorporated in the LP-32 compounds to obtain a good cure with better resistance to compression set. The results in

Table 11 show that with 4 parts of the 50% solution of maleic anhydride in cyclohexanone a satisfactory cure was not obtained after 24 hours with either the IP-32 or the IP-2 compounds. Good adhesion was secured after the 24 hour cure, but the compounds were soft and tacky. After 48 hours of immersion in SR-6, the adhesion was fair to poor.

The compounds containing 8 parts of the 25% maleic anhydride solution did not cure within 48 hours. The IP-32 and IP-2 sealant compounds prepared with 4 parts of this solution possessed good working life, cured to a good hardness in 24 hours and had good adhesion before and after two days of immersion in SR-6 fuel. After seven days of immersion in SR-6, the IP-32 compound had good adhesion but the IP-2 sealant adhesion was poor. Compared to a commercial IP-2 base sealant compound, the IP-32 sealant cured to a higher hardness and in general possessed better adhesion properties. The IP-2 sealant compound prepared with 2 parts of maleic anhydride (solid) gave better adhesion after seven days of immersion in SR-6 than the IP-2 sealant containing 4 parts of the 25% maleic anhydride solution.

6. Effect of Phenolic Resin BK-3962 on "Thiokol" IP-2

Previously the Bakelite resin BK-3962, reacted readily with IP-2 at room temperature to give a fairly tough rubber-like material that might possess merit for integral fuel cell applications. Additional work was done with compositions containing only IP-2 and BK-3962, and also with the latter as an additive in the standard IP-2 control formulation.

From the results in Table 12, it is apparent that BK-3962, either with IP-2 alone or as an additive, did not possess any merit as an improved sealant compound for general application as these compounds had a very short working life of 5 to 10 minutes. However, the IP-2/BK-3962 compounds were not attacked by JP-3A fuel after one month of immersion and therefore, may be useful as a protective coating for IP-2 base sealants.

D. INVESTIGATION OF "THIOKOL" IP-2 AND IP-32 INTEGRAL FUEL CELL SEALANT COMPOUNDS

Two-package mix sealant compounds were formulated with "Thiokol" IP-2 and IP-32 and with the optimum concentrations and types of adhesion additives and curing agents investigated in the foregoing studies. The data obtained in this study were to be used in the compounding of sealant compounds with the pentamethylene dichloride/formal and hexamethylene dichloride/triglycol/formal and other promising experimental polymers which were developed.

The results in Table 13 show that 4 parts of a 25% solution of maleic anhydride in cyclohexanone was satisfactory as an adhesion additive in the base IP-2 sealants. These sealants possessed satisfactory working life, good curing characteristics and satisfactory adhesion properties both before and after aging the base sealant compounds at 120°F for seven days and at room temperature for one month. However, this additive was not as desirable with the IP-32 sealant since a satisfactory cure at room temperature was not obtained in the films on aluminum panels after aging the base compound for 30 days at 80°F. The IP-2 sealant containing the phenolic resin adhesion additive BR-6741 was generally not as satisfactory as those containing maleic anhydride.

The IP-32 sealant compound possessed lower moduli and a higher ultimate elongation before and after aging at 212° and 250°F and after 24 hours of immersion in SR-6 fuel than comparable IP-2 sealant compounds. The commercial sealant compound was generally not as good as the IP-2 base sealants prepared and evaluated in this study.

E. EFFECT OF WD-6/SARAN F-120 BASE REVERSE PHASE ON THE PROPERTIES OF THE HEXAMETHYLENE DICHLORIDE/TRIGLYCOL/FORMAL/TERPOLYMER

A small quantity of a WD-6/Saran Base Reverse Phase in the terpolymer sealant compound might provide a protective coating for the polymer and thereby improve its physical properties after immersion in aromatic fuel; therefore, ten parts (solid basis) of a Base Reverse Phase containing 74.7% of "Thiokol" WD-6 and 25.3% of Saran per 100 parts of polymer were compounded with the 50/25/23/2 mole % hexamethylene dichloride/triglycol/formal/TCP terpolymer experimental sealant compound.

The results in Table 14 show that this quantity of Base Reverse Phase did not significantly affect the physical properties of the experimental polymer sealant compound either before or after immersion in SR-6 fuel.

F. INVESTIGATION OF NEW TYPES OF FILLERS

Aerosil and Ex. Silica 54-EP-88, very fine silicon dioxides, were evaluated as fillers in a "Thiokol" LP-32 formulation cured with the lead peroxide/lead stearate/sulfur system at room temperature and were found to be excellent reinforcing agents for the liquid polymer. The use of 15 parts of these fillers resulted in a rubber with hardness and tensile strength comparable to that obtained with 30 parts of Pelletex SRF-3, and also in higher ultimate elongation. Higher hardness, tensile and tear strength and ultimate elongation were obtained with 15 parts of these fillers than with 15 parts of Pelletex SRF-3, whereas the rubber containing 15 parts of Aerosil was very resilient (see Table 15 for test data).

A preliminary study was conducted with LP-2 and Aerosil filler employing a soluble cumene hydroperoxide curing system for the development of a translucent sealant material. The data obtained in this study are not presented in this report. However, the best IP-2 translucent sealant compound developed to date and the evaluation data are presented in the Experimental Integral Fuel Cell Sealant Compounds section.

G. ORGANIC CURING SYSTEMS

Cure and adhesion studies were conducted with an integral fuel cell sealant based on "Thiokol" IP-32. The formulation contained a small amount of sulfur and maleic anhydride adhesion additive. It was cured by three systems, viz., lead peroxide/lead stearate paste (C-11), p-quinonedioxime (GMF)/amine and trinitrobenzene/amine. The objective was to develop satisfactory cures and adhesion to aluminum with organic curing systems. The p-quinonedioxime/amine cure was found previously (see p. 71 WADC Technical Report 52-230) to be superior to the lead peroxide curing system for resistance to heat aging in our standard evaluation formulation.

From the data in Table 16, it is apparent that the p-quinonedioxime/amine curing systems yielded a longer working life and a slower cure at room temperature than did the lead peroxide cure. An elastomer with hardness and adhesion to aluminum comparable to that obtained with lead peroxide was achieved with a p-quinonedioxime/2,4,6 tri(dimethylaminomethyl) phenol system after a 72 hour cure at room temperature. Satisfactory cures and good adhesion were obtained with some of these systems after 24 hours at room temperature and subsequent heating at 158°F for 5 hours. Trinitrobenzene/triethanolamine/calcium oxide did not provide a satisfactory cure at room temperature alone; however, good cures and satisfactory adhesion were obtained after 24 hours at room temperature plus 5 hours at 158°F (see Table 17). The effect of heat aging on the physical and adhesion properties of the rubbers cured with these systems was not investigated.

TABLE 7

PROPERTIES OF "THIOKOL" LP-32 COMPOUNDS

Compound No.	43351-4	34395-1	34395-2	34395-3
	Control			
LP-2	100	--	--	--
LP-32	--	100	100	100
Zinc sulfide	50	50	50	50
Lead stearate	1.4	1.4	1.4	1.4
Lead peroxide	7.5	7.5	7.5	7.5
Sulfur	--	--	0.1	0.25
	Vulcanizate Properties (Cured 24 Hrs. at 77°F)[a]			
	b / c / d	b / c / d	b / c / d	b / c / d
Shore A hardness	48/49/--	43/ 43/--	43/ 43/ --	45/ 47/--
100% Modulus, lb/sq in.	150/175/150	75/ --/50	110/100/ 60	100/100/ 75
300% Modulus, lb/sq in.	310/350/240	150/--/100	175/150/150	--/150/100
Tensile strength, lb/sq in.	490/475/290	350/300/200	460/600/290	460/625/275
Elongation, %	480/475/340	870/1075/970	810/1150/950	800/1125/900
Tear strength, lb/in.	50/ 50/--	57/ 73/--	71/107/--	83/103/--
Compression set, %				
At 1 hour				
158°F	67	>100	90	54
-40°F	33	64	62	54
Torsional test	b/c	b/c	b/c	b/c
Relative modulus				
T_5, -°F	54/46	48/e	50/49	50/50
T_{10}	57/52	55/--	54/54	55/55
T_{50}	64/60	60/--	63/62	62/61
T_{100}	66/61	64/--	66/68	66/64
Absolute modulus				
G_{rt}, lb/sq in.	152/113	84/--	94/93	104/109
$G_{5,000}$, -°F	62/58	61/--	65/63	63/62
$G_{10,000}$	65/62	65/--	68/66	66/64
$G_{20,000}$	68/65	68/--	70/69	69/67

(Table continued and footnotes on next page.)

TABLE 7 (Contd.)

PROPERTIES OF "THIOKOL" LP-32 COMPOUNDS

Compound No.		43351-4	34395-1	34395-2	34395-3
Tension-retraction, %					
TR10, -°F		60	60	59	60
TR30		55	30	44	45
TR50		47	5	15	17
TR70		33	+20	+10	+7
TR10 - TR70		27	80	69	67
Swelling volume, %					
SR-6	1 day	14	15	19	16
	1 month	16	4	13	17
SR-10	1 day	2	1	5	2
	1 month	2	0	4	2
JP-3A	1 day	4	4[f]	3[f]	3[f]
	1 month	9[f]	8[f]	6[f]	10[f]

a Unless specified otherwise, the specimens were unaged and untreated.
b Unaged.
c Aged 72 hours at 212°F.
d Test specimens immersed in SR-6 @ 80°F for 24 hours and tested while wet.
e Rubber quite thermoplastic. Specimen stretched during aging at 212°F too thin for torsional test.
f Surface of test specimen attacked.

TABLE 8

EFFECT OF 1 PART OF MALEIC ANHYDRIDE ON ADHESION OF "THIOKOL" LP-2 BASE SEALANT COMPOUND

Compound No.	34397-1	34397-2	34397-3	34397-4
LP-2	100	100	100	100
Pelletex SRF-3	30	30	30	30
Maleic anhydride	1	1	1	1
C-8 Resin (BR-18774)[a]	--	0.5	--	--
Paraplex 5B[b]	--	--	20	--
Paraplex G20[c]	--	--	--	20
C-11 (parts/100 parts of base compd.)	9.7	9.6	8.4	8.4
Working life, hr.	1	1	4	1
Shore A hardness				
After 24-hr. cure	60	60	40	48
After 48-hr. cure	60	64	45	51
Adhesion characteristics				
After 24-hr. cure				
Unaged	Good	Good	Tacky, undercured	Very poor
Aged[d]	Tacky, undercured	Good	--	--
After 24-hr. cure & 48 hr. in SR-6				
Unaged	Good	Poor	--	Very poor
Aged[d]	Tacky, undercured	Poor	--	--
After 24-hr. cure & 7 days in SR-6				
Unaged	Poor	Poor	--	--
Aged[d]	Tacky, undercured	Poor	--	--
After 7-day cure				
Aged[d]	Tacky, undercured	Good	--	--

[a] Epoxide type polymer manufactured by Bakelite Corporation.
[b] Special maleic alkyd polyester manufactured by Rohm and Haas Company.
[c] Sebacic acid type polymer manufactured by Rohm and Haas Company.
[d] Base sealant compound and accelerator aged 30 days at 80°F.

TABLE 9

EFFECT OF 2 PARTS OF MALEIC ANHYDRIDE ON ADHESION OF "THIOKOL" LP-2 BASE SEALANT COMPOUND

Compound No.	43352-1	43352-2	43352-3	43352-4	43352-5	43352-6	43352-7	43352-8
LP-2	100	100	100	100	100	100	100	100
Pelletex SRF-3	30	30	30	30	30	30	30	30
Maleic anhydride	2	2	2	2	2	2	2	2
C-8 Resin (BR-18774)[a]	--	0.5	--	--	--	--	--	--
Paraplex 5B[b]	--	--	10	5	--	--	--	--
Paraplex G20[c]	--	--	--	--	10	5	--	--
BR-6741[d]	--	--	--	--	--	--	10	5
C-11 (parts/100 parts of base compd.)	9.6	9.5	8.9	9.2	8.9	9.2	8.9	9.2
Working life, hr.								
Unaged	2	1.75	2.75	2.5	2	1.5	No cure in 48 hr.	
Aged[e]	No cure in 48 hr.	0	--	--	--	--	--	--
Shore A hardness								
After 24-hr. cure								
Unaged	60	57	58	57	58	59	--	--
Aged[e]	No cure in 48 hr.	61	--	--	--	--	--	--
After 48-hr. cure								
Unaged	63	60	60	60	60	63	--	--
Aged[e]	No cure in 48 hr.	62	--	--	--	--	--	--

(Table continued and footnotes on next page.)

TABLE 9 (Contd.)

EFFECT OF 2 PARTS OF MALEIC ANHYDRIDE ON ADHESION OF "THIOKOL" LP-2 BASE SEALANT COMPOUND

Compound No.	43352-1	43352-2	43352-3	43352-4	43352-5	43352-6	43352-7	43352-8
Adhesion characteristics								
After 24-hr. cure								
Unaged	Good	Good	Poor	Poor	Poor	Poor		
Aged[e]	No cure in 48 hr.	Good	--	--	--	--		
After 24 hr. cure & 48 hr. in SR-6								
Unaged	Good in spots	Good	Poor	Poor	Poor	Poor		
Aged[e]	No cure in 48 hr.	Good	--	--	--	--		
After 24-hr. cure & 7 days in SR-6								
Unaged	Fair in spots	Good	Poor	Poor	Poor	Poor		
Aged	No cure 48 hr.	Good	--	--	--	--		
After 7-day cure								
Unaged	Good	Good	Poor	Poor	Poor	Poor		
Aged[e]	No cure in 48 hr.	Good	--	--	--	--		

[a] Epoxide type polymer manufactured by Bakelite Corporation.
[b] Special maleic alkyd polyester manufactured by Rohm and Haas Company.
[c] Sebacic acid type polymer manufactured by Rohm and Haas Company.
[d] Phenolic resin manufactured by Bakelite Corporation.
[e] Base sealant compound and accelerator aged 30 days at 80°F.

TABLE 10

EFFECT OF BAKELITE BR-6741 ON ADHESION OF "THIOKOL" LP-2 BASE SEALANT COMPOUND

Compound No.	43353-1	43354-2	43354-3	43354-4	43354-5	43354-6	43353-4
LP-2	100	100	100	100	100	100	--
Commercial LP-2 base sealant	--	--	--	--	--	--	100
Pelletex SRF-3	30	30	30	30	30	30	--
Maleic anhydride	--	--	0.5	0.5	1	1	--
BR-6741[a]	5	2.5	5	2.5	5	2.5	--
Commercial sealant accelerator	--	--	--	--	--	--	12
C-11 (parts/100 parts of base compd.)	9.4	9.6	9.4	9.5	9.4	9.5	--
Working life, hr.	3	3	Did not cure in 5 days	Did not cure in 5 days	Did not cure in 5 days	Did not cure in 5 days	2.5
Shore A hardness After 24-hr. cure	43	45					35
Adhesion characteristics							
After 24-hr. cure							
Unaged	Fair to good	Poor	--	--	--	--	Fair
Aged[b]	Fair to good	--	--	--	--	--	Good
After 24 hr. cure and 48 hr. in SR-6							
Unaged	Good	Poor	--	--	--	--	Fair
Aged[b]	Good	--	--	--	--	--	Good
After 24-hr. cure and 7 days in SR-6							
Unaged	Good	Poor					Good
Aged[b]	Fair to good	--					Fair to good
After 7-day cure							
Unaged	Good	Good					Good
Aged[b]	Good	--					Good

[a] Phenolic resin manufactured by Bakelite Corporation.
[b] Base sealant compound and accelerator aged 30 days at 80° F.

TABLE 11

EFFECT OF MALEIC ANHYDRIDE - CYCLOHEXANONE SOLUTION ON PROPERTIES OF SEALANT COMPOUND

Compound No.	43353-4	43356-1	43356-2	43357-1	43357-2	43358-1	43358-2	43362-4
LP-32	--	100	--	100	--	100	--	--
LP-2	--	--	100	--	100	--	100	100
Commercial LP-2 base sealant	100	--	--	--	--	--	--	--
Pelletex SRF-3	--	30	30	30	30	30	30	30
Sulfur	--	0.1	--	0.1	--	0.1	--	--
Maleic anhydride	--	--	--	--	--	--	--	2
50% Soln. maleic anhydride in cyclohexanone	--	4	4	--	--	--	--	--
25% Soln. maleic anhydride in cyclohexanone	--	--	--	8	8	4	4	--
Commercial sealant accelerator	12	--	--	--	--	--	--	--
C-11 (parts/100 parts of base compound)	--	9.5	9.5	9.2	9.2	9.5	9.5	9.6
Working life, hr.	2.5	3	2.5	No cure in 48 hr.	No cure in 48 hr.	6	4	1.5
Shore A hardness								
After 24-hr. cure	35	7	Too soft	--	--	45	56	38
After 48-hr. cure		--	--	--	--	45	58	55
Adhesion characteristics								
After 24-hr. cure	Fair	Good (undercured)	Good (undercured)	--	--	Good	Good	Good
After 24-hr. cure and 48 hr. in SR-6	Fair	Fair	Poor	--	--	Good	Good	Good
After 24-hr. cure and 7 days in SR-6	Good	--	--	--	--	Good	Poor	Good
After 7-day cure	Good	--	--	--	--	Good	Good	Good

TABLE 12

EFFECT OF OIL-MODIFIED PHENOLIC RESIN ON PROPERTIES OF "THIOKOL" LP-2 POLYMER

Compound No.	43351-4	43351-1	43351-2	43351-3	43351-5	43351-6
	Control					
LP-2	100	100	100	100	100	100
Zinc sulfide	50	--	--	--	50	50
Lead stearate	1.4	--	--	--	1.4	1.4
Lead peroxide	7.5	--	--	--	7.5	7.5
BK-3962[a] (50% solids)	--	100	66.5	100	40	80
Maleic anhydride	--	--	--	2	--	--
Vulcanizate Properties[b]						
Shore A hardness	48	73	63	68	50	58
100% Modulus, lb/sq in.	150	300	250	300	160	160
300% Modulus, lb/sq in.	310	--	375	--	340	310
Tensile strength, lb/sq in.	490	300	375	300	375	360
Elongation, %	480	160	350	100	360	430
Tear strength, lb/in.	50	54	65	44	51	60
Torsional test						
Relative modulus						
T_5, -°F	54	48	41	46	48	50
T_{10}	57	55	53	53	55	56
T_{50}	64	65	66	64	63	64
T_{100}	66	--	69	66	66	66
Absolute modulus						
G_{rt}, lb/sq in.	152	527	340	362	198	272
$G_{5,000}$, -°F	62	55	58	56	61	60
$G_{10,000}$	65	61	62	60	64	62
$G_{20,000}$	68	64	67	64	67	65
Swelling volume, %						
SR-6 1 day	14	21	17	--	12	11
SR-6 1 month	16	27	15	--	8	6
SR-10 1 day	2	1	1	--	2	2
SR-10 1 month	2	6	2	--	1	1
JP-3A 1 day	4	2	2	--	4[c]	4[c]
JP-3A 1 month	9[c]	12	4	--	2[c]	0[c]

[a] Oil modified phenolic resin manufactured by Bakelite Corporation.

[b] Compounds No. 43351-1, -2 and -3 were cured to constant hardness at 77°F. The other compounds were cured 24 hours at 77°F.

[c] Surface of test specimen attacked.

TABLE 13

PROPERTIES OF "THIOKOL" LIQUID POLYMER EXPERIMENTAL SEALANT COMPOUNDS

Compound No.	43374-1	43360-4	43361-3	43368-4	43369-4
	Commercial Sealant	IP-32	IP-2		
	Compounding Recipes				
IP-32	--	100	--	--	--
IP-2	--	--	100	100	100
Commercial sealant compound	100	--	--	--	--
BR-6741	--	--	5	--	--
Pelletex SRF-3	--	30	30	30	30
Sulfur	--	0.1	--	--	0.1
25% Soln. of maleic anhydride in cyclohexanone	--	4	--	4	4
Commercial sealant accelerator	12	--	--	--	--
C-11 (parts/100 parts of base compound)	--	12.6	9.4	12.6	12.6
	Working Properties and Stability of Base Compound				
Working life, hr.					
Unaged	3	> 3.75	> 6.5	2	2.5
Aged 7 days at 120°F	3.5	> 2.5	> 7	3	2.5
Aged 30 days at 80°F	3.5	> 6.5	> 3.25	3.25	>4
Shore A hardness					
Unaged					
After 24-hr. cure	20	52	45	58	60
After 72-hr. cure	35	54	50	61	60
Aged 7 days at 120°F					
After 24-hr. cure	25	45	45	58	53
After 72-hr. cure	30	50	48	58	57
Aged 30 days at 80°F					
After 24-hr. cure	25	too soft	42	60	55
After 72-hr. cure	36	47	50	61	58

(Table continued on next page.)

TABLE 13 (Contd.)

