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NAS 9-11068 FINAL REPORT VOL. 1

DISCUSSION, FIGURES, AND REFERENCES

Production Development of Organic Nonflammable Spacecraft Potting, Encapsulating and Conformal Coating Compounds

S. L. Lieberman 31 Jan. 1974

NASA-CR-134234) PRODUCTION DEVELOPMENT OF N74-21159
ORGANIC NONFLAMMABLE SPACECRAFT POTTING,
ENCAPSULATING AND CONFORMAL COATING
(Furane Plastics, Inc., Los Angeles, Unclas
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Epocast

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furane plastics
INCORPORATED

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NOTICE

PRODUCTION DEVELOPMENT OF ORGANIC NONFLAMMABLE SPACECRAFT POTTING, ENCAPSULATING AND CONFORMAL COATING COMPOUNDS

CONTRACT NAS 9-11068

VOLUME I

DISCUSSION, FIGURES, AND REFERENCES

(31 Jan 1974)

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FORWARD

This research program was sponsored by the Structures & Mechanics Division of the Manned Spacecraft Center, National Aeronautics and Space Administration. Mr. H. F. Kline was the Project Monitor for NASA. The Program was conducted by Furane Plastics, Inc., under Contract No. NAS 9-11068. Mr. Sheldon L. Lieberman was the Program Manager, Principal Investigator, and author of this Final Report.

The author particularly wishes to acknowledge the test support provided by the entire staff, and, in particular, Messrs. D. Pippen and L.Schluter, of the White Sands Testing Facility of NASA-MSC, and to the testing staff of the Delsen Corporation. Appreciation is also extended to Mr. W. Dewar, of Furane, for his technical guidance and support. Finally, credit is given to R/D Industries for the design and development of the Upward Flammability Test Fixture Assembly, and the other special molds and tooling utilized for the Program.

ABSTRACT

The overall program objective was to carry out the production development of a flexible compound which not only functioned in a manned aerospace environment as an effective electrical insulation, but whose flammability characteristics were evidenced by rapid self-extinguishment and minimal thermal (pyrolysis) degradation.

Based upon extensive contacts with vendors, etc., a broad array of non-flammable polymeric specie, and additives generally noted to have flame retarding properties, were considered for pertinence to previously achieved NASA and NASA-contracted efforts in this direction.

The following polymeric matrices were examined: modified silicone and fluorosilicone RTV's, polyesters, epoxies, urethanes, and epoxy-urethanes. Additives were evaluated in conjunction with some of these polymers (i.e. opaque) in order to achieve survival in 10. psia, 30.% oxygen/70.% nitrogen environment, and air. Polyester, epoxy, urethane and, epoxy-urethanes were formulated without additives. These depended upon flame retarding elements on the polymers molecules themselves. Depending upon formulations, it was possible to achieve non-flammable products when tested in the specimen vertical/ignitor underneath mode. Optimization of formulations to obtain a suitable balance between the various properties and flammability resistance led to the final selection of a silicone RTV/additive-loaded compound which meets almost all program requirements. The very low valued properties found are within a realistic level of design toleration.

Complete formulation, processing, and test data is herein provided for this compound, EPOCAST 87517-A/B, and the other formulations prepared by the project. These other formulations included several potentially useful for this program, but which require further development, possibly even synthesis of necessary stable intermediaries.

Upon selection of the optimum compound, a 50. lb. batch was prepared, tested, and shipped to NASA Johnson Spacecraft Center.

This report contains details of those test methods and procedures utilized in the program but which are not either readily available, or are of some special nature. In addition, a description of the special flammability facility previously (Ref. 3-7) designed and then modified for this program is also presented.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont)

TABLE OF CONTENTS (cont)

TABLE OF CONTENTS (cont)

LIST OF TABLES

LIST OF TABLES (cont)

LIST OF TABLES (cont)

LIST OF TABLES (cont)

LIST OF TABLES (cont)

LIST OF ILLUSTRATIONS

LIST OF APPENDICES

SECTION 1

INTRODUCTION

Numerous aerospace applications exist for potting and encapsulating compounds, and conformal coatings. These include connectors, printed circuit boards, wire hardness terminations, circuit breakers, etc. These materials perform such diverse design and fabrication functions as electrical insulation, abrasion and handling protection, physical locating and orienting restraint, shock and vibration isolation, and atmospheric (particularly moisture and high humidity) and bacteriological protection. There are a broad range of conventional off-the-shelf flexible or semi-flexible materials (e.g. urethanes, polysulfides, epoxies, silicones, and polyesters) which could satisfactorily provide these functions and, in fact, are approved for the above usage under various applicable MIL and NASA specifications.

NASA requirements for Shuttle particularly highlight the present necessity of having non-flammable versions of these compounds and coatings. It is essential that these materials, regardless of exposure to cabin atmosphere, provide no fuel to any accidental flame initiation. Such criterion is difficult to accomplish with polymeric moieties, even when no hydrogen is present in the polymer.

Besides the flammability aspect, the material selection criteria for the manned space structures must also consider the critical problems of toxicity resulting from outgassing within the closed ecological system of manned space flight, and such functional criteria as electrical and mechanical performance.

SECTION 2

PROGRAM SCOPE

In addition to the overall Program scope definition established by the Statement of Work (Ref. Appendix A), for the production development of an optimized compound, other constraints were initially applied, some due to obvious technical needs in terms of probability of success, others to budget restrictions. These limitations included:

a. No new polymer synthesis routes would be investigated. "Simple" laboratory and/or shop polymer modifications were not considered as synthesis.

b. Only off-the-shelf materials would be utilized. This did not exclude research materials which had achieved or could achieve rapid pilot plant and/or production status.

c. Formulated compound(s) raw materials' costs were not to exceed approximately $100.00 per pound. Low cost was essential if wider usage by cost conscious hardware-oriented designers was to be accomplished.

d. Emphasis was placed upon the development of elastomeric and/or flexible formulations. This was due to the practical problem of a) achieving the mechanical stability necessary for compound/component bond integrity, and b) protecting the component from shock and vibration resulting from process/installation procedures, as well as operational environments.

It should be noted that the Statement of Work shown in Appendix A was not modified to reflect recent NASA design philosophy regarding Shuttle manned environment. Specifically, final flammability testing at the NASA White Sands Testing Facility and the contamination tests (e.g. outgassing and odor) were run during the final stages of the Program and were conducted in 14.7 psia air instead of the 30 psia oxygen/7.0 psia nitrogen specified in the Statement of Work.

SECTION 3

EXPERIMENT DEFINITION AND TASK SEQUENCE DEVELOPMENT

This program was a logical consequence of several NASA-sponsored (Refs. 3-1 and 3-2) programs, as well as pertinent in-house R & D at the NASA Manned Spacecraft Center. As such it:

1. represents second generation refinements of the above R & D efforts,
2. establishes the logical impetus to pilot plant production of optimized formulation(s),
3. delineates pertinent production variables, and
4. updates property data in accordance with the most recently specified application parameters and their attendant requirements.

Hence, the primary technical approach for this Program is basically derived from both prior art and the above contracted and NASA in-house activities.

A graphic description of the original Program Plan is shown in Figure 3-1. The completion of a specific phase signified a major "Go-No Go" decision point for each formulation. Subsequent modifications of the Program Plan were necessitated by pragmatic changes in testing schedules and NASA in-house testing costs. This resulted in the revised Program Plan shown in Figure 3-2. The phases noted reference the applicable sections of this report.

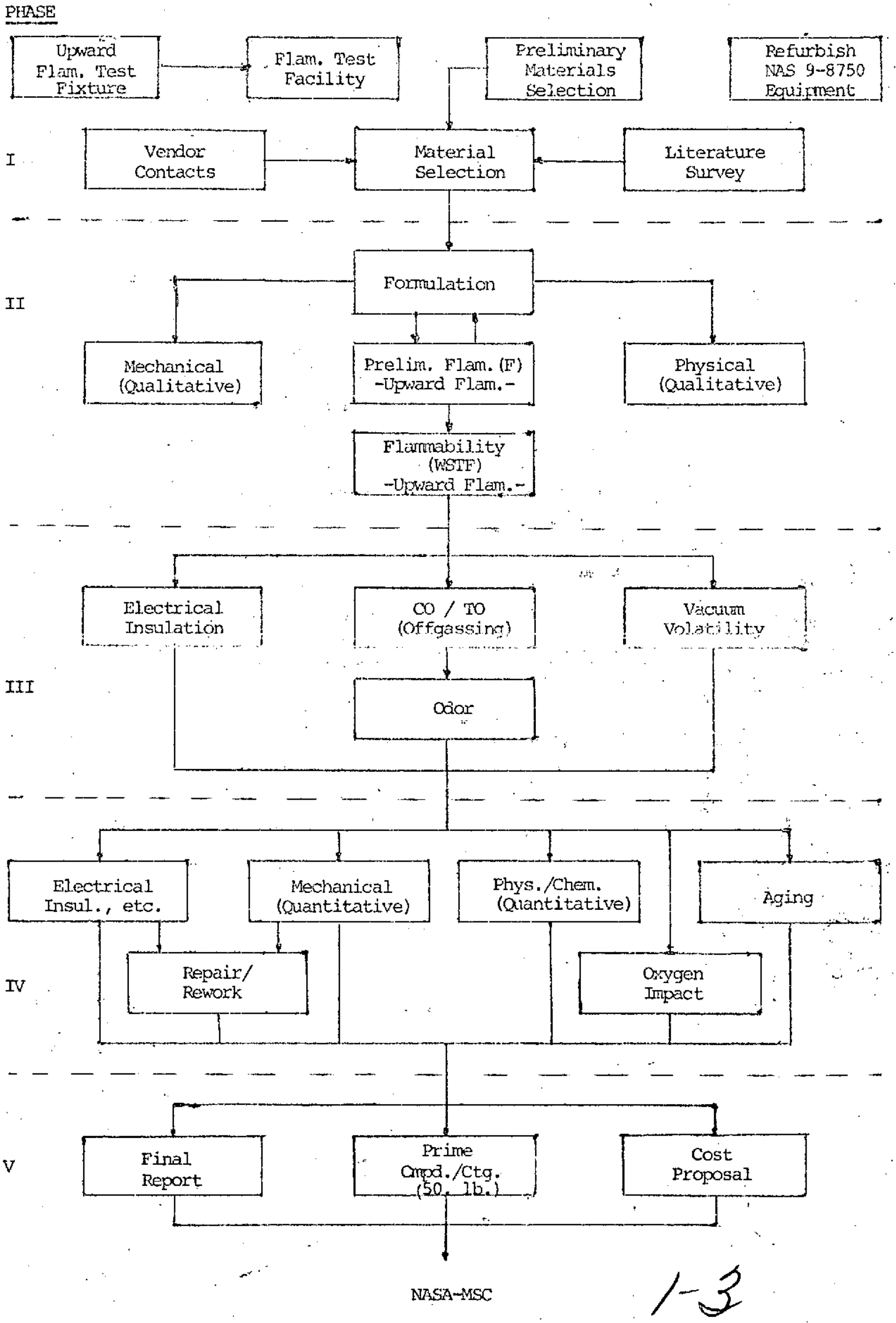
It is seen from Figure 3-2 that preliminary flammability screening tests and preliminary electrical insulation tests were conducted at Furane. Based upon these results, test panels of potentially useful formulations were then submitted to the NASA White Sands Test Facility. This arrangement permitted a high rate of testing in the NASA/ Furane Flammability Test Facility. However, since said Facility only permits testing of 5.0 in., maximum, test specimens, the final testing of the contractually specified (Ref. 3-3) 12.0 in. specimens (Ref. 3-4) was to be conducted by the NASA White Sands Testing Facility (WSTF). It should be noted that the 5.0 in. x 2.5 in specimens conforms to another NASA test document (Ref. 3-5). Subsequently, the 12.0 in. WSTF specimens were modified also to 5.0 in. (Ref. 3-6) and to 8.-9.0 in. for these tests, since, at the time of specimen submission, WSTF's routine mass test capability did not include the option for 12.0 in. test specimens. It now appears that their capabilities include such testing.

3.1 PHASE I: MATERIALS SELECTION

The materials to be developed within this Program had to perform, in addition to their fire protection activity, such diverse design and fabrication functions as

FIGURE 3-1

PROGRAM/TEST PLAN (1)



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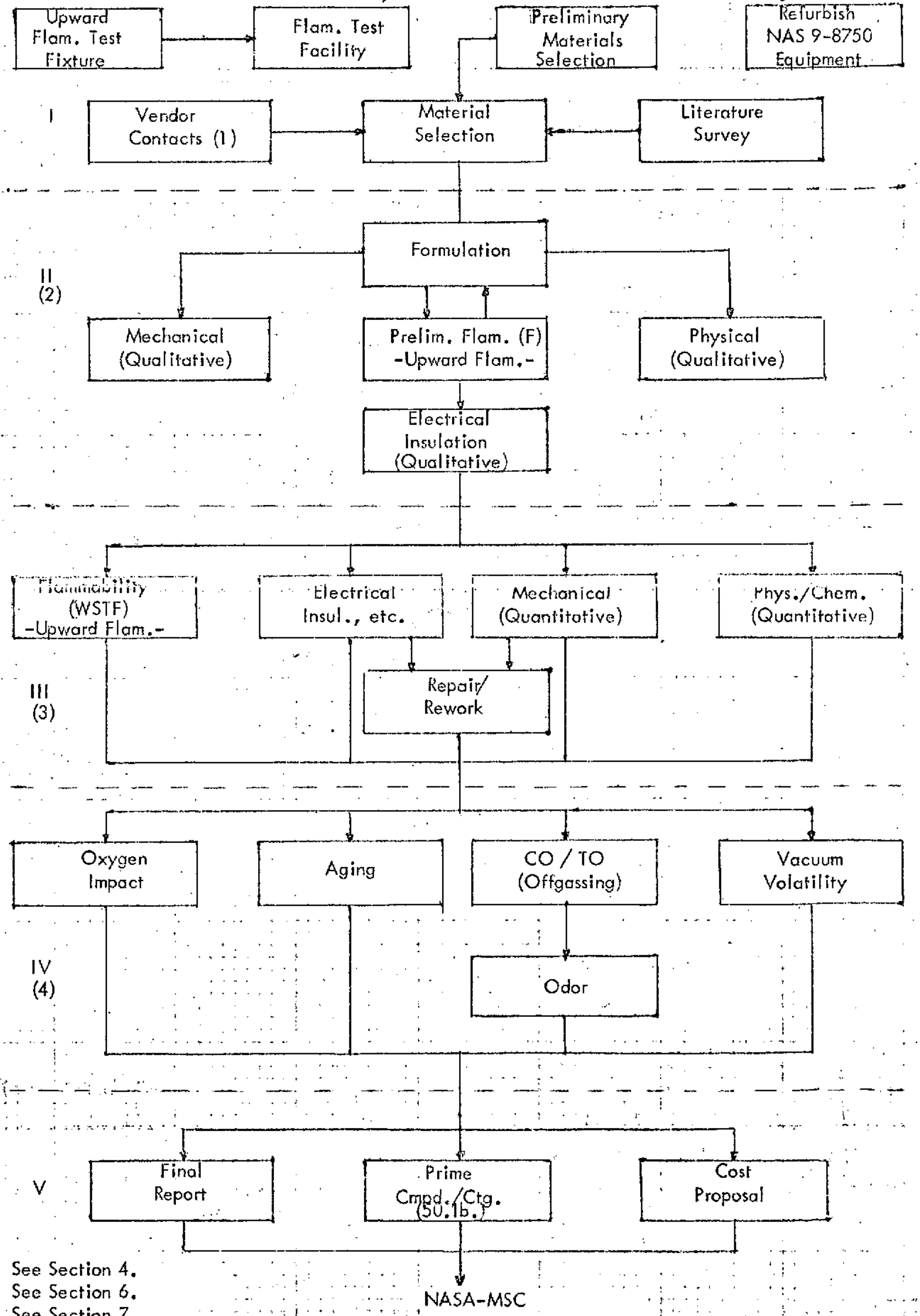
1. Based on Statement of Work, NAS 9-11068, 5 May 1972.

PROGRAM/TEST PLAN (ACTUAL) Figure 3-2



1. See Section 4.
2. See Section 6.
3. See Section 7.
4. See Section 8.

electrical insulation, abrasion and handling protection, physical locating and orienting restraint, shock and vibration isolation, and atmospheric (particularly moisture and high humidity) protection. Further, it was also now desirable that the material have sufficient clarity to permit the observation of the elastomer-covered substrates and components. This was deemed potentially feasible since the cabin environment was prescribed, at the Program's onset, as being 10.0 psia, 30 percent oxygen/70 percent nitrogen, instead of the 16.5 psia, 60 percent oxygen/40 percent nitrogen required by the original development programs. In addition, other desirable parameters included:

a) minimal vacuum volatility
b) minimal toxicity
c) good aging characteristics
d) satisfactory GOX impact response
e) ease of processing to final product in any location (i.e. minimal processing equipment)
f) non-solvent release systems.

In order to accomplish the Program objectives within the prescribed constraints, it was necessary to first assess the state-of-the art primarily of non-flammable monomers and polymers, and secondarily of fire retarding and quenching agents. Further, the pertinent processing, environmental and functional characteristics of potential materials were also sought. Since the binder was clearly the weakest link in the formulation chain, it was essential to contact organizations which were considered potential sources of applicable binder materials and/or data. Since such an investigation had been conducted under NAS 9-8750, only an updating was now required (see Section 4 and Appendix B).

A formulation developed under NAS 9-8750 essentially satisfied the above functional requirements (see Tables 3-1 and 3-2). However, this formulation, F-387, is not clear, has somewhat lower mechanical properties than desired, has a rather high viscosity, and is higher in cost than conventional potting materials.

