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INVESTIGATION OF RESIN SYSTEMS FOR IMPROVED ABLATIVE MATERIALS

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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TRW SYSTEMS

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INTERIM REPORT

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July 25, 1966

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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Liquid Rocket Technology Branch
Stephen M. Cohen

TRW SYSTEMS

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demonstrated to provide greater resistance than conventional resin systems to both fluorine/hydrogen and FLOX/methane propellant combustion environments. This may be viewed as if the charred resin is self-reinforcing. The tests also confirmed that the reinforcement has a major affect on ablative performance. However, it was demonstrated, for these conventional reinforcements, that graphite is preferred for use with fluorine/hydrogen propellant combinations and silica is preferred for use with FLOX/methane propellants. Future composite studies will be devoted to 1) determining the relative contribution to ablative performance provided by the reinforcement and the resin and to 2) improving processing techniques and characteristics of the resin systems so that maximum effect of the resin is manifested in the composite.

In the remaining portion of this program the syntheses, optimization and composite fabrication studies will be continued and scaling-up and composite fabrication activities will be initiated.

In summary, material development tasks are being conducted which are aimed at providing new and improved ablative resins for use in advanced composites to be employed with high energy propellant combinations.

Polyamide-imide "stiff" polymers are being investigated to determine methods for fabrication of neat resin masses ameniable to evaluation in fluorine-containing propellant exhaust environments. New, commercially available modified polyimide resins are being evaluated for processability and resistance to the propellant exhaust environments. Inorganic systems, such as zirconium borides and phosphate bonded oxides, both expected to yield advanced resin matrices, are being investigated for resistance to fluorine-containing propellant exhausts.

Preliminary results of the optimization studies show that the organic resin systems chosen for evaluation are resistant to fluorine/hydrogen and FLOX/methane combustion environments. The water content of the FLOX/ methane exhaust was expected to have a much more degrading effect on the organic resins than the contents of fluorine/hydrogen combustion environment. This does not appear to be the case; further testing in the immediate future will provide more reliable comparative data. Sufficient data for evaluation of the polyalkaline earth acrylates, CPBU, and the inorganic systems also will be available in the near future.

Studies of composite resin systems have proceeded by the choice of a resin system, i. e., polyamide-imide considered optimized in Task II. Initial processing studies involved selection of a suitable impregnation solvent, determination of resin content, volatile content, and staging conditions of preimpregnated fabric reinforcements, and establishment of molding parameters. A new modified polyimide resin system also was selected for evaluation. These two resin systems, employed with the methodology determined for fabrication of composites as thick as 5/8 inch, were made into specimens suitable for evaluation in the propellant exhaust environmental test (PEET). Both graphite and silica reinforcements were used. A graphite fabric-reinforced polybenzimidazole resin, plus phenolic based composites reinforced with carbon, graphite and silica fabric were obtained for comparative use in PEET.

Although the planned test matrix of resin and reinforcements has not yet been completed, evaluation of the preliminary data shows several significant trends. "Stiff" polymers, which yield dense chars, were although not tested, that inorganic resins, particularly those containing elements that had refractory fluorides and oxides, were more likely to survive the FLOX/methane combustion environment.

Synthesis and property determinations to date have been directed to the evaluation of new polyimide "stiff" polymers, preparation of intermediates to the key monomers and determination of their properties. The underlying reasons for selection of these polymer systems were presented in Contract NAS3-4188. These considerations have resulted in the selection of modified polyimide polymer systems containing principally unsaturated cyclic chemical groups which are expected to aromatize during processing or under ablative use conditions. The aromatization step is viewed as resin curing, and as such, is a distinct and novel chemical mechanism for curing of resin masses.

The polyimide resin systems under investigation require the synthesis of new dianhydride monomers bis(5-tetrahydrophthalic anhydride) sulfone and bis(p-3, 4-dicarboxy anhydride phenoxy phenyl) sulfone. During the first half of this program precursors for these monomers have been synthesized, isolated and identified.

Optimization of resin systems, identified for use as advanced ablative materials, is being carried out to improve physical, chemical and processing characteristics. Resins selected for optimization have been studied in the present effort, or are state of the art polymers from commercial sources. Methods for optimization include tailoring of chemical properties and studies of cure cycles, catalysts, and aromatization. Improvement of char yields and processability are the most important goals.

Materials under study include poly cyclized polybutadiene urethane (CPBU), which is being investigated to determine processes which will cause aromatization of saturated ring structures with high char yield as the ultimate goal. Poly (calcium, barium and magnesium) acrylates are being investigated to determine processes which will provide dense resin masses suitable for inclusion into ablative materials fabrication techniques.

SUMMARY

This interim report describes the work performed by TRW Systems during the period 10 January through 1 July 1966 for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-7949. This program is an extension of initial studies conducted under Contract NAS3-4188.

The primary objective of this program is to prepare ablative materials, suitable for use with fluorine-containing propellant systems, from improved resin matrices. This objective is being accomplished through experimental studies on the following consecutive material development tasks:

- Task I - Synthesis and property determinations,
- Task II - Resin formulation optimization,
- Task III - Composite processing parameter studies,
- Task IV - Synthesis scale-up, and
- Task V - Fabrication of ablative composites.

During the first half of this program investigations on the first three tasks were initiated.

Two classes of high energy fluorine-containing propellant environments were identified in Contract NAS3-4188. Each present distinct differences in their reactivity with resins. One class consists of fluorine-containing propellant systems whose combustion products do not include oxygen in any free or combined form, e.g., fluorine/hydrogen; the other class includes propellant combinations which have fluorine- and oxygen-containing exhaust species, e.g., FLOX/methane. In Contract NAS3-4188 it was determined that organic "stiff" polymers were suitable for use in the fluorine/hydrogen combustion environment. It was recommended,

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ABSTRACT

This interim report describes the work performed under Contract NAS3-7949 to advance the state-of-the-art of resin matrices required for improved ablative materials for use with high energy fluorine-containing liquid propellant systems during the period 10 January through 1 July 1966. This is being accomplished through experimental studies on consecutive material development tasks initiated during this period involving synthesis and property determinations, resin formulation optimization and composite processing parameter studies. In future work these tasks will be continued and the objective will be attained through synthesis scale-up and fabrication of ablative composites tasks. This program is an extension of initial studies conducted under Contract NAS3-4188.

Synthesis and property determinations have been directed to preparation and evaluation of new modified polyimide resins based on new anhydride monomers, bis(5-tetrahydrophthalic anhydride) sulfone and bis(p-3, 4-dicarboxy anhydride phenoxy phenyl) sulfone, which offer improved processability. Optimization of resin systems, identified in Contract NAS3-4188 as advanced resin materials is being carried out to improve physical, chemical and processing characteristics. Composite processing studies have been conducted to determine the parameters which affect the fabrication of graphite and silica reinforced polyamide-imide and modified polyimide resins.

Preliminary testing of the resistance of neat resins and composites containing state-of-the-art and advanced resins in fluorine/hydrogen and FLOX/methane combustion environments shows that 1) "stiff" polymers appear to be superior to other types of organic resins, and 2) different reinforcements are preferred in each propellant combination combustion environment -- graphite in fluorine/hydrogen and silica in FLOX/methane.

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1. INTRODUCTION

This program is a continuation of studies performed under Contract NAS3-4188 entitled "Investigation of Resin Systems for Improved Ablative Materials." The objective is the preparation of ablative composites with improved resin matrices suitable for use as advanced nozzles for rocket engines employing high energy propellants, such as fluorine/hydrogen and fluorine-oxygen/methane. Ablative composites employing improved resins will exhibit the following features: low ablation rates, resistance to severe chemical environments, ability to withstand extremely high temperatures for extended periods of time, and capability to perform successfully when subjected to engine duty cycles of varying durations.

Two classes of high energy fluorine-containing propellant environments were identified in Contract NAS3-4188. Each present distinct differences in their reactivity with resins. One class consists of fluorine-containing propellant systems whose combustion products do not include oxygen in any free or combined form (e.g., fluorine/hydrogen); and the other class, propellant combinations which have fluorine oxygen-containing exhaust species (e.g., $FLOX/CH_4$).

In Contract NAS3-4188, analytical and experimental determinations provided 1) the critical parameters which control the effectiveness of resins in the ablative use environment, 2) new resin systems tailored and evaluated experimentally to verify the criteria established for resin ablative utilization, and 3) resins recommended for future studies.

Advanced ablative resin systems identified in Contract NAS3-4188 such as poly (cyclized-1, 2, -butadiene) tolyl urethane, are in various stages of development. The current program (under Contract NAS3-7949) is organized to continue the development and testing of candidate resins through systematic synthesis, property determination, and optimization studies in order to select the most promising resins for composite formulation studies.

In a parallel NASA sponsored program, new fibers and reinforcing agents which improve the properties of composites in fluorine containing high energy propellant combustion environments are being synthesized and fabricated. In this program, composite formulation studies will be conducted to determine the processing and composition parameters required for preparation of composite structures from 1) the resin matrices selected under Contract NAS3-7949, and 2) the advanced fibers and reinforcing agents generated in the parallel program.

The properties of these advanced composite formulations will be determined, and the more promising candidate composite formulations will be selected for scale-up and subsequent fabrication into test specimens for delivery to NASA/Lewis Research Center.

In this report are presented the accomplishments to date on the first three tasks of the program as follows:

- Task I - Synthesis and Property Determinations;
- Task II - Resin Formulation Optimization; and
- Task III - Composite Processing Parameter Studies.

Also included is a list of new technology and three appendices describing detailed laboratory experiments and results.

2. TASK I - SYNTHESIS AND PROPERTY DETERMINATIONS OF RESINS

Under Contract NAS3-4188, materials were determined which offer the potentiality of yielding improved ablative resins in a F_2/H_2 combustion environment. Concerning organic materials, "stiff" polymers, i.e., polymers whose backbones are characterized by a multiplicity of aromatic groups, were experimentally shown to be the most stable among the organic substances investigated. For inorganic materials, zirconium diboride exhibited the best degree of stability. As a result, "stiff" polymers and zirconium diboride polymers were speculated to yield advanced resin matrices for ablative composites.

The objective of this task is to provide polymers which comply with the criteria determined under Contract NAS3-4188. In addition, another objective of this task is to provide polymers which may be readily processed into ablative composites. During this report period a detailed approach has been generated for the synthesis of new "stiff" polymers which are speculated to meet these criteria. Preparation of a new zirconium boride polymer system, as described in Reference 1, requires a major research effort. Initial investigations of this inorganic system have been deferred pending optimization studies (Task II) on the resistance of zirconium diboride in a FLOX/methane combustion environment.

In this section are presented detailed discussions of organic polymers which yield advanced ablative resins, the selection of two candidate systems for synthesis, the accomplishments on the synthesis of these polymers and intermediates to date, and the results of testing of the advanced polymers and intermediates.

2.1 ORGANIC POLYMERS DESIGNATED TO YIELD ADVANCED ABLATIVE RESINS

"Stiff" polymers were selected for synthesis in order to prepare advanced organic ablative resins. These materials are a class of organic polymers having "backbones" which are characterized mainly by a multiplicity of organic aromatic groups.

The selection of "stiff" polymers was based upon results of the program carried out under Contract NAS3-4188. Use testing of candidate "stiff" polymers in a F_2/H_2 flame demonstrated that this class of organic polymers yielded resins which were more stable than commonly used ablative resins, e.g., phenolic and epoxies.

In addition, "stiff" polymers yield resins which exhibit exceedingly high second order transition temperatures, e.g., $\sim 800\ ^{o}C$. Since resins generally do not distort dimensionally at temperatures lower than their second order transition temperature, a high value of this property is attractive for applications where dimensional stability at high temperatures is required. In ablation, it is desirable that the resin be dimensionally stable to a temperature which is greater than the temperature determining the onset of its pyrolysis. In this manner, the resin has improved resistance to erosion by gases of a rocket engine. Because the pyrolysis rate of organic resins procedes significantly at temperatures of 450 ^{o}C and greater, the high thermal stability of "stiff" polymers assures that initial pyrolysis of these materials will occur without significant loss of their mechanical integrity.

2.1.1 "Stiff" Polymer Processing Considerations

The principal problem in the use of available "stiff" polymers is the difficult conditions required for processing. As a result, the objective of the synthesis effort is the preparation of "stiff" polymers which can be readily formed without sacrificing desirable properties. A brief description of the processing difficulties of current "stiff" polymers, and in addition, the processing advantages of the novel polymers of this study, is presented below.

For coating applications, the monomeric precursors of "stiff" polymers, e.g., polyimides, are coreacted in a suitable organic solvent to form "intermediate" polymers in solution. This solution essentially constitutes the varnish which is employed for coating of materials, e.g., glass cloth. During extended heating of the coated material at moderate temperatures, i.e., 120 to 170 °C, to drive off volatile solvent and reaction products, the thermally stable "dead cured" polymer is formed as a coating on the substrate. Upon assembling coated materials into stacked plies, however, fusion of the assemblage into a laminate by "dry bonding" is precluded due to the high second order transition point of the "dead cured" polymer (Reference 2).

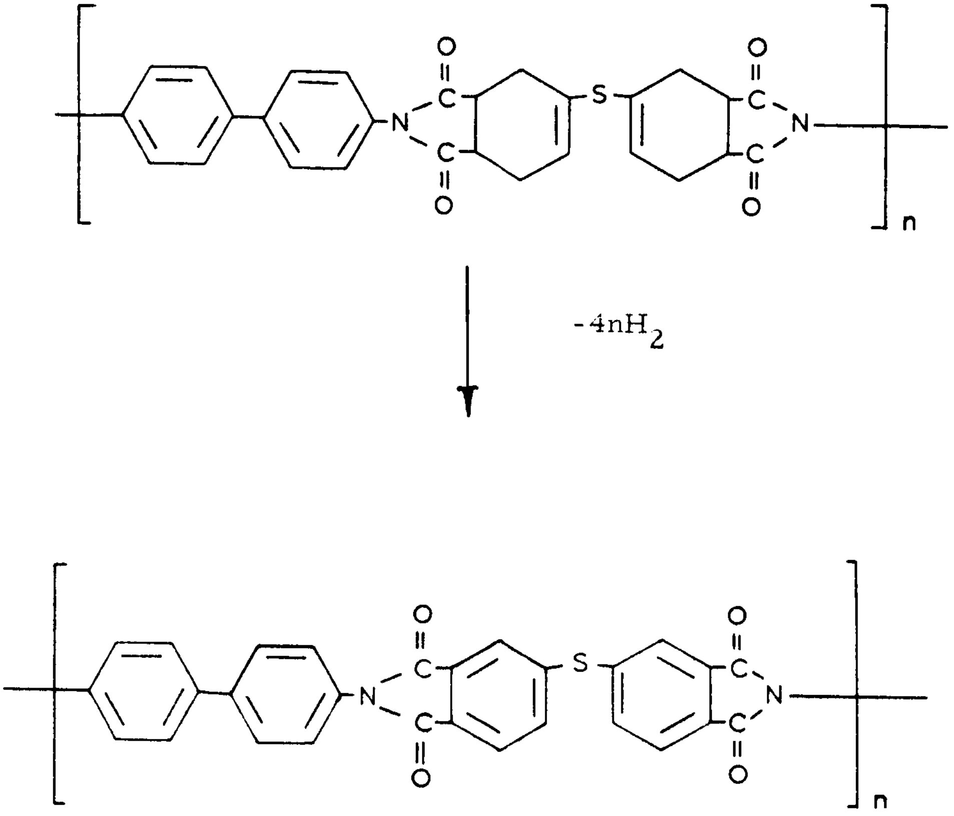
In practice, varnish coated substrates are heated for a specified period of time. The resulting coating thereby contains a polymeric "intermediate" partially advanced to the final polymer, and in addition, some residual solvent. The resinous coating then is said to be "B-staged." The coated materials are assembled into parallel plies and fused with loss of volatiles into laminates by use of heat and pressure.

The preparation of laminates of current "stiff" polymers employing the above method, however, requires high mechanical pressures and temperatures (Reference 3). These pressures are necessary to constrain the laminate in order to avoid the formation of voids by volatiles evolved during processing. These laminating conditions may not damage rugged reinforcing agents, such as glass fabric. However, laminates containing newly developed high modulus "whiskers", or fibrils, e.g., boron carbide fibrils, must be prepared with the use of minimal pressure because these fibrils are friable and subject to being crushed upon application of pressure. Thus, current "stiff" polymers have limited utility when employed in conjunction with advanced reinforcing materials.

The effort of the organic polymer synthesis program is to provide new "stiff" polymers which will significantly enhance the art of processing composites and laminates without sacrifice of their final properties. Composites containing friable reinforcing materials may thereby be readily fabricated because minimal mechanical pressure and reduced temperature may be employed. The resultant composites will be suitable for long term service at elevated temperatures.

"Stiff" polymers that are planned for synthesis in this program have "backbones" characterized mainly by cyclic chemical groups, approximately half of which are aromatic, and those remaining are saturated and/or partially unsaturated. In contrast, the cyclic groups of current "stiff" polymers are mainly aromatic. The presence of saturated and/or partially unsaturated cyclic groups are expected to decrease significantly the second order transition temperature of these polymers relative to that of their aromatic analogues. The decrease of the second order transition temperature is attributed to the greater flexibility of saturated and/or partially unsaturated cyclic chemical groups. Consequently, the polymers are expected to "dry bond" at convenient laminating temperatures (Reference 2). Laminating techniques employing "dry bonding" diminishes the problem of volatiles evolved during lamination, thereby reducing the requirement for high mechanical pressures.

In addition, the saturated and/or partially unsaturated cyclic chemical groups of the polymer are expected to aromatize during "dry bonding" or under ablative use conditions. This aromatization is expected to occur through the liberation of hydrogen from the cyclic groups. In order to facilitate the expulsion of hydrogen, the cyclic groups will be chemically tailored with electron withdrawing chemical substituents, e.g., carbonyl groups. Upon the loss of hydrogen from the polymer, its second order transition temperature will undergo a marked increase. Consequently, the cured polymer will exhibit a high heat distortion temperature, a desirable property for ablative resins. This phenomenon occurs with minimum loss of volatiles evolving from a stable nonsolvated polymeric precursor. The phenomenon may be viewed as constituting resin curing, and as such is a distinct and novel chemical mechanism for the curing of resin masses. This curing reaction is exemplified in Equations (1) and (2).