PROPERTIES OF "THIOKOL" LIQUID POLYMER EXPERIMENTAL SEALANT COMPOUNDS

Compound No.	43374-1	43360-4	43361-3	43368-4	43369-4
	Commercial Sealant	LP-32	LP-2		
	Vulcanizate Properties (Cured 24 hr. @ 77° F)				
	a/b/c/d	a/b/c/d	a/b/c/d	a/b/c/d	a/b/c/d
Shore A hardness	50/76/--/--	44/55/70/--	53/71/80/--	50/62/79/--	48/62/78/--
100% Modulus, lb/sq in.	100/--/--/100	125/190/340/75	160/410/--/150	175/340/590/160	175/300/650/150
300% Modulus, lb/sq in.	275/--/--/240	225/410/--/175	410/--/--/325	500/900/--/500	475/--/--/--
Tensile strength, lb/sq in.	360/470/--/250	450/725/725/340	625/700/490/490	600/1025/775/575	550/840/650/460
Elongation, %	380/90/--/340	670/580/280/680	500/170/60/380	460/350/140/340	360/285/100/270
Tear strength, lb/in.	52/31/--/37	64/187/213/48	85/80/33/50	66/156/120/38	58/133/78/36
Torsional test					
Relative modulus					
T_5, $-^\circ F$	44	46	49	52	51
T_{10}	53	53	55	56	56
T_{50}	65	62	62	62	64
T_{100}	67	66	65	66	66
Absolute modulus					
G_{rt}, lb/sq in.	177	75	122	145	121
$G_{5,000}$, $-^\circ F$	61	63	61	61	63
$G_{10,000}$	65	66	64	64	66
$G_{20,000}$	69	68	68	68	69
Swelling volume, %					
SR-6 1 day	10	15	12	12	12
1 month	5	12	6(cracking)	10	11
SR-10 1 day	2	1	1	0	0
1 month	0	-3	-2(cracking)	-2	-3
JP-3A 1 day	2	2	2	1	1
1 month	1	0	2	0	0
H_2O 1 day	2	7	3	2	2
1 month	10	22	17(cracking)	9	9
Weight/volume loss after aging, %					
7 days at 212° F	9/7	11/13	10/11	13/16	2/0
7 days at 250° F	--	32/38	23/27	31/37	33/39

(Table continued and footnotes on next page.)

TABLE 13 (Contd.)

PROPERTIES OF "THIOKOL" LIQUID POLYMER EXPERIMENTAL SEALANT COMPOUNDS

Compound No.	43374-1	43360-4	43361-3	43368-4	43369-4
	Commercial Sealant IP-32		IP-2		
Adhesion of base compound, lb/in.					
Unaged					
After 24-hr. cure and 48 hr. in SR-6	$>26^e$	$>35^e$	17^f	$>28^e$	$>27^e$
" 24-hr. " and 7 days " "	$>25^e$	$>34^e$	22^g	$>31^e$	$>25^e$
Aged 7 days at 120°F					
After 24-hr. cure and 48 hr. in SR-6	$>15^e$	6.5^e (under-cured)	16^g	$>20^e$	$>18^e$
" 24-hr. " and 7 days " "	14^g	30^g	13^f	4^f	12^f
Aged 30 days at 80°F					
After 24-hr. cure and 48 hr. in SR-6	22^g	h	8^f	$>18^e$	$>20^e$
" . 24-hr. " and 7 days " "	22^e	--	5^f	20^g	11^f

a Unaged.
b Aged 7 days at 212°F.
c Aged 7 days at 250°F.
d Immersed in SR-6 for 24 hours and tested while wet.
e Cohesion failure.
f Adhesion failure.
g Adhesion and cohesion failure.
h Greatly undercured after nine days at room temperature.

TABLE 14

EFFECT OF WD-6 - SARAN BASE REVERSE PHASE ON PROPERTIES OF HEXAMETHYLENE/TRIGLYCOL/FORMAL TERPOLYMER

Compound No.	34384-3	34400-1
	Control	
Polymer No. 20199E[a]	100	100
Pelletex SRF-3	30	30
Maleic anhydride	2	1
BRR-18794[b]	0.5	0.5
BRP (30189-2)[c]	--	19.4[d]
C-11 (parts/100 parts of base compd.)	9.4	8.4

Vulcanizate Properties (Cured 24 Hr. at 77°F)

	Unaged/SR-6[e]	Unaged/SR-6[e]
Shore A hardness	54/--	53/--
100% Modulus, lb/sq in.	225/200	175/125
300% Modulus, lb/sq in.	600/--	550/--
Tensile strength, lb/sq in.	600/250	550/200
Elongation, %	300/120	300/140

a A polyfunctional liquid mercaptan containing 55/25/23/2 mole % hexamethylene dichloride/triglycol dichloride/formal/TCP with a Brookfield viscosity of 285 poises.

b Epoxide type polymer manufactured by Bakelite Corporation.

c Base reverse phase of 51.4% solids containing 74.7% WD-6 latex and 25.3% Saran.

d Equivalent to ten parts (solids basis) of Base Reverse Phase.

e Test specimens immersed in SR-6 at 80°F for 24 hrs. and tested while wet.

TABLE 15

EVALUATION OF AEROSIL AND EX. SILICA 54-EP-88 FILLERS

Compound No.	B47568-1	B47568-2	B47568-3	B47568-4	B47568-7
LP-32	100	100	100	100	100
Pelletex SRF-3	15	30	--	--	--
Aerosil	--	--	15	30	--
Ex. Silica 54-EP-88	--	--	--	--	15
Lead stearate	1.87	1.87	1.87	1.87	1.87
Lead peroxide	10	10	10	10	10
Sulfur	0.1	0.1	0.1	0.1	0.1

Vulcanizate Properties (Cured 24 hr. @ 77°F)

Shore A hardness	44	50	51	54	50
100% Modulus, lb/sq in.	100	150	100	130	125
Tensile strength, lb/sq in.	625	850	875	600	800
Elongation, %	890	800	1050	1300	1030
Tear strength, lb/in.	63	117	90	98	86

TABLE 16

ORGANIC CURING SYSTEMS

Compound No.	B43386-1	B43392-10	B43388-1	B43387-5	B43390-6	B43390-5	B43390-8	B43390-2	B43390-3	B43392-3	B43387-7
LP-32	100	100	100	100	100	100	100	100	100	100	100
Pelletex SRF-3	35	35	35	35	35	35	35	35	35	35	35
Sulfur	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150	0.150
25% Soln. maleic anhydride in cyclohexanone	--	4	4	4	4	4	3	4	4	4	4
GMF	--	--	1.5	3	5	5	5	3	5	7	3
Triethanolamine	--	--	6	6	6	3	3	3	--	--	--
DMP-30	--	--	--	--	--	--	--	--	3	3	6
C-11	16.9	16.9	--	--	--	--	--	--	--	--	--
Working life, hr.	0.5	1.5	Over-night	Over-night	18	18	18	--	--	3.5	Over-night
			Cure[a] and Adhesion Characteristics								
Shore A hardness											
24 hr.	50	50	Soft	Soft	Soft	Soft	Soft	Soft	5	25	Soft
48 hr.	53	51	17	27	Soft	Soft	Soft	10	40	32	21
72 hr.	55	55	30	43	25	Soft	20	20	30	33	50
24 hr. plus 5 hr./158°F.	54	50	40	47	50	42	40	36	36	45	41
Adhesion to aluminum											
24 hr.	None	Good	Soft	Soft	Soft	Soft	Soft	Soft	Soft	Good	Soft
48 hr.	None	Good	Fair	Good	Soft	Soft	Soft	Soft	Good	Good	Soft
72 hr.	None	Good	Good	Good	Good	Soft	Good	Good	Good	Good	Good
24 hr. plus 5 hr./158°F.	None	Good	Good	V. good	Good	Good	Good	Good	Good	V. good	V. good

a Cured at room temperature.

TABLE 17

ORGANIC CURING SYSTEMS

Compound No.	B43392-10	B43392-4	B43391-6	B43392-9
	(Control)			
IP-32	100	100	100	100
Pelletex SRF-3	35	35	35	35
Sulfur	0.15	0.15	0.15	0.15
25% Sol'n. of maleic anhydride in cyclohexanone	4	--	4	4
Calcium oxide	--	--	5	5
GMF	--	5	--	--
DMP-30	--	3	--	--
Ferro 940	--	5	--	--
50% Sol'n. of trinitrobenzene	--	--	8	8
Triethanolamine	--	--	1.5	1.5
Benzoyl peroxide	--	--	--	1
C-11 accelerator	16.9	--	--	--
Working life, hr.	1.5	2.5	--	8

Cure[a] and Adhesion Characteristics

Shore A hardness				
24 hr.	50	25	Soft	5
48 hr.	51	25	Soft	30
72 hr.	55	33	Soft	60
24 hr. plus 5 hr./158°F.	50	25	53	55
Adhesion to aluminum				
24 hr.	Good	Fair	--	Soft
48 hr.	Good	Fair	--	Fair
72 hr.	Good	Good	--	Good
24 hr. plus 5 hr./158°F.	Good	V. good	V. good	V. good

[a] Cured at room temperature.

III. TRANSLUCENT SEALANT COMPOUND DEVELOPMENT

A. INTRODUCTION

This aspect of the program was devoted to the development of a translucent sealant compound for integral fuel cell sealant application that would permit visual inspection during and after application and cure and possess generally improved properties.

The development program was divided into the following general categories:

1. General compounding studies with various commercial epoxy resins and "Thiokol" liquid polysulfide polymers.
2. Improvement of peel adhesive bond strength to aluminum.
3. Regulation and stabilization of cure to obtain better balanced properties.
4. Investigation of polysulfide liquid polymer/polyester and "Thiokol" liquid polymer/liquid polyamide resin systems with and without epoxy resins.
5. Determination of the effect of elevated temperature post cure and plasticization of the polysulfide liquid polymer/epoxy resin systems with WD-2 type latex polymer on the properties of the compositions.
6. Investigation of the cure characteristics and properties of high viscosity polysulfide liquid polymer/epoxy resin systems.

B. GENERAL COMPOUNDING STUDIES WITH VARIOUS COMMERCIAL EPOXY RESINS AND "THIOKOL" LIQUID POLYSULFIDE POLYMERS

1. Introduction

The objective of the work conducted in this phase of the program was to determine the pertinent properties of various liquid polysulfide polymer/epoxy resin systems for integral fuel cell sealant application. Empirical tests were conducted since little information was available on the functionality and molecular weight of the commercial epoxy liquid resins. Primary emphasis was placed on obtaining a composition with the stress-strain, heat resistance, low temperature and fuel resistance properties considered necessary for integral fuel cell sealants.

2. Compounding Studies with Bakelite, Araldite and Epon Epoxy Resins

The following commercial epoxy resins were evaluated in clear formulations with a 50/50 mixture of "Thiokol" LP-32/LP-33 and LP-33 alone:

Bakelite BRR-18794
Araldite CN-502
Araldite CN-503
Araldite CN-504
Araldite E-133
Araldite E-134
Epon E-828

The ratios of "Thiokol" liquid polymer to epoxy resin investigated were 1/1, 2/1, 3/1 and 1/2. In a few compounds, the "Thiokol" liquid polymer/epoxy resin ratios were varied from the foregoing in an attempt to obtain better properties; different epoxy resins were combined for the same reason. In these general studies, all of the formulations were cured with 10 parts of DMP-30 per 100 parts of epoxy resin.

In Table 18, the properties of the sealant compounds prepared with a 1/1 ratio of "Thiokol" liquid polymer to epoxy resin are recorded. The properties of the clear sealants formulated with 2/1 and 3/1 ratios are recorded in Tables 19 and 20; Table 21 contains the properties of compositions prepared with various liquid polymer/epoxy resin ratios and combinations of various epoxy resins. A summarized review of the results is as follows:

a. All of these compositions were clear.

b. In practically all cases, the hardness, tensile and tear strengths and elongations of the compositions were a direct function of the liquid polymer/epoxy resin ratio. As the ratio of liquid polymer to epoxy resin was increased, softer, weaker but more elastomeric materials were obtained. For some of the liquid polymer/epoxy resin compositions this is graphically illustrated in Figures 1, 2, 3 and 4.

c. In general, hardness, tensile and tear strengths were lowered by heat aging the compositions for 72 hours at 212° F. The ultimate elongations of 1/1 "Thiokol" liquid polymer/epoxy resin materials were generally increased somewhat by heat aging, whereas, in the 2/1 and 3/1 liquid polymer/epoxy resin compounds it decreased on heat aging.

d. Low temperature flexibilities (modified Mil-S-5043, Aer, test) of the 2/1 liquid polymer/epoxy resin compositions were much better than those of the 1/1 compositions. With the exception of the material containing E-133, a ratio of 3/1 did not significantly enhance this property.

e. The low temperature torsional stiffness properties of some of the 2/1 liquid polymer/epoxy resin materials were fair, whereas, the 3/1 compositions were superior by comparison in this property. However, all of the clear compositions that were tested for low temperature torsional stiffness were inferior to the LP-2 base sealant compounds in this respect. Low temperature torsional stiffness properties of the 1/1 materials could not be determined since they were too stiff.

f. Extraction in SR-6 fuel increased considerably when the liquid polymer/epoxy resin ratio was increased from 1/1 to 2/1. A few of the 3/1 ratio materials were subjected to this test, but the results were not considered reliable since the test strips agglomerated. The SR-6 extraction values of the latter compositions would presumably be higher than those of the other two ratios.

g. In general, the resistance of the 1/1 liquid polymer/epoxy resin compositions to volume swell in SR-6, SR-10 and JP-3A fuels was slightly better than that of the 2/1 materials. Compositions tested in JP-3A fuel were not attacked during a one-month immersion period. The better compositions also have satisfactory resistance to volume swell in water at 80° F.

h. Although a number of the 1/1 liquid polymer/epoxy resin materials passed a 2-inch radius flexibility test at 212° F after aging for 72 hours, the films were relatively weak and "short" at this temperature and adhesion to an aluminum panel was poor.

i. Compositions prepared with a 1/2 ratio of liquid polymer/epoxy resin were too brittle to be of value for integral fuel cell sealants and were not evaluated.

j. A 2/1 ratio of LP-33 to CN-503/E-133 possessed physical properties that were comparable to those of "Thiokol" LP-2 base sealants. However, the material became soft and weak after heat aging and had a relatively high SR-6 fuel extraction value. Presumably this and similar clear compounds were plasticized with unreacted liquid polymer.

k. An elastomeric composition with all of the requirements considered necessary for integral fuel cell sealant application was not obtained.

l. Formulations were developed which gave comparatively hard compositions of high modulus, high tensile and tear strengths, and relatively low ultimate elongations (see Table 18). One of these (Compound No. 45014-4) had a tensile strength of over 3,000 lb/sq in. and a tear strength greater than 400 lb/in. Most of these compositions had low SR-6 fuel extraction values, which indicated that the reaction between the epoxy resin and polysulfide liquid polymers was approximately complete. The low temperature flexibility of these materials, as determined by a modified Mil-S-5043 (Aer) test, was poor and their coefficients of expansion appeared to be much greater than that of aluminum.

m. A number of elastomeric compositions of low moduli, with properties approaching those of the present LP-2 base sealants were prepared (see Tables 19, 20, and 21). However, these materials generally became much softer and their tensile and tear strengths were significantly lower after heat aging at 212° F. Their relatively high extraction values in SR-6 fuel signified that a complete reaction of the "Thiokol" liquid polymer with the epoxy resin was not obtained.

n. The amount of "Thiokol" liquid polymer in the clear compositions apparently must be greater than that of the epoxy resin to obtain a good balance of tensile and tear strength and ultimate elongation. However, a complete cure was not obtained in such compositions, as indicated by relatively high extraction values in SR-6 fuel.

Several attempts were made to cure compositions containing "Thiokol" liquid polymer and Araldite liquid epoxy resin AN-101 at room temperature. AN-101 was specifically designed for adhesive applications. It was not possible to cure these systems with DMP-30, triethylenetetramine or hardener HN-951.

A number of clear formulations were prepared with Araldite SN-985, which was reported to be very elastic and to adhere well to most metals, and "Thiokol" liquid polymers. Cures were not obtained at room temperature.

3. Investigation of Epiphen Epoxy Resins

Epiphen epoxy resins XR-823 and XR-881, manufactured by the Borden Chemical Company, were thought to be of a different structure than the other epoxy resins which were studied. Since they are not made with an aromatic compound, they might be completely aliphatic in structure. Compatibility and cure were made with XR-881 and XR-823 and "Thiokol" liquid polymers LP-32, LP-33 and ZL-174. A ratio of 1/1 liquid polymer/epoxy resin was employed and the compositions were cured at room temperature with the catalysts supplied by the Borden Chemical Company.

From the data in Table 22 it is evident that these epoxy resins were not completely compatible with LP-32 and LP-33 in the ratio of 1/1 liquid polymer/epoxy resin. Cures were obtained but the compositions were not clear nor were the physical properties good at room and elevated temperatures. Epiphen XR-823 was compatible with ZL-174 and the compound cured at room temperature. However, the material did not have encouraging physical properties either at room or elevated temperature. Some additional work would be required before the merits of these epoxy resins for the formulation of clear sealant compounds with "Thiokol" liquid polymers can be definitely established. They may be compatible with the higher molecular weight liquid polymers in higher or lower liquid polymer/epoxy resin ratios.

C. ADHESION ADDITIVE STUDIES

1. Introduction

Since films of the liquid polysulfide polymer/epoxy resin compositions prepared in this program were deficient in peel adhesive bond strength to aluminum, studies were conducted with additives in an attempt to improve this property.

2. Solution of Maleic Anhydride

A 50% solution of maleic anhydride in cyclohexanone was evaluated as an adhesion additive in compositions containing 1/1 and 2/1 ratios of 50/50 LP-32/LP-33 "Thiokol" liquid polymer to CN-502 epoxy resin. Two and four parts of the maleic anhydride solution per 100 parts of the "Thiokol" liquid polymer were used.

The data in Table 23 show that the 50% maleic anhydride solution retarded the cure of the liquid polymer/epoxy resin compositions, which were cloudy and weak. However, the additive did not appear promising for improving the adhesion properties of the compositions to aluminum.

3. Beetle Resin 216-8

Beetle 216-8, was evaluated as an adhesion additive in the same compositions used in the maleic anhydride solution additive study. Three and 6% by weight of the CN-502 epoxy polymer were replaced with the Beetle resin.

From the data in Table 24, it is apparent that the Beetle resin increased the working life of some of the compositions. In the 1/1 liquid polymer/epoxy resin ratio compounds it retarded the cure considerably, but in the 2/1 liquid polymer/epoxy resin ratio compositions it appeared to accelerate the cure slightly. When 3% of the epoxy resin was replaced with the Beetle resin and used with CN-502 alone, the cure rate was not appreciably affected. However, replacing 6% of the CN-502 with Beetle 216-8 retarded the cure somewhat. The beetle resin was of no significant value for improving the peel bond adhesion properties of any of the compositions to aluminum, but it enhanced "leveling" of the films.

D. REGULATION AND STABILIZATION OF CURE TO OBTAIN BETTER BALANCED PROPERTIES AT LOW, NORMAL AND ELEVATED TEMPERATURES AND AFTER HEAT AGING

1. Introduction

Various compounds such as benzyl mercaptan, allyl glycidyl ether and phenolic resins were investigated in liquid polysulfide polymer/epoxy resin systems for regulation and stabilization of cure and to improve the low temperature flexibility and physical properties at room and elevated temperatures and after heat aging. The effect of catalyst structure and concentration on these properties were also studied.

2. Effect of Reducing the Functionality of the Epoxy Resin on the Properties of "Thiokol" Liquid Polymer/Epoxy Resin Compositions

Studies were conducted with formulations containing small amounts of benzyl mercaptan to determine its effect on the properties of the cured compositions. This monofunctional mercaptan can act as a chain-stoppering agent for the thiol-terminated liquid polymer and/or react with the epoxy groups in the epoxy resin to reduce its functionality. Since the latter reaction apparently has preference, the liquid polymer/epoxy resin composition should not be as highly cross-linked, therefore being more elastomeric and having better resistance to heat aging.

According to the results in Table 25, a formulation containing a 1/1 ratio of 50/50 LP-32/LP-33 and CN-502 and 0.05 part of benzyl mercaptan per 100 parts of "Thiokol" liquid polymer resulted in a softer and more extensible but weaker composition than a comparable formulation without benzyl mercaptan. However, after heat aging, the composition became much harder and stronger but "shorter". The physical properties of the heat aged samples were in the same range as the unaged physical properties of the control. Also, the composition containing the benzyl mercaptan had a much longer working life than did the controls. In the other formulations, the effects of benzyl mercaptan were inconsequential and were no better than the control with respect to "shortness" when tested at 212° F after 72 hours of aging.

Some additional work was done with clear formulations containing 1/1 and 2/1 liquid polymer/epoxy resin ratios of 50/50 LP-32/LP-33 to CN-503 epoxy resin and 0.25 and 0.75 part of benzyl mercaptan per 100 parts of CN-503. Ten parts of DMP-30 catalyst per 100 parts of CN-503 were used to cure the compositions at room temperature.

The data in Table 26 show that benzyl mercaptan did not improve the unaged or heat aged physical properties of the compositions nor the strength and extensibility of the materials at 212° F. The compositions containing benzyl mercaptan as well as the controls became somewhat softer after 72 hours aging at 212° F.

The monofunctional epoxide, allyl glycidyl ether, was investigated for possible reduction of the functionality of the epoxy resin in clear formulations through dilution. Formulations containing 1/1 and 2/1 ratios of 50/50 LP-32/LP-33 to CN-502 with 2.5 parts of allyl glycidyl ether per 100 parts of epoxy resin were evaluated. The results in Table 27 show that generally a shorter working life was obtained with the allyl glycidyl ether formulations; all of the compositions were softer, weaker and more extensible than the controls. However, the compositions became much harder, stronger and less extensible after heat aging and all but one of the compositions had lower SR-6 extraction values than the controls. Also, one composition (No. 45032-2) showed some improvement with respect to "shortness" at 212° F. On this basis, the use of allyl glycidyl ether for this purpose would merit some additional work.