The comparative results from NAS 9-8749 are also shown in Tables 3-1 and 3-2. A brief review of each formulation is presented herein:

a) Formulation 1015 (Emerson & Cuming) (Ref. 3-8)

The electrical properties of this formulation are, at best, initially marginal, and appear to seriously degrade in a vacuum. It is seen that neither heat (i.e. 250°F) nor the moisture cycle, either alone or in conjunction with each other, causes the degradation evidenced when a 1×10^{-4} torr vacuum is added to the environment. A review of the formulation doesn't readily pin-point the causitive agent(s). Therefore, this fluorocarbon-based, solvent release system had a low level of interest.

b) Formulation SC (Emerson & Cuming) (Ref. 3-8)

As in the case of E&C 1015 above, this sealer coat formulation is based upon a solvent release fluorocarbon elastomer and was also given a low priority.

c) Formulation QC-15 (Emerson & Cuming) (Ref. 3-8)

The data shown in the tables clearly reveals the futility of pursuing this formulation in terms of this program's criteria. Therefore, no further experimental effort was expended upon it.

d) Formulation MRTA-5 (Emerson & Cuming) (Ref. 3-8)

As in the case of Formulation 1015, a serious degradation occurs in the electrical properties subsequent to vacuum exposure. Again, the cause is uncertain, particularly since Furane does not have copies of the original laboratory reports of said data.

This is a polyester-based system. According to the material vendor (Ref. 3-9), the cured resin typically has an elongation of 1.4%. Since a) this is completely irreconcilable with the required 125% min., and b) the alumina in the formulation can only further reduce the elongation, it was decided to eliminate this specific formulation from further consideration. New formulations based upon non-styrenated halogen-containing polyesters, with a limited amount of conventional flexible polyesters, and no alumina, would be prepared by the Contractor. This route could have conceivably led to a transparent or semi-transparent, flexible, nonflammable cured system.

It was further intended that if the other properties were satisfactory but if this clear system could not meet this Program's flammability requirement, Dechlorane 604 would be added until a suitable formulation was achieved.

As seen in Tables 3-1 and 3-2, the NASA developed formulation, SG-12 KI, also did not sufficiently comply with the Program's requirements.

Hence, modifications, at best, would be necessary for the above systems. On the other hand, the changed criteria presented an opportunity to examine some entirely new systems (e.g. epoxies and urethanes) which might provide significant advantages while meeting the revised flammability criterion. In reviewing new candidate materials and systems, some simplistic guidelines were utilized. For example, thermoplastic and emulsion-based materials were immediately rejected, as were all rigid systems. Similarly, materials requiring cures in excess of 150°F were also deleted from further consideration.

Therefore, it was relatively easy to decide whether to eliminate or retain most materials from the program. However, in the case of a few materials it was somewhat more difficult to ascertain their usefulness; a more detailed analysis then ensued. For example, BUSORB 34 (diethyl-3-acetyl-4-hydroxybenzyl phosphonate: Buckmann Laboratories) is suggested as an ultraviolet absorber by the manufacturer. As such, it had potential as an anti-aging additive. In addition, its phosphorus could aid fire retardation and minimize afterglow. But it is seen from Table 3-3 that, with respect to the three flame promoting elements of hydrogen, carbon, and oxygen:

a) its hydrogen content is between that of a typical addition reaction silicone RTV and a fluorinated version, and
b) its carbon and oxygen contents are significantly higher than either silicone,

thereby probably negating to some extent the benefits provided by the phosphorous. Further, the similarity of the carbon, hydrogen, and oxygen quantities to that of the highly flammable acrylic polymer is even more significant. It is interesting to note that the manufacturer recommends (Ref. 3-10) 0.3 to 0.6 phr "...for long term light color and clarity" of a conventional polyester resin. Whereas for "self-extinguishing properties with good light stability...in a halogenated (polyester) resin with 35% styrene...", 3. to 5. phr is recommended. As a result of these facts, it was decided to reject the material for this Program.

On the other hand, dibromobutenediol was tentatively retained because of its elemental analysis (i.e. low levels of carbon, hydrogen, and oxygen, and a high level of bromine, see Table 3-3), its difunctional reactivity, and its linear configuration, even though formulation difficulties were anticipated in developing a suitable flexible urethane casting material with it.

Highly flammable methyl methacrylate polymer is also shown in Table 3-3 for comparison only.

Based upon an analysis of the available data, the delineation of processing/functional requirements, and a determination of the relative significance of such information, candidate polymeric matrices and flammability reducing agents were selected for preliminary formulation. (See Section 6). As noted above, principal emphasis was on the minimization of hydrogen content, preferably by replacement with free-radical forming halogen atoms, thereby increasing the endothermic character of the compound. Secondary consideration was given to minimum carbon. Unless otherwise noted in this report, the various formulation materials were used in the "as received" condition. Since many were vendor proprietary products, the chemical identification and quantity of their constituents were often not available.

3.2 PHASE II: PRELIMINARY SCREENING

Materials selected from the Phase I investigation were compounded into cured formulations. Qualitative physical and mechanical test strips (see Section 5.4) were also prepared. Promising ones were further fabricated into flammability test specimens and tested in a 3.0 psia oxygen/7.0 psia nitrogen environment. Insulation resistance block specimens were then prepared from those candidate formulations which were self-extinguishing in less than 5.0 in. These electrical test specimens were subjected to a preconditioning high humidity (95%), elevated temperature (71 °C) environment.

All data shown in the various tables of this report (see Section 6) which are identified with the sub-title of "Characteristics" were developed from the thin strip specimens. Due to the small size of the strip specimen, testing was limited to those forces simply provided by the hands and between the fingers. For example, crack resistance was carried out by folding the strip in half so that the crease was in the width dimension, and the faces met within approximately 1/4 in. from the crease line. While in the folded condition, a crack propagation evaluation was then performed by making a small slit in the convex surface of the fold with a scalpel. Such tests, while being extremely simple and fast to run, are clearly quite subjective by nature and, hence, were only indicative of a trend and/or were a gross approximation of a property.

3.3 PHASE III: FINAL SCREENING

The results of Phase III, consisting of those tests shown in the applicable portion of Figure 3-2, are discussed in complete detail in Section 7. In addition to flammability, the tests selected for this phase were based upon the widest evaluation of conventional properties (i.e. electrical, mechanical, and physical/chemical properties) with the minimum number of tests. This data increased the confidence level in the usage of the formulation since diverse types of test data are generally of more initial use to designers than a heavy emphasis on just one property (e.g. electrical data only). For example, the cured materials are exposed to mechanical loads when a) they are handled and shipped, b) installed, c) launched, d) relocated, and e) used to position other materials (e.g. wire harnesses). Since it is not practical to initially test materials to each and every load environment anticipated, various basic tests were used to categorize the materials for subsequent material selection and specific application evaluation. These basic tests included tensile, elongation and tear.

Since realistic utilization of the final material must involve some processing and fabrication by the electrical component's manufacturers and assemblers, it was considered necessary to determine the feasibility of rework and repair techniques with the material. The techniques were verified by fabrication of a typical repair and determining the quality of the repair with a moisture/resistance test.

3.4 PHASE IV: PRODUCT CHARACTERIZATION

This phase, as shown in Figure 3-2, involved additional tests which provide preliminary design data for manned space applications as, for example, the Shuttle.

3.5 PHASE V: PILOT PLANT PRODUCTION

Upon NASA's selection of the optimum formulation, a 50. pound batch was prepared for delivery to NASA for their further testing and evaluation.

3.6 SYSTEMS AND PROCEDURES

3.6.1 Identification

Source and batch data were maintained for all formulations and processing materials. A number was consecutively assigned to each formulation. Individual batches and duplicate specimens of a given formulation were also noted via this technique. For example, 003-05-12 designates the twelfth specimen prepared from the fifth batch of formulation system number 3. Test data were keyed to these numbers.

3.6.2 Data Retention

Each formulation and flammability test was recorded on data sheets shown in Appendices C and G, respectively, and filed as an individual unitized package so that access to all data for each was immediately available. The formulation/Processing Data Sheet provides for the complete description of formula, tooling, processing conditions and observations, and an analysis of pertinent qualitative physical and mechanical properties.

SECTION 4

MATERIAL VENDOR CONTACTS

Appendix B is a list of vendors which were contacted in this Program for such items as data and samples of their flame retarding monomeric/polymeric moieties and/or additives. Whenever data were received from a supplier, they were assessed for formulation pertinence. The criteria for their analysis has been delineated (see Section 3). The list does not include information received during the performance of NAS 9-8750 unless it was received again as a result of the updated inquiry in this Program.

SECTION 5

SPECIAL APPARATUS AND TEST PROCEDURES

5.1 FLAMMABILITY TEST FACILITY

Due to the Project's need to expeditiously evaluate the flammability performance of candidate formulations, it was necessary to conduct preliminary flammability screening tests at the Contractor's facility. Applicable equipment available from NAS 9-8750 was on the premises and only required refurbishment and some modification for utilization in the upward flammability test mode. Briefly, the basic design of the equipment is as follows:

A cylindrical section of a surplus vacuum processing system was used as the basic test chamber. (Expendable and/or surplus materials and components were used wherever possible to minimize cost.) This structure had various ports which were used with only minor modifications. The entire facility and system design was then oriented with respect to this cylinder. Figure 1 (Appendix E) is a block diagram of the final unit and the subsystems of which it is comprised. The interconnecting distribution systems for the electrical power, environmental test atmospheres (oxygen and nitrogen), purging (nitrogen), vacuum, and venting systems are specifically shown in Figure 2, Appendix E. Tables 1 and 2 of Appendix E further identify materials and components of the test facility. Numerous brass, stainless steel, iron, and copper fittings and tubing were utilized in the assembly of the system. Flexible pressure lines were also used in order to simplify assembly. The remaining pertinent design details of the basic system have been reported in Reference 3-7, and a photograph of the entire facility is shown in Figure 5-1 of said reference.

A successful "dry run" was carried out prior to utilization to particularly assure compliance with the vacuum and pressurization requirements of the Upward Propagation Test (Appendix D) specified in the Statement of Work (Appendix A).

5.2 UPWARD FLAMMABILITY TEST FIXTURE ASSEMBLY

Changed test requirements necessitated designing a suitable test fixture assembly which could be accommodated in the present NASA/Furane Flammability Test Facility with minimum modification of the Facility. The drawings for the new test fixture have been incorporated into the total set of drawings for said Facility (see Appendix E, Figures 14 to 21, inclusive). Several minor changes were also made in the original set of drawings. Thus, the pyrex light port, shown in Appendix E, Figure 1, has been replaced with the fixture's base plate (see Appendix E, Figure 15).

The fixture's design does not cause any interference in the flammability testing of either the 1/4" x 1/4" x 1" embedded wire specimens or the potted connectors used for NAS 9-8750 type testing.

Only minor difficulties were encountered in the fabrication, cleaning, and assembling of the fixtures.

The Window Base Plate (P/N 11810) and Power Base Plate Assembly (P/N 11820) are shown in Figures 5-1, 5-2, and 5-3 in various stages of assembly. Similarly, the Test Specimen Holder Assembly (P/N 11830) is seen in Figures 5-4 and 5-5. The completed Fixture Assembly is shown in Figure 5-6. The Fixture Assembly, with a typical specimen (i.e. F-387) and silicone RTV/nichrome V ignitor, is seen in Figure 5-7.

Upon completion of the Test Facility modification, the set-up shown in Figure 5-7 was used to verify operational test procedures (Appendix F) and test system functionality. Figure 5-8 shows a completed run made in 14.7 psia air with a sample of Formulation 387.

A general check-out and operational procedure for utilizing the Upward Flammability Test Fixture Assembly in the NASA/Furane Flammability Test Facility has been prepared (Appendix F). It essentially conforms to the new flammability test requirements of this program. A copy of Furane Drawing No. 10010C is also provided in Appendix F (page F-8) since it designates the components referred to in the specification. Similarly, we are including (Appendix G) a copy of the "Flammability Test Conditions/Results" Data Sheet which was utilized for each specimen tested.

It should be noted that the chamber for the NASA/Furane Flammability Test Facility is significantly smaller than those used by NASA for this purpose. Effects of a) total available oxygen, and b) oxygen partial pressure were therefore examined. Specimen F-481-1A-2 was tested in accordance with Appendix F in 3.0 psia oxygen/7.0 psia nitrogen. Specimen F-481-1A-4 was formulated from the same batch as F-481-1A-2, cast in the same thickness, and simultaneously cured with it. Half of F-481-1A-4 was carefully covered lengthwise with aluminum foil so that the exposed edges adjacent to the covered faces were also covered. A pair of steel plates, cut to the covered surface area, was bolted through the specimen near the axial center line of the specimen, and clamped into the fixture with the specimen at the other edge of the steel plates. It was the object of this configuration to "guard" half of the specimen from both heat and flame. This partially sandwiched specimen was tested exactly the same as F-481-1A-2, including the use of a full size silicone RTV ignitor. The results, seen in Figure 5-9, indicate that there appeared to be sufficient oxygen present for the full size specimen since F-481-1A-1 was a duplicate of F-481-1A-2 in all respects.

In order to evaluate the effect of partial pressure, F-481-1A-3 was tested in 6.0 psia oxygen/4.0 psia nitrogen. This specimen was identical to the others in formulation and processing. It is evident from Figure 5-10 that the increase (twice) in oxygen partial pressure, keeping the total pressure constant, causes a dramatic increase in specimen degradation.

In other words, the degradation seemed to be more proportional to the partial pressure rather than to the total available oxygen. A review of WSTF data appears to substantiate this. It is apparent that the test is reasonably consistent (see Table 6-5) and that the chamber seemed to be of sufficient capacity for the specified environment and specimen size.