(1)

(2)

The decrease in flexibility of the partially saturated cyclic groups of the polymer which occurs during transformation from a partially saturated to an aromatized state (Equations 1 and 2) is shown using Drieding Stereo Models in Figure 1. The cyclic rings undergo a transformation from three dimensional flexible to a two dimensional rigid state. Associated with this transformation, the second order transition temperature of the polymer is expected to undergo a marked increase.

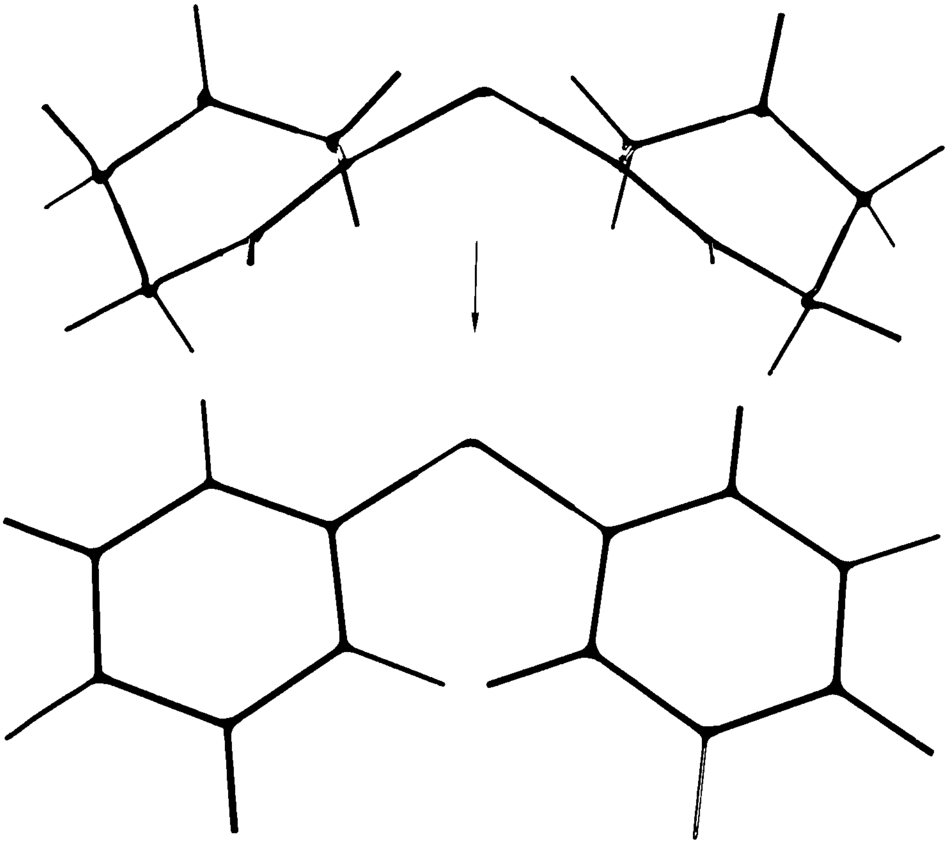


Figure 1. Dreiding Stereo Models Showing Transformation from Flexible, Three Dimensional, Partially Saturated Rings to Rigid Aromatic Rings

In practice, the new "stiff" polymers will be employed for the preparation of laminates in the following fashion: Resin varnishes will be prepared in the manner analogous to current art (Reference 4). Materials will be wetted with these varnishes, and the coated materials will be heated until all solvent has been removed and the remaining polymer (100 percent solids) has been fully reacted to the final stage. The coated materials will be arranged as stacked plies and "dry bonded" into laminates upon the application of comparatively minimal pressure and moderate temperatures. The amount of time the laminate is held at elevated temperatures will determine the extent of induced aromatization, or cure, of the resin. In applications where the laminate is expected to yield a long service life at high temperatures, it is desirable to aromatize all of the cyclic chemical groups of the polymer. Partial aromatization of the cyclic groups during cure may be sufficient for ablative requirements, the remaining aromatization being accomplished by pyrolysis during engine firing.

The advantages of the new "stiff" polymers compared to current "stiff" polymers are summarized below:

a) Lamination is effected without the need of residual solvent and/or partially advanced polymer in the "B-staged" material, thereby minimizing an extended "kiss contact" stage in laminate formation, during which period premature precipitation of intractable resin may occur. In addition, resin flow from between the plies on application of pressure is minimized, thus preventing the formation of resin-starved areas within the laminate.

b) The "B-staged" polymer is advanced chemically to the finalized material by elimination of hydrogen gas. In contrast, advancing current "B-staged" polymers is accomplished by the evolution of water, phenol, and/or ammonia. The evolution of the low molecular weight, high diffusivity gas, hydrogen, rather than higher molecular weight volatiles allows the utilization of low mechanical pressure in laminate preparation.

c) The relatively small weight loss to prepare a fully cured polymer reduces the amount of laminate shrinkage during cure.

d) The above delineated features are expected to contribute significantly to laminating process reproducibility.

2.1.2 "Stiff" Polymer Synthesis Considerations

Synthesis of the new "stiff" polymers is required in order to produce laminates which will exhibit the foregoing processing features. Such polymers are neither commercially available, described in the literature, nor according to the best of our knowledge, planned for synthesis elsewhere.

The new "stiff" polymers selected for synthesis are termed generically polyimides and/or polypyrrones which, as a class, are currently being investigated as thermally stable resins (References 4 and 5). These polymers are prepared by condensing a cyclic monomer containing two acid anhydride groups with either 1) a monomer containing two primary amines or 2) a monomer containing four primary amines arranged in adjacent pairs on aromatic rings.

The "stiff" polymer synthesis task is concerned with the preparation of new cyclic monomers which contain two acid anhydride groups. The diamines and tetramines will be selected from commercially available materials. Dianhydride monomers containing specific cyclic groups were selected for synthesis, rather than analogous cyclic diamines, because the new anhydride compounds are considered more likely to yield polymers which aromatize thermally by hydrogen evolution.

The dianhydrides required for the preparation of new modified polyimides consist of two types:

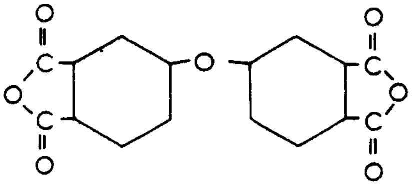
a) One type of dianhydride compound (Type I) yields cyclic, fully saturated groups in their respective polymers.

b) The other type (Type II) yields partially saturated cyclic groups.

The synthesis of the necessary dianhydrides has not been described in the chemical literature. Thus, an exploratory synthesis program has been undertaken. Also, in order to provide a useful monomer for comparative experiments, a new aromatic dianhydride, Type III, will be synthesized. Specific monomers of each of the three types are described chemically in the following paragraphs. In addition, a series of diimide monomers are described. These materials are required for studies of thermal aromatization processes.

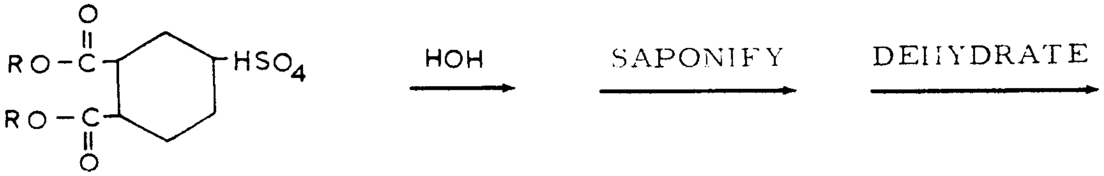
2. 1. 2. 1 Type I Monomers

A number of specific monomers, which should yield polymers containing saturated cyclic chemical groups, are structurally depicted here, together with their possible synthesis routes. Monomer A yields the polyimide ether resin system recommended in Reference 1, however, it utilizes a different synthesis procedure designed to give higher molecular weight products, and has the capability of permitting "B-staging".



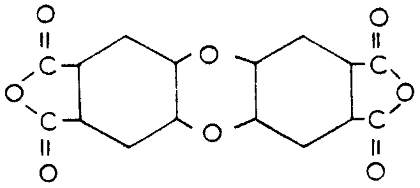
MONOMER A

(3)



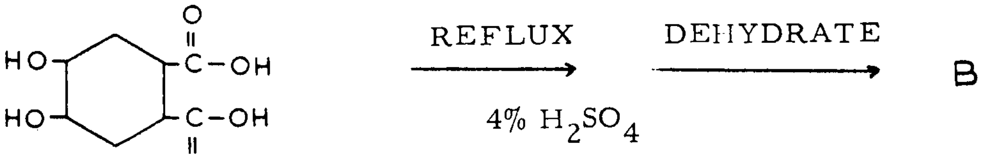
SYNTHESIS A

(4)



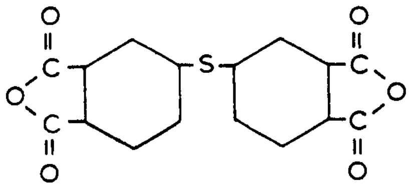
MONOMER B

(5)

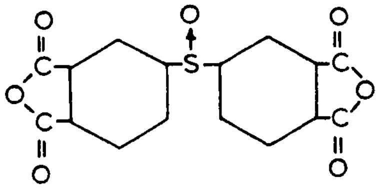


SYNTHESIS B

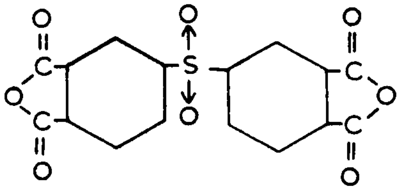
(6)



MONOMER C

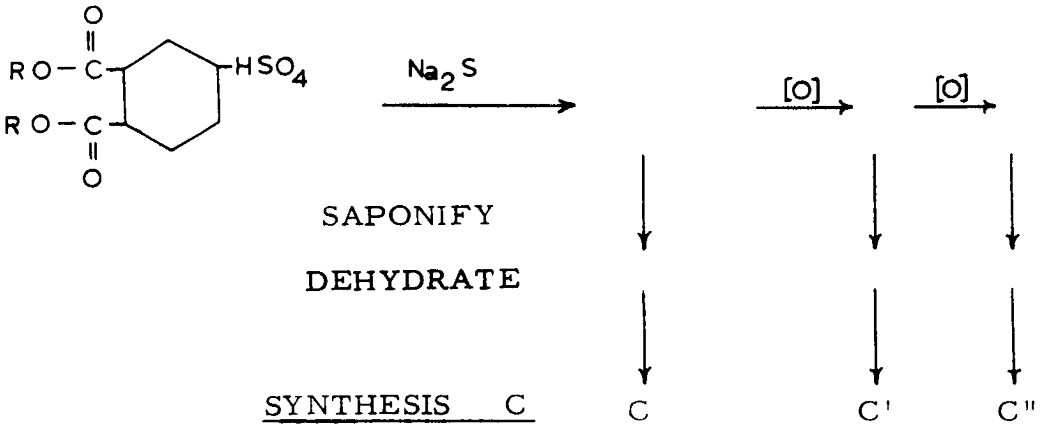


MONOMER C'



MONOMER C"

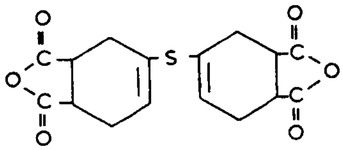
(7)



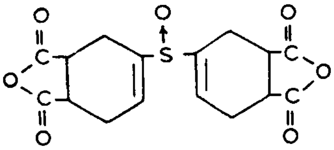
(8)

2.1.2.2 Type II Monomers

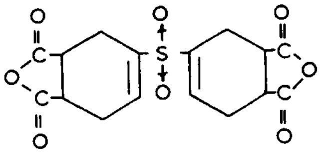
A number of specific monomers which should yield polymers containing partially saturated cyclic chemical groups are structurally depicted here, together with their possible synthesis routes.



MONOMER D



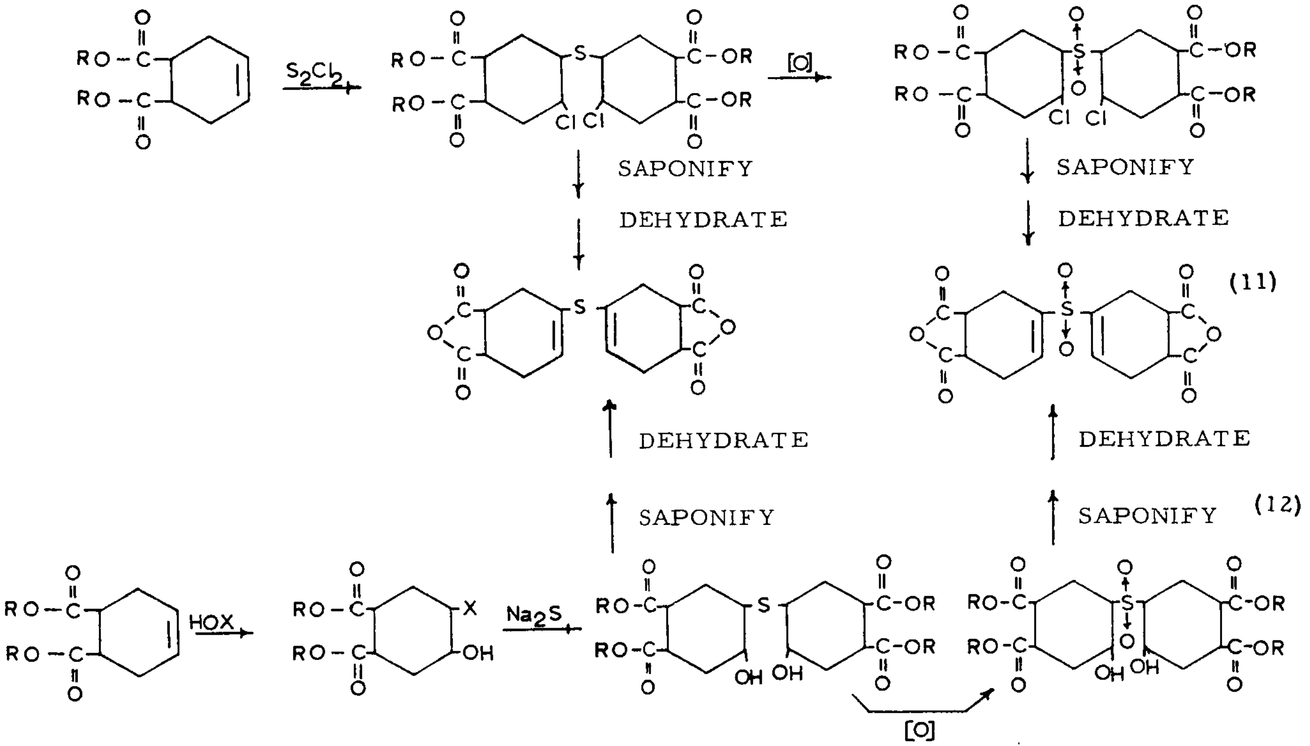
MONOMER D'



MONOMER D''

(9)

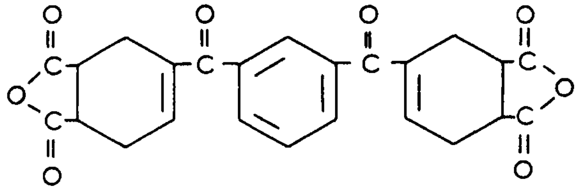
(10)



(11)

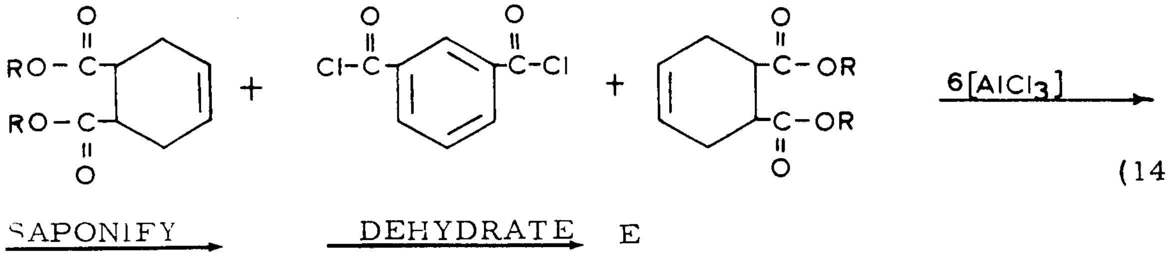
(12)

SYNTHESIS D



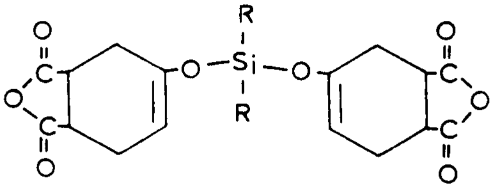
(13)

MONOMER E



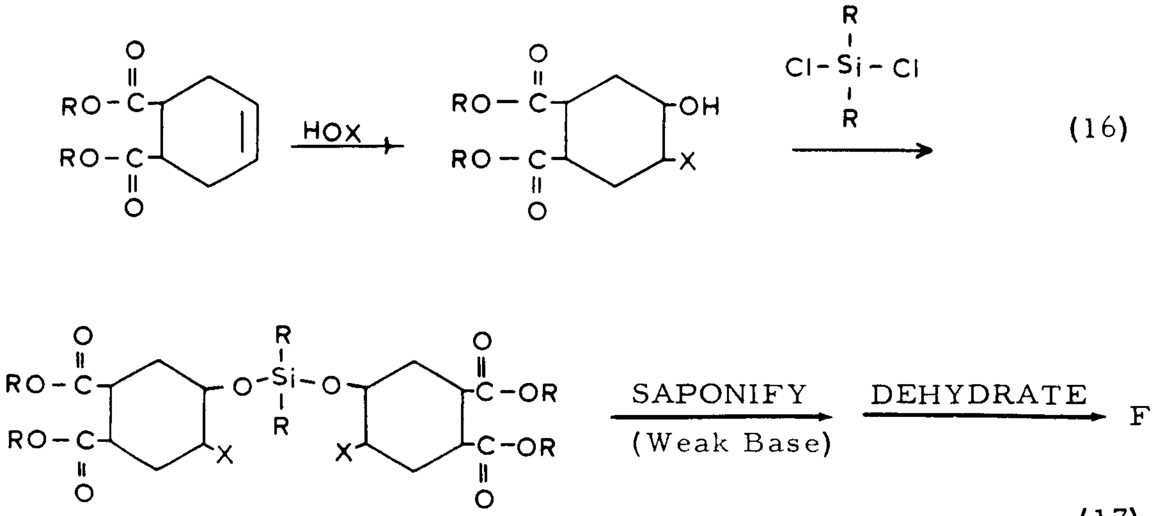
(14)