3. Studies with Phenolic Resins CTL-91-LD and BR-6741

Phenolic resins CTL-91-LD and Bakelite BR-6741 were investigated in a liquid polymer/epoxy resin system to determine their effect on cure characteristics and physical properties at room and elevated temperature.

Formulations containing a 1/1 ratio of 50/50 LP-32/LP-33 to CN-503 with 25 and 50 parts of BR-6741 and CTL-91-LD respectively per 100 parts of CN-503 were evaluated with DMP-30 as the catalyst. The data in Table 28 show that both phenolic resins retarded cure and were not completely compatible in these concentrations. Physical characteristics of the cured compounds were not generally as good as the control and all of the materials were weak and short at 212° F. Resin CTL-91-LD was evaluated further in the same liquid polymer/epoxy resin formulation in concentrations of 10, 100 and 200 parts of epoxy polymer. Ten parts of CTL-91-LD was slightly incompatible, whereas 100 and 200 parts were completely compatible (see Table 29). The physical characteristics of these cured materials were not as desirable as those of the control for an integral fuel cell sealant. Also, the compositions containing 10 and 100 parts of CTL-91-LD were weak at 212° F. The material containing 200 parts of the phenolic resin was flexible at 212° F but became brittle on cooling to room temperature.

In the concentrations tested, these phenolic resins did not show promise for improving the properties of liquid polymer/epoxy resin compositions for integral fuel tank sealant compounds.

4. Study of Styphen 1 for Possible Reduction of the Functionality of the Epoxy Resin

Styphen 1, tris(α-methylbenzyl) phenol, could conceivably react with the epoxide groups in the epoxy resin and/or with the thiol terminals on the "Thiokol" liquid polymer. However, it was thought that the former reaction would have preference and that Styphen 1 might reduce the functionality of the epoxy resin thereby decreasing the extent of cross-linking in the polysulfide liquid polymer/epoxy resin compositions.

A number of compatibility and cure studies were conducted with Styphen 1 in compositions containing only "Thiokol" liquid polymers and in liquid polymer/epoxy resin systems with DMP-30 as the catalyst. Data for the most significant of these studies are recorded in Table 30. Styphen 1 was very compatible with the liquid polysulfide polymers, but room temperature cures were not obtained. Room temperature cures were obtained with the liquid polymer/CN-502 resin compositions containing the additive which was completely compatible (see No. 47614-4).

Additional work was done with Styphen 1 in compositions containing a 1/1 liquid polymer/epoxy resin ratio with several different epoxy polymers to obtain physical property data. Twenty-two parts of the additive per 100 parts of epoxy resin were used since the preliminary studies indicated this to be the optimum concentration. Data in Table 31 show that a compound (No. 47637-4) containing CN-504 possessed well balanced physical properties which were not changed by heat aging. The compound containing E-134 epoxy resin had very good physical properties for a sealant compound except being brittle after heat aging. All of the compositions were weak at 212° F, and poor in low temperature properties. With the exception of one compound (No. 47637-5) the SR-6 fuel extraction of these materials was quite high indicating that the reaction was not complete. Styphen 1 was of no significant value for obtaining a clear, liquid polymer/epoxy resin composition with good strength and flexibility at an elevated temperature.

5. Effect of Lower Concentration of DMP-30 Catalyst on Properties of Clear Compounds

Studies were conducted with systems containing "Thiokol" liquid polymer and Bakelite epoxy resin BRR-18794, and "Thiokol" liquid polymer and Araldite CN-503 epoxy resin with 5 and 7 parts, respectively, of DMP-30 in lieu of 10 parts per 100 of epoxy resin.

The data in Table 32 show that in the formulations containing BRR-18794, the physical properties with 10 parts of DMP-30 were better balanced than those with 5 parts.

The compositions with CN-503 and 7 parts of DMP-30 were softer and more elastomeric but weaker than the materials cured with 10 parts of the catalyst. Also, they became much harder and stronger but "shorter" after heat aging, indicating that the compositions were not fully cured at room temperature (see Nos. 45019-3 and-4 in Table 32). A decrease in the catalyst concentration in these formulations did not result in more suitable compositions for integral fuel tank sealant applications.

6. Evaluation of Triethylenetetramine and Tetraethylenepentamine as Catalysts

Triethylenetetramine was investigated as a catalyst for curing compositions containing a 50/50 mixture of LP-32/LP-33 polymers with Araldite CN-502 and CN-503 epoxy resins. Seven parts of triethylenetetramine per 100 parts of epoxy resin were used in this study since this concentration was recommended as the optimum for 100% epoxy formulations. From the results in Table 33, it is apparent that with the exception of one formulation the compositions cured with triethylenetetramine were harder than those cured with DMP-30. However, all of the compositions cured with triethylenetetramine were cloudy but one, which was crumbly.

A similar study conducted with compositions containing mixtures of 50/50 LP-32/LP-33 or LP-33 alone with BRR-18794 and 10 parts of triethylenetetramine per 100 parts of epoxy resin showed that the 50/50 LP-32/LP-33 compositions were cloudy but the LP-33 compositions were clear (see Table 34). Also, in the 2/1 liquid polymer/epoxy resin formulations, the cured compositions were crumbly so that this amine did not appear to be as satisfactory as DMP-30.

Tetraethylenepentamine and triethylenetetramine were also investigated as catalysts for curing a 1/1 ratio of liquid polymer LP-33/CN-502 at room temperature to obtain better physical properties both before and after heat aging and at an elevated temperature than were obtained with DMP-30. The data in Table 35 show that the compositions cured with tetraethylenepentamine and triethylenetetramine possessed considerably lower cure rates and were inferior to the control formulation catalyzed with DMP-30 in over-all physical properties both before and after heat aging.

7. Co-Curing Agent Studies

Cup cure studies were conducted with trinitrobenzene and cumene hydroperoxide as co-curing agents in a very elastomeric formulation (LP-33, CN-503, E-133) catalyzed with DMP-30 to cure fully the unreacted "Thiokol" liquid polymer. Four and 2 parts of trinitrobenzene per 100 parts of liquid polymer were tried. The physical properties of the control composition with DMP-30 were in the range of LP-2 base sealant compounds but the SR-6 extraction value was high. The data in Table 36 show that the trinitrobenzene system retarded cure and was unsatisfactory.

Another study was conducted with cast sheets prepared from the same liquid polymer/epoxy resin formulation employing cumene hydroperoxide in concentrations of 6, 4 and 2 parts per 100 parts of "Thiokol" liquid polymer as a co-curing agent. In the cup cure study cumene hydroperoxide was affective as a co-curing agent. However, the compositions did not appear to be as tough and extensible as the control material cured with DMP-30 alone (see Table 37).

The data in Table 38 show that the cast sheets prepared from the cumene hydroperoxide co-cure compositions were very slow curing at room temperature. Since the formulation containing 4 parts of cumene hydroperoxide cured better than the one with 2 parts of the peroxide, it is evident that cumene hydroperoxide did not retard cure. The previous cup cure studies showed cumene hydroperoxide to be effective as a co-curing agent. However, the exotherm generated is not available in a cast sheet as in a cup cure where the reaction heat is more confined and consequently accelerates the cure. The cast sheets were weak and short at an elevated temperature and contained many small bubbles which were no doubt formed by the liberated oxygen from the cumene hydroperoxide. Further evaluation of them was discontinued.

E. INVESTIGATION OF POLYSULFIDE LIQUID POLYMER/POLYESTER AND LIQUID POLYSULFIDE POLYMER/LIQUID POLYAMIDE SYSTEMS

1. Introduction

The liquid polysulfide polymer/epoxy resin compositions developed thus far did not possess the balance of physical properties considered necessary for integral fuel cell sealant application. Therefore, polyesters and polyamides were investigated in "Thiokol" liquid polymer and liquid polymer/epoxy resin systems to determine whether translucent reaction products with improved properties at an elevated temperature were obtainable.

2. Studies with "Thiokol" Liquid Polymer/Vibrin Polyester Systems

In the compatibility study conducted with Vibrin X-1047 and "Thiokol" liquid polymers and liquid polymer/epoxy resin compositions, the data in Table 39 show that it was compatible with a low liquid polymer concentration but was not completely compatible with a high concentration of liquid polymer; however, all of the formulations were clear. Compositions containing equal amounts of liquid polymer, epoxy resin and X-1047 were compatible.

A study was made with formulations containing Vibrin X-1047 and polysulfide liquid polymers 50/50 LP-32/LP-33, LP-33 and LP-38 (ZL-174) cured with DMP-30 catalyst to determine the cure characteristics and evaluate the physical properties. The data in Table 40 reveal that the X-1047 only formed a soft gel with the catalyst but, that with the exception of one compound (No. 46299-6), cures were obtained with the 1/1 and 1/2 Vibrin/liquid polymer ratio compositions at room temperature. All of these materials were resilient, "short" and weak at room temperature and "short" and weak at 212° F.

Three compositions containing equal parts of Vibrin X-1047, epoxy resin CN-502 and liquid polysulfide polymers 50/50 LP-32/LP-33, LP-33 and LP-38 (ZL-174) were cured with DMP-30 catalyst and evaluated. The data in Table 41 show that these compositions cured rapidly at room temperature and were very resilient, but all were very "short" and weak at 158° F, and were not an improvement over the liquid polymer/epoxy resin control.

3. Investigation of Polyester PDL-7-669

The results of compatibility studies in Table 42 show that PDL-7-669 was not too compatible with "Thiokol" liquid polymers but was more compatible with the low molecular weight polysulfide polymer LP-38 (ZL-174). Compositions containing 90 parts of PDL-7-669 and 10 parts of liquid polysulfide polymer (50/50 LP-32/LP-33; LP-33 and (ZL-174) LP-38) were evaluated for room temperature curing characteristics with Luperco ATC and a 1/1 combination of Laminac Catalyst No. 347 and 6% Hexogen Cobalt as catalysts. The results of this study are recorded in Table 43. Compared to a PDL-7-669 control, these cures were softer and not brittle.

Formulations containing 1/1 and 1/2 PDL-7-669/liquid polymer ratios with liquid polysulfide polymers of 50/50 LP-32/LP-33, LP-33 and LP-38 (ZL-174) respectively, and catalyzed with 10 parts of DMP-30 catalyst per 100 parts of PDL-7-669 were studied for room temperature curing characteristics. All of the cured compositions were soft, resilient, weak and "short" at room and elevated temperature (see Table 44).

Polyester PDL-7-669/liquid polysulfide polymer reaction products did not show promise for integral fuel cell sealant materials.

4. Studies with Polyamide Resins 100-S and 110

Polyamide resins 100-S and 110 were evaluated in liquid polysulfide polymers and liquid polymer/epoxy resin systems to determine whether adhesion properties for a sealant compound could also be obtained. Due to the high viscosity of these polyamides, they were dispersed in the liquid polymer and liquid polymer/epoxy resin systems at elevated temperature.

Compatibility studies were conducted with polyamide resins 100-S and 110 and "Thiokol" liquid polymers 50/50 LP-32/LP-33, LP-33 and LP-38 (ZL-174). From the data in Table 45, it is apparent that these polyamide resins were very incompatible with the liquid polysulfide polymers. Since it was reported that these polyamides were compatible and reacted with some epoxy type resins, studies were made with systems containing these polyamides and epoxy resins CN-502 and CN-503 and evaluated (see Table 46). Additional work was conducted with formulations containing equal parts of "Thiokol" liquid polymers and CN-503 and 22 parts of the polyamides per 100 parts of CN-503. These compositions were also very incompatible. Compositions were prepared with fifty-five parts of epoxy resin and 11 parts of LP-38 per 100 parts of polyamide. The data in Table 47 show that some of the compositions cured on heating at 212° F, but the components were not completely compatible and their properties were not encouraging for integral fuel tank sealants.

F. EFFECT OF ELEVATED TEMPERATURE POST CURE ON PROPERTIES OF "THIOKOL" LIQUID POLYMER/EPOXY RESIN COMPOSITIONS

Four different polysulfide liquid polymer/epoxy resin compositions were cured to constant hardness at room temperature with DMP-30 and were then subjected to a post cure of 2 hours at 300° F to determine the effect on the toughness and extensibility of the materials at elevated temperature. The data in Table 48 show that the post cure did not improve the over-all physical properties of the compounds at either room or elevated temperature.

G. PLASTICIZATION OF POLYSULFIDE LIQUID POLYMER/EPOXY RESIN SYSTEMS

Fifteen per cent (by weight of epoxy polymer) of dried WD-2 polymer was dissolved in epoxy polymers BRR-18794, CN-502, CN-503, CN-504 and E-134 by heating at 212° F. Formulations comprising equal parts of 50/50 LP-32/LP-33 and the epoxy polymers containing the WD-2 polymer were prepared and cured at room temperature with DMP-30. It was theorized that incorporating the WD-2 might improve the flexibility, extensibility and low and elevated temperature properties of the compound.

The data in Table 49 show that the WD-2 polymer increased the working life of the liquid polymer/epoxy resin compositions but was of no value for improving the over-all physical properties of the materials for integral fuel cell sealant application at either room or elevated temperatures. Further investigation of these compounds was discontinued.

H. INVESTIGATION OF HIGH VISCOSITY LIQUID POLYSULFIDE POLYMER/EPOXY RESIN COMPOSITIONS

Formulations with "Thiokol" LP-2 and three different epoxy polymers were studied to determine the effect of a high molecular weight polymer on the cure characteristics and properties of the clear compositions.

In one composition a 2/1 liquid polymer/epoxy resin ratio was used and cured with DMP-30 at room temperature. The data in Table 50 show that the LP-2/epoxy resin compositions possessed better cure characteristics than those of comparable compounds prepared with the lower molecular weight LP-33. The results indicated that high viscosity liquid polymer/epoxy resin ratios could be used with LP-2 rather than with LP-33 to obtain an elastomeric compound with lower fuel extraction and better balanced properties.

Additional objectives of this study were to obtain good peel bond strength to aluminum and low fuel extraction. A WD-2 type crude (SP-931), containing some thiol terminals, was redistributed with LP-33 to obtain a high viscosity (1600 poises) thiol-terminated polysulfide polymer. Theoretically a high molecular weight polymer should require less epoxy resin for a complete cure, resulting in a polymer chain less cross-linked and more flexible. Compositions containing 1/1, 1/4, and 4/1 liquid polymer/epoxy resin ratios were then prepared with this redistributed WD-2 type polymer and cured at room temperature with DMP-30 catalyst. The 1/1 and 1/4 liquid polymer/epoxy resin compounds were too brittle for testing, but the 4/1 compositions were elastomeric. From the data in Table 51 it is apparent that the 4/1 liquid polymer/epoxy resin compounds containing CN-503 and CN-504 possessed encouraging physical properties both before and after heat aging for an integral fuel cell sealant material as they were rubber-like and their low temperature torsional stiffness properties were quite comparable to those of an LP-2 base sealant compound. However, they were weak at an elevated temperature and their SR-6 fuel extraction values were relatively high. They were relatively slow curing at room temperature. Investigation of high viscosity polysulfide liquid polymer in liquid polymer/epoxy resin compositions should be continued.

TABLE 18

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 1/1

Compound No.	30184-1	45041-1	43019-1	45014-2	45014-3	45014-4	43039-1	45004-2
	BRR-18794		CN-502		CN-503		CN-504	
50/50 LP-32/LP-33	100	--	100	--	100	--	100	--
LP-33	--	100	--	100	--	100	--	100
BRR-18794	100	100	--	--	--	--	--	--
CN-502	--	--	100	100	--	--	--	--
CN-503	--	--	--	--	100	100	--	--
CN-504	--	--	--	--	--	--	100	--
DMP-30	10	10	10	10	10	10	10	10
Working life, hr.	0.5	--	1	1.75	0.5	1	0.75	0.5
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature								
	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	>100/90	100/86	96/94	100/85	100/85	100/85	90/90	95/80
Tensile strength, lb/sq in.	2300/935	3690/910	1690/2075	1390/950	2750/2525	3400/1475	1070/1240	1075/600
Elongation, %	20/50	60/80	20/20	<10/80	<10/70	<10/60	70/75	95/95
Tear strength, lb/in.	200/10	--/65	180/185	215/110	320/265	415/220	150/115	115/60
Low temperature flexibility								
Passed, °F	10	--	--	-30	RT	-10	-10	-10
Failed, °F	0	--	-20	-40	35	-20	-20	-20
Adhesion at failure	Poor	--	Poor	Poor	Poor	Poor	Poor	Poor
Elevated temperature flexibility								
(7 days at 212° F)	Failed	--	--	Passed	--	Passed	--	--
Adhesion	Poor	--	--	V. Poor	--	V. Poor	--	--
Short	Yes	--	--	Yes	--	Yes	--	--
SR-6 extraction, %	1.5	4.9	6.8	11.5	3.3	5.8	3.1	5
Swelling volume, %								
SR-6 1 day	0	--	2	2	2	1	2	2
1 month	0	--	2	8	3	4	2	2
SR-10 1 day	0	--	0	1	1	1	1	1
1 month	1	--	-2	-2	1	1	0	-1
JP-3A 1 day	0	--	0	1	1	1	1	1
1 month	0	--	0	0	2	1	1	1
H_2O 1 day	0	--	2	2	--	--	--	2
1 month	3	--	6	6	--	--	--	10

(Table continued and footnotes on next page.)

TABLE 18 (Contd.)

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 1/1

Compound No.	43045-1	45014-5	43041-1	45004-1	45014-6	45014-7
	E-133		E-134		E-828	
50/50 LP-32/LP-33	100	—	100	—	100	—
LP-33	—	100	—	100	—	100
E-133	100	100	—	—	—	—
E-134	—	—	100	100	—	—
E-828	—	—	—	—	100	100
DMP-30	10	10	10	10	10	10
Working life, hr.	0.5	1	0.5	0.25	0.75	0.75
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature						
	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	100/97	100/85	100/94	98/100	>100/80	>100/75
Tensile strength, lb/sq in.	1430/1650	1520/1335	2525/2160	1275/2575	2000/975	2590/610
Elongation, %	60/30	10/80	10/20	20/70	<10/110	<10/90
Tear strength, lb/in.	190/250	290/170	370/—	233/275	190/100	470/55
Low temperature flexibility						
Passed, °F	—	-10	-10	-10	-10	0
Failed, °F	RT	-20	-20	-20	-20	-10
Adhesion at failure	Poor	Poor	Poor	Poor	Poor	Poor
Elevated temperature flexibility (7 days at 212° F)	Passed	Passed	—	Passed	Passed	Passed
Adhesion	Poor	V. Poor	—	Poor	Poor	Poor
Short	Yes	Yes	—	Yes	Yes	Yes
SR-6 extraction, %	7.5	6.6	3.5	2.8	3.5	6.5
Swelling volume, %						
SR-6 1 day	0	1	2	2	1	1
1 month	4	1	4	6	2	1
SR-10 1 day	0	2	2	1	1	1
1 month	-1	2	1	2	1	1
JP-3A 1 day	-1	1	2	2	2	2
1 month	0	2	2	2	1	1
H_2O 1 day	-1	—	—	—	1	2
1 month	4	—	—	—	5	6

a Unaged.
b Heat aged 72 hours at 212° F.

TABLE 19

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 2/1

Compound No.	30175-1	45028-2	43006-2	43011-1	43010-2	43019-2	43039-2	45028-1
	BRR-18794		CN-502		CN-503		CN-504	
50/50 LP-32/LP-33	100	--	100	--	100	--	100	--
LP-33	--	100	--	100	--	100	--	100
BRR-18794	50	50	--	--	--	--	--	--
CN-502	--	--	50	50	--	--	--	--
CN-503	--	--	--	--	50	50	--	--
CN-504	--	--	--	--	--	--	50	50
DMP-30	5	5	5	5	5	5	5	5
Working life, hr.	1	1.75	2.25	1.5	1.5	1.25	1.25	2
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature								
	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	93/67	90/56	73/64	33/33	92/80	73/48	50/50	48/30
100% Modulus, lb/sq in.	--/--	920/--	525/300	50/--	--/--	450/125	140/160	130/50
300% Modulus, lb/sq in.	--/--	--/--	--/--	150/--	--/--	--/--	--/--	280/--
Tensile strength, lb/sq in.	1140/160	920/175	525/360	150/70	1075/640	640/150	220/180	290/85
Elongation, %	50/25	100/70	100/100	320/340	80/60	150/150	175/125	310/230
Tear strength, lb/in.	95/0	90/5	44/30	19/18	110/35	75/30	30/20	30/15
Torsional test								
Absolute modulus								
G_{rt}, lb/sq in.	2570	2244	587	82	--	227	471	324
$G_{5,000}$, - ^{o}F	+37	+35	+20	36	--	10	6	15
$G_{10,000}$	2	2	32	40	--	27	32	32
$G_{20,000}$	Broke	33	50	46	--	41	46	49
Low temperature flexibility								
Passed, ^{o}F	-30	--	-60	-60	-50	-50	-60	--
Failed, ^{o}F	-40	--	-70	-70	-60	-60	-70	--
Adhesion at failure	Poor	--	Poor	Good	Poor	Poor	Poor	--

(Table continued on next page.)

TABLE 19 (Contd.)