UPWARD FLAMMABILITY TEST FIXTURE ASSEMBLY
- WINDOW BASE PLATE & POWER BASE PLATE ASSEMBLY -
P/N 11810 & P/N 11820

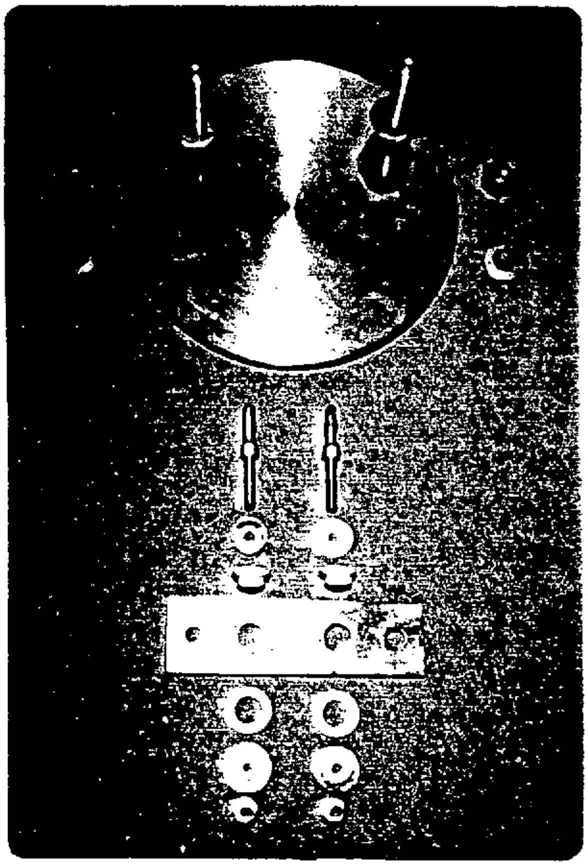


FIGURE 5-1

UNASSEMBLED

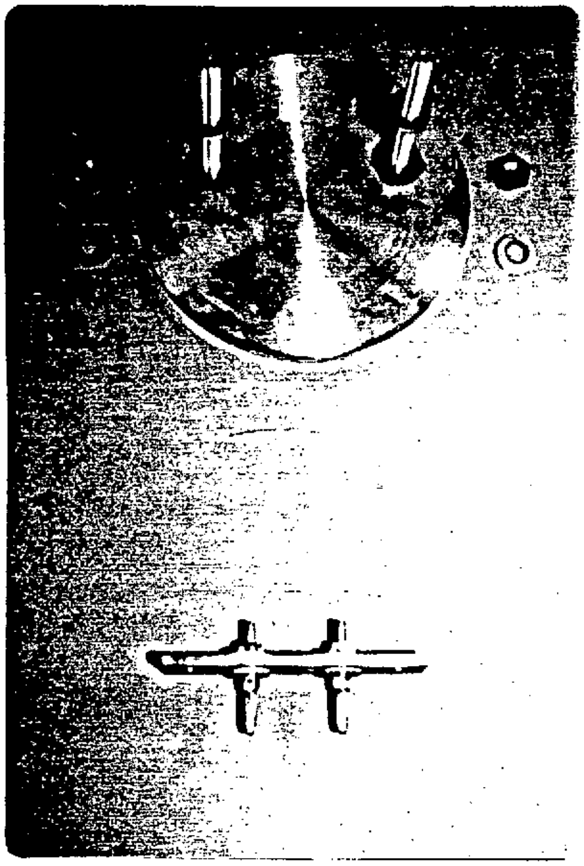


FIGURE 5-2

PARTIALLY ASSEMBLED

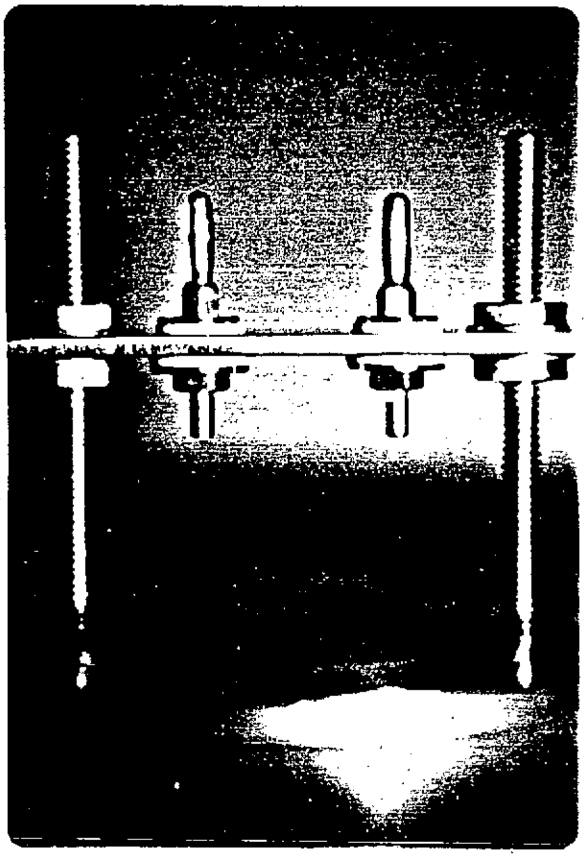


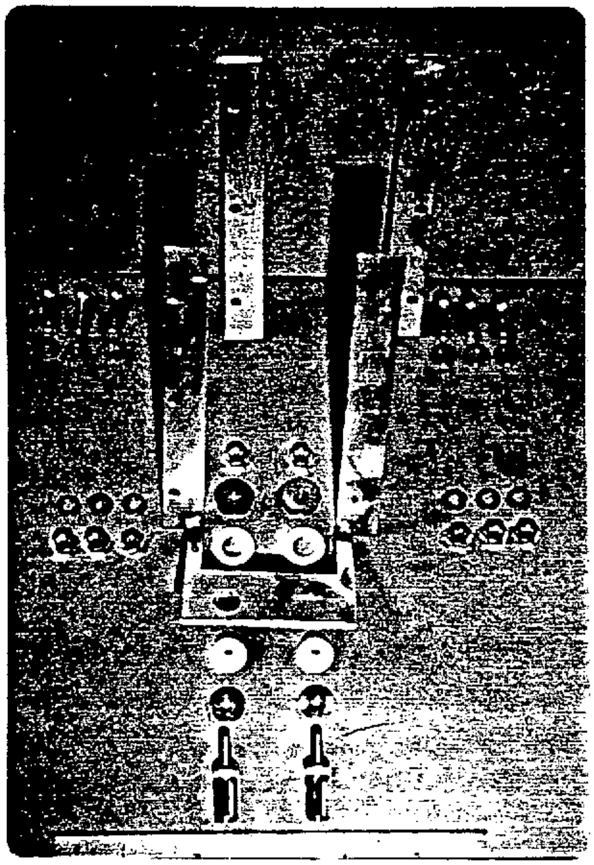
FIGURE 5-3

ASSEMBLED

1-13

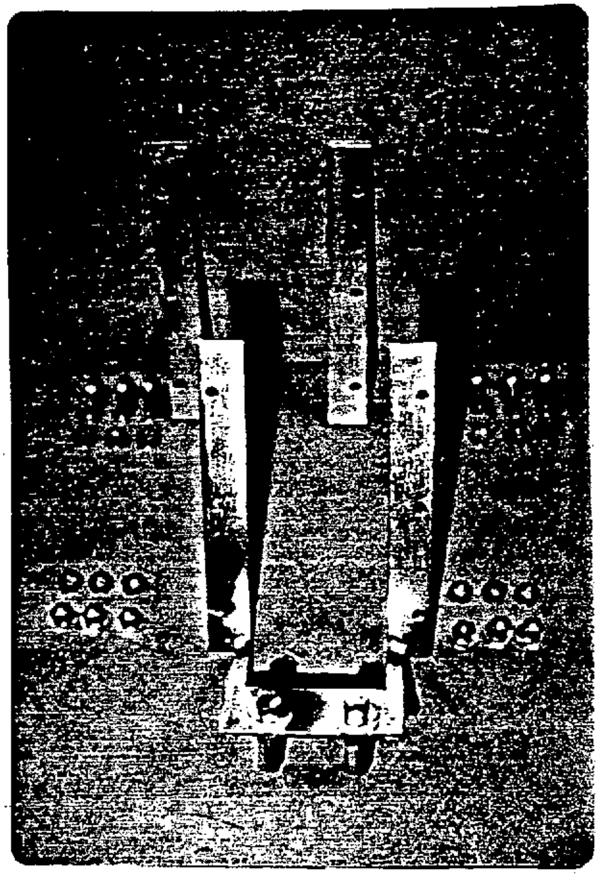
UPWARD FLAMMABILITY TEST FIXTURE ASSEMBLY
- TEST SPECIMEN HOLDER ASSEMBLY -
P/N 11830

FIGURE 5-4



UNASSEMBLED

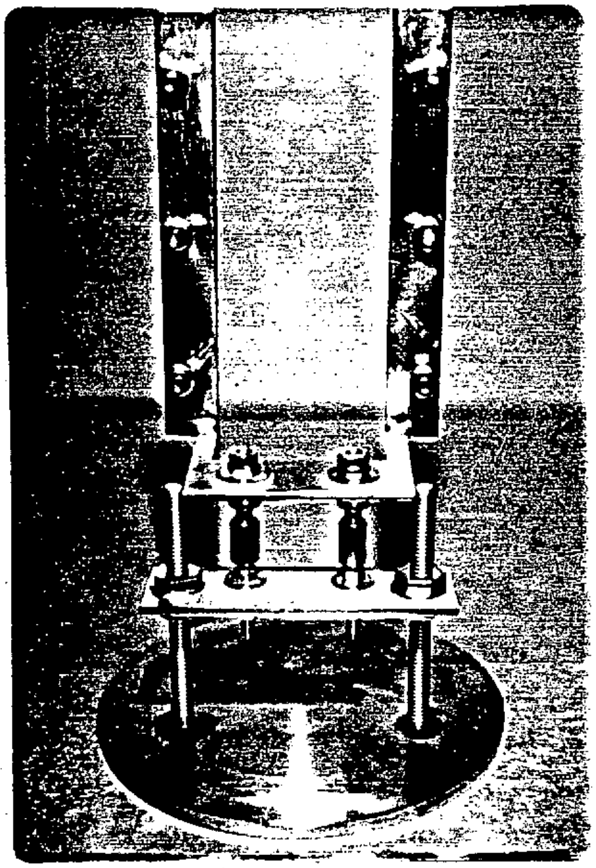
FIGURE 5-5



PARTIALLY
ASSEMBLED

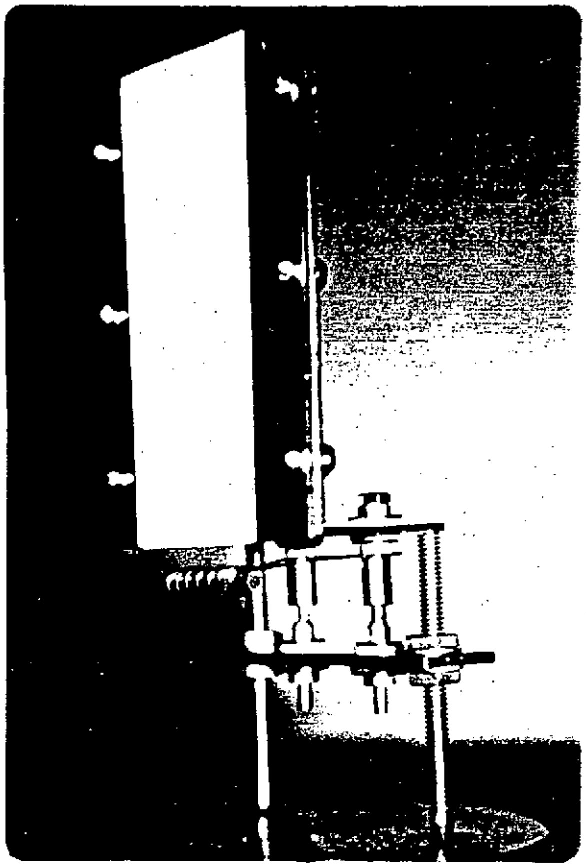
UPWARD FLAMMABILITY TEST FIXTURE ASSEMBLY

FIGURE 5-6



COMPLETED ASSEMBLY

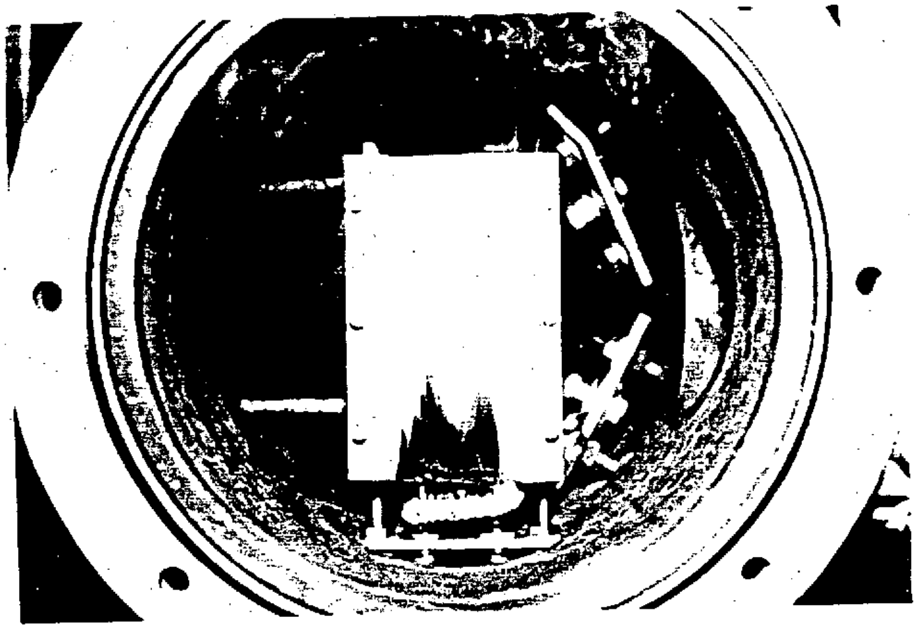
FIGURE 5-7



ASSEMBLY, SPECIMEN, AND IGNITOR

UPWARD FLAMMABILITY TEST FIXTURE ASSEMBLY

Figure 5-8

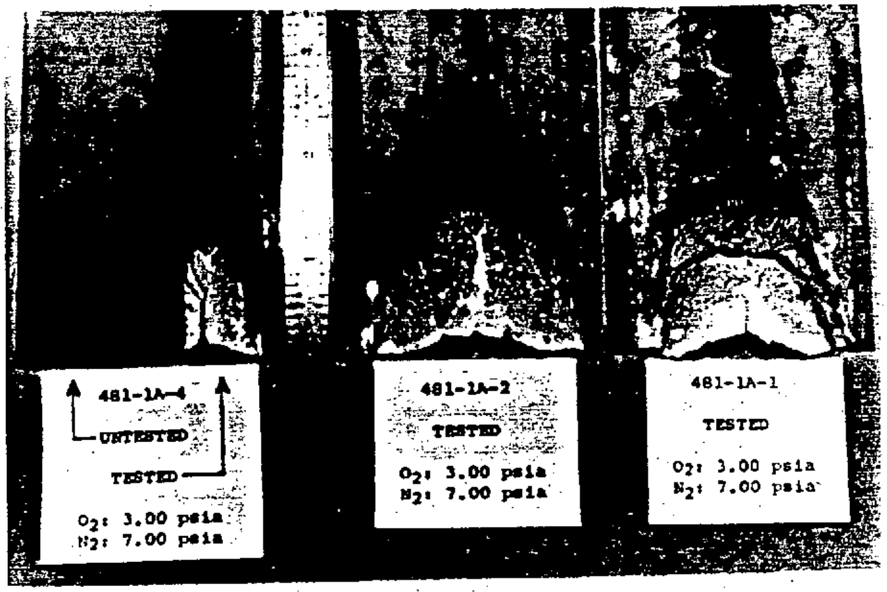


- DRY RUN IN 14.7 PSIA AIR -
(Formulation 387)

FLAMMABILITY TEST

- OXYGEN EFFECTS -

FIGURE 5-9



VERIFICATION

FIGURE 5-10

5.3 SILICONE RTV/NICHROME V IGNITOR

The upward flammability test (Appendix D) requires the use of an electrically heated silicone RTV ignitor. However, the test specification does not a) delineate the grade of nichrome wire, or b) define the dimensional tolerances for the silicone RTV.

The Contractor was informed (Ref. 5-1) that the Technical Monitor's laboratory utilized chromel A. The Contractor therefore used this 80% nickel/20% chromium alloy, but has procured it as Nichrome V.

The Contractor was further informed (Ref. 5-2) that the silicone RTV was cured in commercially available soda straws, and that some cured to a 0.27 inch diameter, with 0.22 inch diameter being nominal in the specification. The Contractor subsequently submitted (Ref. 5-3) RTV samples (F-459-1,2) which it had cured for 24 hours at room temperature in straws from 3 separate sources. The straw molds resulted in diameters ranging from 0.205-0.0225 inches. Just prior to shipment of these rods, the Contractor received a Contract Modification (Ref. 5-4) to apply a ± 0.03 inches tolerance to the specified diameter. On this basis, all of the straw molded rods are allowable.

The Contractor has found that injection into the straws with a Semco air pressurized gun operating initially at 40 psi and 65 psi at the final stages (i.e. increasing viscosity with time), resulted in completely void free rods. For example, a 6.75 inch rod was cut into 0.25 inch rods. These were then cut axially in half. None of the exposed surfaces showed any voids when examined with a magnifying glass. In addition, the cut ends of 37 (1.25 inch) rods also showed no voids. Previous attempts to use a vacuum sucking technique were unsuccessful.

5.4 STRIP MOLD

It was deemed advisable to fabricate a thin specimen of each formulation in order to obtain a better qualitative "feel" for handling characteristics, flexibility, memory, crack initiation and propagation, tear strength, etc. (see Section 3.2). To this end, a number of very simple and inexpensive strip molds were fabricated from aluminum sheet, pressure sensitive Teflon tape, and spring-loaded paper clips. The resultant specimens were approximately 3-1/4 in. x 3/4 in. x 0.065 in.

5.5 SHEET MOLD

The sheet stock were cast to "stops" between 1/4 in. thick glass plates. Spring clips were used to apply continuous pressure to the metal "stops." Teflon TFE, Tedlar, and polyethylene provided good release from all formulations used to prepare test sheets. Mylar suitably released only from the silicone and fluorosilicone RTV's. Commercial polyethylene bags made from seamless layflat tubing was a convenient technique to use with the glass plates. However, wrinkles sometimes occurred with these bags when low viscosity formulations were cured at 150°F. This was primarily due to thermal distortion of the polyethylene. Hand fabricated bags made from Tedlar had some built-in wrinkled caused by unevenness in heat sealing the seams.

5.6 INSULATION RESISTANCE TEST AND MOLD

As shown in Figure 3-2, a formulation which satisfactorily passes the upward flammability test is then given a qualitative electrical insulation test. Preconditioning the test specimen (Figure 1 of Reference 5-5) with the "moisture cycle" is considered sufficiently drastic to eliminate most of those which would not likely be electrically suitable. In order to simplify and expedite this preliminary evaluation, the standard cycle (i.e. 75-160°F/95% R.H/1 day per cycle/5 days) was modified to 160°F/95% R.H./4.5 days. This permitted a) inserting specimens at any time into the environmental chamber, b) utilization of an additional, but simpler, environmental chamber, and c) comparison of cyclic versus constant environment on the formulations selected for the full characterization. The same molds were also used for the more precise cyclic testing.

The "qualitative" chamber was a desiccator with water in its base. It was heated from below by four 150 watt thermostatically controlled light bulbs, all enclosed in a 3.0 in. wall polyurethane box. Temperature was readily maintained within ± 3°F.

The qualitative electrical tests were carried out with a Type 1230A, "DC Amplifier and Electrometer" (General Radio Co.) and an external 500 v. D.C. supply. Measurements were made before and after moisture exposure.

SECTION 6

FORMULATIONS DEVELOPMENT: PRELIMINARY SCREENING

Based upon an analysis of prior art, including the aforementioned NASA-supported and in-house programs, the most promising formulations were the following generic polymeric species:

a) Silicone RTV (modified SG-12 KI) (Ref. 3-7)
b) Fluorosilicone RTV (modified F-387) (Ref. 3-7)
c) Polyester (modified MRTA-5) (Ref. 3-8)
d) Epoxy
e) Urethane
f) Epoxy-Urethane

6.1 SILICONE RTV FORMULATIONS

6.1.1 Formulation

Initial and primary consideration within this group was given to the prior NASA-MSC in-house and contracted efforts previously reported (Ref. 3-7), and conveniently referred to as Formulation SG-12 KI:

Sylgard 186 (Dow Corning)	100. pbw
ammonium phosphate, monobasic (open source)	75. "
Glass Frit No. 7570 (Corning Glass)	50. "
Sylgard 186 Curing Agent (Dow Corning)	10. "

The poor electrical properties of this system (Ref. 3-7, Table 9-8) were attributed to the monobasic ammonium phosphate. This chemical's, as well as the glass frit's, physical form would also not be conducive to reinforcing the polymer; hence the poor tensile strength. As presently constituted, this formula had an extremely low probability of meeting the requirements of this program. It was therefore our intention to examine the following modifications of the basic formula:

a) Substitute an ammonium polyphosphate (i.e. Phos-Chek P/30; Monsanto) for the monobasic ammonium phosphate. A few pertinent comparisons are:

	$NH_4H_2PO_4$	P/30
1) solubility (gm/100 ml water)	22.7 (0°C) 173.2 (100°C)	1. (room temperature)
2) pH	3.8-4.4 (1)	6.5 (2)
3) phosphorus (%)	30.	32.

Note: 1. 5% solution at 25°C.
2. 10% slurry at room temperature.

It should be noted that noticeable leaching and terminal corrosion was observed when insulation resistance specimens of SG-12 KI were subjected to the moisture cycle. It was felt that substitution of the P/30 would significantly alleviate these two problems.

b) Reduce the respective quantities of the phosphate and of the glass frit. This would further minimize the leaching due to the high water solubility of the phosphate and corrosion problems attributable to its low pH. It was anticipated that this would also improve the mechanical strength properties.

These formulation modifications (F-475, -476, -477, -478, and -479) are shown in Table 6-1, as is F-480 which was prepared to compare these additives to Dechlorane 604 (Hooker), the chlorinated/brominated organic flame retardant used in F-387 (see Table 6-1), when used in conjunction with the Sylgard 186 and at the same concentration. Test specimens were also made from the Sylgard 186 alone to further enhance the perspective of the resultant data.