SYNTHESIS E



(15)

MONOMER F



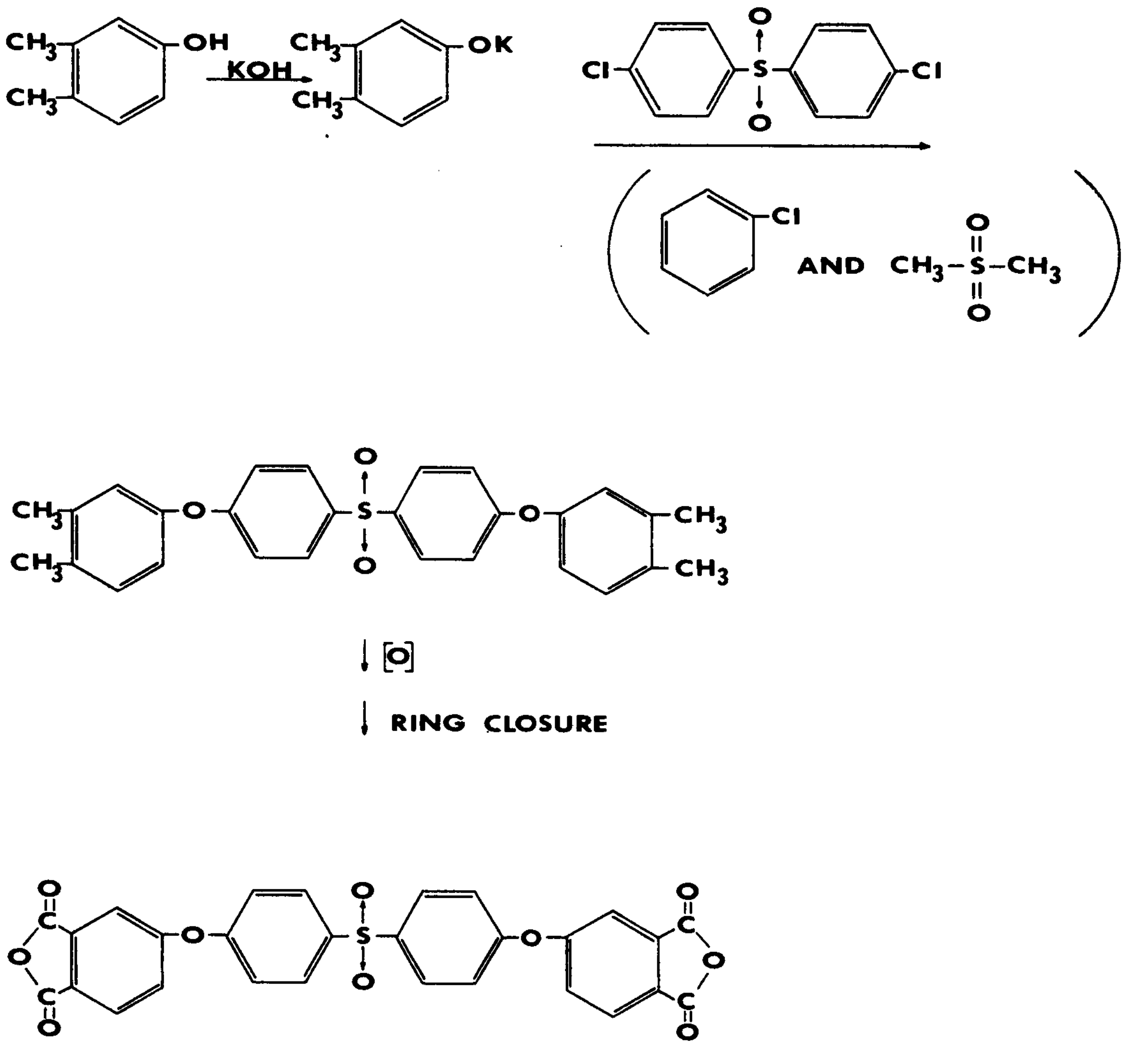
(16)

(17)

SYNTHESIS F

2.1.2.3 Type III Monomers

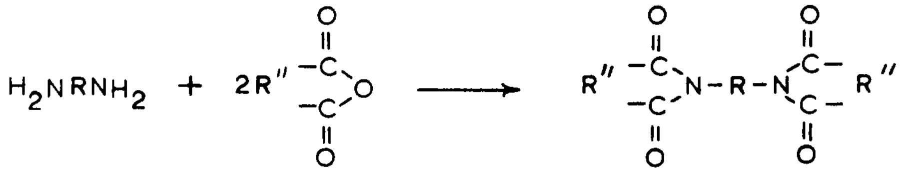
The following sequence of reactions describes the preparation of a high molecular weight aromatic dianhydride for comparative purposes.



MONOMER G

2.1.2.4 Diimide Monomers

Synthesis of a series of diimide monomers were prepared in the first quarter of this program. The principal objective was to evaluate thermogravimetric analysis (TGA) data for each monomer for the purpose of determining the conditions under which aromatization will take place. The monomers and their properties are given in Appendix A (1-9). The typical reaction used in their preparation is shown below:



(21)

2.1.3 Synthesis/Modification of a Commercially Available "Stiff" Polymer

Polybenzimidazole resins have been identified as commercially available "stiff" polymers which have outstanding high temperature properties. These resins are expected to withstand the F_2/H_2 combustion atmospheres and temperatures. However, they were found to be difficult to use in the preparation of high reliability laminates. This difficulty stems from the fact that water/phenol or water/ammonia plus solvents are volatiles evolved upon completion of the curing reaction causing voids during the laminating process. (Reference 6.) Suitable laminating processes, therefore, must be determined, and careful controls on time, temperature and pressure must be exercised.

It was proposed by TRW that modifications of the polymer by incorporation of biphenyl or ether groups will minimize the laminating problems. Under Air Force contracts, the Narmco Division of Whittaker Corporation, however, are presently modifying their polybenzimidazole polymers to make them more ameniable for lamination (Reference 7). It appears appropriate to evaluate the Narmco materials prior to preparing polymer modifications of polybenzimidazoles by TRW.

2.2 MONOMERS SELECTED FOR POLYMER SYNTHESIS

Exploratory synthesis of the Type I, II and III monomers, with the exception of Monomer F, were carried out in order to determine whether they could be prepared readily. The results of these studies indicated the feasibility for preparation of a set of monomers. From this set, the following two monomers were selected for preparation of advanced thermally stable polymers:

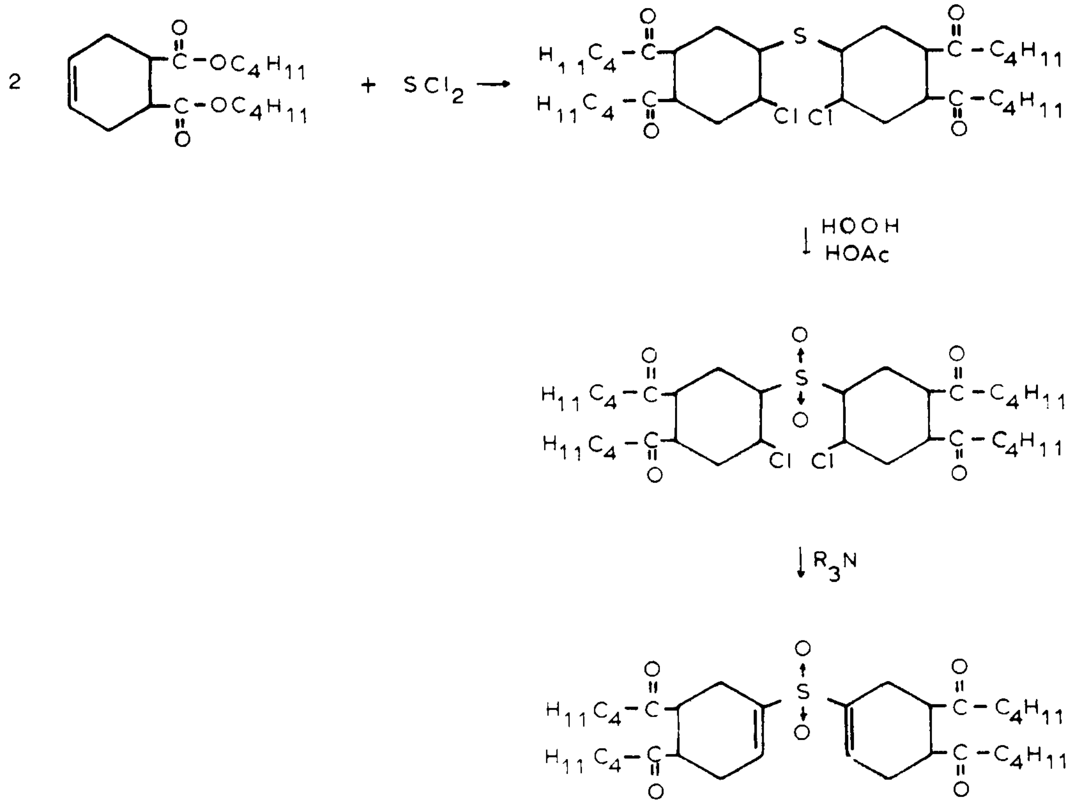
- bis(5-tetrahydrophthalic anhydride) sulfone; and
- bis(p-3,4-dicarboxy anhydride phenoxy phenyl) sulfone.

Details concerning the selection of monomers are given below.

2.2.1 Bis(5-Tetrahydrophthalic Anhydride) Sulfone

Bis(5-tetrahydrophthalic anhydride) sulfone (Monomer D"), was selected for primary emphasis in the synthesis program on the basis of consideration of the feasibility of its successful synthesis and the tendency of its derived polymers to aromatize with minimal degradation of their "backbones" at elevated temperatures. Dianhydride monomers containing saturated cyclic groups, Type I, in contrast to Type II monomers, were determined to yield polymers which may undergo appreciable scission of their "backbones" under conditions which may induce aromatization of their cyclic groups. In addition to these features, bis(5-tetrahydrophthalic anhydride) sulfone is expected to react readily with primary amines. As a result, this monomer should yield high molecular weight polymers which are required for obtaining resins with suitable mechanical properties.

The synthesis route which has been determined for the preparation of bis(5-tetrahydrophthalic anhydride) sulfone employs materials which are readily available and relatively inexpensive. Synthesis of the monomer is expected to be accomplished through the route indicated in Equations 22 through 24.



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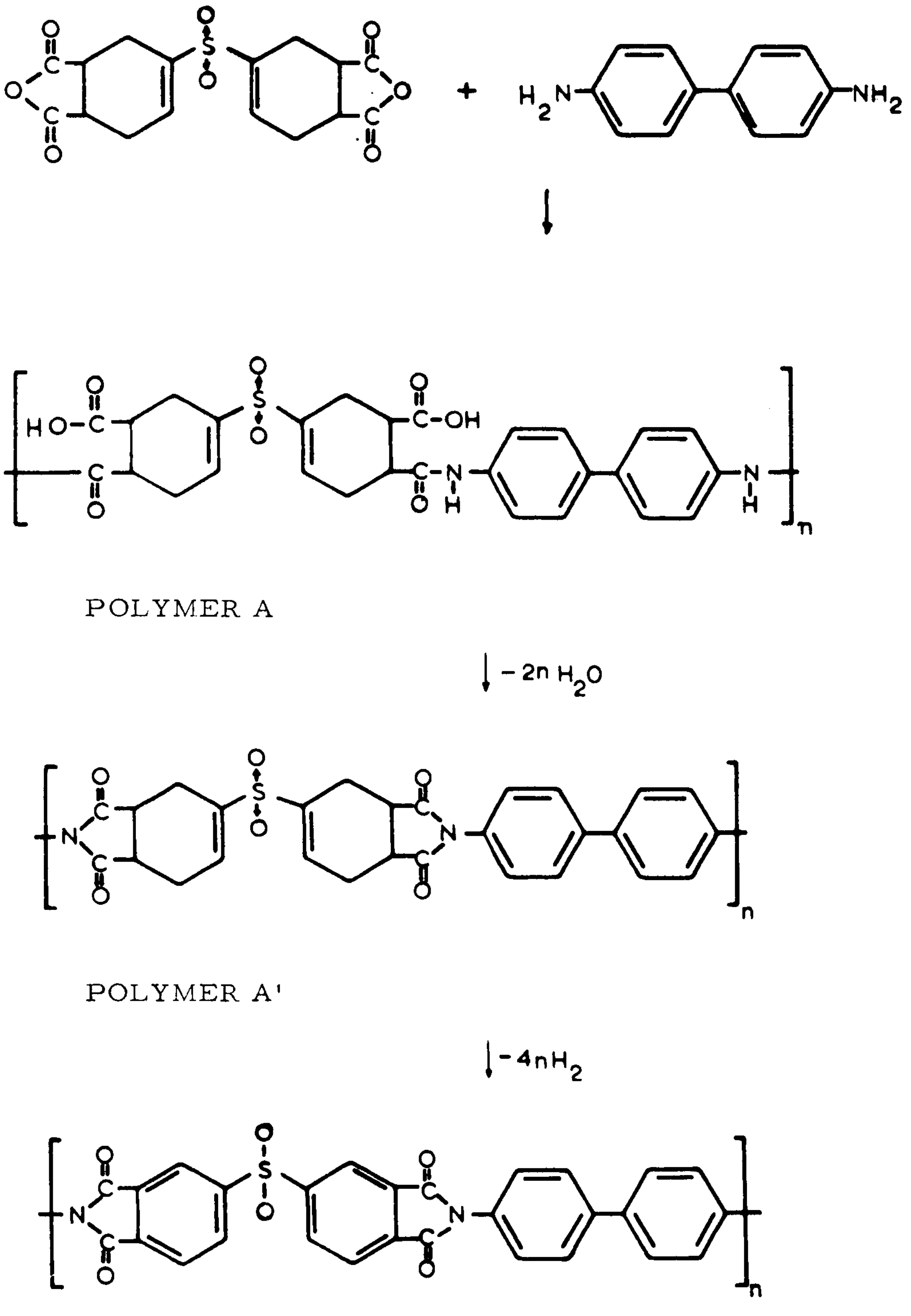
(23)

(24)

Bis(5-tetrahydrophthalic anhydride) sulfone will be reacted with selected organic polyamino compounds to yield advanced polymers. Figures 2 and 3 show examples of the synthesis routes for the formation of thermally stable polymers employing benzidine and diamino benzidine, respectively, as organic polyamino monomeric constituents.

These polymers offer significant processing advantages over state of the art, fully aromatic analogues, because of the decreased amount of volatile matter evolved during cure. In state of the art polyimides the aromatic analogue of polymer A shown in Figure 2 is representative of

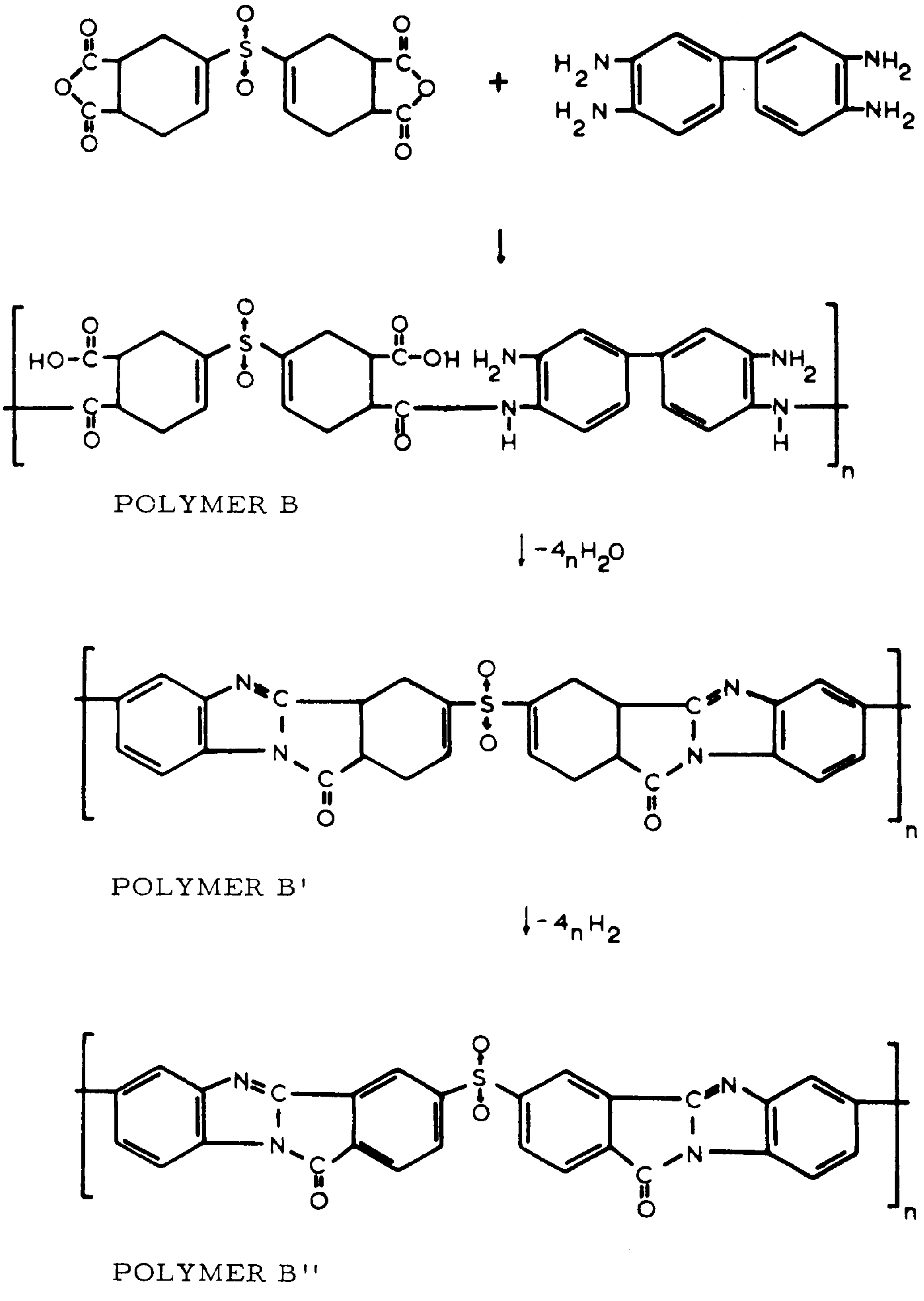


POLYMER A

POLYMER A'

POLYMER A''

Figure 2. Polyimide Synthesis Example Employing bis(5-Tetrahydrophthalic Anhydride) Sulfone



POLYMER B

POLYMER B'

POLYMER B''

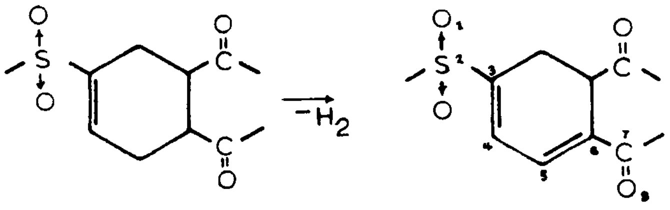
Figure 3. Polypyrrone Synthesis Example Employing bis(5-Tetrahydrophthalic Anhydride) Sulfone

the chemical composition of the B-staged resins. In addition, it generally contains some residual solvent. The final cured C-stage in the current aromatic analogue is represented by polymer A'.