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 2/1

Compound No.		30175-1	45028-2	43006-2	43011-1	43010-2	43019-2	43039-2	45028-1
		BRR-18794		CN-502		CN-503		CN-504	
SR-6 extraction, %		8.2	6	13.6	6.5	11.4	—	13.5	10.2
Swelling volume, %									
SR-6	1 day	2	2	6	—	3	—	6	45^d
	1 month	6	9	4^c	—	8^c	—	2^c	—
SR-10	1 day	1	-2	1	—	2	—	0	20^d
	1 month	-1	0	-3	—	0^c	—	-2	—
JP-3A	1 day	2	-3	2	—	3	—	1	4
	1 month	5	-3	2	—	4^c	—	-2	9
H_2O	1 day	—	2	—	—	3	—	—	4^c
	1 month	—	16	—	—	5^c	—	—	18

(Table continued on next page.)

TABLE 19 (Contd.)

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 2/1

Compound No.	43025-1	43026-1	43041-2	43041-4	43018-1	45028-3
	E-133		E-134		E-828	
50/50 LP-32/LP-33	100	—	100	—	100	—
LP-33	—	100	—	100	—	100
E-133	50	50	—	—	—	—
E-134	—	—	50	50	—	—
E-828	—	—	—	—	50	50
DMP-30	5	5	5	5	5	5
Working life, hr.	1	1	1.25	1.25	—	1.5
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature						
	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	93/75	89/30	87/67	60/42	96/55	95/40
100% Modulus, lb/sq in.	—/—	125/30	620/—	150/—	—/—	1085/100
300% Modulus, lb/sq in.	—/—	225/—	—/—	—/—	—/—	—/—
Tensile strength, lb/sq in.	875/300	225/50	620/350	260/200	1450/190	1275/100
Elongation, %	55/80	300/200	130/90	240/50	50/60	130/115
Tear strength, lb/in.	65/30	50/10	110/25	40/20	210/0	180/15
Torsional test						
Absolute modulus						
G_{rt}, lb/sq in.	1030	163	1870	157	2560	2134
$G_{5,000}$, - °F	0	0	$\not<$ 4	17	$\not<$ 32	$\not<$ 27
$G_{10,000}$	25	15	27	30	0	22
$G_{20,000}$	50	35	42	42	38	60
Low temperature flexibility						
Passed, °F	—	-20	-60	—	-40	—
Failed, °F	-20	-40	-70	—	-50	—
Adhesion at failure	Poor	Poor	Poor	—	Poor	—
SR-6 extraction, %	14.2	13.9	8	—	12.6	10.5

(Table continued and footnotes on next page.)

TABLE 19 (Contd.)

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 2/1

Compound No.		43025-1	43026-1	43041-2	43041-4	43018-1	45028-3
		E-133		E-134		E-828	
Swelling volume, %							
SR-6	1 day	4	2	3	8	4	2
	1 month	3	37	14	13^c	6	38
SR-10	1 day	1	2	1	1	1	1
	1 month	0	15	2	1	-3	0
JP-3A	1 day	1	14^c	2	4	2	1
	1 month	2	24	3	4	-3	2
H_2O	1 day	2^c	5	—	—	2	2^c
	1 month	5	13^c	—	—	2	11^c

a Unaged.
b Heat aged 72 hours at 212° F.
c Cloudy.
d Test specimen stretched.

TABLE 20

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 3/1

Compound No.	30181-1	43006-1	43010-1	43039-3	43029-1	43041-3	43018-2
	BRR-18794	CN-502	CN-503	CN-504	E-133	E-134	E-828
50/50 LP-32/LP-33	100	100	100	100	100	100	100
BRR-18794	33.3	--	--	--	--	--	--
CN-502	--	33.3	--	--	--	--	--
CN-503	--	--	33.3	--	--	--	--
CN-504	--	--	--	33.3	--	--	--
E-133	--	--	--	--	33.3	--	--
E-134	--	--	--	--	--	33.3	--
E-828	--	--	--	--	--	--	33.3
DMP-30	3.33	3.33	3.33	3.33	3.33	3.33	3.33
Working life, hr.	1.25	3	2	2	2	--	2
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature	a/b	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	89/60	27/--	65/45	30/25	40/22	55/37	65/48
100% Modulus, lb/sq in.	--/--	75/--	360/100	70/30	75/50	190/--	425/125
300% Modulus, lb/sq in.	--/--	150/--	--/--	125/--	--/--	--/--	--/--
Tensile strength, lb/sq in.	700/150	150/--	460/125	140/50	140/50	300/100	525/125
Elongation, %	80/40	300/--	140/120	355/275	215/190	235/130	160/100
Tear strength, lb/in.	37/0	0/--	50/20	20/10	20/0	50/10	60/0
Torsional test							
Absolute Modulus							
G_{rt}, lb/sq in.	865	--	806	79	201	258	184
$G_{5,000}$, - °F	8	--	24	41	40	30	28
$G_{10,000}$	32	--	40	50	48	44	46
$G_{20,000}$	51	--	53	54	55	58	56

(Table continued and footnotes on next page.)

TABLE 20 (Contd.)

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH A "THIOKOL" LIQUID POLYMER/EPOXY RATIO OF 3/1

Compound No.	30181-1	43006-1	43010-1	43039-3	43029-1	43041-3	43018-2
	BRR-18794	CN-502	CN-503	CN-504	E-133	E-134	E-828
Low temperature flexibility							
Passed, °F	--	-70	-50	--	-60	-40	-40
Failed, °F	--	-80	-60	--	-70	-50	-50
Adhesion at failure	--	Poor	Poor	--	Fair	Poor	Poor
SR-6 extraction, %	2.2	8.1[c]	--	9.8[d]	25.4	7[c]	--
Swelling volume, %							
SR-6 1 day	2	--	10	10	8	6	15[e]
1 month	10	--	10[e]	27[e]	30[e]	6[e]	-2
SR-10 1 day	2	--	1	2	1	2	2
1 month	2	--	-2[e]	30	4	1	-2
JP-3A 1 day	2	--	3	12	-4	2	2
1 month	2	--	2[e]	22	-4[e]	2	--
H_2O 1 day	--	--	2	--	6	--	3[e]
1 month	--	--	6[e]	--	18[e]	--	5

a Unaged.
b Heat aged 72 hours at 212° F.
c Test strips agglomerated; result is dubious.
d Formed a lump due to solution.
e Cloudy.

TABLE 21

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH VARIOUS "THIOKOL" LIQUID POLYMER/EPOXY RATIOS AND BLENDS OF EPOXY RESINS

Compound No.	43029-2	43032-1	43031-1	43031-2	43031-3	43037-2	43037-3	43024-1
	CN-502		CN-503	CN-502/CN-503		CN-503/E-133		E-828
50/50 LP-32/LP-33	100	—	—	100	—	—	100	—
LP-3	—	—	—	—	—	—	—	100
LP-33	—	100	100	—	100	100	—	—
CN-502	40	66.6	—	25	25	—	—	—
CN-503	—	—	44.5	25	25	25	25	—
CN-504	—	—	—	—	—	—	—	—
E-133	—	—	—	—	—	25	25	—
E-828	—	—	—	—	—	—	—	160
DMP-30	4	6.66	4.45	5	5	5	5	16
Liquid polymer/epoxy ratio	2.5/1	1.5/1	2.25/1	2/1	2/1	2/1	2/1	1/1.6

Properties of Cast Sheets Cured to Constant Hardness at Room Temperature

	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	65/42	80/50	50/30	80/60	55/35	62/30	65/60	96/>100
100% Modulus, lb/sq in.	250/90	350/100	125/—	325/—	140/—	145/33	200/—	—/ c
300% Modulus, lb/sq in.	—/—	—/—	—/—	—/—	—/—	335/—	—/—	—/—
Tensile strength, lb/sq in.	467/100	450/125	250/50	440/275	210/50	360/54	290/350	3360/—
Elongation, %	180/180	170/170	355/200	145/95	250/185	380/230	210/105	10/—
Tear strength, lb/in.	43/24	65/30	51/0	64/12	38/0	50/20	40/15	245/—

(Table continued and footnotes on next page.)

TABLE 21 (Contd.)

PROPERTIES OF CLEAR SEALANT COMPOUNDS WITH VARIOUS "THIOKOL LIQUID POLYMER/EPOXY RATIOS AND BLENDS OF EPOXY RESINS

Compound No.	43029-2	43032-1	43031-1	43031-2	43031-3	43037-2	43037-3	43024-1
	CN-502		CN-503	CN-502/CN-503		CN-503/E-133		E-828
Torsional test								
Absolute modulus								
G_{rt}, lb/sq in.	--	386	161	672	137	250	--	--
$G_{5,000}$, $-^{o}F$	--	1	11	7	15	11	--	--
$G_{10,000}$	--	18	26	26	28	31	--	--
$G_{20,000}$	--	35	40	44	35	40	--	--
Low temperature flexibility								
Passed, °F	-80	-50	--	--	--	-30	--	--
Failed, °F	--	-60	--	--	--	-40	--	--
Adhesion at failure	Fair	Poor	--	--	--	Poor	--	--
SR-6 extraction, %	10.2	9.4	8	16.9	d	10.5	9.0	--
Swelling volume, %								
SR-6 1 day	8	3	15	2	2	4	2	2
1 month	6[e]	6[e]	36	2[e]	6[e]	37[e]	6[e]	2
SR-10 1 day	2	-3	5	0	-6	2	1	2
1 month	1	-4	35	1	17	26	2	1
JP-3A 1 day	5	0	22	-1	-20	4	2	2
1 month	5	0	56	-1	-12	22	2	1
H_2O 1 day	5	--	--	--	--	--	--	2
1 month	10	--	--	--	--	--	--	3

a Unaged.
b Heat aged 72 hours at 212° F.
c Too brittle for testing.
d Test strips partially dissolved.
e Slightly cloudy.

TABLE 22

CURE STUDIES WITH EPIPHEN EPOXY RESIN/"THIOKOL" LIQUID POLYMER SYSTEMS

Compound No.	47619-1	47619-2	47619-3	47619-4	47619-5	46719-6	47619-9	47619-10	47633-1	47633-2
LP-32	--	--	--	--	100	100	--	--	--	--
LP-33	--	--	--	--	--	--	100	100	--	--
ZL-174 (LP-38)	--	--	--	--	--	--	--	--	100	100
XR-881	100	--	100	--	100	--	100	--	100	--
XR-823	--	100	--	100	--	100	--	100	--	100
219-140, Catalyst for XR-823	--	10	--	--	--	10	--	10	--	10
219-88, Catalyst for XR-881	20	--	--	--	20	--	20	--	20	--
DMP-30	--	--	10	10	--	--	--	--	--	--
Working life, min.	>3.5 hr.	25	20	15	--	15	>2 hr.	40	20	10
Cup Cure Characteristics Determined at Room Temperature										
Shore A hardness[a]										
24 hr.	98	90	>100	98	20	75	35	100	--	--
48 hr.	>100	90	>100	>100	85	75	73	100	--	--
72 hr.	>100	90	>100	>100	85	85	73	100	70	95
96 hr.	--	--	--	--	--	--	--	--	70	95
Characteristics of cured compounds	Clear, brittle	Sponged, short	Opaque, brittle	Clear, brittle	Cloudy weak, short	Opaque, weak, short	Opaque, weak, short	Opaque, slightly brittle	Slightly grainy, short	Clear, short
Characteristics after 24 hr. at 212°F	Short weak	b	b	b	Short, weak	Short, weak	Short weak	Short, weak	Short, weak	Short, weak
Adhesion to aluminum	Poor	--	Poor	Poor	Poor	Poor	Good	Poor	Poor	Poor

[a] Instantaneous reading.

[b] Compounds too brittle to die out test specimens.

TABLE 23

EFFECT OF MALEIC ANHYDRIDE ON CURE CHARACTERISTICS AND ADHESION PROPERTIES OF CLEAR COMPOUNDS

Compound No.	46252-5 (Control)	46252-6 (Control)	46252-1	46252-2	46252-3	46252-4
50/50 LP-32/LP-33	100	100	100	100	100	100
CN-502	100	50	100	100	50	50
50% Solution maleic anhydride in cyclohexanone	--	--	2	4	2	4
DMP-30	10	5	10	10	5	5
Working life, hr.	1.5	1.5	1.75	3.5	>3.75	>3.5
Cup Cure Characteristics Determined at Room Temperature						
Shore A hardness	a/b	a/b	a/b	a/b	a/b	a/b
24 hr.	68/65	25/20	60/55	60/55	15/10	10/5
48 hr.	80/75	55/50	65/60	65/60	45/40	30/20
72 hr.	80/75	60/55	65/60	75/70	45/40	35/30
96 hr.	85/82	65/60	80/70	85/80	50/45	45/30
144 hr.	92/87	65/63	85/77	90/92	55/45	48/32
168 hr.	90/85	68/60	85/80	88/80	55/45	48/30
Remarks on cure after 168 hr.	Clear, tough, short	Clear, tough, extensible	Slt. cloudy weak, short	Slt.cloudy weak, short	Cloudy weak short	Cloudy, weak extensible
Film Characteristics After Seven Days Cure at Room Temperature						
Cure	Soft	Soft	Soft,	Soft slt.tacky	Soft	Soft, tacky
Adhesion	Poor	Fair	Tack	Tack	Poor	Poor
Clarity	Clear	Clear	Clear	Clear	Cloudy	Cloudy

a Instantaneous reading.
b Five-second reading.

TABLE 24

EFFECT OF BEETLE 216-8 RESIN ON CURE CHARACTERISTICS AND PROPERTIES OF "THIOKOL" LIQUID POLYMER/EPOXY RESIN COMPOSITION

Compound No.	46261-1 (Control)	46261-2	46261-3	46261-4 (Control)	46261-5	46261-6	46261-7	46261-8	46261-9 (Control)
50/50 LP-32/LP-33	100	100	100	100	100	100	--	--	--
CN-502	100	97	94	50	48.5	47	97	94	100
Beetle 216-8	--	3	6	--	1.5	3	3	6	--
DMP-30	10	9.7	9.4	5	4.85	4.7	9.7	9.4	10
Working life, hr.	0.5	1.0	1.1	1.25	1.6	1.6	0.4	0.4	0.3
Cup Cure Characteristics Determined at Room Temperature									
Shore A hardness	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b
24 hr.	80/78	50/45	50/40	20/10	25/15	15/10	95/95	85/85	95/95
48 hr.	80/75	50/40	50/40	25/15	45/40	30/20	95/95	85/85	93/93
72 hr.	83/80	50/45	50/45	30/20	48/45	35/25	95/95	85/85	95/95
144 hr.	85/85	60/55	60/50	35/30	60/55	45/35	98/98	88/88	95/95
168 hr.	85/85	70/60	70/65	45/40	65/60	50/45	100/100	90/90	95/95
192 hr.	85/85	70/60	70/65	45/40	65/60	50/45	--/--	90/90	95/95
Properties after 192 hr. cure	Not brittle, tough, sl., extensible	Not brittle, tough, extensible	Not brittle, tough extensible	Not brittle, tough, extensible	Not brittle, tough, extensible	Not brittle, tough, extensible	Brittle, not tough	Brittle, not tough	Brittle, not tough
Adhesion to aluminum	Fair to good	Soft, fair to good	Soft, fair to good	Soft, fair to good	Soft, fair to good	Soft, fair to good	Brittle, poor	Brittle, poor	Brittle, poor

a Instantaneous reading.
b Five-second reading.

TABLE 25

EFFECT OF BENZYL MERCAPTAN ON PROPERTIES OF CLEAR "THIOKOL" LIQUID POLYMER/EPOXY COMPOUNDS

Compound No.	43019-1 (Control)	45039-1	45014-3 (Control)	45039-3	43037-3 (Control)	45020-1
	CN-502		CN-503		CN-503/E-133	
50/50 LP-32/LP-33	100	100	100	100	100	100
CN-502	100	100	--	--	--	--
CN-503	--	--	100	100	25	25
E-133	--	--	--	--	25	25
Benzyl mercaptan	--	0.05	--	0.05	--	0.05
DMP-30	10	10	10	10	5	5
Liquid polymer/epoxy ratio	1/1	1/1	1/1	1/1	2/1	2/1
Working life, hr.	1	> 2.75	0.5	> 2.25	1	0.75
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature						
	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	96/94	70/>100	100/85	>100/100	65/60	70/73
100% Modulus, lb/sq in.	--/--	150/--	--/--	--/--	200/--	190/--
300% Modulus, lb/sq in.	--/--	--/--	--/--	--/--	--/--	--/--
Tensile strength, lb/sq in.	1690/2075	170/1870	2750/2525	2100/2490	290/350	250/430
Elongation, %	20/20	240/20	<10/70	30/30	210/105	190/95
Tear strength, lb/in.	180/185	40/126	320/265	335/200	40/15	35/32
Heat aging characteristics after 72 hr. at 212° F[c]	Discolored short	Discolored short	Discolored short	Discolored short	Discolored short	Discolored short

a Unaged.
b Heat aged 72 hours at 212° F.
c Specimens tested at 212° F.

TABLE 26

EFFECT OF BENZYL MERCAPTAN ON PROPERTIES OF CLEAR COMPOUNDS

Compound No.	46263-5 (Control)	46263-6 (Control)	46263-1	46263-2	46263-3	46263-4
50/50 LP-32/LP-33	100	100	100	100	100	100
CN-503	100	50	100	50	100	50
Benzyl Mercaptan	—	—	0.75	0.38	0.25	0.125
DMP-30	10	5	10	5	10	5
Working life, hr.	0.5	1.0	0.5	1.0	0.75	0.8

Properties of Cast Sheets Cured to Constant Hardness at Room Temperature[a]

	46263-5 (Control)	46263-6 (Control)	46263-1	46263-2	46263-3	46263-4
	b / c	b / c	b / c	b / c	b / c	b / c
Shore A hardness	>100/100	95/78	>100/100	80/72	>100/100	90/72
100 % Modulus, lb/sq in.	d/--	800/--	d/--	--/--	d/--	725/--
Tensile strength, lb/sq in.	--/2790	840/500	--/2450	475/465	--/2890	725/440
Elongation, %	--/20	110/85	--/30	90/90	--/30	100/95
Tear strength, lb/in.	--/261	117/31	--/233	93/37	--/259	102/30
Low temperature flexibility						
Passed, -°F	--	50	--	40	--	40
Failed, -°F	0	60	0	50	0	50
Adhesion at failure	Poor	Poor	Poor	Poor	Poor	Poor
Elevated temperature flexibility						
(7 days @ 212°F)	Passed	Passed	Passed	Passed	Passed	Passed
Adhesion	Poor	Poor	Poor	Poor	Poor	Poor
Short and weak	Yes	Yes	Yes	Yes	Yes	Yes
Extraction in SR-6, % after 24 hr.	8	10	4	9.5	5	12

a Unless specified otherwise, the specimens were unaged and untreated.
b Unaged.
c Heat aged 72 hours at 212°F.
d Too brittle to die out test specimens.

TABLE 27

EFFECT OF ALLYL GLYCIDYL ETHER ON PROPERTIES OF CLEAR LIQUID POLYMER/EPOXY SEALANT COMPOUNDS

Compound No.	43019-1 (Control)	45032-1	43006-2 (Control)	45032-2	45014-3 (Control)	45032-3	43010-2 (Control)	45032-4
	CN-502				CN-503			
50/50 LP-32/LP-33	100	100	100	100	100	100	100	100
CN-502	100	100	50	50	--	--	--	--
CN-503	--	--	--	--	100	100	50	50
Allyl glycidyl ether	--	2.5	--	1.25	--	2.25	--	1.25
DMP-30	10	10	5	5	10	10	5	5
Liquid polymer/epoxy ratio	1/1	1/1	2/1	2/1	1/1	1/1	2/1	2/1
Working life, hr.	1	0.75	2.25	1.25	0.5	0.75	1.5	1
Properties Determined on Cast Sheets Cured to Constant Hardness at Room Temperature								
	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	96/94	60/95	73/64	60/91	100/85	90/97	92/80	55/86
100% Modulus, lb/sq in.	--/--	75/--	525/300	75/580	--/--	270/--	--/--	65/--
300% Modulus, lb/sq in.	--/--	75/--	--/--	170/--	--/--	--/--	--/--	130/--
Tensile strength, lb/sq in.	1690/2075	75/2225	525/360	170/580	2750/2525	270/2920	1075/640	130/620
Elongation, %	20/20	390/10	100/100	360/100	<10/70	190/20	80/60	300/90
Tear strength, lb/in.	180/185	12/195	44/30	25/70	320/265	85/230	110/35	22/50
SR-6 extraction, %	6.8	4	13.6	8.4	3.2	4.6	11.4	3.5
Heat aging characteristics 72 hr. at 212°F[c]	Short	Short	Short	Quite flexible	Short	Short	Short	Short

a Unaged.
b Heat aged 72 hours at 212°F.
c Specimens tested at 212°F.

TABLE 28

COMPATIBILITY AND CURE STUDY WITH "THIOKOL" LIQUID POLYMER/EPOXY RESIN/PHENOLIC RESIN SYSTEMS

Compound No.	47604-1 (Control)	47604-2	47604-3	47604-4	47604-5
50/50 LP-32/LP-33	100	100	100	100	100
CN-503	100	100	100	100	100
BR-6741	--	25	50	--	--
CTL-91-LD	--	--	--	25	50
DMP-30	10	10	10	10	10
Working life, hr.	0.5	0.5	0.4	0.5	0.5
Appearance of mix	Clear	Very Cloudy	Very Cloudy	Cloudy	Cloudy

Cup Cure Characteristics at Room Temperature

	a / b	a / b	a / b	a / b	a / b
Shore A hardness					
48 hr.	100/100	65/60	70/65	55/50	80/75
72 hr.	100/100	80/75	80/75	70/65	92/90
96 hr.	100/100	90/85	80/75	80/70	95/90
192 hr.	100/100	90/85	85/80	90/85	95/93
216 hr.	100/100	93/90	90/88	90/85	98/95
Properties at room temperature	Clear, tough sl. brittle	Opaque, short, not extensible, not tough	Opaque, short, not extensible, not tough	Opaque, short not extensible, not tough	Opaque, short, not extensible, not tough
Characteristics after heating 24 hr. at 212°F	Short, weak	Short, weak	Short, weak	Short, weak	Short, weak

a Instantaneous reading.
b Five-second reading.