The cure/post cure cycle for these formulations (see Table 6-3) was basically as originally suggested by NASA (Ref. 6-1) and as utilized in our previous activities (Ref. 3-7) with the basic formula.

6.1.2 Evaluation

Table 6-4 tabulates various qualitative properties which supplement the preliminary flammability data and, hence, provides further insight into the potential of each formulation. All of the data shown in Table 6-4 were obtained from cast strips, approximately 3-1/4" x 3/4" x 0.065". The Table also lists the hardness and specific gravity of the respective formulations. The latter data are derived from the flammability test specimens.

It is seen from Table 6-4 that all of the formulations of this series tested to date readily comply with this Program's Statement of Work "Mandatory" requirement (Appendix A) of 30.-85. Durometer A. However, it is also seen that the 25 phr Phos-Chek P/30 formulation (F-478) is the only one which even barely passes the "Target" value of 1.25 for the specific gravity. It is to be noted that the original SG-12 KI also does not meet the specific gravity requirement (i.e. 1.58: Ref. 3-7). The remaining physical and mechanical properties shown in Table 6-4 are generally comparable to those achieved with the "original" (see Table 9-5, Ref. 3-7), and appear to be adequate for the intended applications.

The preliminary flammability test data for these formulations are shown in Table 6-5. The ignition time noted in the tables was based upon the start of the actual burning of the ignitor until power was turned off. Start of specimen burning time was also based upon the start of the ignitor burning since it was not visually feasible to clearly differentiate between the two burnings.

It was noted that, in almost all cases, the specimens of this series deformed near the burning ignitor so that sometime during the test one side of the test specimen was more exposed to the ignitor than the other (i.e. the bottom of the test specimen tended to buckle away from the ignitor, regardless how tightly the test specimen was clamped in place. In fact, the specimen was still clamped in place upon the test's completion.). This behavior created a situation whereby the side more exposed to the ignitor picked up the black soot from the burning ignitor, while the opposite side only seemed to be covered with the test specimen's soot. This was clearly seen with such formulations as F-475, -476, and -477. These produced a white soot.

A specimen's zone of flammability degradation was determined by vigorously scraping the surface of the specimen on the side less exposed to the ignitor's soot. Generally, three zones resulted:

Zone 1: Base of specimen (i.e. closest to ignitor), extensive degradation (e.g. embrittlement, cheesyness, curling or other deformation, etc).
Zone 2: Minor surface degradation (tactile evidence).
Zone 3: Minimal surface degradation (visual evidence: discoloration).

The maximum distance of Zone 2 was used as the self-extinguishment distance, since Zone 3 could reasonably be due to a lower zone's flame. The specimens for F-477 and -478 showed a somewhat anomolous behavior in that they had a zone of no degradation at all approximately in the center of the specimen (i.e. between the two sides) between Zones 2 and 3. It is not clear why this occurred, and only with these specimens. It may be that some peculiar buckling occurred during the burning stage. F-480-1, and -2 also behaved differently. They were considerably curled in the burn zone.

It is seen from Table 6-5 that when the P/30 and frit are reduced from 75 and 50 phr, respectively (F-475), to 50 and 25 phr, respectively (F-476), there are no significant differences in the flammability characteristics of the specimens (e.g. flame-out time, residue in original configuration, or distance to self-extinguishment). However, when a reduction is further made in the P/30 to 25 phr (F-477), there are noticeable changes in all three characteristics. When the remaining frit is deleted, the flame-out time doesn't change, but there is evidence of increased degradation in the quantity of residue and in the degradation distance. When only the frit is present, the flame-out time doubles, but less degradation is observed. It is apparent that the P/30's decomposition when heated causes the greater material degradation, whereas its presence definitely limits the burn time. As a comparison (F-480), Dechlorane 604 was used at a weight level comparable to the weights of P/30 (F-478) and frit (F-479). The flame-out time and residue percentage were improved, but the Zone 2 distance was double that of F-479 due to the presence of some surface char for a greater distance.

The base polymer system for the series shown in Table 6-1 (except for F-387), Sylgard 186 (Dow Corning), was evaluated in the unfilled state (F-481). Its flame-out time was even less than when the frit alone was used, and its residue was greater than when just P/30 was present. In addition, its self-extinguishment (SE) distance was less than that of the specimens which contained P/30 at less than a 50 phr level, or the ones with Dechlorane 604.

Based on the data in Table 6-5, F-476 appeared to be the best compromise of this series.

6.2 FLUOROSILICONE RTV FORMULATIONS

6.2.1 Formulation

Furane's F-387 (Ref. 3-7) is the primary starting point in our fluorosilicone optimization effort. Its formulation is as follows:

RTV 77-033 (Dow Corning)	100. phr
DECHLORANE 604 (Hooker)	150. "
RTV 77-033 C.A. (Dow Corning)	10. "

It is apparent from Table 3-1 (and summarized in Table 3-2) that this formulation came closest to meeting the mandatory requirements shown in Table 3-1.

An effort was made to substantially reduce the D-604 since this would improve all other properties than the flammability resistance. Since the latter was now less of a problem, the D-604 reduction was not unreasonable. However, the raw material cost would go up commenserately as the 77-033 is approximately $70.00/lb. and the D-604 is approximately $5.00/lb. In addition, the basic polymeric system, RTV 77-033 became unavailable. (It could be made available if a sufficiently large order, e.g. $50,000.00 or approximately 700 lbs., based on a non-production cost of $70.00/lb. is placed with the vendor) (Ref. 6-2). A closely related version, RTV 94-531, was available and, hence, was substituted. This material differs from the RTV-77033 by having 0.205% by weight of free carbon also present. Although not evaluated for this program, a similar product, RTV 77-024 (Dow Corning), was previously investigated (Ref. 3-7). It contained 0.031% by weight of free carbon. The fire retardant characteristics of the RTV 77-033 (Dow Corning) were found to be superior to that of the RTV77-028. The RTV 94-531 was evaluated as a substitute for the RTV 77-033 since the presently specified gaseous test environment contains less oxygen.

The formulations shown in Table 6-6 were processed as described in Table 6-7. F-387-20 and F-387-21 were prepared to a) evaluate the effect of thickness upon flammability characteristics since Appendix D does not specify specimen thickness, and b) test the new Upward Flammability Test Fixture Assembly. F-470, -471, and -472 utilized the RTV 94-531. For comparison, Sylgard 186 was also combined with the Dechlorane 604 (F-467 and -468). In fact, all of the formulations shown in Table 606 (except for the unmodified RTV 94-531: F-470) contain various proportions of D-604.

6.2.2 Evaluation

It is evident from comparing the data in Table 6-4 with the data of Table 6-8 that the fluorosilicone RTV's, as compared to the Sylgard 186, deteriorate the mechanical properties. It was also observed that the silicone/fluorosilicone blend, F-474, had an apparent viscosity higher and more thixotropic than either of the polymeric moieties alone, possibly indicating some incompatibility.

It is seen from Table 6-9 that increasing the specimen's thickness of F-387 resulted in less burning time and less degradation, particularly in the SE distance.

When comparing the differing Dechlorane 604 contents of F-387 and -473, the SE distance data and the residue percentages for these two were quite consistent with their said contents; the flame-out times were less so.

The applicability of RTV 94-531 to this program is seen with F-470 (no D-604), F-472 (75 phr D-604), and F-471 (150 phr D-604). The flame-out times and SE distances were consistent with the D-604 present. However, in this group the residue percentages were less clearly delineated.

At a 75 phr D-604 level, the RTV 77-033 based formulation (F-473) had a shorter flame-out time, slightly lower residue, and essentially the same SE distance as the RTV 94-531 type (F-472). When 150 phr D-604 was used, the RTV 77-033 (F-387) and the RTV 94-531 (F-471) types appeared to have somewhat similar flammability characteristics when tested as specified herein, and when thickness differences are taken into consideration.

F-474, a blend of RTV 77-033 and Sylgard 186, was formulated with 75 phr D-604. When compared to F-468, it is seen from Table 6-9 that the latter also appears to have better flammability characteristics within this comparison.

6.3 POLYESTER FORMULATIONS

Potentially interesting materials for a polyester-based flame retardant elastomeric system are tabulated in Table 6-10. A series of pre-blends were formulated as shown in Table 6-11. These were catalyzed with either a ketone (i.e. methyl ethyl ketone) peroxide/cobalt naphthanate system (Table 6-12) or a redox promoted aromatic diacyl peroxide (i.e. 2,4-dichlorobenzoyl peroxide) system (Table 6-13). Anticipating that the brominated polyester would be somewhat more difficult to cure than a non-halogenated one, higher than "typical" quantities of the promotor or accelerator were used in order to better assure a cure. The respective processing steps are shown in Tables 6-14 and 6-15. Except as otherwise noted, the temperatures specified in these two tables were the approximate minimums necessary to achieve sufficient fluidity to blend the ingredients by simple hand stirring. All of the blending was carried out with stainless steel spatulas and aluminum dishes. None of the blends were degassed at this stage of their investigation, but this probably would have been required for panel fabrication.

The characteristics of these pre-blends are tabulated in Table 6-16. It is seen from this table that:

a) the DMAP (dimethyl allyl phosphonate: Weston Chemical Co.) is the best diluent of the three, and
b) the isophthalic and the bisphenol polyesters have poor compatibility.

The characteristics of the catalyzed blends, both in the uncured and in the cured states, are shown in Table 6-17. It is evident from this table that the ketone peroxide/cobalt system was better than the other one. In addition, the incompatibility of the isophthalic and the bisphenol polyesters is also evident in these data.

Based upon the "cured" properties, F-493 is clearly the preferred formulation among those tabulated in Table 6-17. The room temperature specimen was only slightly tacky after 24 hours, and appeared "cured" in 48 hours. It, like the 150°F cured specimen, had poor tear but was quite flexible. When given a post cure of 150°F for 24 hours, the room temperature specimen increased in hardness, was less flexible and had gone from a very slight grey to a bright blue. It should be noted that the allyl part of the DMAP was probably the cause of the non-tacky nature of F-493. The allyl and phosphorous parts of this diluent should also improve the aging characteristics of the base polyester system.

The flame retardant components of F-493 are 13.8% bromine and 4.58% phosphorous. This compares with 29.6% chlorine/bromine for F-387. However, F-493, or a similar one, is transparent, whereas F-387 is a white opaque system.

Tertiary butyl peroctoate was substituted for the MEKP-5 in the modified F-493 formulations (see Table 6-18). It is evident from Table 6-19 that inadequate cures resulted.

It is seen in Table 6-17 that the mechanical strength properties, particularly tear and tensile strengths, were quite poor. Modifications of the basic F-493 formulations were then carried out to determine whether a reduction in DMAP (F-505), reduction in the flexibilizing resin (F-504), or a reduction in the cobalt naphthanate promotor (F-503) could provide any significant improvement in the strength of the polymer. Qualitatively, none showed (see Table 6-19) a significant improvement. However, F-503, as compared to F-493, was less "cheesy," had slightly better cohesion, and would have a longer can stability due to its lower promotor content.

Although the polyesters formulated at that point in the program showed promise in their flame retardancy (i.e. immediately self-extinguishing in air when ignited with a match), clarity, flexibility, and lack of porosity, their poor cohesion, tear resistance, etc., considerably lower their usefulness. In an attempt to achieve some improvements in the mechanical properties, formulations were prepared from the basic F-493 and F-503 systems, varying catalyst and accelerator (see Table 6-20), cured slowly (see Table 6-21), and characterized (see Table 6-22). Insufficient improvements were obtained. Therefore, further work with all of these polyester systems was discontinued.

6.4 EPOXY FORMULATIONS

6.4.1 Phase I

It is well known that epoxies generally, and halogenated ones in particular, have low elongations (i.e. less than 5%) unless such epoxy coreacting materials as polysulfides or polyamides are used as flexibilizers. Unfortunately, these flexibilizers tend to significantly reduce the thermal stability, tensile and tear strengths, and electrical properties (especially after exposure to high humidity) of the product. In addition, commercial halogenated epoxy systems are generally either of very high viscosity or are solid. Therefore, it was the initial objective of this phase to evaluate various reactive epoxide-type liquid flexibilizers in conjunction with the brominated epoxies of interest. These included several long chain polyglycol diepoxides from Dow Chemical Co. (i.e. D.E.R. 732 and 741) (see Table 6-23).

The D.E.N. 438 (epoxy novalac: Dow Chemical Co.) was also tried as a possible aid in offsetting any thermal degradation which may result from the use of even the epoxy flexibilizers.

Epoxy preblends were prepared (see Table 6-24) to determine compatibility and/or cure of some of these materials. D.E.H. 61 (Dow), diethylene triamine (DETA), triethylene tetramine (TETA), and ZZLA-0826 were used as liquid co-hardeners. The D.E.H. 61, a polyamine, was specifically recommended by the supplier, Dow Chemical Co., as particularly suited for their D.E.R. 741 where high elongation, low shrinkage, and nearly colorless transparency are required. The DETA and TETA had been found to be effective room and low temperature hardeners. The ZZLA, a polyamine, is used in high impact epoxy systems.

It was assumed, based upon the high impact data presented by the vendor (Ref. 6-3), that maximum flexibility and elongation would be achieved with the simple combination of D.E.R. 741/D.E.H. 61. It was not certain whether an adequate cure could be obtained at 150°F (66°C) since the vendor also states that "D.E.H. 61 is not completely soluble in D.E.R. 741 at resin temperatures lower than 70°C. To insure thorough mixing of the two components the resin should be preheated to approximately 80°C." A specimen, F-513, was prepared (see Table 6-24) and cured at 150°F (see Table 6-25). The blend went from an apparently non-homogenous mixture (see Table 6-26) to a clear, rubbery, elongating, but tacky casting (see Table 6-27). It was assumed that solubility occurred as a result of a) exotherm and/or b) vendor's temperature recommendations having a built-in safety factor.

In an effort to reduce the surface tack, half of the required D.E.H. 61 was replaced with an excess of DETA (F-514, -516) and an excess of TETA (F-515, -517). It is seen from Table 6-27 that tack was reduced but with some reduction in polymer strength. A parallel set of specimens were prepared in which the DETA (F-519, -521) and the TETA (F-520, -522) were stoichiometrically correct. Tack was completely eliminated but crack propagation was worsened. Since over-catalization of an epoxy is known to be deleterious to its thermal properties, further consideration was limited to F-521 and -522. F-521 had slightly better flexibility than F-522. It was therefore initially selected for evaluation with the brominated epoxies.

D.E.R. 732 was also evaluated with DETA (F-523) and the catalytic blend, F-519, used for F-521 (see F-524). The latter was more flexible than the correspondingly cured F-521. Also, F-523 and -524 were both more flexible than any of the D.E.R. 741 formulations except for F-513. However, both F-523 and -524 were quite cheesy, had no crack resistance, and had essentially no adhesion to their aluminum foil casting dishes. Therefore, work with D.E.R. 732 was discontinued.

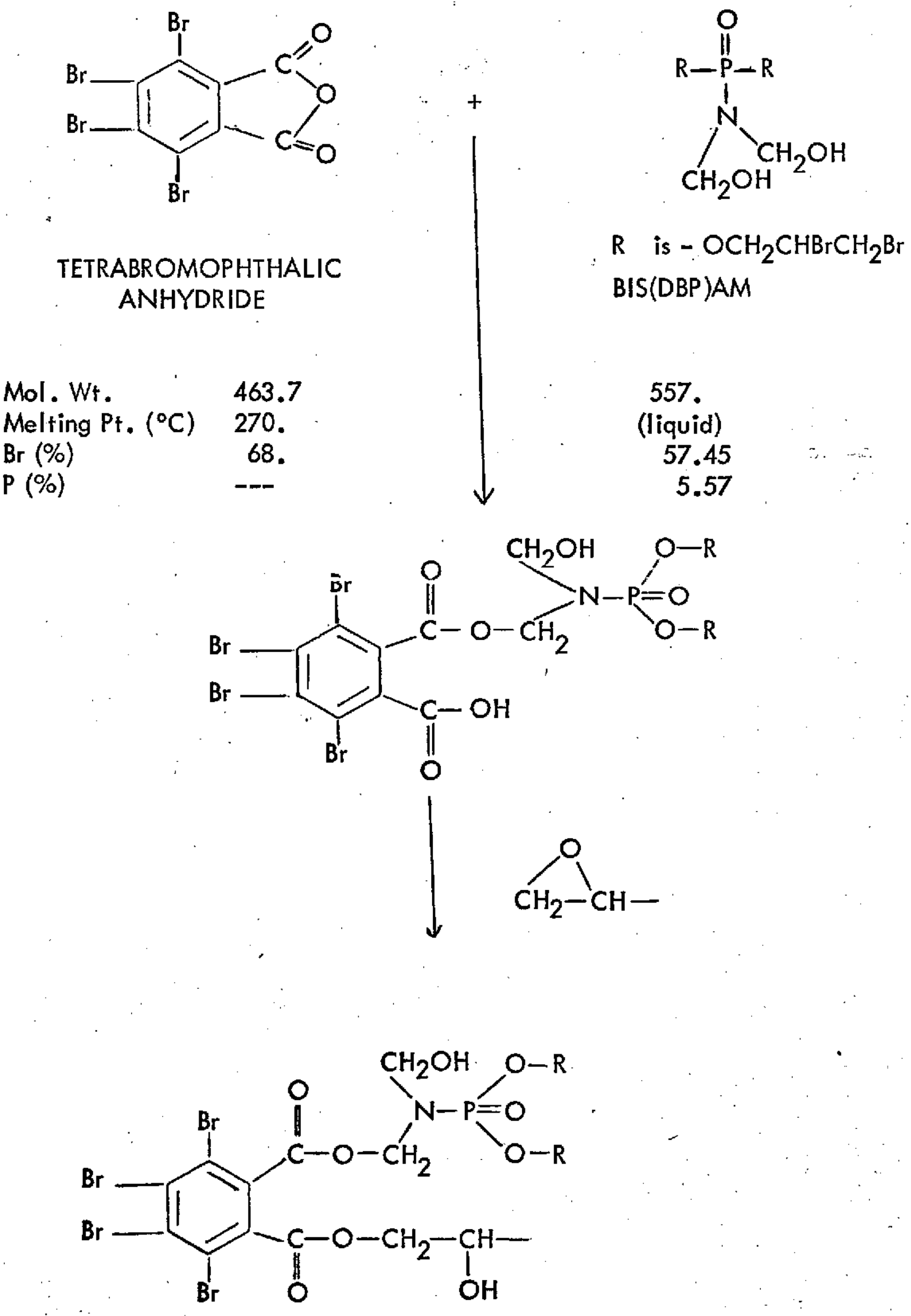
In summary, the relative flexibilities of these cured preblends were, in decreasing order: F-513 > 523-1A, B; 524-1A, B > 516-1A, B > 517-1A, B > 521-1A, B > 522-1A, B; 518-1A, B.