In contrast, the B-stage of the polymer system being synthesized in this program is represented by polymer A', which has minimal residual solvent. Curing the resin to the final polymer (polymer A'') occurs with the liberation of hydrogen, whereas comparable C-staging of current polyimides occurs with the liberation of water. A similar advantage exists for polypyrrones.

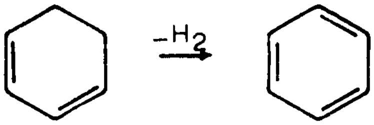
From these considerations it is seen that the volatile content generated from final cure of the modified polyimides of this program is 22% w/w of that evolved from analogous state of the art aromatic polyimides. Comparison of the cure of analogous polypyrrones shows that use of bis(5-tetrahydrophthalic anhydride) sulfone reduces the volatile content even further (to 11% w/w). The advantage of the markedly reduced amount of volatiles liberated in the formation of the final polymer facilitates the preparation of compact, void-free laminates. In addition, the volatile is a high diffusivity gas, hydrogen, which readily vacates the laminate, thereby further reducing the possibility of void formation. As a result, high mechanical pressures should not be required in laminate preparations.

The facility of the polymers in Figures 2 and 3 to dehydrogenate readily is based on the premise that the following indicated reaction is promoted by the chemical structure of the sulfone monomeric constituent.



(25)

Here it is observed that a conjugated system involving eight atoms is produced upon the evolution of one mole of hydrogen. The formation of the resonance stabilized eight-atom system, numbered in the above formula, provides the driving force for the dehydrogenation step. This phenomenon may be compared to the following well-known reaction:



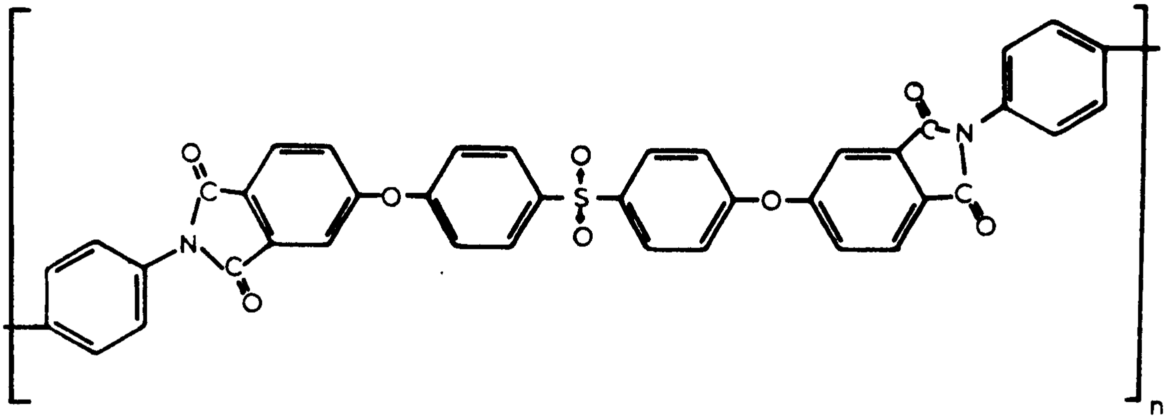
(26)

where the formation of a six-atom resonance stabilized atom system, benzene, facilitates the dehydrogenation of the parent compound, cyclohexadiene. Elimination of a second mole of hydrogen from the sulfone monomeric constituent to form the aromatized polymer should proceed readily after the first mole of hydrogen has been eliminated from the structure.

2.2.2 Bis(p-3,4-Dicarboxy Anhydride Phenoxy Phenyl) Sulfone

Bis(p-3,4-dicarboxy anhydride phenoxy phenyl) sulfone (Monomer G) also was selected for synthesis. The high molecular weight of this Type III monomer leads to stiff polymer synthesis where the amount of volatile matter evolved is significantly reduced, relative to that evolved in the synthesis of current "stiff" polymers. As a result, the ease of preparation of laminates is enhanced. Examples of stiff polymers prepared by condensing bis(p-3,4-dicarboxy anhydride phenoxy phenyl) sulfone with benzidine or diaminobenzidine are given in Figure 4. Comparative evaluation of Type II and Type III monomers in stiff polymers provides the means for determining the significance of the processing advantages of polymers which "cure" by aromatization of their cyclic chemical groups.

POLYIMIDE



POLYPYRRONE

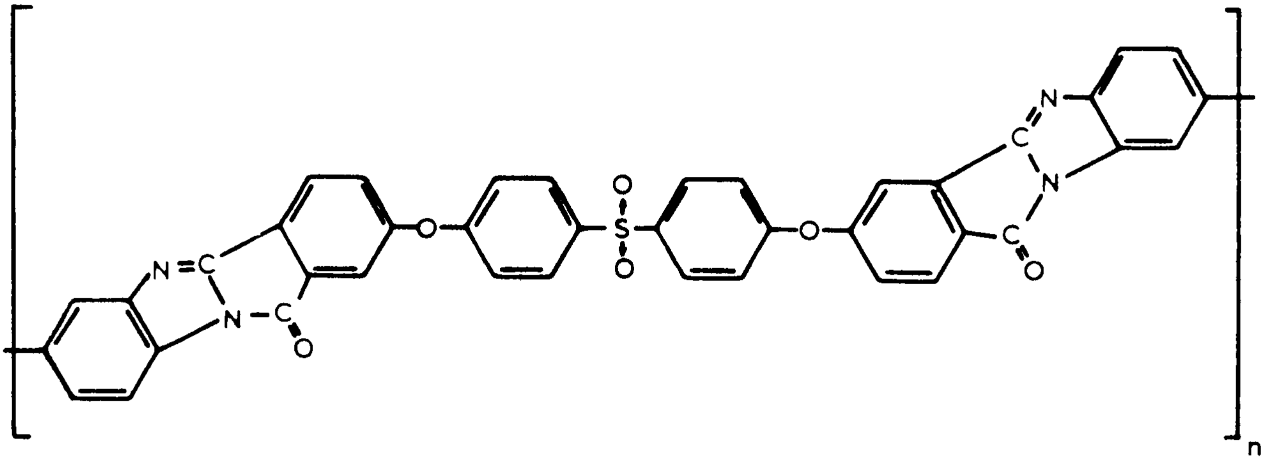


Figure 4. "Stiff" Polymers Obtained From bis(p-3,4-Dicarboxy Anhydride Phenoxy Phenyl) Sulfone

2.3 SYNTHESIS PROGRAM RESULTS

This section describes the progress and accomplishments of the synthesis program to date. Details of the compounds synthesized and identified to date are given in Appendix A.

The synthesis of bis(5-tetrahydrophthalic anhydride) sulfone is currently being undertaken using sulfur dichloride. Initial studies employing sulfur monochloride did not yield the desired precursor from which the sulfone may be prepared. The sulfur dichloride approach will eliminate the oxidation difficulty found using the sulfur monochloride product.

Reaction conditions were determined which gave 40% w/w yield of bis(p-3,4-dimethyl phenoxy phenyl) sulfone. This material is the precursor of bis(p-3,4-dicarboxy phenoxy phenyl) sulfone, from which the dianhydride derivative will be prepared. Analytical determinations to date confirm the structure of the synthesis product.

A general discussion of the progress of the effort in Task I of this program is given in the following sections.

2.3.1 Investigation of the Synthesis of Bis(5-Tetrahydrophthalic Anhydride) Sulfone Employing Sulfur Monochloride

Di-n-butyl tetrahydrophthalate was reacted with sulfur monochloride to form the β-chloro-sulfide adduct (Appendix A). Although the sulfide adduct was apparently synthesized in high yield, it was found to resist oxidation to the sulfone under conditions given in the literature employing hydrogen peroxide in acetic acid (Reference 8). The adduct's resistance to oxidation was attributed to the presence of elemental sulfur which formed concurrently with the formation of the adduct. The elemental sulfur was dispersed colloidally in the reaction mixture, and it was found to be difficult to remove.

Higher temperatures were employed in order to force the oxidation of the adduct. Under these conditions, oxidation of the β-chloro-sulfide adduct was effected; however, deesterification of the adduct was also found to occur. The latter was not an undesirable result because deesterification of the adduct must be effected subsequently in order to prepare the corresponding dianhydride required for polymer synthesis.

In view of the above results, deesterification of the adduct in aqueous acetic acid was attempted in order to prepare the tetrabasic acid derivative. Isolation of the tetrabasic acid derivative was viewed as a means of separating the β-chloro-sulfide adduct from the elemental sulfur so that oxidation of the material may take place under mild conditions. The material that was isolated was found to melt in the range 110 to 120 °C. Elemental analysis of the material showed that it was essentially free of chlorine and rich in sulfur (See Table I). The absence of chlorine in the product was an unexpected result, because the chlorine in the chemical structure provides the means whereby unsaturation is induced into the ring. Retention of the chlorine in the molecule was expected because the chemical literature indicates that dehydrochlorination of β-chloro-sulfides, in contrast to β-chloro-sulfones, is difficult to effect.

It was speculated that, under the conditions employed for the deesterification of the adduct, hydroxyl groups and acetate groups displaced the chlorine groups in the chemical structure of the material. Consequently, the material was considered to be essentially a mixture of Compounds B and C given in Table I, and addition of the monoacetate of B.

The product was oxidized by hydrogen peroxide in acetic acid according to the procedure described in the literature for the oxidation of sulfides to sulfones (Reference 8). Oxidation was carried out prior to receiving the elemental determination showing the absence of chlorine. The material isolated melted in the range 120 to 130 °C, approximately 10 ° higher than the parent material.

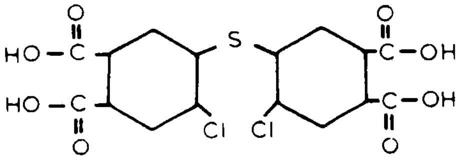
The oxidized material was found to be very hygroscopic when exposed to the atmosphere, whereas the parent material did not display this property. The oxidized material in air absorbed water to the extent that it became self-dissolved, the solution being very viscous and sticky to the touch.

TABLE I

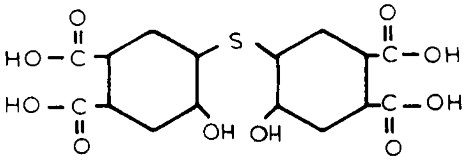
COMPARISON OF POSTULATED AND DETERMINED ELEMENTAL ANALYSES

COMPOUNDS	COMPOSITION				
	C % w/w	H % w/w	Cl % w/w	S % w/w	ACID meq/g
Found for Adduct	46.35	5.03	0.88	10.90	8.87
Compound A (Expected product)	43.34	4.51	16.03	7.22	9.03
Compound B (Postulated)	47.30	5.46	0.00	7.89	9.85
Compound C (Postulated)	49.98	5.31	0.00	7.35	8.16

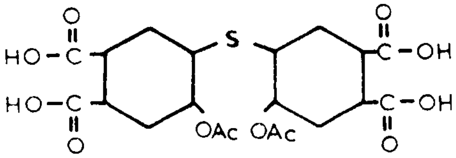
Compound A



Compound B



Compound C



2.3.2 Investigation of the Synthesis of Bis(p-3,4-Dimethyl Phenoxy Phenyl) Sulfone

Bis(p-3,4-dimethyl phenoxy phenyl) sulfone is the precursor of bis(p-3,4-dicarboxy phenoxy phenyl) sulfone, from which the dianhydride derivative will be prepared. Reaction conditions for the preparation of this material have been determined which provide up to 40% yield of the product (See Appendix A). The product was found to melt at 118 to 120 °C. A thin layer chromatogram of the product indicated the absence of contaminants, and an infrared spectrum confirmed the presence of phenyl ether linkage and the absence of hydroxyl groups.

2.4 PROPERTY DETERMINATIONS

Evaluation experiments have been selected which will rank the ablative performance of new candidate resins relative to that of other ablative resins. The ranking will determine systems suitable for optimization relative to improving ablative performance and composite processing.

The evaluation experiments are:

- Thermogravimetric analysis
- Propellant exhaust environmental tests

Thermograms of advanced polymer system precursors are presented in Appendix A. Thermograms of recommended polymer systems are located in Appendix B. From these curves a measure of the char yield is obtained.

A description of the propellant exhaust environmental test (PEET) apparatus and its operation is given in Section 3.8.1 and Appendix C.

Several other property determinations also will be conducted on the candidate resins. The properties to be determined include thermal decomposition temperature, density, thermal conductivity and specific heat. These properties were shown in Contract NAS3-4188 to provide critical information concerning the effectiveness of resins in ablative matrices. Detailed discussions of these methods are described in the final report of Contract NAS3-4188 (Reference 1).

3. TASK II - RESIN OPTIMIZATION

The work on Contract NAS3-4188 identified either newly synthesized or commercially available resin systems suitable for use as advanced ablative materials. Several of these resin systems require optimization to improve their overall ablative performance in fluorine-containing combustion environments. Optimization of resin matrices requires an ordered investigation of resin properties, and a determination of methods for improvement of the properties. The major object of this task is to evaluate candidate resins, optimize the properties critical to ablative performance, and select the most promising resins for use in Task III, Composite Studies.

Resins from the following three sources are being optimized in this program:

- Contract NAS3-4188: Cyclized polybutadiene urethane (CPBU), polyalkaline earth acrylates, phosphate bonded oxides, polyamide-imides, and zirconium borides.
- Contract NAS3-7949: Resin systems selected and synthesized in Task I.
- Commercial Sources: Monsanto - Skybond 700 (polyimide), and Narmco - Polybenzimidazole.

Optimization of the resins will be carried out by:

- Tailoring chemical structures to improve char yields, mechanical properties and processability; and
- Studying the effect of cure cycles, char promoters, and aromatization catalysts.

Evaluation of resin systems will be carried out by:

- Mechanical, thermal and chemical property assessments; and
- Propellant Exhaust Environment Test (PEET) evaluation.

Selection of resin systems for incorporation into Task III, Composite Studies, will be made from data analysis of the evaluations performed and assessment of the degree of improvement to be imparted to the composite material. Details are given below describing the approaches and progress for optimization of the various resins.

3.1 POLY(CYCLIZED 1,2-POLYBUTADIENE) TOLYL URETHANE

Poly (cyclized 1,2-polybutadiene) tolyl urethane (CPBU) has been identified as a readily processable resin system which, although it has good properties at elevated temperatures, does not form good chars under the ablative conditions. The chemical structure of CPBU is believed to consist principally of a series of fused cyclohexane rings which on selective dehydrogenation could result in a fused aromatic structure. Subsequent pyrolysis would increase the char yield significantly to approach that obtained for difficult-to-process polyphenylene resins. The approaches taken to cause the dehydrogenation of CPBU are both thermal and thermal plus catalytic.

Identification of the temperature at which dehydrogenation would take place was determined by evaluation of the thermogravimetric analysis (TGA) curve shown in Figure 5. Temperatures taken below and above the major point of inflection, i.e., 285 and 425°C, respectively, were selected and the CPBU exposed to 24 hours aging at each temperature under vacuum. The sample aged at 285°C lost approximately 8% of its original weight; it was then subjected to a conventional TGA to determine if dehydrogenation had taken place. The results are shown in Table II and do not indicate that the char yield had been altered appreciably. The sample aged at 425°C lost approximately 90% of its weight and was judged unsuitable for further analysis.