TABLE 29

COMPATIBILITY AND CURE STUDY WITH "THIOKOL" LIQUID POLYMER/EPOXY RESIN/PHENOLIC RESIN SYSTEMS

Compound No.	47604-1 (Control)	47606-1	47606-2	47606-3
50/50 LP-32/LP-33	100	100	100	100
CN-503	100	100	100	100
CTL-91-LD	--	10	100	200
DMP-30	10	10	10	10
Working life, hr.	0.5	--	--	--
Appearance of mix	Clear	Sl. Cloudy	Clear	Clear

Cup Cure Characteristics at Room Temperature

	a / b	a / b	a / b	a / b
Shore A hardness				
24 hr.	100/100[c]	85/80	100/100	30/10
120 hr.	100/100	95/90	100/100	30/10
144 hr.	100/100	95/93	100/100	30/10
168 hr.	100/100	95/91	100/100	30/10
Properties at room temperature	Clear, tough, sl. brittle	Opaque, short, sl. brittle, not tough	Clear, very brittle, not tough, not extensible	Clear, short, not tough
Characteristics after 24 hr. at 212°F	Short, weak	Short, weak	Rubber-like, weak	Flexible, became brittle on cooling to room temperature

a Instantaneous reading.
b Five-second reading.
c Readings are for 48, 72, 96, 192 and 216 hours cure.

TABLE 30

CURE STUDIES WITH "THIOKOL" LIQUID POLYMER/EPOXY RESIN/STYPHEN 1 SYSTEMS

Compound No.	46285-1 (Control)	47611-1	47611-2	47621-2	47614-4	47614-1	47611-8
50/50 LP-32/LP-33	100	--	100	100	100	100	100
CN-502	100	--	--	100	100	100	100
Styphen 1	--	100	100	10	28	66	100
DMP-30	10	10	10	10	10	10	10
Liquid polymer/ epoxy ratio	1/1	--	--	1/1	1/1	1/1	1/1
Working life, hr.	0.5	--	--	0.75	0.6	0.75	1.9
Cup Cure Characteristics Determined at Room Temperature							
	a / b			a / b	a / b	a / b	a / b
Shore A hardness							
24 hr.	60/55	No cure	No cure	60/55	--/--	40/30	40/30
48 hr.	65/60	No cure	No cure	60/55	--/--	--/--	--/--
96 hr.	80/75	No cure	No cure	--/--	85/80	--/--	--/--
120 hr.	80/75	No cure	No cure	75/70	85/80	40/30	70/60
144 hr.	--	--	--	75/70	85/83	45/40	70/60
Properties after compounds attained constant hardness	Tough Extensible, clear	--	--	Tough, extensible, clear	Very tough extensible, clear	Tough, extensible, clear	Tough, very extensible clear
Characteristics after heating 24 hr. at 212°F	Short	--	--	Short	Soft, flexible, not short, weak	Thermoplastic, soft, tacky	Thermoplastic, soft, tacky

a Instantaneous reading.
b Five-second reading.

TABLE 31

PROPERTIES OF CLEAR COMPOSITIONS CONTAINING STYPHEN 1

Compound No.	47637-1	47637-2	47637-3	47637-4	47637-5
50/50 LP-32/LP-33	100	100	100	100	100
Styphen 1	22	22	22	22	22
BRR-18794	100	--	--	--	--
CN-502	--	100	--	--	--
CN-503	--	--	100	--	--
CN-504	--	--	--	100	--
E-134	--	--	--	--	100
DMP-30	10	10	10	10	10
Liquid polymer/epoxy ratio	1/1	1/1	1/1	1/1	1/1
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature[a]					
	b / c	b / c	b / c	b / c	b / c
Shore A hardness	>100/85	60/95	95/95	95/95	98/98
100% Modulus, lb/sq in.	d/--	75/--	550/--	475/--	300/d
Tensile strength, lb/sq in.	--/625	75/1150	550/1790	475/550	740/--
Elongation, %	--/75	230/65	115/65	100/85	205/--
Tear strength, lb/in.	--/73	20/196	165/222	110/110	258/--
Properties at 212° F after 24 hr. aging	Short, weak	Sl. extensible, weak	Short, weak	Short, weak	Short, weak
Low temperature flexibility					
Passed, °F	R.T.	R.T.	--	R.T.	--
Failed, °F	20	20	R.T.	20	R.T.
Adhesion at failure	Poor	Good	Poor	Poor	Poor
Elevated temperature flexibility (7 days at 212° F)	Passed	Passed	Passed	Passed	Passed
Adhesion	Poor	Good	Poor to fair	Poor to fair	Fair
Volume swell, %					
SR-6 1 day	0	2	2	2	1
1 month	-1	0	6	10	3
SR-10 1 day	-1	0	1	1	2
1 month	-1	-5	0	-2	0
JP-3 1 day	-1	4	2	0	1
1 month	-1	0	1	1	0
H_2O 1 day	-1	3	2	1	1
1 month	3	1[e]	4[e]	15[e]	6[e]
Extraction in SR-6, %					
24 hr.	6	17	13	12	5
Total 72 hr.	10	21	16	18	8

[a] Unless specified otherwise, the specimens were unaged and untreated.

[b] Unaged.

[c] Heat aged 72 hours at 212° F.

[d] Too brittle to die out test specimen.

[e] White film on specimen.

TABLE 32

EFFECT OF LOWER CONCENTRATION OF CATALYST ON PROPERTIES OF CLEAR "THIOKOL" LIQUID POLYMER/EPOXY COMPOUNDS

Compound No.	30184-1	45002-1	45041-1	45014-1	45014-3	45019-3	43010-2	45019-4
			BRR-18794				CN-503	
50/50 LP-32/LP-33	100	100	--	--	100	100	100	100
LP-33	--	--	100	100	--	--	--	--
BRR-18794	100	100	100	100	--	--	--	--
CN-503	--	--	--	--	100	100	50	50
DMP-30	10	5	10	5	10	7	5	3.5
Liquid polymer/epoxy ratio	1/1	1/1	1/1	1/1	1/1	1/1	2/1	2/1
Working life, hr.	0.5	1.25	--	0.5	0.5	0.5	1.5	--
Properties Determined on Cast Sheets Cured to Constant Hardness at Room Temperature								
	a/b	a/b	a/b	a/b	a/b	a/b	a/b	a/b
Shore A hardness	>100/90	>100/100	100/86	>100/90	100/85	70/96	92/80	25/72
100% Modulus, lb/sq in.	--/--	--/--	--/--	--/--	--/--	135/--	--/--	35/--
Tensile strength, lb/sq in.	2300/935	2110/1775	3690/910	2400/875	2750/2525	170/2060	1075/640	95/420
Elongation, %	20/50	10/10	60/80	<10/90	<10/70	220/30	80/60	320/75
Tear strength, lb/in.	200/100	135/171	--/65	210/75	320/265	40/180	110/35	10/25
Low temperature flexibility								
Passed, °F	10	--	--	10	RT	--	-50	--
Failed, °F	0	--	--	0	35	0	-60	--
Adhesion at failure	Poor	--	--	Poor	Poor	Poor	Poor	--
Elevated temperature flexibility								
(7 days at 212°F)	Failed	--	--	Failed	--	--	--	--
Adhesion	Poor	--	--	Poor	--	--	--	--
Short	Yes	--	--	Yes	--	--	--	--

a Unaged.
b Heat aged 72 hours at 212°F.

TABLE 33

EVALUATION OF TRIETHYLENETETRAMINE AS A CATALYST IN CLEAR "THIOKOL" LIQUID POLYMER/EPOXY COMPOUNDS

Compound No.	45019-1	45021-1	45019-2	45021-2	45019-3	45021-3	45019-4	45021-4
	CN-502				CN-503			
50/50 LP-32/LP-33	100	100	100	100	100	100	100	100
CN-502	100	100	50	50	--	--	--	--
CN-503	--	--	--	--	100	100	50	50
Triethylenetetramine	--	7	--	3.5	--	7	--	3.5
DMP-30	7	--	3.5	--	7	--	3.5	--
Liquid polymer/epoxy ratio	1/1	1/1	2/1	2/1	1/1	1/1	2/1	2/1
Working life, hr.	1	0.75	1.25	24.75	0.5	2.25	1	0.5
Cup Cure Characteristics Determined at Room Temperature								
Shore A hardness								
24 hr.	30	85	15	Too soft	25	100	10	Too soft
72 "	60	85	30	" "	50	100	20	40
120 "	60	95	30	" "	55	100	20	55
144 "	--	95	--	" "	--	100	--	55
Appearance at constant hardness	Clear tough	Cloudy crumbly	Clear extensible	Cloudy very soft	Clear tough	Cloudy crumbly	Clear extensible	Cloudy crumbly

TABLE 34

EVALUATION OF TRIETHYLENETETRAMINE AS A CATALYST IN CLEAR "THIOKOL" LIQUID POLYMER/BRR-18794 COMPOSITIONS

Compound No.	43046-1	43048-1	43046-4	43048-4	43046-2	45048-2	43046-5	43048-5
50/50 LP-32/LP-33	100	100	—	—	100	100	—	—
LP-33	—	—	100	100	—	—	100	100
BRR-18794	100	100	100	100	50	50	50	50
Triethylenetetramine	—	10	—	10	—	5	—	5
DMP-30	10	—	10	—	5	—	5	—
Liquid polymer/epoxy ratio	1/1	1/1	1/1	1/1	2/1	2/1	2/1	2/1
Working life, hr.	0.75	0.75	0.5	>0.5	1	>1.25	0.75	>1.0
Cup Cure Characteristics Determined at Room Temperature								
Shore A hardness								
24 hr.	90	85	90	90	92	70	92	52
48 hr.	92	85	95	90	95	70	95	52
72 hr.	95	96	95	90	95	75	95	52
120 hr.	95	96	95	90	95	76	95	52
Appearance after 120-hr. cure	Tough short clear	Tough short cloudy	Tough short clear	Tough short clear	Tough short clear	Crumbly cloudy	Tough short clear	Slightly crumbly clear

TABLE 35

EVALUATION OF AMINES AS CATALYSTS FOR CURING "THIOKOL" LIQUID POLYMER/EPOXY RESIN CLEAR COMPOSITIONS

Compound No.	45014-2 (Control)	46295-1	46295-2
LP-33	100	100	100
CN-502	100	100	100
Triethylenetetramine	--	10	—
Tetraethylenepentamine	--	—	10
DMP-30	10	—	—
Working life, hr.	1.75	1.5	1.25

Properties of Cast Sheets Cured to Constant Hardness at Room Temperature[a]

	b/c	b/c	b/c
Shore A hardness	100/85	40/90	40/85
100% Modulus, lb/sq in.	--/--	85/--	85/--
Tensile strength, lb/sq in.	1390/950	85/660	85/630
Elongation, %	<10/80	125/80	100/65
Tear strength, lb/in.	215/110	6/33	7/20
Characteristics after heating 24 hr. at 212° F	Weak, short	Weak, short	Weak, short
SR-6 extraction, % 24 hr.	11.5	11.4	14.1

a Unless specified otherwise, the specimens were unaged and untreated.
b Unaged.
c Heat aged 72 hours at 212° F.

TABLE 36

CURE CHARACTERISTICS OF CLEAR "THIOKOL" LIQUID POLYMER/EPOXY COMPOUND CONTAINING TRINITROBENZENE AS A CO-CURING AGENT

Compound No.	46258-5 (Control)	46258-1	46258-2	46258-3	46258-4
LP-33	100	100	100	100	100
CN-503	25	25	25	25	25
E-133	25	25	25	25	25
Trinitrobenzene[a]	--	8	8	4	4
Accelerator B[b]	--	--	2.4	--	2.4
DMP-30	5	5	5	5	5
Working life, hr.	1	>2.7	>2.5	>2.5	>2.5
Cup Cure Characteristics Determined at Room Temperature					
	c/d	c/d	c/d	c/d	c/d
Shore A hardness					
24 hr.	50/45	too soft	too soft	25/20	20/10
48 hr.	--/--	20/10	10/0	55/45	55/45
96 hr.	--/--	23/12	12/0	65/55	--/--
120 hr.	--/--	30/20	20/0	65/55	--/--
144 hr.	85/80	--/--	20/0	60/50	65/60
168 hr.	85/80	30/20	20/0	60/50	65/55
Appearance after 168-hr. cure	Clear tough extensible	Opaque gummy	Opaque gummy	Opaque weak extensible	Opaque weak extensible

---

a A 50% solution in nitromethane.
b Composed of 12% VYHH, 40% sulfur, 48% methyl ethyl ketone.
c Instantaneous reading.
d Five-second reading.

TABLE 37

CURE CHARACTERISTICS OF CLEAR "THIOKOL" LIQUID POLYMER/EPOXY COMPOUND CONTAINING CUMENE HYDROPEROXIDE AS A CO-CURING AGENT

Compound No.	46251-4 (Control)	46251-1	46251-2	46251-3
LP-33	100	100	100	100
CN-503	25	25	25	25
E-133	25	25	25	25
Cumene hydroperoxide[a]	--	8.5	5.7	2.8
DMP-30	5	5	5	5
Working life, hr.	0.8	0.7	0.6	0.6

Cup Cure Characteristics Determined at Room Temperature

	b/c	b/c	b/c	b/c
Shore A hardness				
24 hr.	Too soft	Too soft	Too soft	Too soft
48 hr.	40/30	55/50	40/30	30/20
72 hr.	50/45	65/60	65/60	50/45
96 hr.	60/55	85/80	70/65	70/60
144 hr.	71/62	93/87	89/80	76/68
168 hr.	70/60	93/90	90/85	78/70
Appearance after 168-hr. cure	Tough extensible clear	Not tough short clear	Not tough short clear	Quite tough slightly extensible clear

a The effective concentration is 70%.
b Instantaneous reading.
c Five-second reading.

TABLE 38

CURE CHARACTERISTICS OF "THIOKOL" LIQUID POLYMER/EPOXY RESIN COMPOSITION CONTAINING CUMENE HYDROPEROXIDE CO-CURING AGENT

Compound No.	46294-1	46294-2
LP-33	100	100
CN-503	25	25
E-133	25	25
Cumene hydroperoxide[a]	5.7	2.8
DMP-30	5	5
Working life, hr.	0.5	1.25

Cure Characteristics of Case Sheets at Room Temperature

	b / c	b / c
Shore A hardness		
96 hr.	Too soft	Too soft
120 hr.	52/45	28/20
240 hr.	60/50	30/20
456 hr.	88/80	58/50
Remarks	Numberous small bubbles in cast sheet	Numerous small bubbles in cast sheets
Characteristics after 24 hr. at 212°F	Weak, short	Weak, short

a The effective concentration is 70%.
b Instantaneous reading.
c Five-second reading.

TABLE 39

COMPATIBILITY STUDIES WITH "THIOKOL" LIQUID POLYMERS AND VIBRIN X-1047

Compound No.	46281-1	46281-2	46281-3	46281-4	46281-5	46281-6	46281-7	46281-8	46281-9	46281-10
Vibrin X-1047	90	10	90	10	90	10	33.3	33.3	33.3	5
50/50 LP-32/LP-33	10	90	--	--	--	--	33.3	--	--	--
LP-33	--	--	10	90	--	--	--	33.3	--	--
ZL-174	--	--	--	--	10	90	--	--	33.3	--
CN-502	--	--	--	--	--	--	33.3	33.3	33.3	5
Appearance of mix	Clear fluid	Cloudy fluid	Clear fluid	Sl. cloudy fluid	Clear fluid	V.sl.cloudy fluid	Clear fluid	Clear fluid	Clear fluid	Clear fluid

TABLE 40

CURE STUDIES WITH "THIOKOL" LIQUID POLYMERS AND VIBRIN X-1047

Compound No.	46299-7	46299-1	46299-2	46299-3	46299-4	46299-5	46299-6
Vibrin X-1047	100	100	100	100	50	50	50
50/50 LP-32/LP-33	--	100	--	--	100	--	--
LP-33	--	--	100	--	--	100	--
ZL-174 (LP-38)	--	--	--	100	--	--	100
DMP-30	10	10	10	10	5	5	5
Working life, min.	> 4.5	0.2	0.2	0.1	0.3	2	> 3
Cup Cure Characteristics Determined at Room Temperature							
Appearance of mix	Clear	Cloudy, sl. viscous	Sl. cloudy-fluid	Clear fluid	Cloudy, sl. viscous	Sl. cloudy fluid	Clear fluid
Shore A hardness							
96 hr.	Soft gel	28	40	35	33	5	Soft gel
120 hr.	Soft gel	30	40	35	33	5	Soft gel
144 hr.	Soft gel	30	45	35	35	5	Soft gel
Remarks after 144-hr. cure	Clear	Resilient-short,weak sl. cloudy	Resilient short,weak sl. cloudy	Resilient short,weak clear	Resilient short,weak sl. cloudy	Resilient short,weak sl. cloudy	Clear
Characteristics after 24-hr. at 212°F	--	Short, weak	Short, weak	Short, weak	Short, weak	Short, weak	--

TABLE 41

CURE STUDIES WITH CLEAR COMPOSITIONS CONTAINING "THIOKOL" LIQUID POLYMERS/VIBRIN X-1047/EPOXIDE RESIN

Compound No.	43901-1 (Control)	46291-1	46291-2	46291-3
Vibrin X-1047	--	100	100	100
50/50 LP-32/LP-33	100	100	--	--
LP-33	--	--	100	--
ZL-174 (LP-38)	--	--	--	100
CN-502	100	100	100	100
DMP-30	10	10	10	10
Working life, hr.	1.0	1.3	1.3	1.3

Cup Cure Characteristics Determined at Room Temperature

	a / b	a / b	a / b	a / b
Shore A hardness				
24 hr.	81/81	55/50	55/50	55/50
48 hr.	84/84	60/55	60/55	60/55
96 hr.	--/--	60/55	60/55	60/55
120 hr.	100/100	60/55	60/55	60/55
Remarks after 120-hr. cure	Tough, not extensible	Tough, extensible v. resilient	Sl. tough, sl. short, v. resilient	Sl. Tough, sl. short, v. resilient
Characteristics at 158°F after heating 2 hr.	--	V. short, weak	V. short, weak	V. short, weak

a Instantaneous reading.
b Five-second reading.

TABLE 42

COMPATIBILITY TESTS WITH "THIOKOL" LIQUID POLYMERS AND PDL-7-669[a]

Compound No.	46265-8	46265-7	46265-6	46271-1	46271-2	46266-7	46266-6	46266-5
PDL-7-669	90	70	50	30	10	90	70	50
50/50 LP-32/LP-33	10	30	50	70	90	—	—	—
LP-33	—	—	—	—	—	10	30	50
Appearance of mix	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy

Compound No.	46271-3	46271-4	46266-10	46266-9	46266-8	46271-5	46271-6
PDL-7-669	30	10	90	70	50	30	10
50/50 LP-32/LP-33	—	—	—	—	—	—	—
LP-33	70	90	—	—	—	—	—
ZL-174 (LP-38)	—	—	10	30	50	70	90
Appearance of mix	Sl.cloudy	Sl.cloudy	Sl.cloudy	Sl.cloudy	Sl.cloudy	V. sl. cloudy	V. sl. cloudy

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a No cure in 72 hours.

TABLE 43

CURE STUDIES WITH "THIOKOL" LIQUID POLYMERS AND PDL-7-669

Compound No.	46265-1 (Control)	46265-3 (Control)	46265-2	46265-4	46265-5	46266-1	46266-2	46266-3	46266-4
PDL-7-669	100	100	100	90	90	90	90	90	90
50/50 LP-32/LP-33	--	--	--	10	10	--	--	--	--
LP-33	--	--	--	--	--	10	10	--	--
ZL-174 (LP-38)	--	--	--	--	--	--	--	10	10
Luperco ATC	1	--	--	1	--	1	--	1	--
Laminac catalyst 347	--	1	0.5	--	1	--	1	--	1
6% Hexogen Cobalt	--	1	0.5	--	1	--	1	--	1
Cup Cure Characteristics at Room Temperature									
Appearance of mix	Clear	Clear	Clear	Cloudy	Cloudy	Cloudy	Cloudy	V. sl. cloudy	V. sl. cloudy
Set time, hr.	No cure	$>4.5<20$	$>28<52$	No cure	1	No cure	0.2	No cure	0.2
Shore A hardness		a/b	a/b		a/b		a/b		a/b
24 hr.	No cure	80/75	--/--	No cure	43/--	No cure	43/43	No cure	45/45
48 hr.	No cure	90/90	--/--	No cure	40/--	No cure	48/48	No cure	45/45
96 hr.	No cure	95/95	78/75	No cure	48/--	No cure	48/48	No cure	48/48
120 hr.	No cure	95/95	83/83	No cure	48/--	No cure	48/48	No cure	48/48
Remarks after 120-hr. cure	V. cloudy	Brittle	Short	Cloudy	V.short	Cloudy	V.short	Clear	V.short

a Instantaneous reading.
b Five-second reading.