A D.E.R. 741/ZZLA-0826 formulation (F-518) was also prepared since ZZLA-0826 (liquid polyamine: Union Carbide Corp.) was reported (Ref. 6-4) to improve impact strength with only a room temperature cure. The resultant casting was less flexible than the others and had almost as poor mechanical properties as the D.E.R. 732 formulations. This direction was also discontinued.

If it were possible to react tetrabromophthalic anhydride with bis (DBP) AM (bis dibromopropanol phosphoryl dimethylol amide: White Chemical Corp.), the resultant molecule would have a methylol group at one end, a carboxyl group at the other, and a bromine and phosphorous content of 57.% and 2.53%, respectively (see Figure 6-1). Since the anhydride structure would now be opened a low temperature cure (possibly accelerated by a tertiary amine) with a flexibilized brominated epoxy might be feasible. Unfortunately, solubility (1:1 mole ratio) could not be obtained (F-534) at a temperature low enough to prevent volatilization of, presumably, the bis (DBP) AM. In order to avoid the problem with the bis (DBP) AM, an attempt (F-535) was made to dissolve the anhydride in the D.E.R. 741. However, when the blend was heated, a hard insoluble layer formed. This was probably a reaction product between the two ingredients. An effort was also made to incorporate phosphorous into the molecular structure by trying to dissolve DBP-ES (mono dibromopropanol maleate: White Chemical Corp.) in DMAP (F-512), reacting the two together via a free radical initiator, and utilizing the available carboxyl groups to then react with a flexibilized brominated epoxy preblend. Even when heated the solubility was obviously quite low. These routes were discontinued since time did not permit the level of research effort which might be necessary to achieve a useful product.

FIGURE 6-1

POTENTIAL REACTION SEQUENCE OF TETRABROMOPHTHALIC ANHYDRIDE, BIS(DBTP)AM, AND EPOXY



	TETRABROMOPHTHALIC ANHYDRIDE	BIS(DBP)AM
Mol. Wt.	463.7	557.
Melting Pt. (°C)	270.	(liquid)
Br (%)	68.	57.45
P (%)	---	5.57

6.4.2 Phase II

Based upon the results with the epoxy preblends, the D.E.R. 741 was used to dissolve various semi-solid/solid brominated (i.e. 44. - 51.5%) epoxies (F-525, -526, and -527) in a 1:1 weight ratio. F-525 and -526 required at least 212°F to solubilize the brominated epoxy in the D.E.R. 741, whereas F-527 was carried out at 150°F. In fact, when the ERX-67 (n,n-diglycidyl-2,4,6-tribromoaniline: Shell Chemical Co.) was melted first, it stayed fluid as a supercooled liquid. This permitted even room temperature blending. This resultant preblend also remained in a low viscosity state (i.e. in excess of 2 weeks). The other two preblends tended to become cloudy and increase in viscosity when stirred at room temperature.

Each of the flexibilized brominated epoxy preblends were catalyzed with F-519 (F-528, -529, and -530) (see Table 6-28). Their precured characteristics are tabulated in Table 6-29. When cured (see Table 6-30), these resulted in clear yellow castings with poor flexibility and high hardness (see Table 6-31). The specimen with ERX-67 (F-527) was somewhat more flexible than the other two. In addition, as stated above, the ERX-67 preblend had the lowest viscosity, highest bromine content, and was the most stable at room temperature. The ERX-67 was therefore utilized in the final epoxy formulation phase.

Improved flexibility was sought first by a reduction in the ERX-67 (F-531). By calculation, this would reduce the bromine content from 23.8% (F-530) to 20.4% (F-531). The resultant casting was also too stiff. F-533 was then prepared with only D.E.H. 61 as the hardener. The mechanical properties were generally satisfactory except that some tack was present. Its bromine content was calculated as 20.0%. F-536 was then prepared by replacing 10.0% of the D.E.H. 61 with an equivalent amount of DETA. F-537 was also prepared. It had 20.0% of its D.E.H. 61 replaced by an equivalent amount of DETA. Of these formulations, F-537 appears more suitable (see Table 6-31), even though it is not clear why its hardness was less than F-536. Its bromine content is 20.3%. As a gross estimate of potential performance, the comparison shown in Table 6-32 is provided.

An attempt was made to flexibilize the epoxy by adding an amine cured silicone RTV, RTV 602 (G.E. Co.). If feasible, its very low viscosity would also be useful. The specimen, F-532, was too stiff for use herein (see Table 6-31).

Since aging properties were of interest, part of each specimen was given an extended post cure in order to obtain some accelerated indication of the cured formulation's stability with time. A qualitative indication was obtained by considering changes in color, flexibility, and hardness. Table 6-31 shows that color remained unchanged and hardness generally changed only slightly. The flexibility of all of these specimens decreased in the following order: F-533-1A, 536-1A, 537-1A > 533-1B, 537-1B, > 531-1A > 531-1B > 532-1A > 532-1B > 530-1A > 530-1B > 529-1A > 529-1B > 528-1A > 528-1B.

It is evident that the variation in a given specimen's cure was less significant than the formula variations. It was further assumed that any nonreacted epoxide rings would act as a scavenger of HBr; the latter being a potential product of long term aging of the cured material, thereby tending to stabilize the system and minimize release of the HBr to the environment.

6.4.3 Preliminary Flammability Evaluation

The basic F-537 formulation (see Table 6-28) was prepared as a two-part system (see Table 6-33) to a) prepare a large batch in order to assure greater uniformity in the anticipated test specimens required for flammability, electrical resistance, etc., and b) evaluate the potential packaging problems (viscosity, etc.) of this system as it would be used in a production operation. F-597 was prepared by warming the two components at 150°F for approximately 20. minutes to assure easier blending. It was degassed for almost 6. hours, with some degassing still noticeable at the end. The blend was homogenous, contained no lumps or coarse particles, and was a clear orange colored, low viscosity fluid.

The catalyst portion of the system, F-598, was simply blended by stirring and was not degassed. This resulted in a homogenous, clear, light yellow, watery thin liquid which showed no evidence of lumps or coarse particles.

The catalized batch, F-600-3B, was utilized for the flammability specimens (see Table 6-34) and was specifically designated as F-600-3-6. As seen from Table 6-35, the specimens self-extinguished in less than 6.0 inches, but did show some signs of melting. Since the evidence was not sufficiently conclusive, this formulation's evaluation was continued into the qualitative electrical tests.

6.5 URETHANE FORMULATIONS

6.5.1 Phase I

Initial consideration was given to some potential urethane precursors which contain bromine and/or phosphorus (see Table 6-36) since urethanes could be cured at low temperatures, had high strength, and might not require flame retardant additives which would tend to opacify the compound. If Brominex 160P (bromine/phosphorus-containing dihydroxy polyol: Swift Chemical Co.) is used as a baseline for comparison of the other polyols with respect to their weight efficiency, it would appear from Table 6-37 that the B-160P is less efficient than any of the four combinations available with the Vircol 82 (phosphonate dihydroxy polyol: Mobile Chemical Co.) or Fyrol 6 (diethyl N,N-bis(2-hydroxy ethyl) amino methyl phosphonate: Stauffer Chemical Co.) shown (note: Isonol FRP-8 was dropped from further evaluation since its weight efficiency is obviously considerably lower than the Vircol 82 or Fyrol 6.). For example, the combination of FR-1138 (dibromoneopentyl glycol: Dow Chemical Co.) and Vircol 82 would result in the same amount of bromine and phosphorus as in Brominex 160P, but would have a total weight of only 79. grams as compared to 100. grams of Brominex 160P. However, total formula weight efficiency must take into consideration the weight penalty of the non-bromine, non-phosphorous isocyanates required for cure. A tabulation of the comparable hydroxyl equivalents of various polyol combinations is shown in Table 6-38. The dibromobutenediol (DBBD) was arbitrarily selected for the comparative calculations since its hydroxyl equivalents (0.447) were close to that of the FR-1138 (0.435). It is seen from Cases 1, 3, and 4 that:

a) Brominex 160P has considerably less hydroxyl equivalents than any of the potential combinations which would provide the same percentages of bromine and phosphorus in the polyol(s), and

b) the DBBD/Vircol 82 system has 13.5% less equivalents than the DBBD/ Fyrol 6 system.

But when a typical diisocyanate, Isonate 143L, a low viscosity version of diphenyl methane diisocyanate (Upjohn), is added in stoichiometric quantities (see Table 6-39, Cases 1, 3, and 4), there is less difference in the bromine (6.5%) and phosphorus (6.1%) contents between the two DBBD systems. On the other hand, the Brominex 160P/Isonate 143L system contains approximately 9.21% additional bromine and approximately 0.69% additional phosphorus than the other two. This is comparable to increases of 41.8% and 42.4%, respectively. Therefore, the B-160P was used as the base polyol for the formulations shown in Table 6-40.

Similarly, the various diisocyanates were compared. Cases 1, 5, and 6 of Table 6-39 show that:

a) there is no significant difference in the use of either Isonate 143L or PAPI 901, a modified polymethylene polyphenylisocyanate (Upjohn), with respect to the final bromine or phosphorus contents and,

b) only slight difference (less than 5%) between the phosphorus contents of the Brominex 9107 and the other two exist.

Since the Vircol 82 is a water white, very low viscosity compound, it was considered as a reactive diluent which should also improve clarity, degassing, flexibility, and the phosphorus content. Effects upon the bromine and phosphorus contents are also noted in Tables 6-38 and 6-39. For example, the addition of 20.0 parts by weight of Vircol 82 to a B-160P/I-143L system reduces the bromine content from 31.2% to 24.5%, and increases the phosphorus content from 2.32% to 3.41%. This represents a 21.4% decrease in bromine, but a 47.0% increase in phosphorus.

It should be noted that the calculations for actual materials used in the formulations were modified (see Cases 9 and 10 of Table 6-38, and Cases 11, 12, and 13 of Table 6-39) when lot data (see Table 6-41) were found to be significantly different from the vendor's reported data.

Except for F-561 and -563, all of the formulations in Table 6-40 adhered to the industry accepted practice of using 1.2 times the stoichiometric quantity of the diisocyanate component.

The series of F-541, -542, and -543 were to determine the effect of, and need for, a reaction accelerator with the basic B-160P/I-143L system. Even when cured and post cured for a total of 100. hours (see Table 6-42), F-541 showed (see Table 6-43) the need for some acceleration. But 0.2% (based on polyol weight) of either stannous octoate (T-9) or dibutyl tin dilaurate (DBTD) (T-12: M&T Chemicals Inc.) was too much. When reduced to 0.04%, the stannous octoate system (F-546) seemed to be better cured and had less voids than the DBTD one, F-548. Also, it is reported that "...dibutyl tins have a tendency to accelerate heat degradation." (Ref. 6-6). PAPI 901, both without T-9 (F-544), and with 0.2% (F-552) and 0.04% (F-554) of T-9 was also formulated with Brominex 160P. This was likewise carried out with Brominex 9107 (F-551, -553, and -555, respectively). The results with PAPI 901 are similar to those with the Isonate 143L. Namely, the non-accelerated formulas had no voids, the 0.04% ones had either very few voids (I-143L) or had no voids (PAPI 901), and the 0.2% ones were both almost of a foamed structure. All of the Brominex ones were void free.

To further optimize the accelerator quantity, 0.08% stannous octoate was tried with the Brominex 160P and each of the three diisocyanates(F-558, -559, and -560). All three were void free.

Assuming proper stoichiometry was present, the rates of gelation for these three different diisocyanate systems appeared to be as follows:

$$\text{I-143L} > \text{PAPI 901} \gg \text{B-9107}$$

F-561 was similar to F-559, except that an additional 10.0% of PAPI 901 was added to see if the tear resistance could be improved since its functionality was approximately 2.3 rather than 2.0. No significant difference in tear was noted, but F-561 had slightly less tack in the respective cured/post cured specimens.

F-557 was similar to F-554 except that 20.0 pbw of the polyol was added. No gel occurred even after 7 days at 150°F. Data review revealed a calculation error in the amount of PAPI 901. The experiment was re-run (F-562). The latter was found to be slightly stiffer than the F-554.

As noted above, vendor's data (see Table 6-36) and lot data (see Table 6-41) were not sufficient similar in all cases for maintaining appropriate stoichiometry; recalculation of applicable equivalent weights were required. Subsequent formulations reflected these changes.

A series of formulations were next made to prepare flammability and electrical insulation specimens. F-563 had excellent adhesion to the Mylar film heretofore used to fabricate sheet specimens. The sheet also was filled with considerable voids (note: 1.3 times stoichiometric I-143L was used). The electrical specimen cured before all the voids released at the surface. A similar one (F-567) was prepared using only a 1.2 times stoichiometric quantity of Isonate 143L. Although the insulation specimen did not have a mass of voids on the surface, voids were found on all surfaces. But both the strip and sheet (silicone coated fiberglass cloth release on both sides) had few voids. F-565 was prepared with PAPI 901 instead of the Isonate 143L, using Tedlar and a silicone coated fiberglass cloth as the release agents for the sheet. The sheet released well on both surfaces. The insulation specimen was similar to the F-567 one. However, the strip specimen had considerable voids on the bottom.

Specimens were prepared (F-564) which also contained 10.0 pbw Vircol 82. The cast sheet adhered to the Mylar film on one side and released quite well from a thin Teflon TFE sheet on the other side. Its strip specimen did not cure at all, but except for the exposed tops of the sheet and electrical insulation specimen, these cured well. F-572 was prepared similar to F-564 except the 0.15% T-9 was used instead of 0.10%. Increased voids were noted, particularly in the strip and insulation block. However, the strip was more cured. In order to reinforce the apparent conclusion, F-575 was prepared using 0.25% T-9. Block and strip specimens were almost foamed. On the other hand, the sheet specimen had very few voids.

All previous sheets were cast between separable films, using a natural rubber tubing as a dam. F-575 was poured into a polyethylene bag which was heat sealed on three sides. As seen from Table 6-42, all cast specimens were first degassed under 29 in. mercury vacuum. Nevertheless, voids appeared in the specimens, even in the F-575 sheet, shortly after they were put in the 150°F oven. Dissipation of the voids prior to gelation (or even significant rise in viscosity) was obviously required. Increasing the T-9 accentuated the problem. Further, the block and strip molds, being of separable parts, were not air sealed. A strippable mold sealer was considered for the exterior of each since isocyanates are extremely moisture sensitive, including to the moisture in air. These molding difficulties are discussed in greater detail in Section 6.8.

6.5.2 Phase II

A cursory attempt was made to prepare a two package urethane prepolymer system with Brominex 160P, in conjunction with Isonate 143L (F-576), PAPI 901 (F-579), and Brominex 9107 (F-582), respectively (see Tables 6-44 and 6-45). The cured systems were F-577, -580, and -583, respectively. An additional group was formulated from the same set of prepolymers and a blend of Brominex 160P and stannous octoate (0.15 parts per 100. parts of polyol) (F-571). This latter group is comprised of F-578, -581, and -584, respectively. Although quantities of the ingredients were in accord with comparable formulations in Table 6-40 which all gelled (see Table 6-43), none of the prepolymer-type "cured" samples were sufficiently gelled to pursue this direction herein since time did not permit the more extensive R&D required in this type of formulation.

6.5.3 Preliminary Flammability Evaluation

The specimens for this test were prepared as shown in Tables 6-40 and 6-42. As seen from Table 6-46, the specimens self-extinguished in less than 6.0 inches, and showed no signs of melting, sparking, or sputtering. Therefore, this formulation was included in the qualitative electrical insulation test phase.

6.6 EPOXY-URETHANE FORMULATIONS

6.6.1 Pre-Reacted Urethanes

In an effort to combine the easier curing characteristics of epoxies with the greater natural resilience of urethanes, it seemed desirable to attempt their marriage. Based upon commercially available materials, the simplest approach was to use an epoxy which contained a pre-reacted urethane (XD 3599.01: Dow Chemical Co.) (Refs. 6-7 and 6-8) to flexibilize the system. ERX-67 was also added to assist in flammability protection (see Tables 6-47 and 6-48). The DMAPA-cured system was suggested by Dow (Ref. 6-9). It is evident from Table 6-49 that insufficient flexibility was achieved with these formulations. No further effort was warranted.