Optimization by addition of dehydrogenation catalysts was also studied. As a control, a platinum catalyst on an alumina base was added at a concentration of 0.4% Pt with respect to the CPBU. Platinum is a well-known dehydrogenation catalyst and might, therefore, display a point of inflection in the TGA curve giving data useful in evaluating

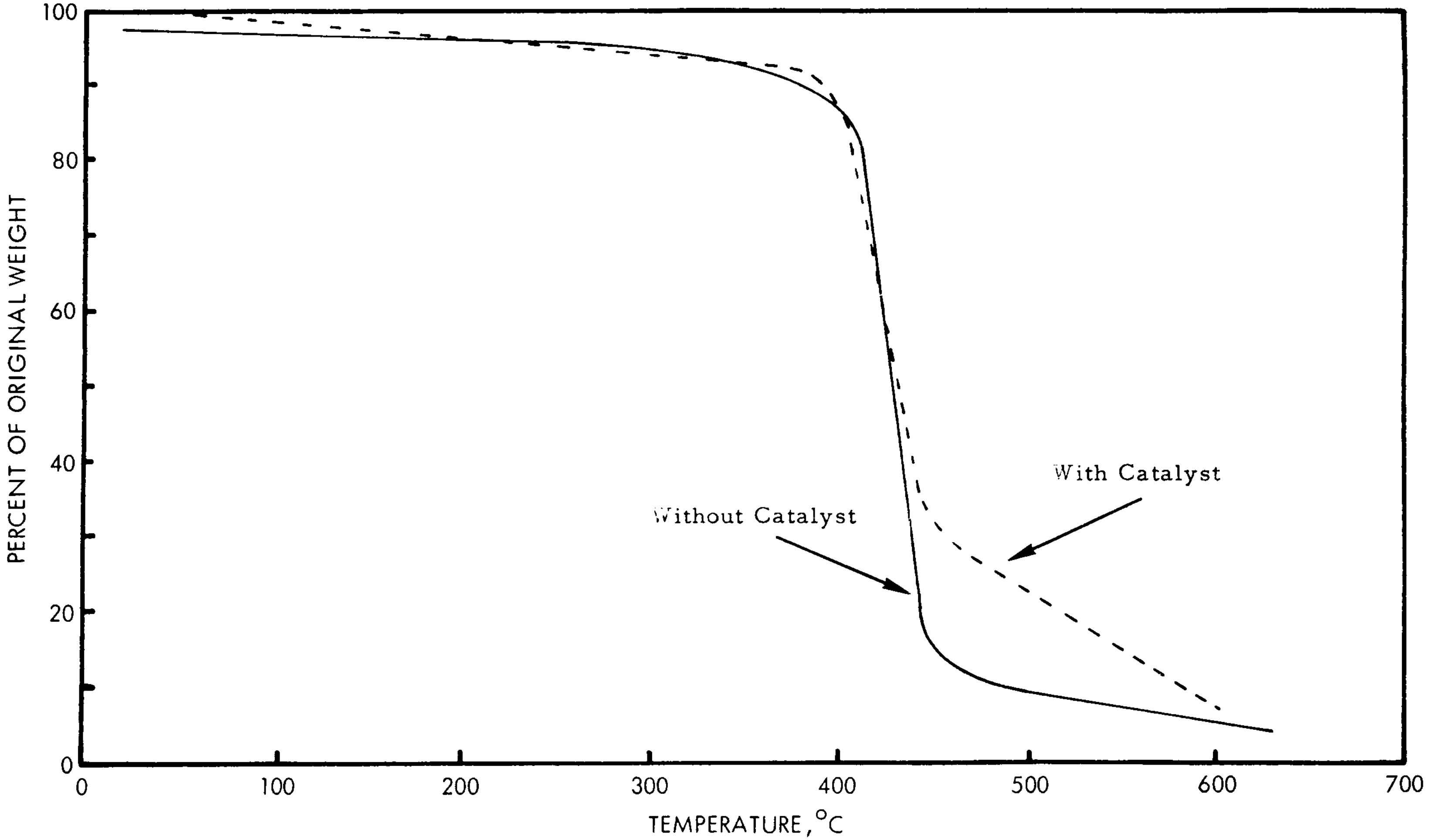


Figure 5. Effect of Platinum Catalyst on the Thermograms of Poly (Cyclized 1, 2-Polybutadiene) Tolyl Urethane
Environment: 0.025 torr Pressure
Scan Rate: 3 °C/Minute

TABLE II

THERMAL AND CATALYTIC DEHYDROGENATION STUDIES ON CYCLIZED POLYBUTADIENE URETHANE (CPBU)

Specimen	Catalyst	Pre-aging Conditions	Temperature at Percent Weight Loss, °C			Weight Lost by Pre-aging % w/w
			25% w/w	50% w/w	75% w/w	
1	None	None	420	430	440	---
2	None	24 Hrs at 285 °C	420	430	440	8%
3	None	24 Hrs at 425 °C	---	---	---	90%
4	0.4% Pt	None	400	410	420	---
5	0.4% Pt	18 Hrs at 350 °C	410	430	480	70%
6	0.5% FeAA	None	390	410	420	---

* **Results of thermogravimetric analyses.**

Environment: 25-inch Hg vacuum; Scan Rate: 3°C/Minute.

dehydrogenation processes. The resulting TGA curve showed no trends, and further showed that overall decomposition of CPBU took place at approximately 20°C lower than the uncatalyzed version (see Table II). A similar platinum-containing sample was subjected to 18-hour isothermal aging at 350°C in vacuum. Approximately 70% of the original weight was lost; a standard TGA curve was obtained on the remaining residue. A slight improvement in the char yield (see Figure 5) was obtained.

A second series of catalysts shown to be useful for increasing char yields of isoprene rubber in solid rocket case liners under ablative conditions, is also under investigation for their applicability to CPBU. These materials are zinc acetonyl acetonate and nickel acetonyl acetonate. First evaluations were done with ferric acetonyl acetonate (FeAA) at 0.5% concentration, since the material was on hand. The results of a single TGA curve are presented in Table II and show that the overall decomposition temperature of the CPBU was lowered 20-30°C. There was no point of inflection in the curve to show dehydrogenation had taken place.

Several theories may be advanced concerning the data presented above. The foremost are:

1. The conditions required for dehydrogenation have not yet been determined,
2. CPBU decomposes below its dehydrogenation temperature, or
3. CPBU does not dehydrogenate appreciably.

In order to show that 2) or 3) above are controlling the results of this optimization study, several more tests are being considered. Both zinc and nickel acetonyl acetonates will be studied, as well as the incorporation of tributyl phosphate with the metallic acetonyl acetonates. Tributyl phosphate, while indicated for use as a char promoter in the isoprene rubber liner mentioned above, it is not expected to be compatible with the CPBU.

3.2 POLYALKALINE EARTH ACRYLATES

Poly (calcium, magnesium and barium) acrylates were developed during Contract NAS3-4188 and have been identified as organo metallic resin systems which do not depend solely upon carbonaceous chars to maintain strength during ablation. The oxides of the alkaline earth metals have been shown to be theoretically both thermally and chemically stable to the combustion gases produced by the fluorine/hydrogen propellant class and most likely to survive exposure in FLOX/methane propellant class combustion environments. Methods for synthesis of these resins have been developed and are reported in the Final Report, Contract NAS3-4188 (Reference 1).

The object of the present optimization study is to provide neat resin specimens for fluorine-containing Propellant Exhaust Environment Test (PEET) evaluation by new processing methods which could be applicable to scale-up.

After cursory exploratory investigations, a new molding procedure for providing PEET evaluation specimens has been developed. Essential details of this procedure are described below:

- Prepare 115 mesh (max) ground polymer by swelling with water and squeeze out excess water by hand in paper toweling.
- Place wet mass directly into mold (1-1/4-inch diameter standard "metallurgical mounting" type may be used) at room temperature.
- Place loaded mold in molding press, also at room temperature.
- Slowly increase pressure to 30,000 psi (over 5 minutes) and increase temperature to 350°F over 30 minutes.
- Maintain the mold at 30,000 psi and 350°F for an additional one hour period.
- Release pressure and remove part from mold.

Good coherent fused specimens were obtained from this procedure and PEET specimens were prepared by machining. The density of the product was lower than that obtained using the vacuum hot press method described in Reference 1. The magnesium and barium analogs of the same polymer will be prepared and tested by the PEET evaluation in the near future.

3.3 PHOSPHATE BONDED OXIDES

Phosphate bonded oxide resin masses were prepared and tested in fluorine/hydrogen flames as reported in the Final Report of Contract NAS3-4188. These materials appear to be attractive in that the oxides were chemically stable to the flame. Mechanically the materials lack ductility and are susceptible to thermal shock. Optimization of these materials is expected to be difficult in that no prior art has been developed to show how ductile materials may be made.

Various routes for optimization have been hypothesized. It is important, however, to determine the degree of resistance the material tested during Contract NAS3-4188 has to FLOX/methane combustion environments. If significant improvement is realized, additional emphasis will be placed on enhancing the ductility of this inorganic resin. An approach under consideration consists of incorporation of a resistant oxide, such as calcia, baria and magnesia. The degree of improvement offered by this approach also may depend on the particle size of the oxide filler.

Optimization studies to date are concerned with the manufacture of a suitable test specimen for FLOX/methane PEET evaluation. Machining of the specimens is a particularly difficult task, but specimens are expected to be produced and tested during the next month.

3.4 POLYAMIDE-IMIDE RESINS

The evaluation of this organic "stiff" polymer was carried out in Contract NAS3-4188 in fluorine/hydrogen flames. As the best evaluated organic polymer, it has been selected for optimization in this program. Optimization of this commercially available resin from Amoco Chemical Corporation has entailed the development of a suitable molding technique for neat resin specimens.

The polyamide-imide resin is available in forms suitable for both impregnation varnish (AI-11) and compression molding (AI-13). Although chemically equivalent, the molding version is in curled flake form, and appears to be more fully imidized. A new vacuum mold (see Figure 6). was designed and fabricated to produce samples for PEET evaluation without need for machining (other than the thermocouple well). The curled flake form of this polymer has posed several problems in the use of the new mold since the flakes have a very low bulk density and, further, will not compact when below their melting point. A process has been devised, however, which produces the required samples from the new mold in shorter cycles than were possible using the large vacuum compression hot mold in Contract NAS 3-4188.

After cursory exploratory studies the following procedure was used for preparation of neat polyamide-imide resin plugs:

- Preheat mold and press to 500°F minimum, 550°F maximum.
- Charge mold cavity with excess polyamide-imide AI-13 particles.
- Close press until the O-rings seal and evaculate the mold at 1-10 Torr for 5 minutes.
- Apply pressure to 6000 psi and maintain until mold force has seated.
- Open mold and recharge with AI-13 particles.
- Close press until O-ring seals and repeat evacuation for 5 minutes.
- Heat the mold to 580°F minimum (thermocouple located between mold halves next to O-ring).
- Raise pressure to 6000 psi and maintain. If mold force does not seat within 2 minutes, raise pressure until seating is accomplished.

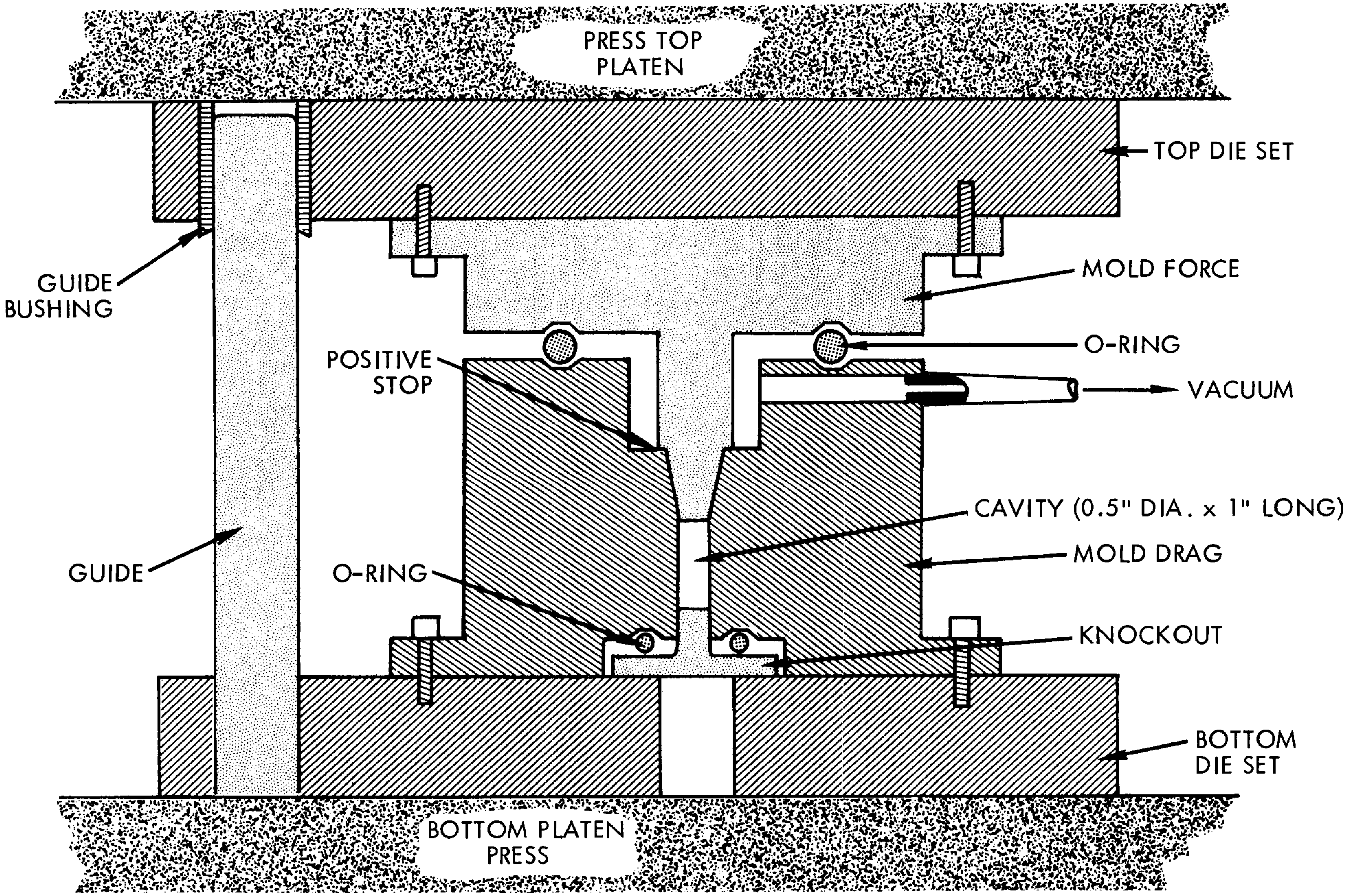


Figure 6. Vacuum Compression Mold for Preparation of PEET Specimens (Half Section Shown Closed)

- Reduce and maintain pressure at 6000 psi, with temperature at 600-625°F for one hour.
- Cool the mold to 350°F while maintaining pressure at 6000 psi.
- Remove mold from press and employ "knock-out" to remove part.
- Examine part for fusion, voids, cracks, etc., and if it passes inspection machine the thermocouple well.

Plugs obtained by this process were compact, fused resin masses, free of voids and cracks.

3.5 ZIRCONIUM BORIDE POLYMERS

In addition to the new "stiff" polymers under consideration, zirconium boride polymers are expected to yield advanced ablative resins. Under Contract NAS3-4188, zirconium diboride was found experimentally to have resistance to fluorine containing flames. Evaluation of zirconium diboride in FLOX/methane combustion environments, however, is required in order to provide the basis for the value of synthesis of zirconium boride polymers. Such evaluations are planned during the next quarter.

3.6 POLYIMIDE RESINS

In addition to the polyimide resins tested in Contract NAS3-4188 (DuPont SP-1 and SP-2), a new polyimide resin produced by Monsanto (Skybond 700) has recently been added to those resins of commercial origin whose properties appear to be of interest for evaluation in fluorine/hydrogen and FLOX/methane flames. The exact chemical structure of the resin is proprietary, however, it has been found to be much more processable than the DuPont polyimides in laminating.

The manufacture of a neat resin specimen for PEET evaluation is the object of this task. Laminating of the material seems to be analogous to the process used for the polyamide-imide resin. It will be necessary to make a molding powder from the predissolved Skybond 700 lamination varnish, and to then determine molding methods. Neither task appears to present undue difficulties. Specimens are expected to be available for testing in the next month.

3.7 POLYBENZIMIDAZOLE RESIN

Chemical optimization of polybenzimidazole resins, currently being carried out by the Narmco Division, Whittaker Corporation, is not in the scope of this contract. Evaluation and recommendation after exposure to PEET flames is, however, a function of this contract. Narmco had promised delivery of a piece of neat polybenzimidazole resin for testing in May; the sample has not yet been received. According to sources at Narmco, delay has been caused by scarcity and difficulty in producing the resin. Samples have again been promised for delivery in August.

3.8 PEET EVALUATION OF NEAT RESINS

Specimens of neat materials described earlier in this section, as well as neat materials for comparative purposes, were subjected to FLOX/methane Propellant Exhaust Environment Test (PEET) evaluation. This section describes the PEET test set-up and modifications incorporated for use of FLOX/methane propellant combinations and presents the results of the candidate neat resin systems.

3.8.1 Propellant Exhaust Environmental Test (PEET)

The propellant exhaust environmental test apparatus (PEET) described under Contract NAS3-4188, has been redesigned to permit the evaluation of the resistance of ablative resins to exhaust species of advanced propellant combinations, such as fluorine/hydrogen and FLOX/methane. The operational mass flow rates of fluorine or FLOX in the redesigned apparatus and its use are described below. Detailed operating procedures for the use of the PEET apparatus and preparation of FLOX mixtures are given in Appendix C.

The experimental arrangement of PEET apparatus components is pictured in Figure 7. This figure shows the fluorine gas cyclinder installed in a barracade (lower right); the hydrogen flowmeter (upper left); the HF trap (lower left); the fluorine flowmeter (upper right); the inert atmosphere shield (which provides an argon cover atmosphere to eliminate contamination of the hot combustion products, upper right); and the propellant torch (center of picture). At the top is the stainless steel hood and fire shower heads. The propellant torch assembly is a Beckman Instruments Company flame spectroscopy burner which is modified in a manner similar to that described by Collier (Reference 9). The modification incorporates an internal Monel sleeve which permits compatible flow of fluorine or FLOX. Not shown are 1) the hydrogen gas cylinder (located external to the room), 2) the nitrogen purge cyclinder (whose lines are seen emerging from the left), and 3) the argon gas cylinder.

The redesign of the apparatus was based on incorporating the following features into the equipment employed under Contract NAS3-4188. Improved safety and versatility of operation resulted from:

a) Explosion proof solenoid (electrically) operated service valves replacing remote mechanically operated service valves.

b) 316 stainless steel Hoke valves employing standard flare-type tubing fittings replacing brass constructed valves.

c) Check-valves installed at necessary points in the apparatus preventing the possibility of fluorine or FLOX gas from coming into contact with the non-fluorine resistant valves.

d) A new Coppus blower ventilating system increasing the removing rate of the combustion fumes.