TABLE 44

CURE STUDIES WITH "THIOKOL" LIQUID POLYMERS AND PDL-7-669

Compound No.	47607-1 (Control)	47607-2	47607-3	47607-4	47607-5	47607-6	47607-7
50/50 LP-32/LP-33	—	100	—	—	100	—	—
LP-33	—	—	100	—	—	100	—
ZL-174 (LP-38)	—	—	—	100	—	—	100
PDL-7-669	100	100	100	100	50	50	50
DMP-30	10	10	10	10	5	5	5
Working life, hr.	—	0.5	0.5	0.5	> 2.5	> 2.5	—
		Cup Cure Characteristics Determined at Room Temperature					
Appearance of mix	Clear	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Sl. cloudy
Shore A hardness		a / b	a / b	a / b	a / b	a / b	
24 hr.	No cure	35/20	40/30	25/20	30/25	No cure	No cure
120 hr.	No cure	25/20	35/30	35/30	40/35	15/10	No cure
144 hr.	No cure	25/20	40/30	35/30	40/40	15/10	No cure
168 hr.	No cure	25/20	40/30	35/30	45/40	15/10	No cure
Remarks after 168-hr. cure	—	Resilient, short, weak	Resilient, short, weak	Resilient, short, weak	Resilient, short, weak	Resilient, short, weak	—
Characteristics after 24 hr. at 212°F	—	Short, weak	Short, weak	Short, weak	Short, weak	Short, weak	—

a Instantaneous reading.
b Five-second reading.

TABLE 45

COMPATIBILITY STUDIES WITH "THIOKOL" LIQUID POLYMERS AND POLYAMIDE RESINS 100-S AND 110

Compound No.	46279-2	46279-1	46269-7	46279-5	46279-4	46279-3	46279-8	46279-7	46279-6
50/50 LP-32/LP-33	90	70	50	--	--	--	--	--	--
LP-33	--	--	--	90	70	50	--	--	--
ZL-174 (LP-38)	--	--	--	--	--	--	90	70	50
100-S	10	30	50	10	30	50	10	30	50
Remarks[a]	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.

Compound No.	46280-2	46280-1	46280-4	46280-3	46280-6	46280-5
50/50 LP-32/LP-33	90	10	--	--	--	--
LP-33	--	--	90	10	--	--
ZL-174 (LP-38)	--	--	--	--	90	10
110	10	90	10	90	10	90
Remarks[a]	N.C.	S.C.	N.C.	S.C.	N.C.	S.C.

Code: N.C. - Not Compatible
S.C. - Slightly Compatible

[a] Compositions heated at 212°F and stirred to facilitate dispersion and then cooled to room temperature.

TABLE 46

COMPATIBILITY STUDIES WITH "THIOKOL" LIQUID POLYMER/EPOXY RESIN/POLYAMIDE POLYMER SYSTEMS

Compound No.	46269-9	46269-4	46279-9	46279-10	46279-11	46280-10	46280-7	46280-8	46280-9
50/50 LP-32/LP-33	--	--	100	--	--	--	100	--	--
LP-33	--	--	--	100	--	--	--	100	--
ZL-174 (LP-38)	--	--	--	--	100	--	--	--	100
100-S	100	100	100	100	100	--	--	--	--
110	--	--	--	--	--	100	100	100	100
CN-502	100	--	100	100	100	100	100	100	100
CN-503	--	100	--	--	--	--	--	--	--
Remarks[a]	C. Cured at 212° F	C. Cured at 212° F	N.C. Soft gel, liquid	N.C. Partial cure separation	N.C. Partial cure separation	S.C. No cure	N.C. No cure	N.C. No cure	N.C. No cure

Code: C. - Compatible
N.C. - Not compatible
S.C. - Slightly compatible

[a] Compositions heated at 212° F and stirred to facilitate dispersion and then cooled to room temperature.

TABLE 47

COMPATIBILITY STUDIES WITH "THIOKOL" LIQUID POLYMER/EPOXY RESIN/POLYAMIDE RESIN SYSTEMS

Compound No.	46287-1	46287-2	46287-3	46287-4	46287-5	46287-6
50/50 LP-32/LP-33	100	100	—	—	—	—
LP-33	—	—	100	100	—	—
ZL-174 (LP-38)	—	—	—	—	100	100
CN-503	100	100	100	100	100	100
100-S	22.2	—	22.2	—	22.2	—
110	—	22	—	22	—	22
Appearance of mix[a]	N.C.	S.C.	N.C.	S.C.	N.C.	N.C.

Compound No.	46296-2	46296-4	46296-6	46296-8	46296-10	46296-12
ZL-174 (LP-38)	11	11	11	11	11	11
100-S	100	—	100	—	100	—
110	—	100	—	100	—	100
CN-502	55	55	—	—	—	—
CN-503	—	—	55	55	—	—
CN-504	—	—	—	—	55	55
Appearance of mix[a]	Clear, cured	Sl.cloudy not cured	Sl.cloudy, cured	Not cured	Sl.cloudy, cured	V. sl. cloudy, not cured
Shore A hardness						
24 hr.	95	No cure	90	No cure	80	No cure
48 hr.	95	No cure	90	No cure	80	No cure
72 hr.	98	No cure	>100	No cure	92	No cure
96 hr.	98	No cure	>100	No cure	92	No cure
Remarks	Separation of ZL-174, tough, sl.cloudy	—	Sl.brittle, sl.cloudy	—	Short, sl.cloudy	—

Code: N.C. - Not compatible
S.C. - Slightly compatible

[a] Compositions heated at 212° F and stirred to facilitate dispersion and then cooled to room temperature.

TABLE 48

EFFECT OF POST CURE ON PROPERTIES OF "THIOKOL" LIQUID POLYMER/EPOXY RESIN COMPOSITIONS

Compound No.	45004-1	45041-1	45014-4	47602-1
LP-33	100	100	100	--
LP-3	--	--	--	100
Araldite E-134	100	--	--	100
CN-503	--	--	100	--
BRR-18794	--	100	--	--
DMP-30	10	10	10	10
Working life, hr.	0.25	1.0	1.0	0.25

Properties of Cast Sheets Cured to Constant Hardness at Room Temperature

	a / b	a / b	a / b	a / b
Shore A hardness	90/95	100/85	96/90	95/90
100% Modulus, lb/sq in.	950/--	--/--	--/--	1150/--
Tensile strength, lb/sq in.	950/940	3750/625	1725/880	1175/850
Elongation, %	130/65	65/55	65/70	105/65
Tear strength, lb/in.	192/202	326/171	267/190	298/194
Characteristics after 24 hr. at 212°F	Short, weak	V. short, weak	Short, weak	Short, weak

a Unaged.
b Samples post cured 2 hr. at 300°F.

TABLE 49

EFFECT OF WD-2 POLYMER ON PROPERTIES OF "THIOKOL" LIQUID POLYMER/ EPOXIDE RESIN CLEAR COMPOSITIONS

Compound No.	30184-1	47644-1	45014-3	47644-2	43019-1	47644-3	43039-1	47644-4	43041-1	47644-5
50/50 LP-32/LP-33	100	100	100	100	100	100	100	100	100	100
BRR-18794	100	100	--	--	--	--	--	--	--	--
CN-503	--	--	100	100	--	--	--	--	--	--
CN-502	--	--	--	--	100	100	--	--	--	--
CN-504	--	--	--	--	--	--	100	100	--	--
E-134	--	--	--	--	--	--	--	--	100	100
WD-2 Latex polymer[a]	--	18.5	--	18.5	--	18.5	--	18.5	--	18.5
DMP-30	10	10	10	10	10	10	10	10	10	10
Working life, hr.	0.5	1.8	0.5	2.5	1	1.5	0.75	1	0.5	1
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature										
	b / c	b / c	b / c	b / c	b / c	b / c	b / c	b / c	b / c	b / c
Shore A hardness	>100/90	>100/100	>100/85	55/>100	96/94	f	90/90	>100/>100	100/94	>100/100
Tensile strength, lb/sq in.	2300/935	d / d	2750/2525	e / d	1690/2075	--/--	1070/1240	1720/1530	2525/2160	1330/1865
Elongation, %	20/50	--/--	<10/70	--/--	20/20	--/--	70/75	35/15	10/20	45/20
Tear strength, lb/in.	200/100	--/--	320/265	--/--	180/185	--/--	150/115	307/229	370/380	266/233
Properties at 212°F after 72 hr. aging	Weak, short	--	Weak, short	--	Weak, short	--	Weak, short	Weak, short	Quite tough, flexible, short	Quite tough, flexible, short

a Polymer contained 5% moisture.
b Unaged.
c Heat aged 72 hr. at 212°F.
d Too brittle for testing.
e Material yielded; stress too low to measure on test machine.
f Unsatisfactory cure; too soft.

TABLE 50

"THIOKOL" LP-2/EPOXY RESIN CLEAR COMPOSITIONS

Compound No.	43046-5	47622-1	45028-3	47622-7	43033-5	47622-4
LP-2	--	100	--	100	--	100
LP-33	100	--	100	--	100	--
BRR-18794	50	50	--	--	--	--
Epon-828	--	--	50	50	--	--
CN-504	--	--	--	--	50	50
DMP-30	5	5	5	5	5	5
Working life, hr.	0.75	1.5	1.5	1.3	3.25	1

Cup Cure Characteristics at Room Temperature

	a / b	a / b	a / b	a / b	a / b	a / b
Shore A hardness						
24 hr.	80/75	90/90	75/70	82/75	Too soft	65/60
48 hr.	85/82	90/90	85/82	95/95	Too soft	85/85
72 hr.	90/87	--/--	--/--	95/95	20/10	--/--
96 hr.	--/--	95/95	95/95	95/95	20/10	91/91
120 hr.	90/87	95/95	95/95	95/95	20/10	91/91
Remarks	Tough, not extensible not brittle	Tough, not brittle	Tough, not brittle	Tough, not brittle	Weak, v. extensible	Tough not brittle

a Instantaneous reading.
b Five-second reading.

TABLE 51

PROPERTIES OF HIGH VISCOSITY LIQUID POLYSULFIDE POLYMER/EPOXY RESIN CLEAR COMPOUNDS

Compound No.	47640-3	47640-6	47640-9
High viscosity liquid polysulfide polymer	100	100	100
Liquid polymer/epoxy ratio	4/1	4/1	4/1
BRR-18794	25	—	—
CN-503	—	25	—
CN-504	—	—	25
DMP-30	3.75	3.75	3.75
Properties of Cast Sheets Cured to Constant Hardness at Room Temperature[a]			
	b / c	b / c	b / c
Shore A hardness	85/75	80/85	70/75
100% Modulus, lb/sq in.	—/—	500/—	250/200
Tensile strength, lb/sq in.	700/172	625/420	300/200
Elongation, %	70/35	175/80	250/100
Tear strength, lb/in.	46/40	65/95	47/80
Torsional test			
Relative modulus			
T_5, -°F	49	39	44
T_{10}	57	52	54
T_{50}	71	64	66
T_{100}	78	69	71
Absolute modulus			
G_{rt}, lb/sq in.	680	292	282
$G_{5,000}$, -°F	55	57	60
$G_{10,000}$	59	61	63
$G_{20,000}$	66	66	69
Characteristics after 24 hr. @ 212° F	Short, weak	Sl.extensible,weak	Sl.extensible,weak
Swelling volume, %			
SR-6 1 day	5	4	4
1 month	-7 "short"	-2 "short"	-2 "short"
SR-10 1 day	1	0	0
1 month	1	0	-2
JP-3 1 day	2	2	2
1 month	1 "short"	1	0
H_2O 1 day	2	1	-1
1 month	8 "white film"	6 "white film"	8 "white film"
Extraction in SR-6, % 24 hr.	10	12	—

a Unless specified otherwise, the specimens were unaged and untreated.
b Unaged.
c Heat aged 72 hours at 212° F.

IV. EXPERIMENTAL TRANSLUCENT INTEGRAL FUEL CELL SEALANT COMPOUNDS

A. INTRODUCTION

It was planned to submit one to two pound samples of experimental sealant compounds prepared with the 60/38 and 60/39.5 mole % pentamethylene dichloride/formal copolymers cross-linked with 2 mole % of trichloropropane and 0.5 mole % of tetrachloropropyl formal, but the copolymers were not of satisfactory quality and time did not permit preparation of additional samples.

Several different "Thiokol" liquid polysulfide polymer/epoxy resin compositions were developed from the information obtained in the course of work conducted on this contract for the development of a translucent sealant compound permitting visual inspection during and after application and possessing improved properties in general.

An experimental (LP-2) base translucent integral fuel cell sealant compound was also developed with improved physical properties and resistance to heat aging and fuels which would permit visual inspection during and after application.

B. EVALUATION OF "THIOKOL" POLYSULFIDE LIQUID POLYMER/EPOXY RESIN SEALANT COMPOSITIONS

Two-package mix, translucent compounds were developed from different liquid polysulfide polymer/epoxy resin compositions for possible application as integral fuel tank sealant compounds. The use of 5 and 10 parts of Aerosil in the fluid compositions produced a "buttery" type consistency of good spreading characteristics and no appreciable "run down" during application. Cured films of these compounds were sufficiently clear to permit visual inspection during and after application. Samples of five compounds possessing the best properties for this application and covering a range of physical properties were submitted to Wright Field.

The test data from our evaluation of these compounds are recorded in Table 52. For each composition, the proper amounts of part A and part B were compounded to give the designated liquid polymer/epoxy resin ratio. With the exception of one compound (No. B47569-3), these compounds had a comparatively short working life.

Some compounds (Nos. B47569-7 and B47569-8) cured to constant hardness within 48 hours but other compounds (Nos. B47569-3, -4 and -6) required five to six days. This does not mean that the materials would not be serviceable before this time as the cure time can be decreased by heating at 158°F for three to five hours after a 24 hour room temperature cure. One compound (No. B47569-6) which contained the high viscosity liquid polymer, was cured for three hours at 158°F after the room temperature cure.

All of these compounds passed the Mil-S-5043 (Aer) test requirements for volume change in Type I and Type III fuels, non-volatile extractable materials and discoloration but none of the compositions passed all of the specification tests to which they were subjected. In general, the hardness of the compounds was affected during the resistance to heat test but was not affected otherwise. The resistance to salt water and hydrocarbons and low temperature flexibility test requirements were the most difficult to meet. None of the compounds passed the salt water and hydrocarbons test and only one (No. B47569-6) could possibly pass the low temperature flexibility test.

From the standpoint of over-all properties, three compounds (Nos. B47569-4, -6 and -7) appeared to be the most promising for integral fuel tank sealant application.

C. EVALUATION OF EXPERIMENTAL "THIOKOL" LP-2 BASE TRANSLUCENT SEALANT COMPOUND

Evaluation of the experimental LP-2 base translucent sealant compound showed that it possessed good potentialities for an improved integral fuel cell sealant material.

The data in Table 53 show that the unaged LP-2 experimental sealant compound was of lower hardness and possessed a lower 100% modulus, much higher ultimate elongation, slightly lower tensile strength and much better resistance to heat aging at 212°F and 350°F than the unaged LP-2 base commercial sealant compound. This latter is demonstrated by the markedly better over-all physical properties of the experimental sealant compound after seven days aging at these temperatures and its much lower percentage decrease in weight and volume during aging at 250°F. The hardness of the experimental sealant compound increased after 24 hours aging at 250°F, but did not change appreciably during the remainder of the 168 hours aging. This was not the case with the commercial sealant and is attributed to a "tightening" of the cure rather than the loss of polymer.

The experimental sealant showed exceptionally good resistance to extraction in SR-6 fuel after 72 hours continuous refluxing and was one-sixth that of the commercial sealant compound; the percentage total extractable material did not appreciably increase after 24 hours extraction. This indicated that a good cure was obtained with the experimental sealant material.

The peel adhesive bond strength of the experimental sealant to aluminum and adhesion characteristics both before and after aging the base compound and curing agent for eight days at 120°F, the resistance to salt water and hydrocarbons at 100°F and the working life of the experimental sealant were also studied.

The experimental sealant compound was of a "buttery" consistency and did not "run down" when applied to a vertical surface. It was of slightly lower density than the commercial sealant compound and was sufficiently transparent for visual inspection during and after application and cure. This property should make it a marked improvement over the present commercial paste sealant compounds for obtaining better sealing, easier detection of leaks and lower maintenance costs.

FIGURE I

SHORE A HARDNESS VERSUS "THIOKOL" LIQUID POLYMER/EPOXY RESIN RATIO

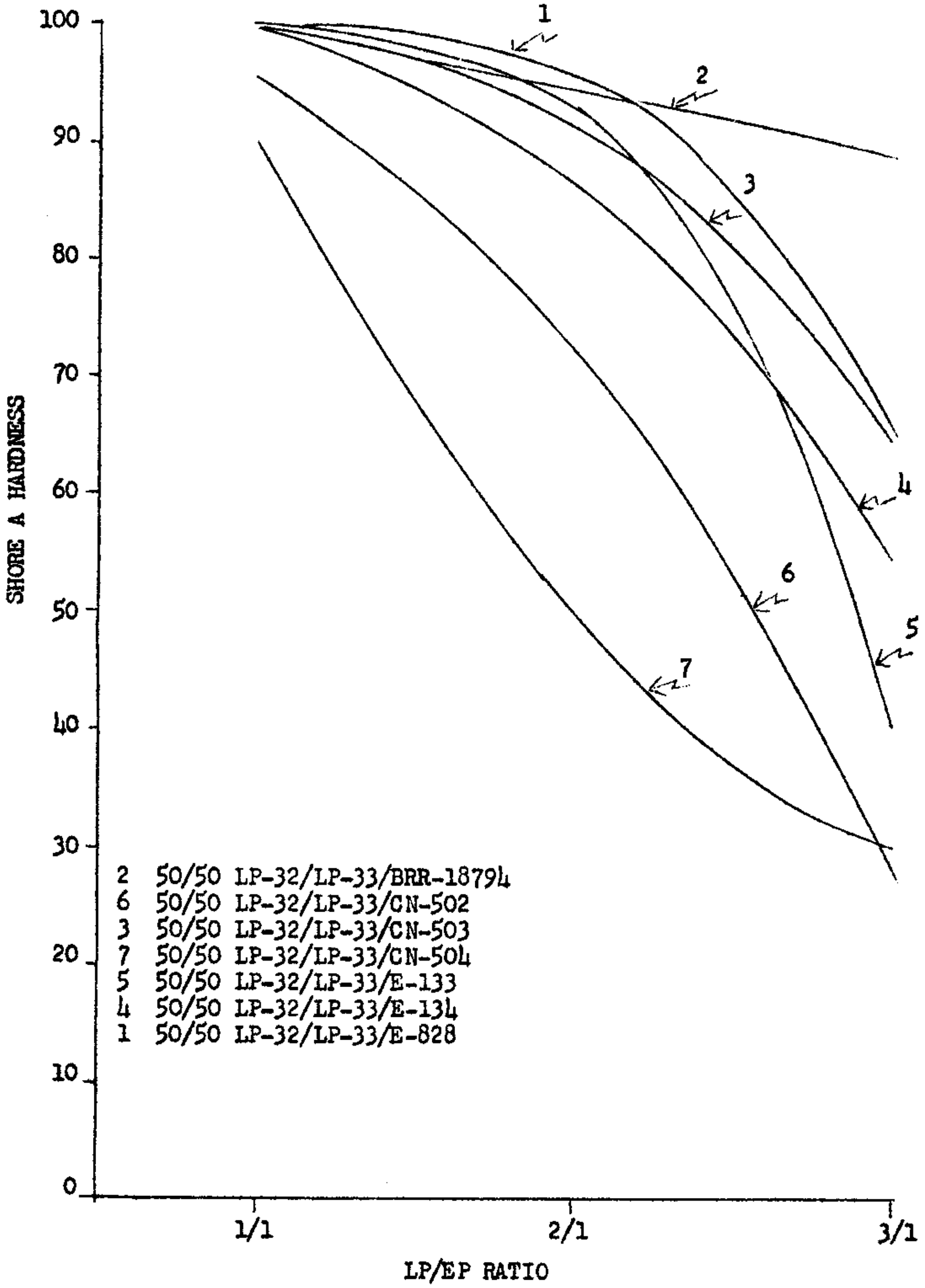
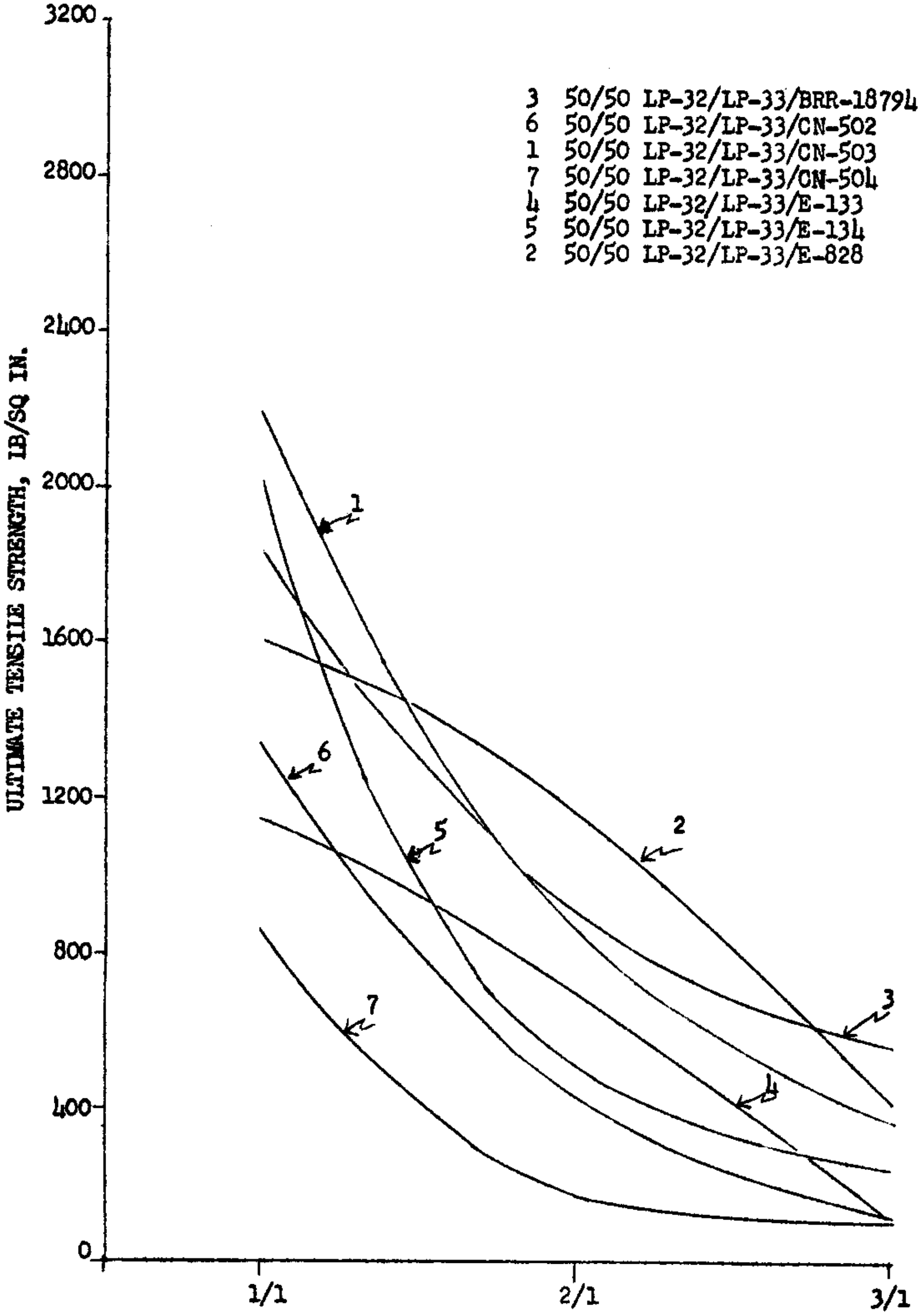