6.6.2 Co-Reacted Epoxy-Urethanes

No source was found for an epoxy-urethane system which was coreacting. The formulations described in Table 6-50 were a preliminary examination of this area. The examination was based upon the rationale shown in Figure 6-2. It is evident from the postulated reaction sequence that the ratio of equivalents are:

diepoxide/dihydroxy polyol/diisocyanate: 1/1/2

If we assume a basic 100. gm for the ERX-67, which has an epoxy equivalent weight of 240., the epoxy equivalents are:

$$E = \frac{100.}{240.} = 0.417$$

Since the same number of equivalents of Brominex 160P are required, its proportionate weight would be:

$$W = (0.417)\ \underset{(1)}{(1316.)} = 548.5 \text{ gm}$$

The proportionate weight of Isonate 143L would be:

$$W = (0.417)\ (2.)\ \underset{(1)}{(144.8)} = 120.5 \text{ gm (stoichiometric)}$$

$$= (1.2)\ (120.5) = 144.6 \text{ gm (practical experience)}$$

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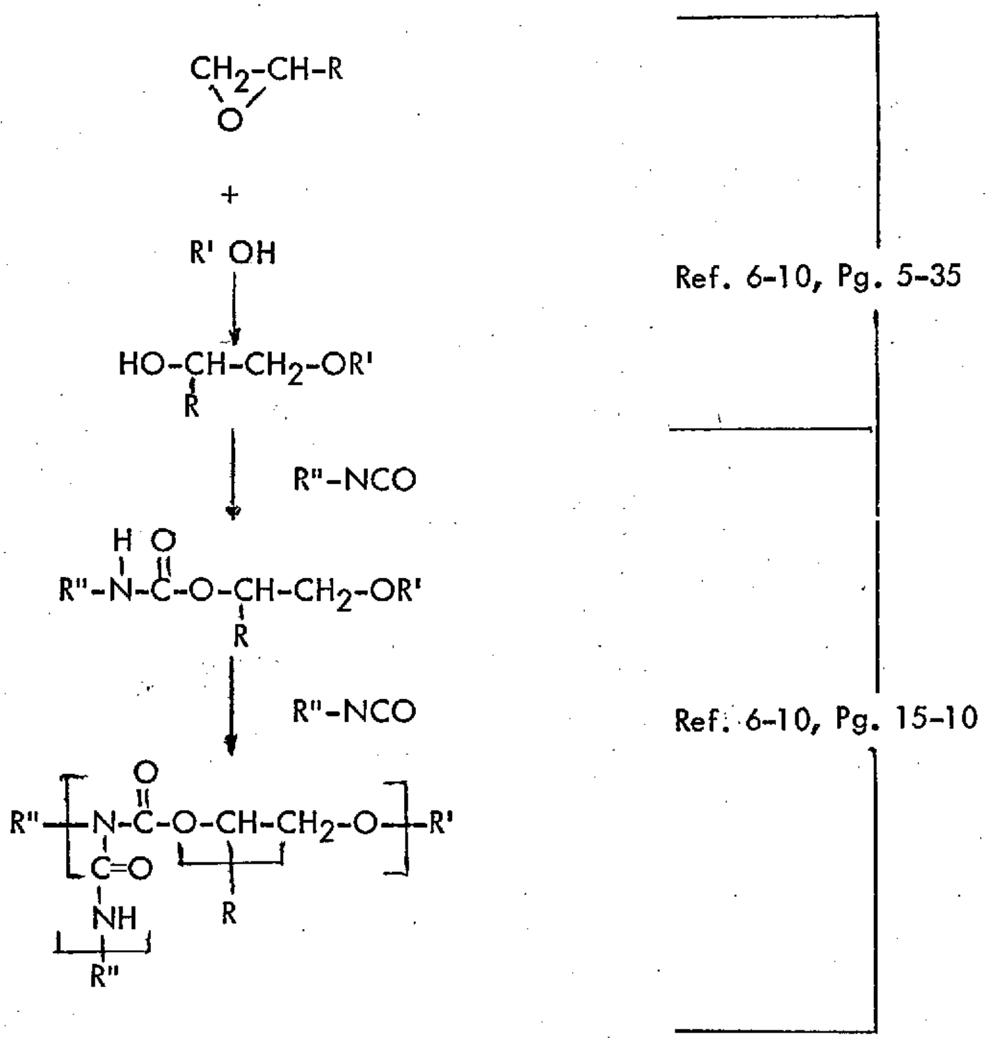
1. See Table 6-41.

FIGURE 6-2

POTENTIAL INTERREACTION OF AN ISOCYANATE, ALCOHOL AND EPOXY



Ref. 6-10, Pg. 5-35

Ref. 6-10, Pg. 15-10

The above quantities would result in bromine, phosphorus, and nitrogen contents in the final compound as shown in Table 6-51.

F-568 and -569 were prepared to determine the compatibility and stability of the ERX-67 with the Brominex 160P and the Isonate 143L. There was no change at either room temperature or at 150°F in the ERX-67/B-160P blend (see Tables 6-52 and 6-53). The surface of the ERX-67/Isonate 143L blend developed a brittle layer (probably due to isocyanate reaction with moist air). F-570 had no tack after a short cure time, no voids in an aluminum cup sample or in one cast in a heat sealed polyethylene bag, negligible voids in the block, and some in the strip and sheet specimens. Again the ones in the strip were at the bottom. Although still quite flexible, the specimens were somewhat harder (i.e. approximately 88 Durometer A) and tougher. Immediate self-extinguishment was also noted with a match in air. Absolutely no melting or dripping was observed during this very qualitative test. This would tend to support the above postulated reaction sequence, since melting or dripping would indicate the presence of a thermoplastic or non-stoichiometric reaction, rather than a thermoset material.

F-573 was similar to F-570 except that 20. pbw of Vircol 82 was also included. The calculated quantity of additional Isonate 143L is:

Component		Wt. (gm)	
Brominex 160P		548.5	(see Table 6-51)
Vircol 82	(0.20) (548.5)	109.70	
Isonate 143L	(52.8) (109.70)/100.	57.9	(see Table 6-39, Case 2)

The potential flame retarding agents are in the quantities as shown in Table 6-54. If Tables 6-51 and 6-54 are compared, it is seen that this addition of Vircol 82 reduces the bromine from 30.7 gm./100. gm. of compound to 25.33 gm./100. gm. of compound (a 17.5% reduction), increases the phosphorus from 1.80 gm./100. gm. of compound to 2.77 gm./100. gm. of compound (a 53.9% increase), and increases the nitrogen (actual) from 2.45 gm./100. gm. of compound to 2.69 gm./100. gm. of compound (a 9.8% increase). The trade-off was considered attractive.

The strip was similar to F-570, the block had more voids, and the sheet had less voids (both sheets were cured between Tedlar films separated by natural rubber tubing). The sheet had approximately an 86 Durometer A.

The use of PAPI 901 instead of Isonate 143L was next considered. Although the former is quite dark in color, its package stability appears to be better. It is also seen from Table 6-39, Cases 1 and 5, that there are no significant differences between the two with respect to their resultant bromine or phosphorus content. Using PAPI 901 instead of the Isonate 143L did not change the epoxy equivalents or the proportionate weight of Brominex 160P. These remained 0.417 and 548.5 gm., respectively. The proportionate weight of PAPI 901 was:

$$W = (0.417)\ (2.)\ (134.4) \underset{(1)}{=} 112.2 \text{ gm. (stoichiometric)}$$

$$= (1.2)\ (112.2) \qquad = 134.7 \text{ gm. (practical)}$$

1. See Table 6-41.

These quantities result in bromine, phosphorus, and nitrogen contents in the cured specimen, F-590 (see Table 6-50), as shown in Table 6-55.

Although the producer of Vircol 82, Mobile Chemical Co., did not officially state it to be so, the contractor eventually surmised that this chemical is a phosphate. Since phosphonates are more hydrolytically stable than phosphates, the use of Fyrol 6 was reconsidered as a possible substitute for Vircol 82. As seen from Table 6-39, Cases 12 and 15, a small reduction in flammability resistance would be expected as a result of the change in reactive diluent. F-589, prepared for comparison purposes, is essentially Case 16 of Table 6-39 since it does not contain ERX-67. This formulation gelled while degassing (i.e. less than 10. minutes). This was no doubt due to the presence of approximately 0.13% of stannous octoate, based upon the weight of Brominex 160P. It may also have been due to some accelerating effect of the Fyrol 6 since F-591 also gelled during degassing, but did so in approximately 30.-40. minutes. In fact, using the same logic, the ERX-67 may have slowed the reactions of F-590 and -591. Since time did not permit a more detailed investigation of this area, and based upon the results shown in Table 6-53, F-590 was arbitrarily selected as the candidate epoxy-urethane formulations for the Preliminary Flammability Evaluation.

6.6.3 Preliminary Flammability Evaluation

It is seen from Table 6-56 that when consideration is given to both burn time and bum distance, F-570 and F-590 were somewhat better than F-573. However, the distinction between F-570 and F-590 was less clear. The former had slightly less burn distance, slightly longer burn time, showed slight sputtering and dripping, and had more of the specimen remaining intact after the test. Both formulations were selected for the preliminary (qualitative) electrical insulation tests.

6.7 PRELIMINARY ELECTRICAL INSULATION EVALUATION

It is immediately evident from Table 6-57 that the urethane formulations were not suitable for this Program. The remaining data were less readily analyzed due to the lack of consistency in some of the data. This was attributed in a large part to the lack of sufficient electrical guarding during these qualitative tests and, to some extent, to variations in patch cords contact resistances. The guarding problem may have also contributed to the generally lower values than what was to be expected. This was later borne out by the qualitative tests run by the Delsen Corp., as seen from Table 6-58.

The exterior physical appearance of the silicone RTV and fluorosilicone RTV specimens were generally quite good when they were cut open axially through the center; no internal voids were observed. The epoxy one had no voids and was transparent, but had a slight tack. Among the epoxy-urethanes, F-590-6 and F-601-1 were extremely porous, especially the latter. This could explain its anomolous values as compared to the other epoxy-urethane specimens. F-570-2A-2 and F-590-3B-5, when cut open as above, showed no internal voids, but there were some on the surfaces, particularly near the mold joints. The moisture cycle definitely affected the surface transparency of all the epoxy-urethanes, but their inside structures were still transparent. The data indicated similar electrical properties between F-570 and F-590. F-590 was finally selected for further evaluation instead of the F-570 formulation because of its apparently better package stability. The two RTV's and the epoxy were also carried into the Final Screening.

6.8 MOLDING DIFFICULTIES

Due to the excellent adhesion generally found with urethanes and epoxies, significant effort was expended in attempting to devise appropriate processing techniques which would permit the casting of both flat sheet and the electrical insulation resistance specimens. The latter particularly engendered difficulties since it was necessary to not only remove the mold from the specimen, but when the viscosity of the uncured resin was sufficiently low, it would tend to creep into the holes which were utilized to project the brass electrical contact pins through the mold and into the specimen. The previous contractual effort, NAS 9-8750, essentially dealt with silicone and fluorosilicone RTV's, and fluoroelastomers. During that phase of the work, sufficient release was achieved by molding against Teflon TFE or Mylar. (The Mylar was used for the flat panels, and Teflon tape, with a pressure sensitive adhesive, was used on the electrical insulation block molds.) When it was decided to increase the production rate of the electrical insulation blocks three-fold, two additional electrical insulation molds were fabricated. They were given a Teflon II coating on all surfaces. In order to get away from the excellent adhesion of the epoxies, urethanes and epoxy-urethanes to the Mylar surface, Teflon TFE, Tedlar, and polyethylene films were tried. For ease of specimen removal from the caul sheets, it was essential that the film used for release also had to be flexible. The thin TFE skived sheeting was considered less desirable, even though it had excellent removal characteristics, since it readily wrinkled and would, therefore, have to be replaced after each molding (cost being a processing factor).

The urethanes and epoxy-urethanes also presented another problem in that they required more attention with respect to degassing due to the isocyanate/water reaction; the water being contained in entrapped air bubbles in the castings. It was therefore considered advisable to carry out final degassing with the resin in the mold. However, due to the size of some of the specimens (i.e. the 12. inch NASA-WSTF flammability specimens), it was found more practical to do the final degassing in a deformable release envelope which could be subsequently placed between the glass caul sheets for cure. Fortunately, polyethylene is commercially available in lay-flat seamless tubing. This is also used commercially to fabricate bags via a heat sealing process. Although this can be done with certain grades of Tedlar, it was not found to be commercially available. Hand sealing of the Tedlar was not found to be a reliable technique. It was hence decided to essentially fabricate the flat sheets with the polyethylene bags even though it did deform at the 150°F cure temperature.

Various methods were attempted in order to alleviate the insulation block problems (i.e. release and void formation). The Teflon II coating gave adequate release except for the end pieces which positioned the above noted brass pins. In order to minimize resin contamination by the usual mold release fluids and greases such as silicones, film-type agents were tried. These included a) vinyl spray-on coating, b) cellulosic spray-on coating, c) polyethylene film bonded to the end pieces with an acrylic pressure sensitive adhesive film, and d) Teflon TFE with a silicone pressure sensitive adhesive. Systems a) and b) bonded quite well to the cured urethane blocks even though they released well from the end blocks. The two Teflon II coated molds were utilized to fabricate epoxy-urethane specimens (F-590-3). Prior to assembly of each mold, one end block was covered on the inside mold surface with the polyethylene system and the other one had the TFE film system attached to it. After extending the end block holes into the films, a minute amount of KEL-F No. 90 grease was inserted into each hole from the outside. The brass rods were then inserted into the end blocks from the film sides for a sufficient distance to permit the end blocks and rods to be assembled with the remaining pieces of each mold. It should be noted that the pins, prior to insertion into the tooling, were sanded with a 320 grit silicon carbide "wet or dry" sandpaper in the dry state. Each pin was then carefully wiped with MEK and oven dried at 150°F (No special primer was utilized for any of the formulations.) After assembly of each mold, one was dipped into a molten was bath at 350°F and quickly removed so that a thin layer of wax covered the exterior of the mold and the pins up to approximately 1/4 inch from the open top of the mold. This mold was allowed to cool to room temperature before adding F-590-3. When both were then filled with the resin, the resin in the non-wax coated one leaked around the joints of the breakaway mold. After approximately three hours of degassing, gas bubbles were seen to be still rising from the surface of both specimens. Following a cure of 17. hours at 150°F, the wax was removed from the exterior of that mold and the side blocks of both molds were carefully removed. The latter operation was easily carried out. Although the exposed surface of each specimen was not tacky, the end block surfaces on the side of the specimens were tacky. It was then noticed that the polyethylene film had adhered to the molding and could not be removed easily. It also appeared that the Teflon film adhesive had not bonded well enough to the end block, so that some resin was able to get into the mold/film interface. Several of the pins were bonded quite tightly in their respective mold holes. In fact, sufficient force was applied to one of the pins to rupture it and yet not break the pin-to-mold bond, or the pin-to-molding bond.

After a 16. hour 15. minute post cure, the bottom plates were removed from both moldings. At this point of the cure cycle the specimens were found to be somewhat harder and released easier from the bottom plates than from the similar surfaced side plates, which were removed at the time of end block removal. It was also seen that there were negligible differences in the void content at the molds' joints.

It was concluded that the wax coating was not a satisfactory mold sealer, especially when one considers the potential for contamination and the obvious increase in mold cleanup time. With respect to the use of either the polyethylene or Teflon films, it is clear that a) neither would be reusable, b) the former is less expensive, and c) Teflon is easier to apply since the adhesive is already present on its back surface. It was deemed advisable to utilize both films in order to establish a somewhat greater history with each before a final selection was made. The 2 mil thick polyethylene was increased to 6 mil to make it more comparable to the Teflon's thickness (i.e. 6.5 mil) and to reduce wrinkling. Final moldings were carried out only with the polyethylene interface.

In order to facilitate degassing of the epoxy-urethanes, the addition of minute amounts of anti-foaming agents to the polyol side of the system was considered. This conceivably added approximately 10. parts per million of non-reactive substances to the cured formulation; probably an acceptable level. This evaluation was carried out in conjunction with a set of experiments to more clearly determine the effects of some processing variables on the problem of outgassing observed during the degassing and the cure cycles. F-570-3 contained no anti-foaming agent. F-586 contained 0.1% AF-2. F-588 contained 0.1% AF-4. These formulations are shown in Table 6-50. The experimental pattern and the results are shown in Table 6-59.

This cursory examination resulted in the following observations and conclusions:

a) Neither 0.1% AF-2 or 0.1% AF-4 caused a significant reduction in voids when added to the resin.

b) Both AF-2 and AF-4 caused a significant reduction in voids when wiped on the strip molds after MEK cleaning.

c) There was no significant difference between AF-2 and AF-4 when used in the above wiping mode.

d) There appeared to be no significant difference in use of either "shop" or reagent grade MEK, with respect to rate of gas generation or retention of gases.

e) No significant difference was observed in the use of either used or new strip molds.

f) Except for a specimen cured at 150°F while in a vacuum, all of the specimens shown had an almost opaque surface coating. (Reaction with moisture in air oven?)

g) The surface coating "cured" prior to lower transparent portion. This probably prevented gases from escaping.

h) The 150°F/vacuum cured specimen also had voids. A lower stannous octoate content might have helped.

i) None of the specimens darkened in the air oven as did similar ones which did not contain ERX-67. (A potential anti-aging property?)

While the above evaluation was being conducted, representative cured samples of each of these formulations were submitted to NASA for contamination studies. The tests and their results are tabulated in Table 6-60. It is seen that the total organics (TO) in all cases are excessive even though the carbon monoxide (CO) is well below the requirement. It is not known whether the differences noted between each of the -NV specimens and between each of the -V specimens are due to inherent experimental error or whether it was caused by material and/or process differences. If the latter, the data are inexplicable since their only differences are the presence or non-presence of the anti-foaming agents. It is also evident that the preconditioning of the specimens significantly improved all of the offgassing tests except "CO."

The vacuum volatility results are also not conducive to clear cut decisions. For example, when no anti-foam agent is present, both weight loss and VCM are reduced after preconditioning. On the other hand, the AF-2 system values increased in both tests. The one with AF-4 increased its weight loss but its VCM was reduced. It is also seen that none of the weight losses were within the specification.

SECTION 7

FORMULATIONS DEVELOPMENT: FINAL SCREENING

Based upon the Preliminary Screening results (see Section 6.), this phase of the program was comprised of additional testing of the following formulations:

a) F-476 (modified silicone RTV)
b) F-471 (modified fluorosilicone RTV)
c) F-537 (epoxy)
d) F-590 (epoxy-urethane)

The quantitative testing for this phase included:

a) electrical properties, including a repair and rework evaluation
b) mechanical properties
c) physical/chemical properties
d) flammability.

7.1 FORMULATION AND PROCESSING

The formulation batches prepared for this phase are tabulated in Table 7-1. Their processing is shown in Table 7-2. In order to expedite the Program, the batches and processing required for the Product Characterization (Phase IV) were simultaneously carried out with the Final Screening phase. The disposition of the fabricated specimens for both phases are tabulated in Table 7-3.