The method of operation for a hydrogen/fluorine or a FLOX/methane exhaust test is described briefly as follows:

> The HF trap is activated, all the system lines are purged with dry nitrogen, the volume surrounding the sample is purged with argon, and the hydrogen

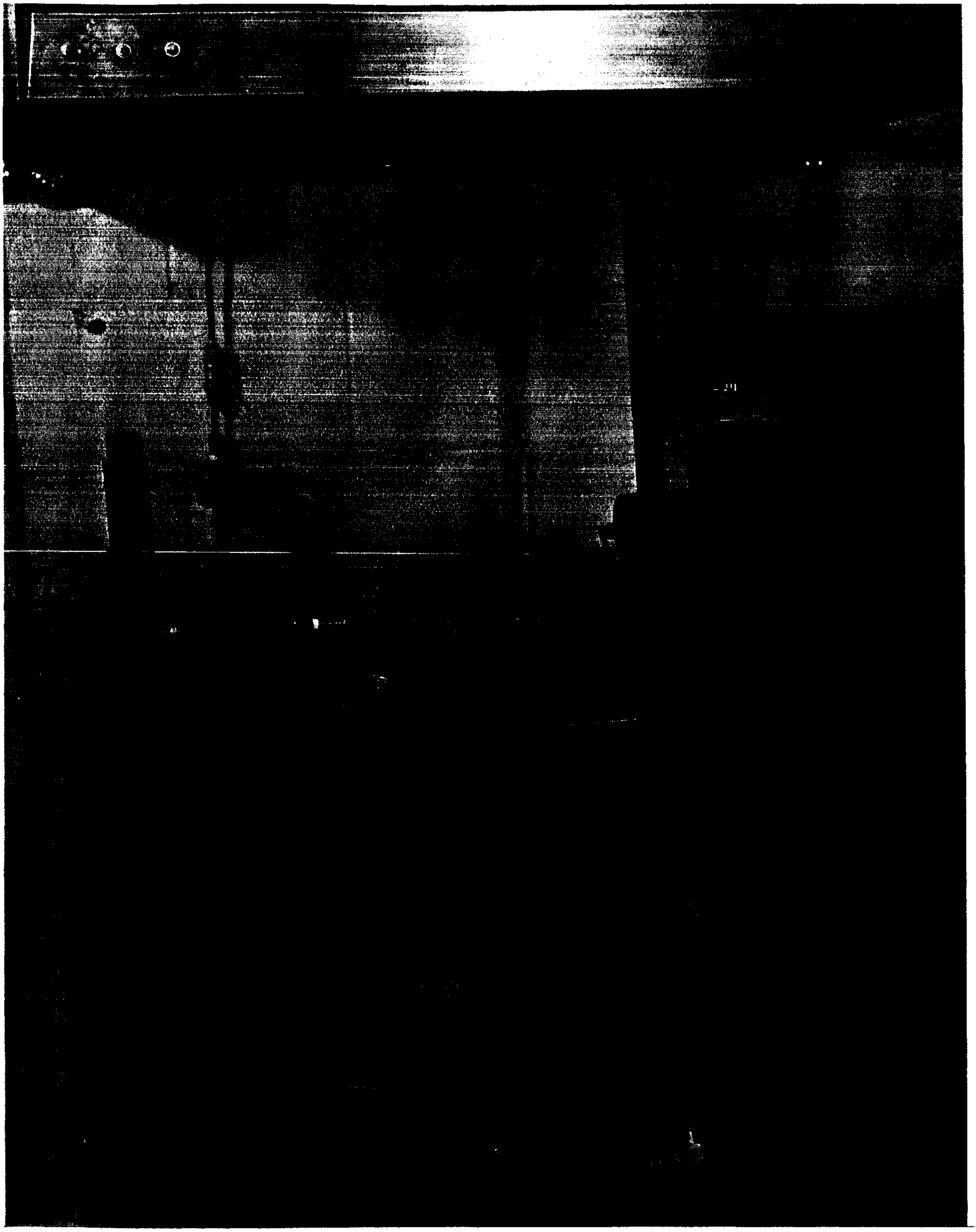


Figure 7. Experimental Set Up of the Propellant Exhaust Environmental Test (PEET) Apparatus

> flow is started. The fluorine is then permitted to flow; upon ignition, the flow rates of the hydrogen and fluorine are adjusted to simulate the operational engine mixture ratios. The test resin sample then is moved into the flame. Because the flame composition and temperatures do not vary appreciably in the radial direction (Reference 10), the sample is located so that the flame "mushrooms" and envelopes the face of the sample to insure a relatively constant thermal flux.

The system is readily adaptable to a fluorine/hydrogen propellant combination, or FLOX/methane propellant combination simply by replacing the fluorine cylinder by a cylinder containing a mixture of F_2/O_2 (FLOX), and the hydrogen cylinder by a cylinder containing methane gas.

Some difficulties were encountered in establishing correct FLOX/methane PEET operation. Several set-backs in schedule occurred when 1) FLOX/methane was found not to be hypergolic and a system redesign was required to incorporate a fluorine/methane lead to initiate combustion, 2) a premature ignition occurred in the tubing upstream from the torch (requiring replacement of the tubing), and 3) two flowmeters, used successfully with the fluorine/hydrogen system, burned out (requiring replacement of the Viton packings with special Teflon packings). Late in the first half of this program, the PEET apparatus was in successful operation, and a number of tests were made.

3.8.2 Results

The neat materials tested and the test results are listed in Table III. Where comparative data are available from Contract NAS3-4188 for 10-second exposures to fluorine/hydrogen combustion environment, it has been included in the same table.

Analysis of the data shows parallels in weight loss between specimens exposed to the combustion environments of FLOX/methane and fluorine/

TABLE III

PEET EVALUATION OF NEAT ABLATIVE MATERIALS

Material Type	FLOX/Methane		Fluorine/ Hydrogen
	Weight Loss,[a] g	Backwall[b] Temperature, °C	Weight Loss,[c] g
Pyrolytic Graphite (Supertemp)	0.0054	360	0.020
Pyrolytic Graphite (Supertemp)	0.022[d]	470	----
JTA Graphite (National Carbon)	0.014	340	0.030
JTA Graphite (National Carbon)	0.016[d]	490	----
SP-1 (Dupont)	0.21	140	0.21
SP-2 (Dupont)[e]	0.41	140	0.36
Epoxy-Novalac[f]	0.53	190	0.55
Polyamide-Imide[g]	0.15	160	0.11
Polycalcium Acrylate[h]	0.85[k]	120	----
Polycalcium Acrylate[i]	1.14[k]	m	0.30
CPBU/Styrene[j]	2.39[k]	290	----
CPBU Standard	2.32[k]	290	0.50

a. 1/2-inch diameter by 1-inch long specimens exposed to 10 second FLOX/CH_4 combustion atmosphere.

b. Thermocouple imbedded in center of specimen 0.5 inches from exposed end.

c. Data from Reference 1, for 10 second exposure to F_2/H_2 combustion environment.

d. Thirty second exposure.

e. Contains graphite powder filler.

f. D.E.N. 438/MNA system.

g. Amoco AI-11.

h. Acrylic Acid Binder.

i. No binder.

j. 75% CPBU/25% Styrene.

k. Excessive spalling during test.

m. Thermocouple inoperative.

hydrogen. Two exceptions, the polycalcium acrylates and the CPBU materials, are evident; these four specimens exhibited excess spalling, and re-tests must be made before the data can be considered reliable.

It was speculated that organic resins would not survive exposure to FLOX/methane combustion products, since the oxygen/water exhaust species would tend to attack any organic, carbonaceous chars produced. The test data show that this is not the case, but rather that the organic polymers tested behaved in a similar manner to that observed for the fluorine/hydrogen system under similar test conditions.

It was also speculated that the FLOX/methane combustion products would have a severe effect on carbon and graphite materials; although this is not evident on the pure graphite materials tested, it is shown by the increase in weight loss on SP-2, a particulate graphite-filled polyimide material, compared to the unfilled SP-1 material.

More samples are planned for PEET evaluation to provide more reliable data, and to reinforce the trends shown by the presented preliminary data. The inorganic systems, i.e., phosphate bonded oxide and zirconium diboride, are undergoing the difficult machining operations required to produce a PEET specimen. Results of PEET evaluations on these materials are expected during the next month.

4. TASK III - COMPOSITE STUDIES

This task consists of laboratory studies of the methods and processing variables required for combining fiber reinforcements with resin systems recommended in Task II. Two of the reinforcements which will be utilized are silica and graphite fibers. Other reinforcements will be supplied from the parallel NASA-supported fibers program being conducted by Texaco Experiment Incorporated. The Texaco materials will probably be in the form of bulk fibers. Receipt of the Texaco reinforcements is expected in the latter stages of this program.

During the first part of this program, experimental studies have been conducted using fiber glass, silica and graphite fibers with two candidate resins. Initial laminating studies were conducted with Style 1581 fiber glass fabric to determine the processing parameters which govern the preparation of composite structures. After establishing the processing parameters and candidate procedures, the more expensive silica and graphite fabrics were used. In this report period processing procedures have been evolved which permit successful processing of 5/8-inch thick laminates from polyamide-imide and modified polyimide resins. As the thickness of the laminates increases, processing difficulties multiply because the elimination of volatile by-products becomes a more difficult task. The composite materials produced to date are the first reported using these two advanced, "stiff" resin systems at these thicknesses. The immediate future work will be directed towards scaling-up the procedure in Tasks IV and V to prepare laminates having a thickness of 1 inch.

In this report period the basic reinforcement impregnation and molding processing parameter variables investigated were:

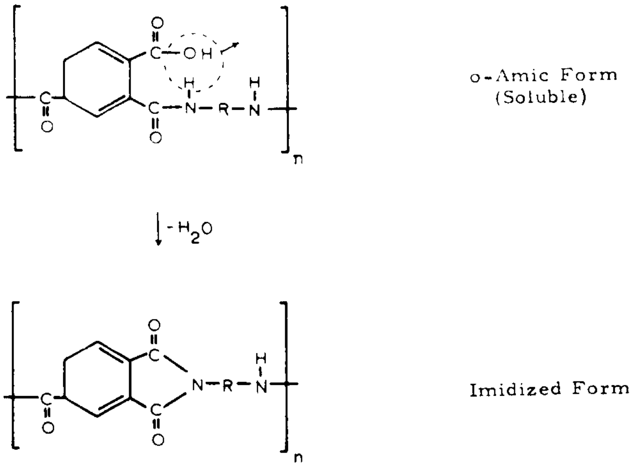
- Resin solids content of impregnating solution;
- Squeeze bar gap for metering resin solution onto fabric;
- B-staging time and temperature; and
- Press molding time, temperature and pressure.

The relatively porosity-free laminates were machined into specimens for PEET evaluation to determine their resistance to fluorine-containing exhaust environments. Presented in this section are details of the investigations of the composites prepared with polyamide-imide and modified polyimide resin systems, and the results of composite PEET evaluation obtained to date.

4.1 POLYAMIDE-IMIDE

Initial Task III laminating studies were performed with the polyamide-imide polymer recommended in Task II. The polyamide-imide polymer is a new aromatic resin supplied by Amoco Chemicals Corporation that can be thermally cured to a product having outstanding thermal stability. This resin is not a copolymer but a single polymer composed of both amide and imide groupings. It is based on trimellitic anhydride. The exact chemical structure is not disclosed by the supplier but they do indicate it is a wholly aromatic polymer. The material is approximately 30 percent imidized and the balance is orthoamic acid. Two types of polyamide-imide polymers based on different diamines are available. The Type 11 material, which is more thermally stable than Type 10, was selected for evaluation.

The predominant curing mechanism for the polymer is a conversion from the soluble ortho-amic form to the insoluble imidized form. This is illustrated below:



The development of processing techniques suitable for the preparation of composite structures using the polyamide-imide resin is segregated into the following two areas:

- Development of reinforcement preimpregnation techniques, and
- Establishment of optimum press molding procedures.

Details of the development of this methodology are presented below.

4.1.1 Preimpregnation Studies

The selection of preimpregnation varnish solvent, solids loading, squeeze bar gap setting and staging conditions was accomplished in these studies to provide optimum conditions for preparation of polyamide-imide preimpregnated fabrics.

The uncured polyamide-imide polymer is soluble in amide solvents such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone. Initial fabric preimpregnation was performed using dimethylformamide as a solvent, but this was discontinued when it was found that this solvent promotes degradation of the polymer. The only solvent used in recent work has been N-methylpyrrolidone.

Initial exploratory studies were conducted using fiber glass reinforcements. The fiberglass-reinforced polyamide-imides were successfully prepared into thin glass fabric laminates using procedures recommended by Amoco. In later studies it was found that thicker laminates of silica and graphite fabrics presented additional problems. It was found that the glass fabric was more easily wetted by the resin than either the silica or graphite. This was probably caused by the Garan finish on the glass fabric; neither the silica nor graphite fabrics had a finish. Competing factors which affect the selection of solids loading of N-methylpyrrolidone varnish include the time required to saturate the graphite and silica fabrics and migration of the resin encountered during subsequent B-staging. The time required to saturate the fabrics thoroughly can be reduced by using a lower solids content. However, the lower solids content caused excessive migration of the resin during the B-staging of the impregnated material in a vertical position. To obtain the desired resin content in the fabric with reasonably rapid fabric wetting, and no serious migration problems, the optimum resin content of the coating solution was found to be 38-41 percent w/w.

The squeeze bar gap setting depends on both the weight of the fabric and the amount of polyamide-imide desired on the fabric. A cursory examination of the effect of squeeze bar gap setting on resin content permitted the selection of a squeeze bar gap setting of 30 mils for the HITCO G-1550 graphite fabric and 40 mils for the HITCO Refrasil C-100-48 silica fabric. These settings provided polyamide-imide contents of 39 to 41% w/w in the preimpregnated fabric.

Oven drying at 350°F for one hour was selected as a procedure for producing a product having a volatile content of approximately 3 percent. Preimpregnation product characterization for volatile content and resin content were performed by standard procedures. The volatile content was obtained by measuring the weight loss that occurs when the sample is heated at 500°F for 20 minutes. The resin content of the resin-impregnated silica fabric was determined by measuring the weight loss of a volatile-free specimen on ignition at 1200°F in air for a period required to obtain constant weight (6 hours usually permitted combustion of all traces of carbonaceous material). The resin content of the impregnated graphite fabric was determined from the difference in weight per unit area between the impregnated volatile-free fabric and the non-impregnated cloth.

The preimpregnation procedure generated in this study is as follows:

- Place the polyamide-imide/N-methylpyrrolidone varnish in a shallow tray and spread the reinforcement fabric over the surface of the liquid.
- When the fabric is thoroughly wetted by the varnish, remove the impregnated fabric from the solution and pass it through a set of squeeze bars.

- Allow the coated fabric to air dry partially, and then place in an oven maintained at 350°F for one hour.
- Remove the dried fabric from the oven and store for subsequent press molding.

4.1.2 Lamination Studies

The establishment of optimum press molding lamination procedures was accomplished through varying B-staging time and temperature, press molding time, temperature and pressure to provide a product which was essentially porosity-free and appeared to have adequate mechanical properties. The results of these studies assisted in establishing the volatile and resin content constraints identified in Section 4.1.1.

Initial moldings of thin (1/8-inch) fiberglass laminates were performed using procedures recommended by Amoco. Successful 1/8-inch laminates were prepared. However, it soon became evident that these procedures were not applicable for thicker laminates. Cure cycle recommendations were requested from the material supplier for moldings ranging up to one inch in thickness, but their studies had only been conducted on 1/8-inch thick laminates. Consequently, new process design information had to be generated.

Early laminates, even when quite thin, frequently blistered and exhibited poor interlaminar adhesion. Lowering the volatile content of the impregnated cloth from approximately 10% to 3% and lengthening the curing time substantially reduced these problems. Brief "bumping" (i.e., sudden release and reapplication of molding pressure) even in the advanced stages of the cure cycle also was found necessary to make satisfactory composites. Exploratory studies in which the B-staging time, temperature, press molding time, temperature and pressure were varied (starting from the Amoco-supplied procedure)has resulted in selection of an overall procedure which makes essentially porosity-free laminates.

Laminates have been made by two means: 1) directly between heated platens, and 2) in a 2.25-inch diameter cylindrical mold. For thicker laminates, including the 5/8-inch thickness required for PEET specimens, the cylindrical mold has been employed. The procedure generated in the exploratory studies for use with graphite and silica fabric is given below:

- Cut the preimpregnated fabric into discs of desired size and stack them as high as needed for final laminate thickness.
- Maintain stacked preimpregnated discs at 500°F (260°C), 100 psig for two hours and "bump" every 15 minutes;
- Increase mold temperature to 550°F (288°C) and maintain it there for one hour while "bumping" from 100 psig every 15 minutes;
- Remove the laminate from the die and condition in a furnace regulated at 288°C for one hour;
- Replace laminate in the die, raise temperature to 600°F (316°C) and apply pressure of 1, 000 psig;
- After 30 minutes, bump the laminate and then cure at 316°C and 1, 000 psig for 90 minutes;

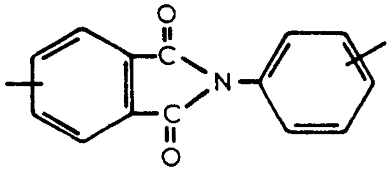
The initial "bumping" which is performed at 500°F is probably necessary to remove entrapped solvent in the laminate interior. The "bumping" that is done at 550 and 600°F probably removes short chain polymer fractions which are volatile at these temperatures. It was unexpected when laminating work was initiated that a successful laminate could result after furnace conditioning at zero applied pressure at 550°F for one hour. It became apparent, however, that this step reduced the tendency for delamination to occur. At the conclusion of this heating period, the laminate swells appreciably in thickness, but the material still retains thermal plasticity. The 1000 psig molding pressure which is subsequently applied to the conditioned laminate compresses the material substantially.

The molding process developed above was primarily directed towards molding thick essentially porosity-free specimens for PEET evaluation. This objective has been attained. It is evident from the PEET evaluation (see Section 4. 3) that further work must be directed towards preparation of polyamide-imide composites which have been post cured to remove residual volatile matter.

4.2 Polyimide Laminates

To aid in the development of processing techniques for preparation of polyimide composites, a second commercial resin was selected for examination. The processing conditions found applicable for this resin, together with those required for preparation of polyamide-imide laminates, will be useful for background information in preparation of laminates from the improved modified polyimides being synthesized in Task I. The new resin selected for evaluation was Monsanto Chemical Company's Skybond 700.

This material is a heat reactive aromatic system which can be thermally cured to a crosslinked polyimide. The chemical structure of the aromatic imide group is shown below.