FIGURE 2

ULTIMATE TENSILE STRENGTH VERSUS "THIOKOL" LIQUID POLYMER/EPOXY RESIN RATIO



LP/EP RATIO

FIGURE 3

ULTIMATE ELONGATION VERSUS "THIOKOL" LIQUID POLYMER/EPOXY RESIN RATIO

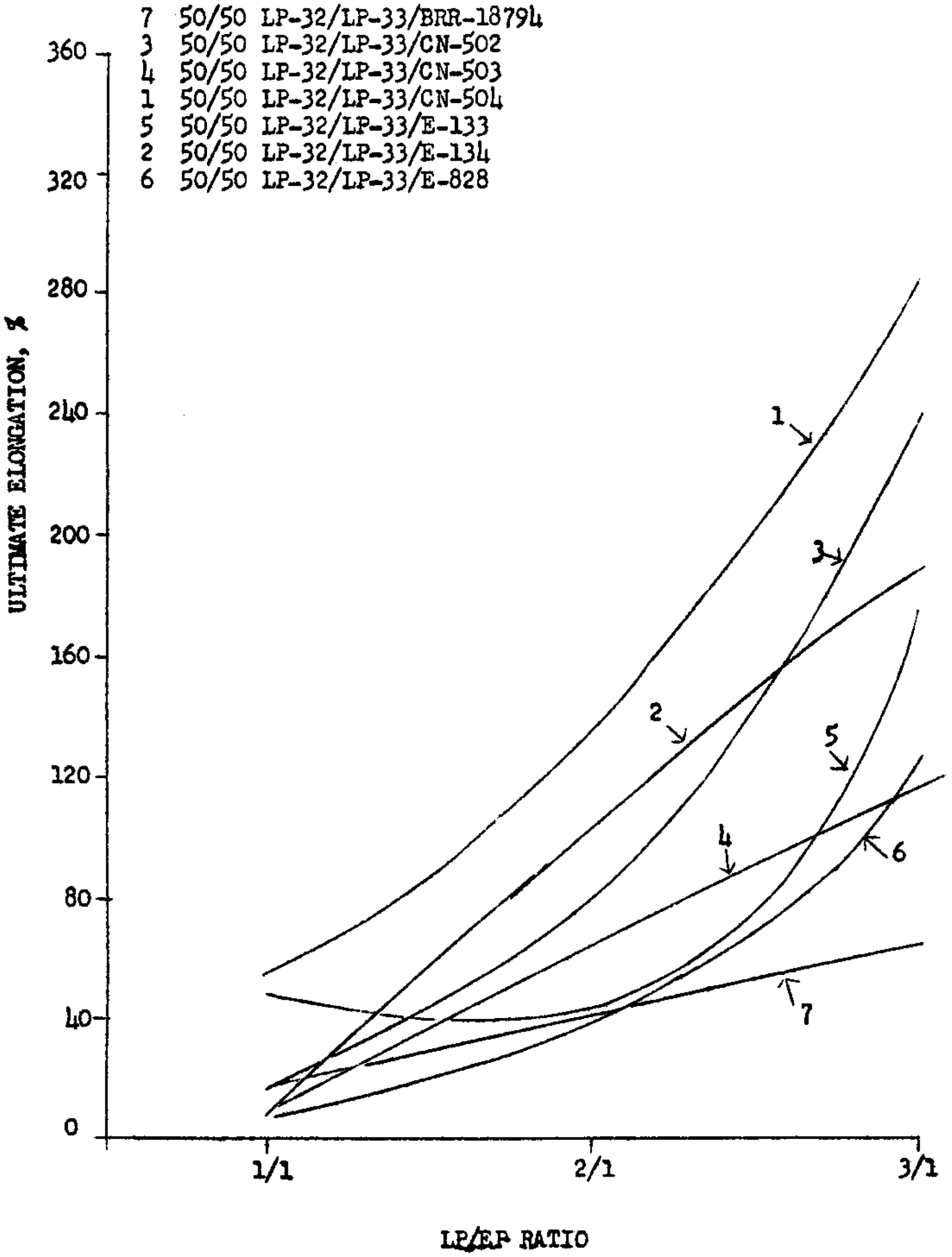


FIGURE 4

TEAR VERSUS "THIOKOL" LIQUID POLYMER/EPOXY RESIN RATIO

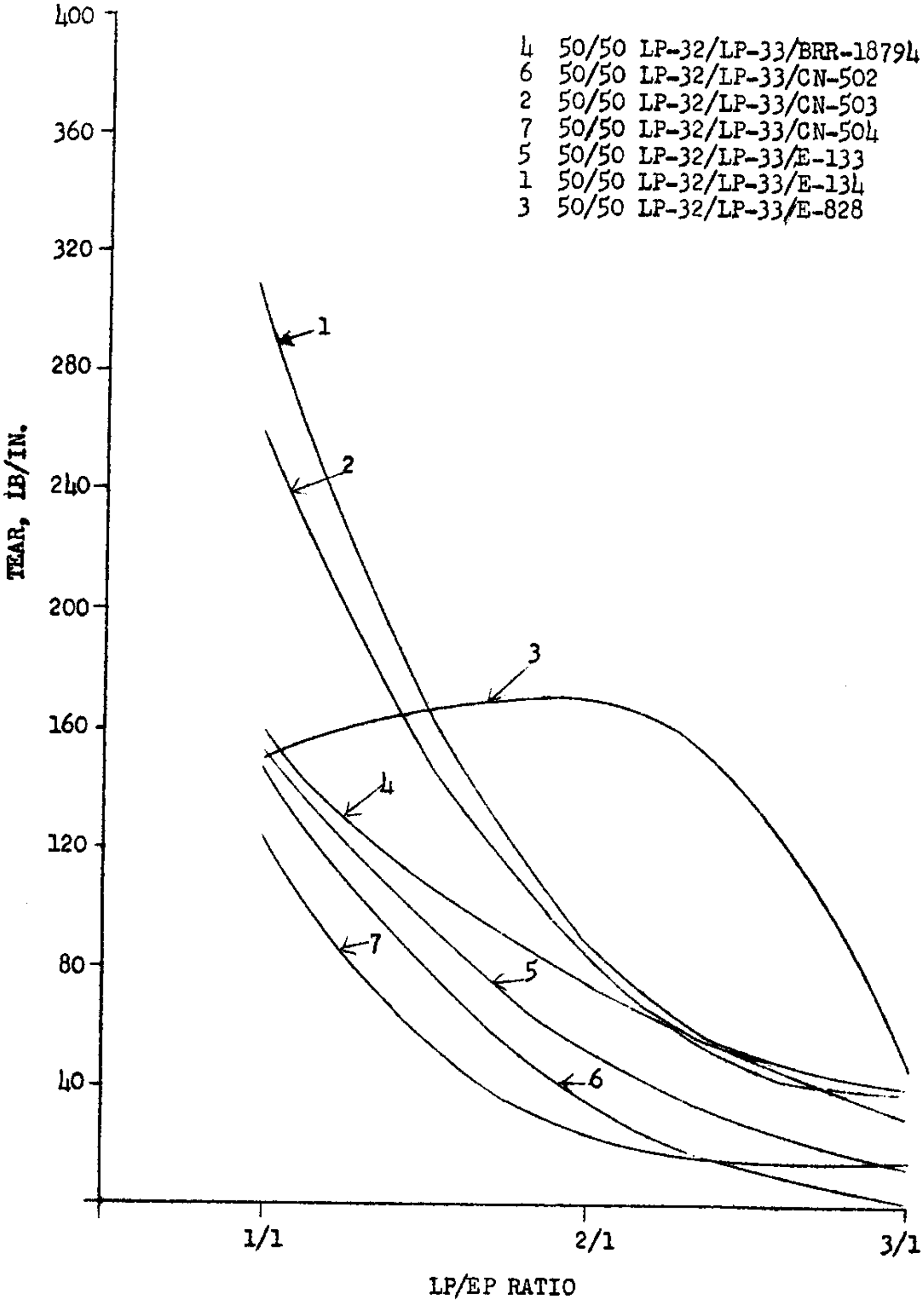


TABLE 52

PROPERTIES OF EXPERIMENTAL "THIOKOL" LIQUID POLYMER/EPOXY RESIN INTEGRAL FUEL CELL SEALANT COMPOUNDS

Compound No.	LP-2 Base Commercial Sealant	B47569-3		B47569-4		B47569-6		B47569-7		B47569-8	
		Part A	Part B	Part A	Part B	Part A	Part B	Part A	Part B	Part A	Part B
50/50 LP-32/LP-33	--	100	--	--	--	--	--	--	--	--	--
LP-33	--	--	--	100	--	--	--	100	--	100	--
High viscosity liquid polymer (1600 poises)[a]	--	--	--	--	--	100	--	--	--	--	--
Liquid polymer epoxy ratio	--	2/1		1.5/1		3.5/1		1/1		1.5/1	
CN-502	--	--	50	--	--	--	--	--	--	--	--
CN-503	--	--	--	--	66.6	--	--	--	--	--	--
CN-504	--	--	--	--	--	--	28.75	--	--	--	--
Epon 828	--	--	--	--	--	--	--	--	--	--	66.6
E-134	--	--	--	--	--	--	--	--	100	--	--
Aerosil[b]	--	--	--	5	5	--	--	5.0	--	5	5
DMP-30[c]	--	5	--	6.66	--	4.32	--	10	--	6.66	--
Cure at Room Conditions											
Days	1[d]	5		6		5	3 hr. @ 158°F	2		2	
Physical Properties											
	e / f	e / f		e / f		e / f		e / f		e / f	
Shore A hardness	58/69	35/80		85/88		87/73		95/97		95/70	
100% Modulus, lb/sq in.	200/512	195/--		--/--		500/375		--/--		--/--	
Tensile strength, lb/sq in.	425/600	200/565		825/1125		510/450		1260/2200		1050/250	
Elongation, %	220/130	440/110		80/50		110/130		85/30		20/80	
Tear strength, lb/in.	30/35	35/75		95/86		70/74		240/250		270/25	

(Table continued and footnotes on next page.)

TABLE 52 (Contd.)

PROPERTIES OF EXPERIMENTAL "THIOKOL" LIQUID POLYMER/EPOXY RESIN INTEGRAL FUEL CELL SEALANT COMPOUNDS

Compound No.	Specification Limits	LP-2 Base Commercial Sealant	B47569-3	B47569-4	B47569-6	B47569-7	B47569-8
Military Specification MIL-S-5043(Aer) Test Data							
Working life, hr.	—	3	2.8	0.6	—	0.5	0.75
Adhesion, lb/in. after 48 hr. in Type III fuel	10 min.	30[g]	4	8.5	11[h]	12.5[h]	10.5[h]
Resistance to heat	No hardening, blistering, cracking or loss of adhesion	Some increase in hardness	Hardness increased, otherwise O.K.	O.K. (passed)	Hardness increased, otherwise O.K.	O.K. (passed)	Hardness decreased, otherwise O.K.
Resistance to salt water and hydrocarbons	No softening, blistering or loss of adhesion. No corrosion of aluminum	Some increase in hardness	Softened somewhat, poor adhesion, otherwise O.K.	Sl. softening, some loss of adhesion, otherwise O.K.	Softened, loss of adhesion, otherwise O.K.	Softened, loss of adhesion	Softened, otherwise O.K.
Low temperature flexibility							
Passed, –°F	70 minimum	Yes	—	—	60	—	—
Failed, –° F	—	—	50	50	70 (Should pass)	50	50
Volume change, %							
After 24 hr. in Type III fuel	20 max.	5(passed)	4(passed)	3.5(passed)	8.5(passed)	3(passed)	1.5(passed)
Dried at 80°F for 48 hr.	-5 max.	1 "	1 "	1 "	1.5 "	1 "	1 "
After 24 hr. in Type I fuel	20 max.	1 "	-1 "	2 "	-1 "	1 "	0 "
Test fluid contamination							
Non-volatile extractible material, mg/100 ml.	60 max.	32(passed)	18(passed)	6(passed)	25(passed)	7(passed)	1 (passed)
Discoloration		V. slight (passed)	None (passed)	None (passed)	None (passed)	None (passed)	None (passed)

(Table continued and footnotes on next page.)

TABLE 52 (Contd.)

[a] A polysulfide crude containing 98 mole % formal and 2 mole % trichloropropane crosslinking agent and some thiol-terminals redistributed with LP-33 to give a high viscosity liquid polymer (1600 poises).

[b] Fine particle size silicon dioxide filler.

[c] 2,4, 6-tri(dimethylaminoethyl) phenol.

[d] Test specimens cut from sheets prepared by milling the compound, after the 24 hour cure, on a cold rubber mill and then molding at 300°F for 10 min.

[e] Not heat aged.

[f] Heat aged 72 hours at 212°F.

[g] Cohesive failure.

[h] Fabric pulled away from stock.

TABLE 53

PROPERTIES OF EXPERIMENTAL "THIOKOL" LP-2 BASE TRANSLUCENT SEALANT COMPOUNDS

Compound No.	LP-2 Base Commercial Sealant Compound	Experimental LP-2 Translucent Sealant Compound (B50155-2)
Commercial sealant	100	--
LP-2	--	100
Aerosil	--	15
25% Solution maleic anhydride in cyclohexanone	--	2
DMP-30	--	1
70% Cumene hydroperoxide	--	6
Commercial sealant curing agent	12	--

Processing Data (Cured 4 hr. @ 77°F)

Working life, hr.	1.7	1.25
Press out, min. @ °F	10/300	10/300
Density, g./cc.	1.62	1.56

Vulcanizate Properties (Cured 24 hr. @ 77°F)

	Unaged	Aged 168 hr. @ 212°F	Aged 168 hr. @ 250°F	Unaged	Aged 168 hr. @ 212°F	Aged 168 hr. @ 250°F
Shore A hardness	51/57[a]	62	70	31/36[a]	50	49
100% Modulus, lb/sq in.	170/230	360	--	100/50	100	75
300% Modulus, lb/sq in.	--/--	--	--	120/150	400	--
Tensile strength, lb/sq in.	375/310	360	290	125/250	415	275
Elongation, %	260/125	100	60	500/550	300	230
Tear strength, lb/in.	64/64	65	35	30/35	60	40
Adhesion, lb/in.[b]						
After 24 hr. cure	17	cohesive failure/[a]--		15/18	cohesive failure	
After 48 hr. in SR-6	33	" " /--		12/17	"	"
Extraction in SR-6, Total %[c]						
After 24 hr.		16			3	
After 48 hr.		21			4	
After 72 hr.		31			5	

(Table continued and footnotes on next page.)

TABLE 53 (Contd.)

PROPERTIES OF EXPERIMENTAL "THIOKOL" LP-2 BASE TRANSLUCENT SEALANT COMPOUNDS

Compound No.	LP-2 Base Commercial Sealant Compound	Experimental LP-2 Translucent Sealant Compound (B50155-2)
Heat aging characteristics at 250°F		
Decrease in weight, %		
After 24 hr.	5	5
After 72 hr.	10.5	5
After 168 hr.	19	6
Decrease in volume, %		
After 24 hr.	6	6
After 72 hr.	12	6
After 168 hr.	23	7
Shore A hardness		
Unaged	57	36
After 24 hr.	65	46
After 72 hr.	70	47
After 168 hr.	78	49
Resistance to salt water and SR-6, 7 days at 100°F	Some increase in hardness Excellent adhesion No blistering or corrosion	No change in hardness Excellent adhesion No blistering or corrosion
Resistance to salt water, and JP-4, 7 days at 100°F	" " "	" " "

NOTE: The base compound and curing agent were thoroughly mixed with a spatula on a glass plate.

a Test sheets cast and cured 24 hr. at 77°F plus 5 hr. at 158°F.
b Test panels cleaned with VM & P Naphtha.
c Soxhlet type extraction.

APPENDIX A

POLYMER PREPARATION PROCEDURES

I. STANDARD REACTION PROCEDURE FOR POLYMER PREPARATION

Reaction

$$ClRCl + Na_2S_x \longrightarrow (-RS_x-)_n + 2NaCl$$

Apparatus

5-Liter, 3-neck round bottom flask fitted with stirrer, reflux condenser, dropping funnel and thermometer.

Procedure

Place 4.8 moles of sodium polysulfide solution of the required rank (about 2 molar concentration) in the flask. Heat with a Bunsen burner and stir. Add, while stirring and heating, 20 ml. of 5% Nekal BX solution and 17 ml. of 50% sodium hydroxide. Then add 117 ml. of 25% magnesium chloride hexahydrate dropwise from the addition funnel.

Continue heating until the temperature of the reaction mixture reaches 200°F. At this point, remove the burner and start adding slowly 4 moles of halide (mixed in the proper molar ratio to give the desired copolymer). The rate of addition should be such that the entire amount will be added over the course of one hour. Temperature of the reaction is controlled partly by the rate of halide addition. If the temperature rises above 200°F, cool the flask by playing a stream of cold water against it.

After the halide has been added, heat the reaction mixture to 212°F and continue heating for one hour. At the end of this time, dilute the reaction mixture with cold water and fill the flask. Continue agitation for a minute or two then stop the stirrer. When the latex has settled, siphon off the supernatant liquid and stir and dilute again, this time with hot water. If the latex is not to be toughened, continue washing in this manner until the supernatant liquid shows no discoloration of lead acetate test paper.

If the latex is to be toughened, stir and heat the latex after removal of the second wash liquid. When the temperature reaches 210°F, add 1 mole of sodium polysulfide (rank 2.25), and maintain the temperature at 200°F for 30 minutes. At the end of this time, dilute the reaction mixture with cold water and wash the latex clean as described above.

When the latex is free of sulfide, remove as much of the supernatant liquid as possible, transfer the latex to a jar and determine the total solids.

Variations

Reactions as large as 5 moles and as small as 2 moles may be conducted in 5-liter flasks. Reactions of one mole and smaller are run in 1-liter, 3-neck flasks. The halides are added over a shorter period of time for the smaller reactions.

Washing time may be greatly shortened by transferring the latex to a large battery jar and using large volumes of wash water.

Possible variations include using dispersing agents other than Nekal BX and condensation nuclei other than magnesium hydroxide.

In cases where the halide is too volatile to permit reaction at 200°F, the halide is added at a temperature that will just cause gentle refluxing. The temperature is raised to 212°F at the end of the halide addition, as stated previously.

If steam distillation is necessary to remove volatile side-reaction products, it is generally done after the latex has been washed twice, although it may be done at any time after the reaction is complete.

II. LIQUID POLYMER PREPARATION

The polymers and copolymers are converted to liquid polymers and copolymers with thiol terminals by reducing some of the disulfide units in the latex to thiols with sodium sulfhydrate and sodium sulfite. The following equation represents the over-all reaction, although it does not indicate the mechanism:

$$RSSR + NaHS + Na_2SO_3 \longrightarrow RSH + NaS{-}R{-} + Na_2S_2O_3$$

The NaS - R - is converted to H-S-R upon acidification.

Procedure

Put the required amount of latex with a total solids of approximately 30% in a beaker. Heat to 180°F with continuous stirring. When this temperature is reached, add sodium sulfhydrate and sodium sulfite (1.1 moles/mole of latex). The amount of sulfhydrate to use is estimated from the durometer reading on a dried filter cake of the latex and from consideration of the inherent properties of the polymer.