7.2 TEST AND EVALUATION

7.2.1 General Properties

The electrical, mechanical, and physical/chemical properties are tabulated by formulation specie as follows:

Modified Silicone RTV	Table 7-4
Modified Fluorosilicone RTV	Table 7-5
Epoxy	Table 7-6
Epoxy-Urethane	Table 7-7

It is seen from Table 7-4 that, except for dielectric strength and a marginal value for power factor, the electrical properties of the modified silicone RTV are quite good. In fact, they have the best overall electrical properties of the four compounds considered in this phase of the program. Even those tested after the moisture cycle appear satisfactory. The extreme range of values found with the single specimen after vacuum exposure and moisture cycling may reflect some anomolous behavior of this specimen rather than being typical of the formulation. The effect of vacuum alone on the resistance is apparently insignificant. Other than having a slightly higher specific gravity than the target value, the remaining property requirements are satisfactorily met.

Although the power factor of the modified fluorosilicone RTV system (see Table 7-5) is clearly better than the modified silicone RTV one, and its dielectric strength is somewhat better, higher dielectric constant and very poor arc resistance, coupled with some lower insulation resistance values, indicate its inferior electrical properties to that of the silicone one. In addition, its mechanical strength properties are definitely worse.

The very poor electrical properties of the epoxy system (Table 7-6) are quite evident. The results possibly indicate a stoichiometric imbalance in the formulation.

The poor elevated temperature electrical resistance values for the epoxy-urethane (see Table 7-7) system, especially when preconditioned with the moisture cycle, reduces its value as an electrical potting compound, together with the poor arc resistance. However, it is seen that its mechanical properties are quite good.

The hardness information for the four formulations is shown in greater detail in Table 7-8, as are the complete details regarding the viscosity determinations shown in Table 7-9. It is seen in the latter table that the modified silicone RTV is thixotropic whereas the epoxy and epoxy-urethane are not.

The properties of the four systems are summarized in Table 7-10. It is clearly evident that, with respect to these data, the modified silicone RTV is the likeliest candidate for production, followed by the epoxy-urethane and fluorosilicone RTV, with the epoxy being of minimal interest. Since there is presently an availability problem with the fluorosilicone RTV base, and its cost is almost an order of magnitude higher than the silicone RTV base, it also has a low level of interest.

It is also apparent that the modified silicone RTV developed in this program is superior to the original SG-12 KI formulation in almost all respects (see Table 7-11). On the other hand, the reverse is true in the case of the comparison (see Table 7-12) between the modified fluorosilicone RTV developed herein and the F-387 formulation of NAS 9-8750.

7.2.2 Final Screening Flammability

As previously discussed in Section 5. (test methods) and Section 6. (test results), the preliminary flammability tests at Furane were conducted with a silicone RTV ignitor in a 10. psia, 30 % O_2/70% N_2 environment, using 5." test specimens. Final testing was to be conducted with the silicone RTV ignitor in the same environment, but using 12." long specimens. This length was specified in order to determine whether the test specimen self-extinguished in less than 6.", as required by the test method stipulated in the Statement of Work.

It is seen from Table 7-13 that the specimens were initially cut and tested by NASA as 5." long specimens. Therefore, it was not feasible to determine whether self-extinguishment could have occurred in less than 6.". In addition, a propane gas ignitor was utilized for the testing instead of the silicone RTV one.

At this time the technical criteria of this study was shifted to the most recent criteria of the Shuttle program. This necessitated the evaluation of the formulations in a 14.7 psia air environment. When longer specimens were used in conjunction with the propane gas ignitor and the revised environment, all of the Furane formulations so tested, met the self-extinguishment requirement. It is also seen that, with respect to the other behavioral aspects (e.g. burn length, burn time, etc.), the modified silicone RTV was the best, the epoxy one was the least desirable, and the epoxy-urethane formulation was somewhere in between but close to the silicone RTV.

SECTION 8

FORMULATIONS DEVELOPMENT: PRODUCT CHARACTERIZATION

As seen from Figure 3-2, Phase IV consisted of the following tests performed by NASA on Furane-prepared (see Table 7-1), -cured (see Table 7-2), and -test distributed (see Table 7-3) material:

a) carbon monoxide (CO) and total organics (TO)
b) odor
c) vacuum volatility
d) oxygen aging
e) oxygen impact

The formulations considered in this section at the start of this phase were:

a) F-476 (modified silicone RTV)
b) F-537 (epoxy)
c) F-590 (epoxy-urethane)

8.1 OUTGASSING (CARBON MONOXIDE/TOTAL ORGANICS)

The test conditions and results are tabulated in Table 8-1. Although the tests were specified to be run in accordance with Reference 8-1, they were actually carried out per Reference 8-2. The major difference between the two procedures, as performed by WSTF (Ref. 8-3), is that the former involves the use of air at ambient pressure, and the latter uses 5. psia pure oxygen. Also, the reference point in calculating total organics (TO) differs between the two procedures. The former is based upon pentane equivalents; the latter on methane. However, the data reported in Table 7-1 have been converted to pentane equivalents.

The effect of a vacuum post cure at 150.°F on the specimens were compared to non-post cured ones. The assumption being that low molecular weight components, both cured and uncured materials, might be readily removed from the "cured" compound by such a treatment. If desirable, such a post cure could usually be incorporated in the preponderance of production molding operations. In the case of each formulation, the weight loss percentage was significantly (i.e. 1/2 to 1/4) reduced by the post cure. On the other hand, the TO data somewhat differs from these results. There is almost a 14:1 reduction in TO for the modified silicone RTV, an insignificant reduction for one epoxy, a slight increase for the other epoxy, and a 3:1 reduction for the epoxy-urethane. Further, it is seen that the post cured silicone RTV and the epoxy-urethane systems had identical weight loss percentages (i.e. 0.0020) but their TO values differed by almost two orders of magnitude. In fact, the epoxy-urethane's TO was more than twice as high as the permissible 100. μgm/gm. Both the epoxy and the modified silicone RTV systems were significantly below this level, regardless of whether they were post cured or not. The lowest value (i.e. 3.4μ gm/gm) was obtained with the silicone. No other value was even close to it.

As seen from the mass spectrometer constituents analysis, the high values for the epoxy-urethane appear to be primarily due to the presence of benzene and, secondarily, to bromoethane. The post cure certainly helped to clean up this system since it removed from detectability chloroethane, ethyl alcohol, methyl ethyl ketone, chlorobenzene, and toluene. In addition, it removed almost 40.% of the bromoethane and approximately 35.% of the benezene. The remaining bromoethane and benzene were the only detectable constituents left in quantities greater than 1.μ gm/gm. Curiously, no nitrogen compounds were detected. Their presence might be expected to some extent if the stoichiometry wasn't exact since two of the raw materials for the formulation are ERX-67 (i.e. n,n-diglycidyl-2,4,6-tribromoaniline) and PAPI 901 (i.e. modified polymethylene polyphenylisocyanate). This would appear to give further credence to the unique reaction described in Figure 6-2.

In all cases, the data in Table 7-1 shows that there was no difficulty in meeting the carbon monoxide (CO) limit of 25.μ gm/gm. The lowest values were obtained with the silicone RTV. The rest had CO values more than a magnitude higher.

8.2 ODOR

Test specimens were taken from the same post cured and non-post cured samples from which the CO/TO specimens were obtained. The conditions and results of the tests are shown in Table 8-2. The silicone RTV, with and without post cure, was the only system which met the requirement of a maximum rating of 2.0, when not diluted either initially for safety reasons, or when not diluted in the test. It is also seen that the post cure of the RTV seemed to remove even the negligible odor present. Post curing of the epoxies did not make much difference when one considers that the 600-1-4B (V) was initially diluted. Since the dilutions were so drastically different for the epoxy-urethane test samples, with and without post cure, it is quite difficult to draw comparison-type conclusions.

8.3 VACUUM VOLATILITY

It is specified (Appendix J) that:

> "The materials shall have a maximum weight loss of 1.0% and a volatile condensable material (VCM) content of 0.1% when tested in accordance with the test procedure...".

It is evident from the data tabulated in Tables 8-3, 8-4, 8-5, and 8-6, and summarized in Table 8-7, that all of the formulations satisfy these requirements. The data (see Figure 8-3) for the one surviving post cured RTV sample, compared to the two non-post cured ones, would seem to infer that the post cure does reduce the VCM. The change in weight loss percentage is less noticeable. The data (see Figure 8-4) for the epoxy-urethane formulation is somewhat contradictory. The weight loss percentage is a little higher for the post cured specimen, while its VCM is lower. A similar situation is seen in Figure 8-5 for one of the epoxy sample sets. On the other hand, the F-600-1-1 epoxy shown in Figure 8-6 has just a reverse set of data trends. Thus, the weight loss percentage is a little lower for the post cured segment, and the VCM is a little higher. It is seen from Figure 8-7 that the epoxy-urethane weight loss is about half that of the epoxies, and its VCM, after post cure, is at least as good as the epoxies.

8.4 OXYGEN AGING

The modified silicone RTV and the epoxy-urethane were given an accelerated aging by exposing them to 300. psi oxygen for 96. hours at 156.°F. The data in Table 8-8 shows no significant change in tensile strength and only a 5.% reduction in percent elongation. The epoxy-urethane evidences a 23.% increase in tensile strength after aging and a 16.5% reduction in percent elongation. Both of these facts would indicate that the polymeric structure was becoming more crosslinked as a result of this environment. However, the "aged" properties were still within the 350. psi and 125.% minimum limits (Appendix A).

It is interesting to note that the initial tensile strength and elongation differences between data obtained by NASA and that obtained by Furane is less than 8. and 4. percent, respectively. But a considerable variation occurs with the epoxy-urethanes. The contractor obtained 54.% higher tensile strength and 32.5% lower elongation.

8.5 OXYGEN IMPACT

Neither the modified silicone RTV nor the epoxy-urethane have any reaction to a mechanical impact of 50. ft. lb. energy while exposed to GOX up to 5000. psia (see Table 8-9). However, pneumatic impact of 1000. psia or greater results in a reaction with both materials. The definition of a "reaction" is as follows:

> "A sample reaction has occurred when, upon completion of an impact test, the sample exhibits discoloration, charring, burning and/or an odor indicative of burning."

Based upon the results shown in Table 8-9, and the relationship between "intended application pressure" and "screening test pressure" (Appendix K, Section 2.2), the maximum intended application pressures for both formulations would be:

Mechanical impact:	3333. psia
Pneumatic impact:	375. psia

SECTION 9

COMPOUND PRODUCTION

Based upon the program's data, the NASA Technical Monitor selected the modified silicone RTV as the optimum compound. The base materials were then procured, processed into the required 50. lb. of uncured compound, given a minimal quality control evaluation, and shipped to NASA. A sample of this batch of the compound was pigmented, cured, and checked for hardness. Reformulation of the same constituents was then carried out to provide a pigmented catalyst for the same end formulation. The preparation of a production procedure applicable to this material is also provided.

9.1 PRODUCTION of 50. lb. EPOCAST 87517-A/B

The materials necessary for the preparation of the selected modified silicone RTV (Furane's production designation: EPOCAST 87517-A/B) were obtained. However, the glass frit was received at a lower weight than what was ordered. Since this material requires a 30. day lead time, it was not deemed advisable to order additional material. This meant that there was very little margin for error or waste, and its quantity became the basing point for calculating the proportionate amounts of the other ingredients for the formulation. The frit was dried at 212.°F for 48. hours, placed while hot in two Tedlar bags, heat sealed, and stored until blending was initiated. Three gallons of the base resin, all from the same batch, was added to a new five gallon polypropylene bucket which had been carefully cleaned with reagent grade MEK and dried until no solvent odor was detected. However, it was also necessary to add some of the same resin from another batch. "Since the curing agent is matched with the resin for each batch to achieve a given pot life, it would be advisable to commingle the curing agents from the two batches in the same proportion as the resins from the two batches" (Ref. 9-1). This recommendation was implicitely followed in the preparation of the compound (Table 9-1).

While the resin was being churned by a Myer's high speed dispenser, the frit was removed from the Tedlar bag and quickly added to the resin. When all the frit had been well blended, the Phos-Chek P/30 was gradually added to the mixture until all of the required amount was present (F-595-2). In order to prevent the blend from overheating, the mixture was allowed to cool to approximately ambient temperature. Approximately three-quarters of a gallon of the mixture was added, while still warm, to a one gallon polypropylene bucket which had been cleaned similarly to the five gallon one. This partial bucket was then carefully blended with the dispenser until the temperature reached approximately 150.°F. This material was then deposited into another cleaned five gallon "poly" bucket. This procedure was repeated five more times, at which time the original five gallon bucket was empty. The mixture, now all in the second five gallon bucket, was reblended in this five gallon bucket. When the temperature had again risen to 150.°F, the one gallon bucket was again three-quarters filled, cooled to room temperature, reblended, and readded to the first five gallon bucket. This was repeated with the remaining material and repeated again from the other bucket. The required quantity was then added to one of the five gallon buckets and the container was sealed with a rubber tubing-gasketed polypropylene lid.

The proper proportions of Sylgard 186 Curing Agent were blended (F-605-1) from the batches from which the resin was derived.

A portion of the two components were then utilized for a minimal quality control evaluation. The viscosity is shown in Table 9-2 for both catalyzed and uncatalyzed compound. The results, and as similarly seen from Table 7-9, indicate that the uncatalyzed portion of the system is definitely thixotropic. Although the data in both tables were obtained with the same viscometer by the same operator, it is seen that a comparison of the two tables raises the obvious question as to why the results were higher at a higher temperature. Considerable care was known to have been taken in preparing both batches, and was carried out by the same operator. The only apparent difference was in the blending methods. The original material was prepared by hand blending. As noted above, considerable mechanical blending at 70.-150.°F was carried out on a Myer's disperser for the production batch.

The catalyzed material was cured into cast flat sheets between Mylar covered glass plates. One was cured at 150.°F for 2. hours (F-596-6B). Another (F-596-6C) was cured at 150.°F for 13. hours. The third one (F-596-6A) was cured at room temperature (approx. 60.-70.°F) until tested for hardness (i.e. 19. days later).

Since the F-595 is white and the F-605 is a colorless clear liquid, the uniform blending of this material is an uncertain step. Our previous experience (Ref. 3-7) with the base resin, Sylgard 186, has shown that it can be readily pigmented with non-toxic inorganics. A sample of the EPOCAST 87517-A/B system was pigmented with 7540 Meteor Cobalt Blue (Harshaw Chemical Co.) and also cast into a similar panel (F-607-1). The casting was made on the same glass plate setup as F-596-6C and simultaneously cured with it at 150.°F for 13. hours. The average results, 19. days after catalyzation, for these four panels are shown as follows:

	Thickness (in.)	Hardness (Durometer A-2)
F-596-6A	0.088	56.
-6B	0.087	56.
-6C	0.094	54.
F-607-1	0.095	53.

Since the hardness requirement is 30.-85. (Durometer A) all of the panels comply. The lack of significant (i.e. within experimental error) differences between the hardness values of four panels should be observed with respect to their differences in cure cycle. It would seem that the pigmenting had little effect upon the hardness. It should also be noted that the previous experimental batch of the unpigmented material had an average hardness (Durometer A-1) value of 58. for an 0.080 panel. It is seen from these data that the thicker panels had lower hardness values. This is possibly a coincidence. On the other hand, the readings may be slightly affected more by the hard surface upon which the measurements were made, in the thinner sections.

After packaging 47.47 lb. of F-595-2 and 3.06 lb. of F-605-1 for shipment, they were sent to NASA Johnson Spacecraft Center as EPOCAST 87517-A and EPOCAST 87517-B, respectively.

9.2 PIGMENTED CATALYST

Since no apparent effect on cure was noted in F-607-1, the possibility of adding the pigment to the curing agent was investigated. F-608-1 was prepared by gradually adding the frit to a mixture of curing agent and pigment. Even an excessive amount of the frit was not enough to stabilize the viscosity so that the blend would remain homogeneous after long time storage. Another blend (F-609-1) was prepared by gradually adding the Phos-Chek P/30 to a mixture of the curing agent and pigment. A highly satisfactory paste was obtained, which also appeared to be thixotropic. In order to keep the total formulation identical to F-607, F-610 was formulated as the other part of a typical two-part system. At the time of completion of this report, this non-required task, including the curing and evaluating of the resultant blend, F-611, was still being conducted. A sample of F-609 and F-610 will be forwarded to the NASA Technical Monitor for his consideration.

9.3 PRODUCTION PROCEDURE

In the production of this modified silicone RTV casting material, there are three basic problems to be considered:

1) pre-drying of the highly hygroscopic glass frit,
2) overheating of the ammonium polyphosphate, Phos-Chek P/30, and
3) minimizing the contact of the glass frit with metallic shearing/dispersing equipment (with the exception of polyethylene lined mills, there is no readily available equipment to process the quantities herein desired without contributing uncontrolled amounts of metallic contamination).