This material is designed for structural, electrical and specialty applications where extended exposure at temperatures up to 700°F is required. Several evaluations have been made for ablative applications, and the results of these have been very favorable. None of these tests have involved fluorine-containing propellants. In one published report (Reference 11) the polyimide material showed approximately 50% less total length loss during ablation than a phenolic impregnated material. The test specimens were reinforced with silica fabric and were tested in a rocket engine exhaust. Kerosene and oxygen were the fuel and oxidizer used. Heat flux was 1550 BTU/ft^2 - sec at Mach 2.45.

As supplied in a solvent dispersion, the resin has the following properties:

Property	Range
Solids	60-64%
Viscosity	2500-7000 cps
pH	4.0-4.7
Specific Gravity	1.15-1.18
Gel Test	75-95 minutes at 135°C

Volatile products given off during molding are mainly aromatic acids, aromatic nitrogenous compounds and solvents.

Processing techniques selected for silica and graphite laminates with this resin were very similar to those used for the polyamide-imide polymer. The 60-64% w/w resin solids solution as supplied was used for coating operations. After cursory exploratory studies, squeeze bar gap settings were selected - 38 mils for silica fabric and 22 mils for use with graphite fabric. A B-staging cycle of 70 minutes at 248°F (120°C) gave a residual volatile content in the impregnated fabric of approximately 3% w/w. Resin contents for both silica and graphite fabrics have usually ranged between 39 and 41 percent. Press molding conditions identical to those evolved for the polyamide-imide system provided composite structures which appeared to be acceptable.

Volatile content of the modified polyimide preimpregnated fabrics were determined by oven heating at 435°F for 10 minutes and determining weight loss. Methods for determining resin content and molding procedures were the same as those used for the polyamide-imide resin.

4.3 PEET EVALUATION OF COMPOSITE ABLATIVE MATERIALS

Composite ablative specimens were subjected to both fluorine/hydrogen and FLOX/methane propellant exhaust environment testing (PEET). Several commercial composites were obtained and tested to provide a comparison with phenolic base graphite, carbon and silica fabric composites and state-of-the-art materials. The commercial materials included a polybenzimidazole/graphite composite. The commercial ablative materials were selected by the manufacturers as being the most likely to survive fluorine-containing combustion environments. The other specimens were prepared by TRW Systems. A list of the composites tested and the results of the PEET evaluation are presented in Tables IV and V. Table IV presents the results of 10-second fluorine/hydrogen PEET evaluations and Table V lists the results of 30-second FLOX/methane PEET evaluations.

Inspection and interpretation of the fluorine/hydrogen PEET results presented in Table IV provides some tentative trends of commercially available ablative composite materials. It appears that graphite fabric reinforcements are superior to silica fabric reinforcements, which are in turn superior to carbon fabric reinforcements. Because only one silica and two graphite reinforced ablative materials were evaluated, additional testing must be conducted on other specimens to provide confidence in these generalized observations.

Assessment of the data in Table V shows that the carbon and graphite reinforced specimens did not perform well. This fact fits the expected theory of attack of carbonaceous materials by FLOX/methane combustion products. It was also speculated that the silica-reinforcements would be attacked by the hydrogen fluoride in the FLOX/methane flame; this, however, did not appear to be the case - in fact the silica reinforced materials were markedly superior in each of the comparative cases, e.g., phenolic, polyamide-imide, and polyimide resins. In general, attack of organic resins by FLOX/methane combustion products did not occur to the extent expected. This finding infers that the chemical compatibility of the exhaust species is indeed a rate dependent phenomenon which is less significant than anticipated previously.

Of the graphite reinforced resin systems, the polybenzimidazole resin was markedly superior. The fact that the TRW Systems prepared candidate "stiff" polymers did not provide the same degree of PEET resistance indicates that improvements in TRW Systems processing methods must be made. The polyamide-imide composites cracked during the PEET evaluation which is believed to arise from residual volatile matter in the finished composite. It is postulated that the

TABLE IV

FLUORINE/HYDROGEN PEET EVALUATION OF ABLATIVE FABRIC REINFORCED COMPOSITES [a]

Sample	Resin Type	Cloth Type	Weight Loss, g	Backwall Temperature, °C [b]
Coast Manufacturing Co.				
4G3036	Phenolic	Graphite	0.10	225
4C1036	Phenolic	Carbon	0.16	127
4C1036-1	Phenolic	Carbon	0.19	144
4C1033-X	Phenolic	Carbon	0.16	182
American Reinforced Plastics Co.				
259 PHC	Phenolic	Carbon	0.29	146
218 PHC	Phenolic	Carbon	0.18	157
Fiberite Corp.				
MX4500	Phenolic	Graphite	0.12	243
MXS-51	Phenolic	Silica	0.13	79
MX4926	Phenolic	Carbon	0.15	165
MXC-51	Phenolic	Carbon	0.17	220

a. Samples exposed to F_2/H_2 combustion environment 10 seconds, 1/2-inch diameter X 1-inch long, reinforcement edgewise.

b. Thermocouple imbedded in center of sample cylinder 0.50-inch from exposed end.

TABLE V

FLOX/METHANE PEET EVALUATION OF ABLATIVE FABRIC REINFORCED COMPOSITES [a]

Sample	Resin Type	Cloth Type	Weight Loss, g	Backwall[b] Temperature, °C
Coast Manufacturing Co.				
4G3036	Phenolic	Graphite	0.53	556
4C1036	Phenolic	Carbon	0.83	331
4C1036-1	Phenolic	Carbon	0.35	307
4C1033-X[c]	Phenolic	Carbon	0.29	315
4C1636-1	Phenolic	Carbon	0.26	480
4C1636-1	Phenolic	Carbon	0.32	450
American Reinforced Plastics Co.				
259 PHC	Phenolic	Carbon	0.79	243
218 PHC	Phenolic	Carbon	0.42	266
185 PHGR	Phenolic	Graphite	0.77	788
Fiberite Corp.				
MX4500	Phenolic	Graphite	0.43	597
MXS-51	Phenolic	Silica	0.22	202
MXS-51[c]	Phenolic	Silica	0.15	200
MX-4926	Phenolic	Carbon	0.39	431
MXC-51	Phenolic	Carbon	0.35	307
U.S. Polymeric Corp.				
X5441	Phenolic	Graphite	0.72	513
FM5064	USP 39	Graphite	0.78	537
85592	Phenolic	Carbon	0.60	322

TABLE V (Cont'd)

FLOX/METHANE PEET EVALUATION OF ABLATIVE FABRIC REINFORCED COMPOSITES [a]

Sample	Resin Type	Cloth Type	Weight Loss, g	Backwall[b] Temperature, °C
Western Backing Co.				
WB8207	Phenolic	Graphite	0.71	602
WB2230	Phenolic	Silica	0.37	e
WB8217	Phenolic	Carbon	0.69	290
WB8249[c]	Phenolic	Graphite	0.60	781
NARMCO Division				
4824	PBI[d]	Graphite	0.40	595
TRW Systems				
RS27	Skybond 700	Graphite	0.75	600
RS28	Skybond 700	Silica	0.34	266
RS29[c]	AI-11[f]	Silica	0.45	348
RS32[c]	AI-11[f]	Graphite	0.64	768

a. Samples exposed to FLOX/methane combustion environment, 30 seconds, 1/2 inch diameter by 1 inch long with reinforcement edgewise.

b. Thermocouple imbedded in center of sample cylinder 0.50 inch from exposed end.

c. Sample split or cracked during test.

d. Polybenzimidazole.

e. Thermocouple inoperative.

f. Amoco polyamide-imide.

cracking would give rise to greater exposed surface area, consequently a high weight loss. In the case of the polyamide-imide resin, a 10-second exposure of the neat resin had a weight loss of 0.15 grams, whereas a 30-second exposure of the silica reinforced material had a weight loss of 0.45 grams. The graphite reinforced polyamide-imide weight loss was 0.64 grams. It is evident that the reinforcements added very little to the general stability of the resin and that the maximum potential improvement of the silica reinforced polyamide-imide was not attained. For these reasons, it is believed the data in Table V for the graphite and silica reinforced polyamide-imide and polyimide composites is not directly representative of what the composite system is capable. The difficulties attendant to the preparation of composites with state-of-the-art "stiff" polymers were discussed in Section 2.1.1 and were identified with poor processing properties. Future studies will focus on processing investigations aimed towards removing residual volatile matter by post curing.

Based on the data discussed above and presented in Tables III, IV, and V, the following trends have been identified. These conclusions are subject to verification by further testing planned in the immediate future.

- In a FLOX/methane combustion environment silica fabric reinforcements are superior to carbon and graphite fabric reinforcements.
- In a fluorine/hydrogen combustion environment graphite fabric reinforcements are superior to silica fabric reinforcements, which in turn, are superior to carbon fabric reinforcements.
- The use of inorganic resins is not indicated as mandatory for either fluorine/hydrogen or FLOX/methane resistant ablative materials.
- "Stiff" polymers, as a class, appear to offer improved resistance to both fluorine/hydrogen and FLOX/methane combustion environments.

5. NEW TECHNOLOGY

The effort during the first half of this program originated the following items of new technology:

a) A new method for processing laminates employing "stiff" polymers as the resin matrices was conceived. The feature of this method is resin curing with hydrogen evolution, thereby aromatizing saturated and/or partially unsaturated cyclic groups in the polymer molecules. In this manner, the resin undergoes a marked increase of its second order transition temperature.

b) In order to expedite the new laminate processing method, new "stiff" polymers were proposed. The new polymers and their dianhydride monomeric precursors, constitute, to the best of our knowledge, new compositions of matter.

c) The strength of resin masses composed of polyalkaline earth acrylates was found to be increased significantly by incorporating polyvinyl alcohol within the resin. The alcohol was incorporated into polyalkaline earth acrylates by swelling the latter material in aqueous polyvinyl alcohol solutions and then drying the swollen mass.

6. REFERENCES

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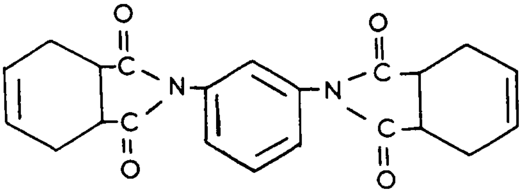
APPENDIX A

SYNTHESIZED MONOMERS AND PRECURSORS

The following monomers were prepared in the laboratory. The procedures used and the properties observed are reported below. The use of each material is reported in the text.

A. 1 m-Phenylene-di-(1, 2, 3, 6-tetrahydrophthalimide)



Procedure A. 1

Take 54.0 g (0.5 mole) of m-phenylenediamine dissolved in 50 ml of dimethylformamide (DMF) and add slowly (from a pressure relieved dropping funnel) to 160 g (1.05 moles) of 1, 2, 3, 6-tetrahydrophthalic anhydride (in 400 ml of refluxing toluene in a 1-liter, three-necked, round bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap and condenser fitted for reflux). Reflux for 24 hours. Observe the amount of liquid in Dean-Stark trap. Treat the hot solution with decolorizing charcoal, filter into 1-liter Erlenmeyer flask, and allow the precipitate to form on cooling. Collect the precipitate on a sintered glass Buchner funnel, wash with fresh toluene and then with isopropanol. Dry the precipitate under vacuum.

Observed Results A. 1

The liquid began to collect immediately on addition of the diamine. At the end of a 24-hour reflux period, 20 ml of liquid had been collected. The theoretical amount of water is calculated at 18 ml. Gas-liquid chromotography showed liquid to be 13 percent DMF or 17.4 ml of H_2O. A white, crystalline solid was collected on the Buchner funnel weighing 164.2 g after drying; this is 87 percent of theoretical yield.

Characterization of Product A. 1

Melting Point: 200 -201°C

Bromine number: 824 mg/g (theoretical: 772 mg/g)

Form: White crystals

Infrared Spectrum: See Figure A-1.

Thermogram: See Figure A-2

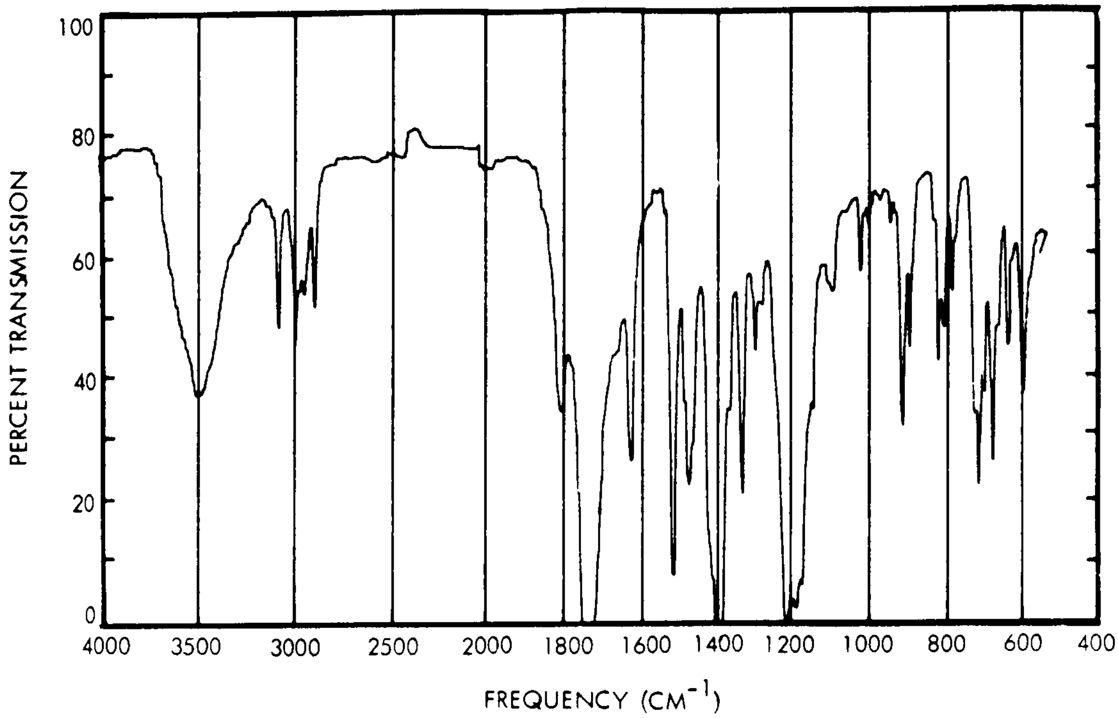


Figure A-1. Infrared Spectrum of m-Phenylene-di-(1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 5.4 mg/g KBr

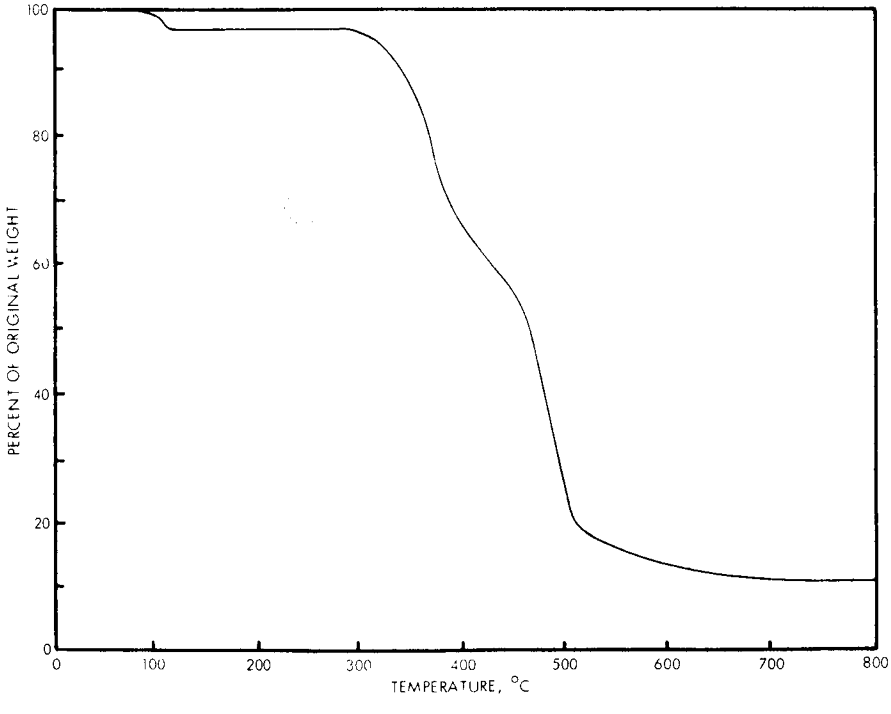
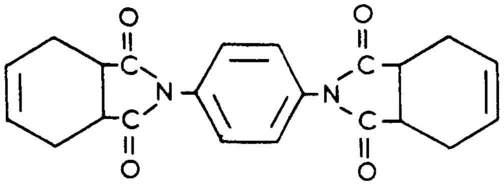


Figure A-2. Thermogram of m-Phenylene-di-(1, 2, 3, 6-Tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3 °C/Minute

A. 2 p-Phenylene-di-(1, 2, 3, 6-tetrahydrophthalimide)



Procedure A. 2

Take 54.0 g (0.5 mole) of p-phenylene diamine dissolved in 200 ml of DMF and add slowly to a stirred, refluxing solution of 159.6 g (1.05 mole of 1, 2, 3, 6-tetrahydrophthalimide in 400 ml of toluene in a 1-liter, three-necked, round bottom flask equipped with a mechanical stirrer, thermometer, Dean-Stark trap, and a reflux condenser. Reflux for 22 hours. Observe the amount of liquid collected in the Dean-Stark trap. Cool to 50°C, and collect white precipitate as in Procedure A-1 above. Wash twice with fresh toluene, and once with acetone. Dry under vacuum.

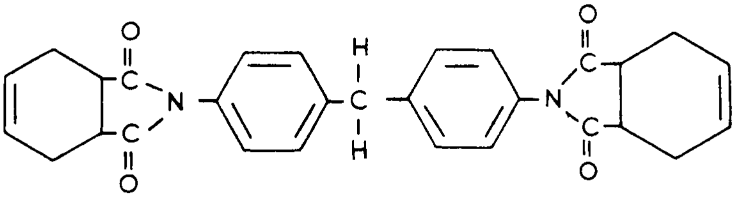
Observed Results A. 2

Liquid collected immediately on addition of diamine. At the end of 22 hours of refluxing, 25.4 ml of liquid had collected. The dry product weighed 164.8 g, which is 87.7 percent of theoretical yield.