After the splitting salts have been added, continue heating at 180°F for 30 minutes. At the end of this time, dilute the latex with cold tap water. Wash the split latex by decantation with hot water until a one-mole sample of the supernatant liquor fails to decolorize a few drops of dilute (light amber color) iodine-potassium iodide solution.

Decant the mixture to half volume and adjust it to pH of 4 with a 50% solution of glacial acetic acid. Dilute with cold water and let the solids settle. Wash the mixture with hot water till a pH of 6 is reached. Pour off all the water and dry the split latex in the oven at 158°F.

III. PREPARATION OF COPOLYMERS BY REDISTRIBUTION

Calculate the amount of each latex needed to yield the desired copolymer. Mix the latices in a beaker and heat with stirring to 180°F. Add sodium polysulfide (rank 2-2.25), 0.1 mole per mole of copolymer and maintain the temperature at 180 F for one-half hour. Dilute the latex with cold tap water, allow it to settle and draw off the supernatant liquid. Continue washing in this manner with hot tap water or until the supernatant liquid shows no discoloration of lead acetate test paper. Draw off the final wash liquid, put the latex in a jar, and determine the total solids.

If it is desired to toughen the polymer during redistribution, use 0.25 mole of sodium polysulfide instead of 0.1 mole per mole of polymer.

IV. PREPARATION OF CRUDE RUBBER BY SPLITTING

Procedure

Put the required amount of latex in a beaker. Heat to 180°F with continuous stirring. When this temperature is reached, add sodium sulfhydrate and sodium sulfite, the latter 11 times the molar quantity of the former. The amount of sulfhydrate to use is estimated from the durometer reading on a dried filter cake of the latex, based on previous experience with the type of polymer being split.

After the splitting salts have been added, continue heating at 180°F for 30 minutes. At the end of this time, dilute the latex with cold tap water. Wash the latex by decantation with cold tap water until a 1 ml. sample (approx.) of the supernatant liquor fails to decolorize an approximately equal volume of dilute (light amber colored) iodine-potassium iodide solution.

When the latex is sulfite-free, as shown by the iodine test, coagulate a small amount of latex by adding a soap (sodium stearate) dispersion and a little 50% acetic acid. If the trial coagulum appears too soft, it is sometimes advantageous to let the split latex stand overnight or longer before coagulating. If the trial coagulum seems to be much too tough, the splitting procedure may have to be repeated on all or part of the latex.

Coagulate the split latex by adding a water dispersion of soap (sodium stearate) containing an amount of soap equal to 1% of the polymer weight and by adding slowly, with stirring, sufficient 50% acetic acid to bring the pH to 4.0. Wash the coagulum two or three times by decantation with hot water to remove the acetic acid. The soap dispersion can be prepared by making a stiff paste of the finely powdered soap in cold water and diluting it rapidly with boiling water. If the coagulum does not form a clump, allow it to settle. In some cases it may be necessary to collect the coagulum on a screen or filter.

Squeeze the coagulum as dry as possible by hand, and mill it on a warm rubber mill until it is dry. Remove from the mill as a sheet.

V. POLYMER STRIPPING PROCEDURES

Stripping with Caustic

While stirring the latex, heat it to 170 F. At this point sodium hydroxide (50% solution) is added, generally at the ratio of 1 mole of sodium hydroxide per mole (segment) of polymer. Maintain the temperature at 170°F for 1 hour. At the end of this time dilute the latex with cold water, allow it to settle, and decant the supernatant liquid. Follow with another wash in the same manner with hot water. A monosulfide strip can follow at this point, or the washing can be repeated until the latex is clean (free of sulfide by the lead acetate test).

Stripping with Sodium monosulfide

This procedure generally follows a caustic strip. Heat the latex to 180°F, and add sodium monosulfide solution (about 2 molar), generally at the ratio of 0.1 mole per mole of polymer segment. Maintain the latex at 180°F for 30 minutes, then dilute with cold water and finally wash by decantation until it is sulfide-free.

Stripping with Sodium Sulfite

Heat the latex to 180°F. Add anhydrous sodium sulfite, 1 mole per mole of sulfur to be stripped and maintain the temperature at 180°F for 30 minutes. At the end of this time, dilute the latex with cold water, allow it to settle and decant. Repeat the washing until a few drops of clear supernatant liquor fails to decolorize about 0.5 ml. of iodine-potassium iodide solution (light amber colored).

APPENDIX B

EVALUATION PROCEDURES

I. COMPOUNDING AND PROCESSING METHODS

A. Experimental Polymers

Most of the experimental polymers were compounded according to the following standard evaluation recipe:

Ingredients	Parts
Experimental polymer	100
Zinc sulfide (ZS-800)	50
Lead stearate	1.4
Lead peroxide	7.5

The compounds were processed by giving them three passes on the paint mill. They were then cured at 77° to 80°F and a relative humidity of 55 to 60% for 24 hours. After curing, the stocks were sheeted on a cold two-roll mill and then molded at 287°F for 10 minutes.

B. Liquid Polysulfide Polymer/Epoxy Resin Compositions

1. General Compounding Studies

All clear sealant formulations were prepared by thoroughly mixing the "Thiokol" liquid polymer with the epoxide resin, heating at 212°F for one-half hour to expel air bubbles, cooling to room temperature and then carefully incorporating the amine catalyst. The liquid was then cast into a mold and cured at room temperature. These sheets were not tested until they attained constant hardness. The "Thiokol" liquid polymers were filtered before use and the 50/50 mixture of LP-32/LP-33 was redistributed by heating for 17 hours at 180°F.

2. Special Studies

a. Adhesion Additive Studies

(1) Maleic anhydride - The maleic anhydride-cyclohexanone solution and DMP-30 were incorporated into the liquid polymer/epoxy resin solution after heating it at 212°F for 30 minutes and then cooling to room temperature.

(2) Beetle 216-8 polymer solution - Same procedure as described in (1) except that the Beetle polymer solution was added to the liquid polymer/epoxy resin solution before heating.

b. Regulation and Stabilization of Cure

(1) Benzyl mercaptan and allyl glycidyl ether studies - Same procedure as outlined in (a-1).

APPENDIX B (Contd.)

(2) Phenolic resin BR-6741 and CTL-91-LD studies - The phenolic, liquid polysulfide and epoxy resins were thoroughly mixed together at room temperature and then the DMP-30 catalyst was incorporated.

(3) Styphen 1 study - Same procedure as outlined in (a-2).

(4) Co-curing agent studies with cumene hydroperoxide and trinitrobenzene - The trinitrobenzene, accelerator B and cumene hydroperoxide were added to the liquid polymer/epoxy resin solution after incorporation of the DMP-30 catalyst.

c. Investigation of Polysulfide Liquid Polymer/Polyester and Liquid Polysulfide Polymer/Liquid Polyamide Systems

(1) Vibrin X-1047 and PDL-7-669 polyester studies - The polyester, liquid polysulfide and epoxy resins were thoroughly mixed together at room temperature and then the DMP-30 catalyst was incorporated.

(2) Investigation of polyamide polymers 100-S and 110. The polysulfide and epoxy resins were mixed together and then the polyamide polymer was added. This mixture was then heated at 212°F to reduce the viscosity of the polyamide polymer and effect dispersion.

d. Study with WD-2 Latex Polymer

WD-2 polymer was separated from the latex by filtration, washed with methyl alcohol and dried. It was then dissolved in the epoxy polymer by heating at 212°F. After cooling to room temperature, the composition was mixed with the polysulfide liquid polymer, heated at 212°F for 30 minutes to expel entrapped air and then cooled to room temperature before incorporating the DMP-30.

e. Investigation of High Viscosity Liquid Polysulfide Polymer/Epoxy Resin Compositions

Five hundred grams of WD-2 type crude containing some thiol terminals was redistributed with 167 gms. of LP-33 by milling and then heating at 212°F for 18 hours. The viscosity of the resultant liquid polymer was 1600 poises.

C. Experimental Integral Fuel Cell Sealant Compounds

All experimental liquid polysulfide polymer base sealant compositions were compounded in two parts; namely, the base compound containing the polymer, filler, adhesion additive and cure regulator additives in one part and the curing agent in the other part. The experimental liquid polymer/epoxy resin sealant compositions were also prepared in two-package mixes. Part A contained the polysulfide liquid polymer and amine catalyst and Part B consisted of the liquid epoxy polymer. In those compositions where Aerosil was used as a "bodying" agent, it was paint milled into one or both parts depending on the viscosity of the component. In all cases, the two component parts were mixed together thoroughly with a spatula on a glass plate for application.

II. EVALUATION METHODS

With the exception of the compression set, adhesion and viscosity determinations, the following tests were conducted on samples cut from 0.75 x 4 x 6 inch molded or cast sheets.

A. Hardness and Stress-Strain Relationship at Room Temperature

Hardness was determined by means of the Shore A durometer at 77°to 80°F. Unless specified otherwise all readings were taken after a 5-second time interval.

The stress-strain relationship, ultimate tensile strength, and elongation were obtained in accordance with the tentative method of test for "Tension Testing of Vulcanized Rubber" ASTM Designation: D412-49T.

B. Tear Strength

Tear strength was determined in accordance with ASTM Designation: D624-48, Die C test specimen.

C. Compression Set

This property was determined on molded plugs at 158° and -40°F in conformance with Method B, ASTM Designation: D395-49T, except that the specimens were subjected to a compression of 25% and exposed to the test temperature for one hour.

The jigs were conditioned for one hour at the test temperature before the samples were tested. Measurements were taken 30 minutes after removal of the specimens from the jig. In the elevated temperature tests, the plugs were cooled at room temperature after removal from the jigs, whereas the plugs tested at the low-temperatures were maintained at the test temperature after removal from the jigs.

D. Torsional Stiffness at Low Temperatures

The low temperature behavior of the compounds was studied with the torsional tester, which is a modification of the tester specified in ASTM Designation: D1043-49T for "Stiffness Properties of Nonrigid Plastics as a Function of Temperature by Means of a Torsional Test". The absolute shear modulus in pounds per square inch at various temperatures was calculated from the degree of twist of the sample. These data were then plotted and the temperatures at which the specimen gave absolute torsional modulus values of 5000, 10,000 and 20,000 lb/sq in. were read from the curve. To determine the relative stiffening of the samples, the torsional modulus obtained at each temperature was divided by that at 64°F. These data were also plotted and the temperatures at which the shear modulus at 64°F (G_{rt}) was increased five (T_5), ten (T_{10}), fifty (T_{50}) and one hundred (T_{100}) times was determined from the graph.

Since the absolute torsional modulus gives a measure of the actual stiffness of the sample rather than the comparative stiffness, emphasis was placed on the absolute values in determining the low temperature stiffness of the compounds.

E. Tension-Retraction

Basically, the tension-retraction test is an adaptation of the T-50 test for determining the "Physical State of Cure of Vulcanized Rubber" ASTM Designation D599-40T. Two-inch T-5 specimens were stretched to 100% elongation on a rack and then immersed in an ethanol(Ponsolve) conditioning bath at -95°F for 10 minutes. The rack was then transferred to the test bath at -95°F and the tension on the specimens was released. After the bath was adjusted to a constant warm-up rate of 2°F per minute, readings were taken every 2.5 minutes as the samples retracted. Temperature versus percentage retraction was plotted and the temperature at which the specimens retracted 10 (TR10), 30 (TR30), 50 (TR50), and 70% (TR70) of the original elongation were determined from the graph. A large temperature differential between the TR10 and TR70 values indicates a low rate of retraction.

F. Solvent Resistance

This test was conducted according to ASTM Designation: D471-49T, Method D, employing SR-6, SR-10 and JP-3A fuels and water. The samples were measured for length after one-day and one-month immersion periods. Percentage volume change was calculated from the increase or decrease in length of the sample.

G. Change in Weight, Volume and Hardness During Heat Aging

The weight, volume and Shore A durometer hardness were determined on 0.075 x 1.5 x 3 inches both before and after various heat aging periods and temperatures in a Fisher forced circulating air oven. The weight of the specimen was determined in air to 0.01 gram and the volume was measured by the loss of buoyancy of the sample in distilled water at room temperature. The percentage weight loss (compound basis) and decrease in volume were calculated.

H. Adhesion

The adhesion characteristics of some of the experimental polymers and LP-2 additives to 24 ST Alclad aluminum were evaluated according to qualification test procedure 4.3.2.3 in specification Mil-S-5043A(Aer). However, this test was not very satisfactory for our use. Our experience has shown that when properly compounded with additives for imparting adhesion, the adhesive strength of the experimental copolymers to aluminum was higher than the cohesive strength and/or that of the cotton fabric. Also, this test requires too much polymer. Therefore, the test was replaced with a "spot" test in which a small quantity of the experimental compound was spread in a layer approximately 0.125 inch thick on 24 ST Alclad aluminum test panel cleaned with VM & P naphtha. The adhesion properties were measured by visual observation and by scraping with a knife after the 24 hour cure at 77° to 80°F and 55 to 60% relative humidity and then after 48 hours of immersion in SR-6 fuel at 80°F. The polymers were rated for adhesion in comparison to the formal control as excellent, good and poor.

I. SR-6 Fuel Extraction

Uniform strips (4.0 grams) cut from the 0.075 inch cast sheets of the liquid polysulfide polymer/epoxy resin compositions were extracted in the apparatus described in Figure 1 in ASTM Designation: D494-46 for 24 hours with SR-6 fuel. The percentage of SR-6 extractables was determined from the amount of material present in the SR-6 fuel.

For the translucent LP-2 sealant compounds the samples were prepared by coating a clean, 0.032 x 1 x 2 inch aluminum panel with a 3/32 inch film of the sealant compound and cured. The coated panel was then cut into two 0.5 x 2 inch strips which were extracted as described above for 24, 48 and 72 hours with SR-6 fuel. The percentage of extractables was determined from the amount of material present in the SR-6 fuel.

J. Elevated Temperature Flexibility

The test specimens were prepared in accordance with qualification test No. 4.3.2.6 in Military Specification Mil-S-5043A(Aer). After the films developed constant hardness, they were aged 72 hours at 212°F and then subjected at 212°F to the bend test described in qualification test No. 4.3.2.6 in Mil-S-5043A(Aer).

K. Strength and Extensibility at Elevated Temperature

Strips approximately 0.125 x 0.5 x 2 inch were pulled manually while at the elevated temperature after the prescribed aging period.

L. Viscosity

All liquid polymers were tested for viscosity before compounding. Measurements were made with the Brookfield viscometer after conditioning the samples for 3 hours at 80°F.

M. Military Specification, Mil-S-5043A(Aer), Requirement Tests Employed For Experimental Sealant Compounds

1. Working and cure time. These properties were determined on 50 g. samples of the liquid polymer/epoxy resin compositions and on 100 g. samples of the experimental sealant compounds.

2. Adhesion, Test No. 4.3.2.3

3. Resistance to heat, Test No. 4.3.2.4

APPENDIX B (Contd.)

4. Resistance to salt water and hydrocarbons, Test No. 4.3.2.5

5. Low temperature flexibility. The test specimens were prepared and tested in accordance with Test No. 4.3.2.6 except that they were tested after conditioning at each test temperature for one hour.

6. Test fluid contamination.

   a. Non-volatile extractable material, Test No. 4.3.2.7.1 Because of limitations in the available test equipment the contaminated test fuel was evaporated at 150°C in lieu of 160° to 165°C as specified in the Air Jet Method of Specification VV-L-791

   b. Discoloration, Test No. 4.3.2.7.3

7. Volume Change, Test No. 4.3.2.9

APPENDIX C

GLOSSARY OF TERMS

1. "Thiokol" LP-2 - A polyfunctional liquid mercaptan with a molecular weight of approximately 4000 and 2.25 rank containing 98 mole % of formal and 2 mole % of trichloropropane cross-linking agent.
2. "Thiokol" LP-32 - A polyfunctional liquid mercaptan with a molecular weight of approximately 4000 and 2.25 rank containing 99.5 mole % of formal and 0.5 mole % of trichloropropane.
3. "Thiokol" LP-3 - A polyfunctional liquid mercaptan with an approximate molecular weight of 1000 and 2.25 rank containing 98 mole % of formal and 2 mole % of trichloropropane.
4. "Thiokol" LP-33 - A polyfunctional liquid mercaptan with an approximate molecular weight of 1000 and 2.25 rank containing 99.5 mole % of formal and 0.5 mole % of trichloropropane.
5. "Thiokol" LP-38 (ZL-174) - A polyfunctional liquid mercaptan with an approximate molecular weight of 500 containing 99.5 mole % of formal and 0.5 mole % of trichloropropane.
6. "Thiokol" WD-6 latex - A water dispersion of a polysulfide polymer of approximately 50% solids. The average particle size is about 6 microns.
7. "Thiokol" WD-2 latex polymer - A polysulfide crude polymer with a composition of 99.5 mole % formal and 0.5 mole % trichloropropane crosslinking agent.
8. "Thiokol" WD-2 type crude (SP-931) - A polysulfide crude polymer containing 99.5 mole % formal and 0.5 mole % trichloropropane split to a small amount of thiol terminals.
9. Accelerator C-11 - Lead peroxide, 100 parts; lead stearate, 18.7 parts; dibutyl phthalate, 50 parts.
10. Accelerator B - VYHH, 12%; sulfur, 40%; methyl ethyl ketone, 48%.
11. Saran F-120 - A polyvinylidene chloride polymer containing approximately 95% vinylidene chloride and 5% acrylonitrile with a viscosity of 1000 cps.
12. Paraplex 5B - A special maleic alkyd polyester manufactured by Rohm and Haas Company.
13. Paraplex G20 - A sebacic acid type polymer manufactured by Rohm and Haas Co.
14. BR-6741 - A phenolic resin manufactured by Bakelite Corporation.
15. BK-3962 - A 50% dispersion of an oil modified phenolic resin in aromatic hydrocarbons manufactured by Bakelite Corporation.

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16. Beetle 216-8 - A 60% solids solution of urea-formaldehyde polymer manufactured by American Cyanamid Company.

17. Styphen 1 - Tris(a-methyl benzyl) phenol manufactured by Dow Chemical Company.

18. DMP-30 - 2, 4, 6-tri(dimethylaminomethyl) phenol manufactured by Rohm and Haas Company.

19. Epoxy type resins:

    BRR-18794 - Bakelite Corporation
    C-8 polymer - Bakelite Corporation
    Epon E-828 - Shell Chemical Corporation
    Epon 1062 - Shell Chemical Corporation
    Araldite CN-502 - Ciba Company, Inc.
    Araldite CN-503 - Ciba Company, Inc.
    Araldite CN-504 - Ciba Company, Inc.
    Araldite E-133 - Ciba Company, Inc.
    Araldite E-134 - Ciba Company, Inc.
    Araldite SN-985 - Ciba Company, Inc.
    Epiphen XR-881 - Borden Chemical Company
    Epiphen XR-823 - Borden Chemical Company

20. Vibrin X-1047 - A liquid polyester containing triallyl cyanurate manufactured by Naugatuck Chemical Company.

21. PDL-7-669 - A polyester containing triallyl cyanurate manufactured by American Cyanamid Company.

22. CTL-91-LD - A 100% solids, heat converting "A" stage phenolic resin manufactured by Cincinnati Testing Laboratories.

23. Polyamide 100-S - Viscous polyamide polymers manufactured by General Mills, Inc.
    Polyamide 110 - Viscous polyamide polymers manufactured by General Mills, Inc.

24. Aerosil - Very fine particle size silicon dioxide filler with a refractive index of 1.55 manufactured by Cabot, Inc.

25. Ex. Silica 54-EP-88 - Very fine particle size silicon dioxide filler manufactured by Columbia-Southern Company.

26. SR-10 fuel - Diisobutylene
    SR-6 fuel - Diisobutylene containing 40% aromatics.

APPENDIX C (Contd.)

27. JP-3A Jet Fuel Specifications:

Gravity, °API	49.0
Reid vapor pressure, p.s.i.	4.0
Freezing point, °F	below 76
Accel. gum, mg./100 ml.	6.3
Residue air jet, mg./100 ml.	6.1
Copper strip corrosion	Pass.
Bromine no.	1.5
Aromatics, % vol.	25
Sulfur, % wt.	0.11
Mercaptan sulfur, % wt.	0.006
Neutralization no., mg. KOH/g. sample	0.08
A.S.T.M. distillation, °F	
IBP	100
5% Rec.	150
10% Rec.	179
20% Rec.	245
30% Rec.	283
40% Rec.	317
50% Rec.	339
60% Rec.	358
70% Rec.	382
80% Rec.	410
90% Rec.	461
E.P.	523
Recovery, %	98.0
Residue, %	1.0
Loss, %	1.0

28. Redistribution - Disulfide interchange.

29. Rank - The number represented by x in the polysulfide formula, Na_2S_x.

30. Splitting - Lowering of polymer molecular weight or chain length by reduction of disulfide bonds with sodium sulfhydrate.

31. Stripping - Removal of sulfur in excess of disulfide from polymer chains. Polymers can be stripped to rank 2.00.

32. Toughening - Increasing polymer molecular weight by removal of low molecular weight fragments.

33. Formal - bis(2-chloroethoxy) methane; bis(2-chloroethyl) formal.

34. Cake hardness - Shore A hardness of the latex polymer cake.

35. GMF-p-quinonedioxime/amine manufactured by Naugatuck Chemical, Division of U. S. Rubber Co.

36. HN-951 - Catalyst for epoxy resin manufactured by Ciba Company, Inc.