The following procedure is designed to minimize the above problems and can produce 50.-100. lb. batches.

a. Prepare a two part modified silicone RTV compound with the following ingredients:

EPOCAST 87517-A

Sylgard 186 (Dow Corning)	100. pbw
Phos-Chek P/30, Reg. (Monsanto)	50. pbw
7570 Glass Frit, 325 mesh (Corning Glass)	25. pbw

EPOCAST 87517-B

Sylgard 186 Curing Agent (Dow Corning)	10. pbw

b. Pre-dry the 7570 Glass Frit at 212.°F, minimum, for 48. hours. The frit is to be no more than 1/4 in. in depth during this drying process. After completion of the drying, and before the frit has cooled, store in pre-weighed Mylar or Tedlar bags. Add a pre-weighed desiccant moisture indicator container to the bag, and immediately heat seal the bag. Reweigh the bag and mark the net weight of the frit on it. Store filled bags, until required, in such a manner as to prevent loss of air tightness.

c. Clean high density polyethylene or polypropylene processing and shipping containers with reagent grade methyl ethyl ketone (MEK). Store sealed until required.

d. Prepare a suitable disperser (e.g. Myer's High Speed Disperser) so that oil and/or grease sources (e.g. bearings) are covered. Clean the blade(s) to remove all sources of contamination such as residual materials from previous runs. Wash the blade(s) with reagent grade MEK until no contamination is observed after wiping with a lint-free paper or fabric which has been soaked with MEK.

e. Weigh out approximately 20.% of the Sylgard 186 needed for the pre-weighed amount of frit in a cleaned processing container.

f. While stirring this resin with the dispersing machine, operating at a blade peripheral velocity of 1700. feet/minute (note: this results in a rolling toroid of material that efficiently provides the shearing force to the mixture), add the frit until it is wetted out and reasonably dispersed. Completely remove the residual mixture from the blade(s) and add it to the container. Cover and store this container until required.

g. Weigh out the remaining Sylgard 186 needed for the pre-weighed amount of frit in a cleaned processing container sufficiently large enough to blend all the ingredients. Use a double shaft blade arrangement for large quantities.

h. While stirring the resin with the dispersing machine, add the Phos-Chek until it is completely wetted out and thoroughly dispersed. Do not allow the temperature to exceed 150.°F.

i. Gradually add all of the premixed resin/frit mixture to the resin/Phos-Chek mixture until a uniform blend is obtained. For ease of blending and/or achieving complete homogeneity in minimum time, repetitive partial blendings are advised. At no time should the mixture's temperature exceed 150.°F. This mixture is now labeled as EPOCAST 87517-A and identified with a lot number and manufacturing date.

j. The Sylgard 186 Curing Agent from the same batch as the resin is reidentified as EPOCAST 87517-B and given the same lot number and manufacturing date as the "A" component. If the resin portion of the "A" component contains resin from two different batches, the curing agents are combined in the same ratio as their resin counterparts.

k. Place 450. ml of the "A" component in a 600. ml beaker. Determine the viscosity at 75. ± 5.°F, using a No. 6 spindle on a Brookfield Model RVT Viscometer at 1. and 2.5 rpm. Determine the specific gravity of the "A" component. Catalyze 175. pbw of "A" with 10. pbw of "B," blend, degas at 29. in.Hg vacuum at room temperature, and redetermine the viscosity. Determine the gel time of 10. gm of the catalyzed formulation.

l. Cast a sheet, approximately 6." x 6." x 0.080 in., minimum. Cure for 2. hours at 150.°F. Determine hardness and specific gravity of the cast sheet.

m. If the materials meet the requirements, they shall be packaged and shipped to the customer.

Manufacturing Costs (manhours):

Weighing and equipment preparation	2. manhours
Production and packaging	4. "
In-process and final product - quality control	2. "
Equipment clean-up	1. "
Total	9. "

The above can produce 50. lb./shift.
Material lead time - 30 days (i.e. Glass Frit) A.R.O.
Furane lead time - 10 working days.

SECTION 10

CONCLUSIONS

10.1 EPOCAST 87517-A/B

a. The following formulation, based upon the modified silicone RTV, F-476/596, was found to have the best balance of thermal, electrical, mechanical, physical and chemical properties of those formulations evaluated in this program.

Sylgard 186 (Dow Corning)	100. pbw
Ammonium Polyphosphate (Phos-Chek P/30, Reg.: Monsanto)	50. "
7570 Glass Frit (Corning Glass)	25. "
Sylgard 186 Curing Agent (Dow Corning)	10. "

b. This formulation met all of the requirements of the Statement of Work (Appendix A) and its modifications, except for the following:

Test	Requirement	T/M (1)	Results (ave.)
Power factor	0.09	M	0.11
Dielectric strength (v/mil)	350., min.	M	240.
Specific gravity	1.25, max.	T	1.40
Clarity	water clear	T	opaque

1. T..... Target value M.....Mandatory value

c. It appears to be suitable for potting, encapsulating, and conformal coatings of electrical and electronic systems requiring immediate self-extinguishment in air or low flammability in augmented oxygen environments. It should be noted that its insulation resistance significantly exceeds the 5. x 10^8 ohms, minimum, required for regular printed circuit boards (Ref. 10-1) and for multilayer printed circuit boards (Ref. 11-2). The high surface (4.7 x 10^{16} ohms) and volume (1.3 x 10^{15} ohms) resistivity, as well as its high arc resistance (127. seconds), are also noteworthy.

d. In comparison to previously developed low flammability systems based upon a silicone RTV system (e.g. SG-12 KI: Table 7-11), EPOCAST 87517-A/B is far superior in all electrical respects except for power factor (significant difference) and dielectric strength (negligible difference). Its mechanical properties are higher, and its hardness and specific gravity are lower. EPOCAST 87517-A/B is, by comparison to SG-12 KI, significantly less affected by the high humidity cycle.

e. EPOCAST 87517-A/B's two part system is readily blended, degassed, and is capable of being applied by spatula, injection or extrusion gun, or even slowly poured. It can also be brushed or dipped with ease; spraying, while possible, would be more difficult unless thinned with a solvent. Similarly, if a very thin electrical coating is desired, it may be possible to dilute the compound with a low boiling perfluorinated solvent to obtain a lower viscosity system. Usage of such solvents may necessitate the frequent agitation of the blend to assure homogeneity during application. Solvent removal would be essentially complete subsequent to a thermal/vacuum post cure.

f. The data indicates that a vacuum/thermal post cure reduces the percent weight loss, percent volatile condensable material (VCM), outgassing (CO/TO), and odor.

g. This polymeric system, while readily processed, is sensitive to contamination, as are all addition reaction silicone RTV's. The "B" component apparently reacts with certain chemical specie, thereby inactivating it. Contact with such materials (or even their vapors) as:

   1. Amines and amine-cured elastomers and plastics, and certain other nitrogen compounds used to cure elastomers and plastics (Refs. 10-3, -4, -5, and -6).

   2. Tin compounds (Ref. 10-3),

   3. Sulfur and sulfur compounds (and their residues), such as are used in organic rubbers (e.g. butyl and chlorinated rubbers) (Refs. 10-3 through 10-7, inclusive),

   4. Acid materials (and their residues) used in some silicone RTV rubbers (Refs. 10-3 through 10-7, inclusive)

   can inhibit cure at the surface, or possibly the entire structure of the compound. This can conceivably create compatibility problems ranging from contacted components and substrates, to tooling and facilities (i.e. cure ovens). Careful selection and cleanliness of contacting materials, equipment, and facilities is therefore maintained during the formulation and cure phases, and can probably be provided in production, or even in the field, with only minimal inconveniences. Where an incompatible material or component can not be avoided, coating it with a barrier or primer to act as an interface will suffice.

h. The ingredients in this formulations are essentially non-toxic from the standpoint of skin absorption. Normal handling and usage should present no particular hazards.

10.2 EVALUATED FORMULATIONS

10.2.1 Modified Silicone RTV Polymers

a. Preliminary flammability tests did not show any significant difference between the presence of 75 or 50 phr of Phos-Chek P/30, or 50 or 25 phr of the 7570 glass frit. A reduction of the P/30 to 25 phr becomes significant. The removal of the frit doesn't change the flame-out time, but there is evidence of increased degradation and in the degradation distance. The P/30 appears to limit the burn time.

b. When Dechlorane 604 is used as the flame retardant instead of P/30 and the frit, the flame-out time and residue percentage improved, but a greater surface char distance is noted.

10.2.2 Modified Fluorosilicone RTV Polymers

a. RTV 77-033 (Dow Corning), the base for F-387, is no longer available. RTV 94-531 (Dow Corning), an available "substitute" does not have quite the same flammability resistance as the original material, especially at lower levels of Dechlorane 604. Other than a slightly lower self-extinguishing distance, this system as formulated herein, has poorer flammability resistance than the EPOCAST 87517-A/B.

b. The mechanical properties of these modified fluorosilicone RTV systems are less satisfactory than the modified silicone RTV ones.

c. The $70.00/lb. cost of the RTV 94-531 is the highest cost precurser used in the program, and is more than a magnitude higher in cost than the Sylgard 186.

d. This system does not meet the Statement of Work requirements for dielectric constant, arc resistance, tear strength, tensile strength, elongation, or specific gravity.

e. In general, the properties of this system were inferior to those obtained with F-387 (see Table 7-12).

10.2.3 Polyester Polymers

a. Brominated, but solid, polyester resins can be satisfactorily dissolved in the phosphorous-containing reactive diluent dimethyl allyl phosphonate (DMAP) and cured at room temperature or 150° F with a ketone peroxide/cobalt system to a clear semi-hard material which has poor mechanical properties such as tear resistance. This material is immediately self-extinguishing with a match ignitor in air and, hence, has some further interest as a clear, flame retarding system.

b. Isophthalic and bisphenol polyesters are not sufficiently compatible with such reactive flame-retarding diluents as DMAP, FYROL Bis-Beta (Stauffer Chemical Co.), or BIS(DBP) H (White Chemical Co.).

c. The pre-blends which consisted of a flexible polyester, a brominated polyester, and a reactive phosphorus-containing polyester, considered in this program, are not adequately cured by either a) redox-promoted aromatic diacyl peroxide (i.e. 2,4-dichlorobenzoyl peroxide), or b) tertiary butyl peroctoate.

10.2.4 Epoxy Polymers

a. The epoxy formulations utilized in this program do not provide a satisfactory balance of flammability resistance in 10. psia, 30.% O_2/70.% N_2, flexibility, and good electrical and mechanical strength. Their slight tack, slight melting during flammability testing, poor odor test results and only fair outgassing resistance indicate a possible stoichiometry imbalance. It should be noted that its weight loss percentage and VCM are higher than the modified silicone RTV and the epoxy-urethane, but are still within the allowable limits.

b. Solid brominated epoxy resins can be solubilized with a reactive, brominated epoxy diluent, ERX-67 (Shell Chemical Co.), to a 75.°F shelf stability of approximately 2. weeks.

c. D.E.R. 741 (Dow Chemical) is also a suitable diluent which can impart some flexibility, but it does not contain any flame-retarding constituents.

d. The flexible amine-cured RTV 602 (G.E.) does not seem to be compatible with the epoxies tested in this program. Even though the individual components are clear, the castings are opaque. They are also quite stiff.

e. It is not feasible to solubilize tetrabromophthalic anhydride in bis dibromopropanol phosphoryl dimethylol amide (bis(DBP)AM: White Chemical Co.) at a low enough temperature at ambient pressure.

Therefore, a preliminary step of reaction between the two moieties could not occur and, hence, a low temperature cure with a flexibilized brominated epoxy pre-blend can not be carried out.

Also, a pre-blend of the anhydride dissolved in D.E.R. 741 is not readily accomplished without causing an insoluble reaction product from forming in part of the mixture.

f. Mono dibromopropanol maleate (DBP-ES: White Chemical Co.) has low solubility in DMAP even when heated. This prevents their being reacted with each other via a free radical initiator, which, in turn, would produce available carboxyl groups which can be reacted with a flexibilized brominated epoxy preblend.

g. The reactive brominated compound, ERX-67, blends with the epoxy flexible (?) resin (D.E.R. 741) (noted in Table 6-24). This preblend system has a very low viscosity, high bromine content, and is stable at room temperature.

h. The high humidity/thermal exposure slightly increased specimen tack.

10.2.5 Urethane Polymers

a. Non-accelerated (e.g. dibutyl tin dilaurate or stannous octoate) formulations of a bromine/phosphorus-containing dihydroxy polyol, Brominex 160P (Swift Chemical Co.), with various diisocyanates have no voids, but are only poorly cured after a minimum of 100. hours at 150.°F.

b. At similar concentrations, stannous octoate gives a better cure and less voids than dibutyl tin dilaurate.

c. Stannous octoate, at an 0.08% level with these diisocyanates and the Brominex 160P, provides void free castings in 55.-100. hours at 150.°F. Although higher concentrations of the stannous octoate shortened the cure time, it increased the void content.

d. The rates of gelation for the three diisocyanates utilized for the urethanes in this program were:

Isonate 143L $>$ PAPI 901 $\gg$ Brominex 9107

e. Castings with Isonate 143L have a much lighter color than those made with PAPI 901.

f. Tedlar film and silicone coated fiberglass cloth release well from urethanes; not so with Mylar film.

g. Urethane systems based upon the formulations herein cured, do not as readily cure as prepolymer systems.

h. The flammability resistance of the urethane system tested in 10. psia 30.% O_2/ 70.% N_2 was not as good as the modified silicone RTV or the epoxy-urethane, but was comparable to the epoxy.

i. None of the urethane formulations conditioned in high humidity and heat are hydrolytically stable.

10.2.6 Epoxy-Urethane Polymers

a. Commercially available pre-reacted epoxy-urethanes are not sufficiently flexible for the applications intended in this program.

b. There are no commercially available co-reacting epoxy-urethane systems, let alone ones which would be flame-retarding.

c. An apparently unique reaction sequence was developed under this program which utilizes, in terms of their respective ratios of equivalents (see Figure 6-2):

diepoxide/dihydroxy polyol/diisocyanate: 1/1/2

Based upon the ingredients used, it is possible to incorporate on the resultant polymeric structure bromine, phosphorus, and nitrogen.

d. Diethyl N,N-bis(2-hydroxy ethyl) amino methyl phosphonate (e.g. Fyrol 6: Stauffer Chemical Co.) appears to accelerate the cure of the co-reacting system developed in this program.

e. PAPI 901, although darker in color, is preferable to the Isonate 143L, because its package stability is apparently better.

f. The moisture/thermal conditioning cycle reduces surface transparency but does not seem to affect the interior.

g. Low electrical resistance at 212.°F, especially after a high humidity/thermal conditioning cycle, and its low arc resistance, minimizes its usefulness as an electrical insulation.

h. Its mechanical strength properties are better than the other formulations so tested.

i. The epoxy-urethane is almost as flame retardant as the modified silicone RTV. They are both self-extinguishing when the ignitor flame is removed. The burn time and burn length is just slightly greater.

j. The outgassing from this formulation is greater than for the modified silicone RTV or the two epoxies tested. Although its carbon monoxide is within the allowable limits, the total organics are very high. However, the vacuum/thermal post cure clearly reduces both values.

k. The effect of vacuum exposure is tolerable; the specifications are met.

l. Odor results, even after a vacuum/thermal post cure, are still unsatisfactory.

m. The target value of 20.%, maximum, change in tensile strength after oxygen aging wasn't met. The elongation value was only a 16.5% difference. Therefore, it is considered satisfactory in this latter regard.

n. This formulation may be used for applications whose limits are:

Mechanical impact: 3333. psia
Pneumatic impact: 375. psia

10.3 GENERAL

a. The modified silicone RTV's are the easiest to fabricate into cured structures; the epoxy-urethanes are the most difficult.

b. Anti-foaming agents added to the epoxy-urethanes do not result in a lower void content. However, wiping the molds with these agents significantly helps in surface void removal.

c. Cured epoxy-urethane specimens containing ERX-67 had a lighter color than those which did not.

d. Production quantities of EPOCAST 87517-A/B can readily be made on available Furane equipment. Contamination by inhibiting materials can prevent cure. Preparation of cured samples and checking their hardness is the simplest method to determine degree of cure.

e. Pigmenting of EPOCAST 87517-A/B does not significantly affect hardness.

SECTION 11

RECOMMENDATIONS

11.1 EPOCAST 87517-A/B

a. Consider the utilization of this formulation for potting, encapsulating, conformal coating, and sealing in aerospace/industrial/commercial industries for such applications as:

- augmented oxygen areas
- electrical/electronic systems
- fuel lines, tanks, and indicators.

b. Evaluate Phos-Chek P/30 "Regular" in comparison with the "fine" grade with respect to processability and end product properties.

c. Reformulate this system so that a non-toxic, non-flammable, etc., pigment is incorporated with the curing agent in such a manner as to stabilize it for extended storage periods (see Section 9.2).

d. Establish appropriate quality control limits which are relevant to specific end product performance.

e. Evaluate the vacuum weight loss and VCM similar to the manner in which the present data was obtained, except that the exposure temperature should be 257.°F instead of 150.°F in order to more realistically compare this formulation with other materials previously tested in accordance with Appendix J.

f. Examine processing variables in greater detail. Consider such factors as:

1) Minimum cure time at ambient and at 150.°F with respect to cured properties,
2) Six month storage life of the "A" and "B" portions on final handling/processing and on cured compound's properties,
3) Optimum vacuum/thermal post cure cycle,
4) Suitable solvent and solvent percentages for low viscosity versions.

g. Carefully solvent clean molds and other substrates (e.g. wire insulation, connectors, etc.), oven dry, if possible, and keep in non-contaminating environment.

h. Verify suitability of the recommended pigment with respect to end product properties.

11.2 EVALUATED FORMULATIONS

a. Improve the mechanical strength of the polyester system and consider its use where a solvent-free, clear, low viscosity, low flammability system is required.

b. Review the stoichiometry of the epoxy system F-600. Note clarity of casting, and potential of good aging properties in oxygen and/or radiation environment due to presence of ERX-67.

c. Further development work is recommended for the epoxy-urethanes to reduce their processing difficulties and improve their electrical properties. This continued interest is due to their low viscosity, low flammability, transparency, minimal effect by the moisture cycle, and high mechanical strength.

   1) Consider the use of Fyrol 6 as a partial substitute for the Brominex 160P since this may accelerate the reaction and lighten the color of the casting.
   2) Determine optimum vacuum/thermal post cure cycle. Particularly note whether post curing removes the bromoethane and benzene on a linear or decreasing exponential curve.
   3) Check stoichiometry with respect to exact hydroxyl and NCO numbers.

d. Evaluate the vacuum weight loss and VCM at 257.°F for the epoxy-urethane.

e. Compare the oxygen aging data for the epoxy-urethanes with specimens exposed to air for 96. hours at 156.°F to determine if a similar hardening of the casting occurs.

f. Also consider use of the epoxy-urethanes in such non-electrical applications as flame retardant sealants.

g. Evaluate ERX-67 as an anti-aging reactive chemical.

SECTION II

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