Characterization of Product A. 2

Melting Point: 300 °C
Form: White crystals
Infrared Spectrum: See Figure A-3
Thermogram: See Figure A-4

A. 3 p, p'-Diphenylmethane-di(1, 2, 3, 6-tetrahydrophthalimide)



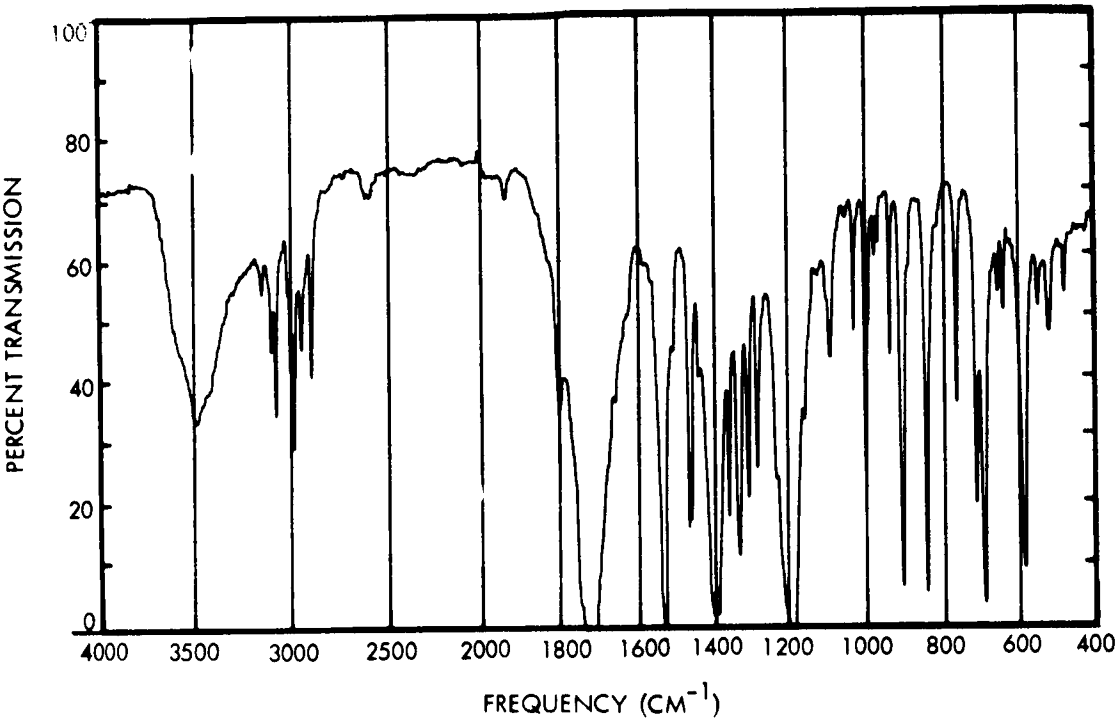


Figure A-3. Infrared Spectrum of p-Phenylene-di-(1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 6.1 mg/g KBr

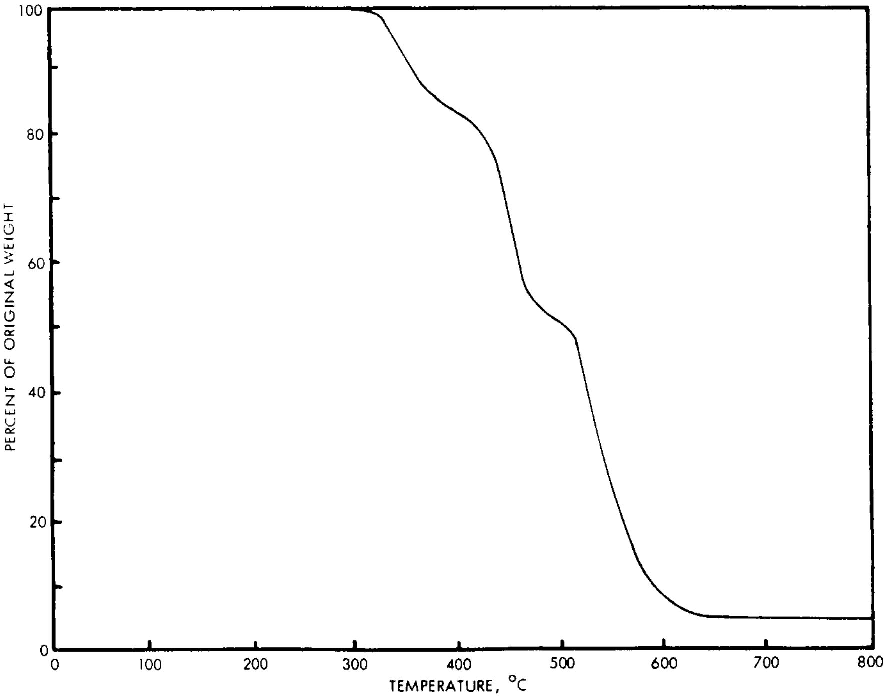


Figure A-4. Thermogram of p-Phenylene di-(1, 2, 3, 6-Tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3 °C/Minute

Procedure A. 3

Dissolve 49.5 g (0.25 mole) of p,p'-methylene dianiline in 50 ml of DMF and add to 76.0 g (0.5 mole) 1,2,3,6-tetrahydrophthalic anhydride in the manner described in Procedure A. 1. Reflux for 20 hours, cool and collect as in examples above. Wash with toluene and isopropanol; dry under vacuum. Recrystalize from toluene/DMF solution and weigh.

Observed Results A. 3

12.4 ml of liquid was collected in the trap after 20 hours refluxing. The dry product weighed 97.9 g, which is 84 percent of theoretical yield.

Characterization of Product A. 3

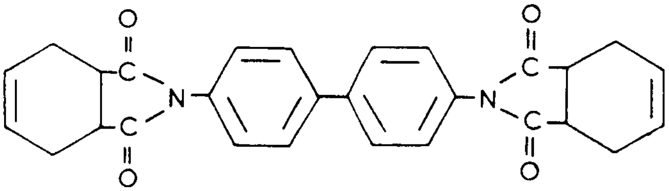
Melting Point: 212 - 216 °C (original)
205 - 216 °C (after recrystalization)*

Form: White crystals

Infrared Spectrum: See Figure A-5

Thermogram: See Figure A-6

A. 4 Benzidine-di(1,2,3,6-tetrahydrophthalimide)



Procedure A. 4

Dissolve 55.2 g (0.3 mole) of benzidine in 150 ml DMF and add to 91.2 g (0.6 mole) of 1,2,3,6-tetrahydrophthalic anhydride in the manner described in Procedure A. 1. Reflux for 20 hours. Filter solution hot, cool, collect precipitate as above, wash with toluene, isopropanol, and finally ether. Dry under vacuum.

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*Broadening of melting point after purification has not yet been explained.

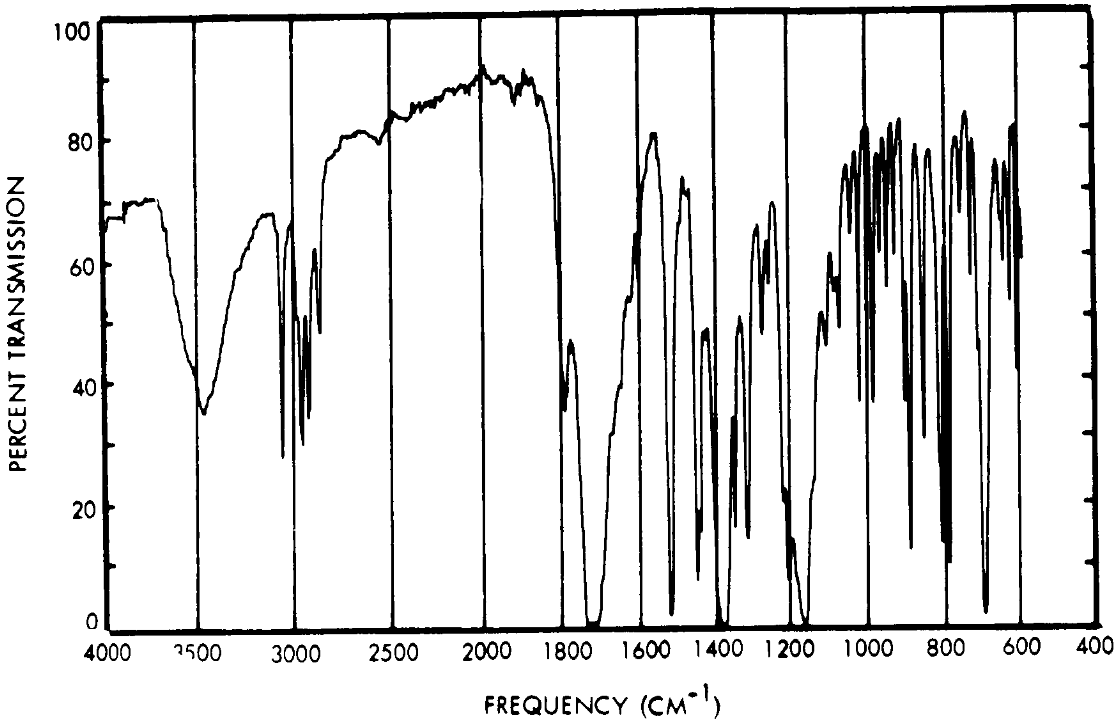


Figure A-5. Infrared Spectrum of p, p'-Diphenylmethane-di(1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 8. 1 mg/g KBr

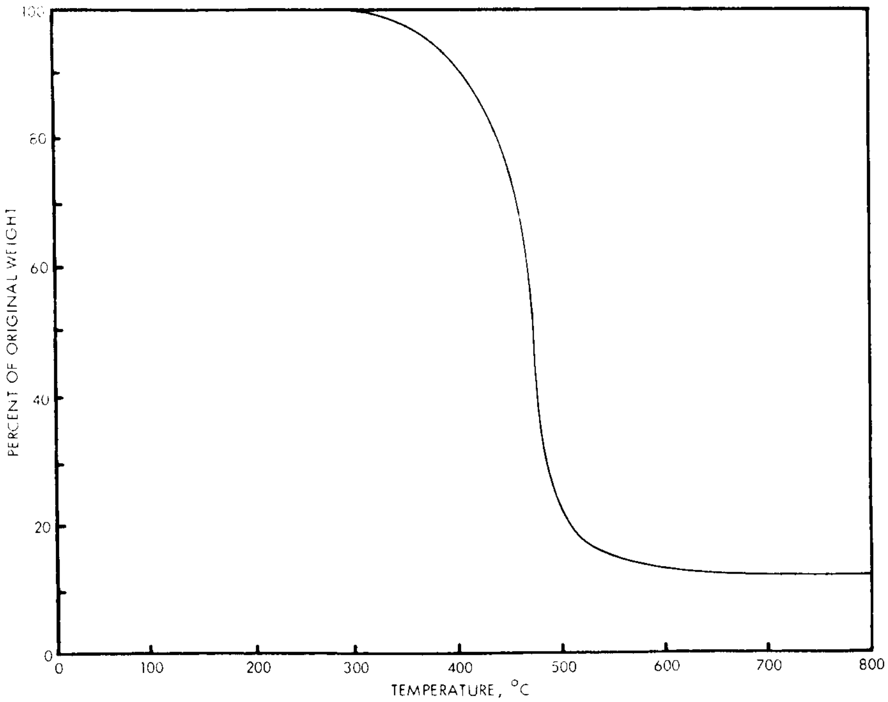


Figure A-6. Thermogram of p, p'-Diphenylmethane-di(1, 2, 3, 6-Tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3 °C/Minute

Observed Results A. 4

18 ml of liquid were collected after 20 hours of refluxing. The dry product weighed 110.5 g, which is 81 percent of theoretical yield.

Characterization of Product A. 4

Melting Point: 299 - 302 °C

Form: White crystals

Infrared Spectrum: See Figure A-7

Thermogram: See Figure A-8

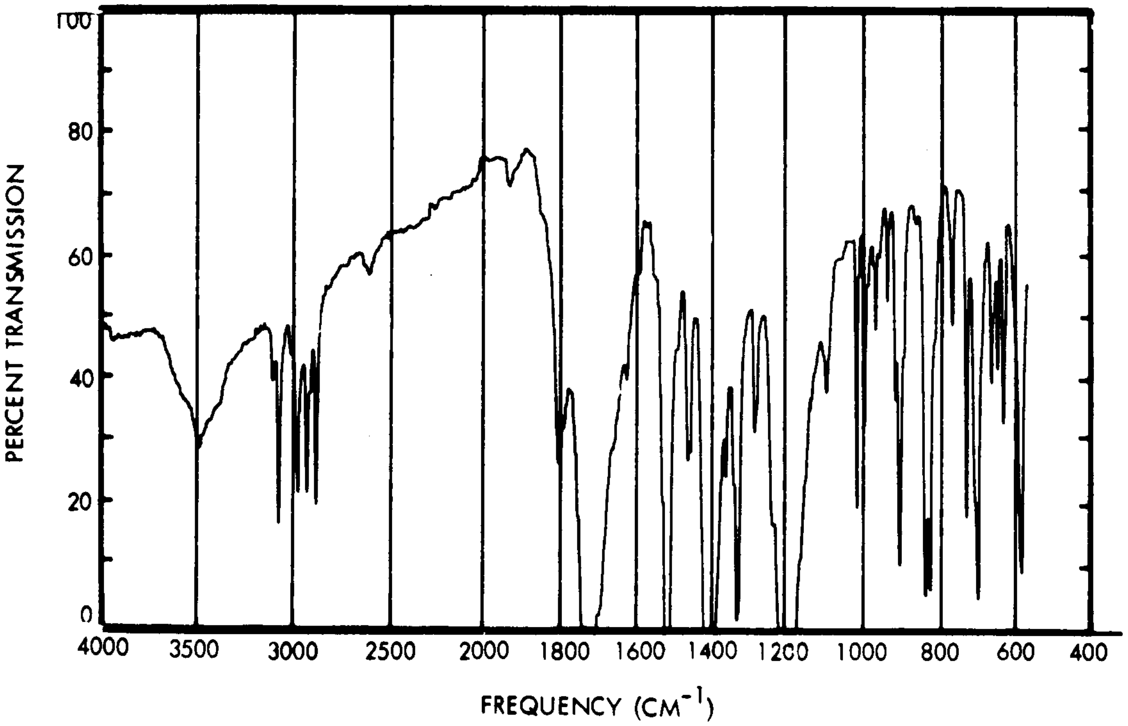


Figure A-7. Infrared Spectrum of Benzidine-di(1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 8.4 mg/g KBr

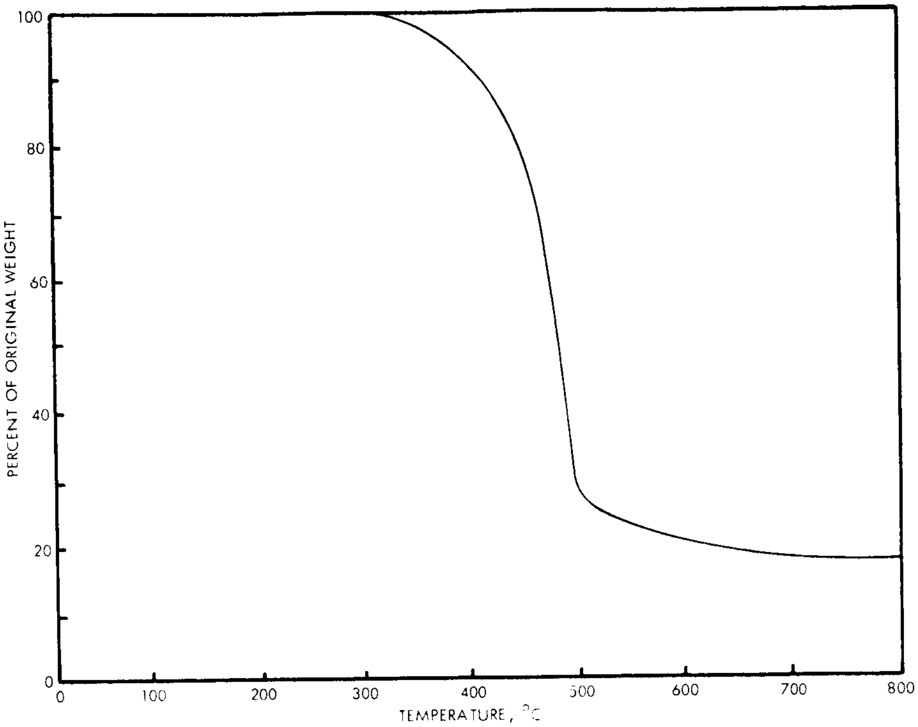
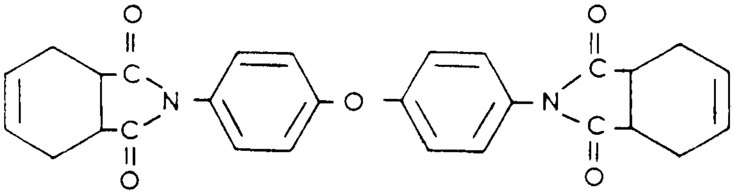


Figure A-8. Thermogram of Benzidine-di(1, 2, 3, 6-Tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3 °C/Minute

A. 5 p, p'-Diphenyl ether-di(1, 2, 3, 6-tetrahydrophthalimide)



Procedure A. 5

Dissolve 60.0 g (0.3 mole) of dianiline oxide in 150 ml of DMF and add to 91.2 g (0.6 mole) of 1, 2, 3, 6-tetrahydrophthalic anhydride in the manner described in Procedure A. 1. Reflux for 24 hours. Filter hot, cool recrystalize precipitate from toluene/DMF mixture after treating with decolorizing charcoal. Dry under vacuum.

Observed Results A. 5

16 cc of liquid were collected after 24 hours of refluxing. The dry product weighed 84.9 g which is 60.4 percent of theoretical yield.

Characterization of Product A. 5

Melting Point: 42 - 44 °C

Form: Faintly pink crystals

Infrared Spectrum: See Figure A-9

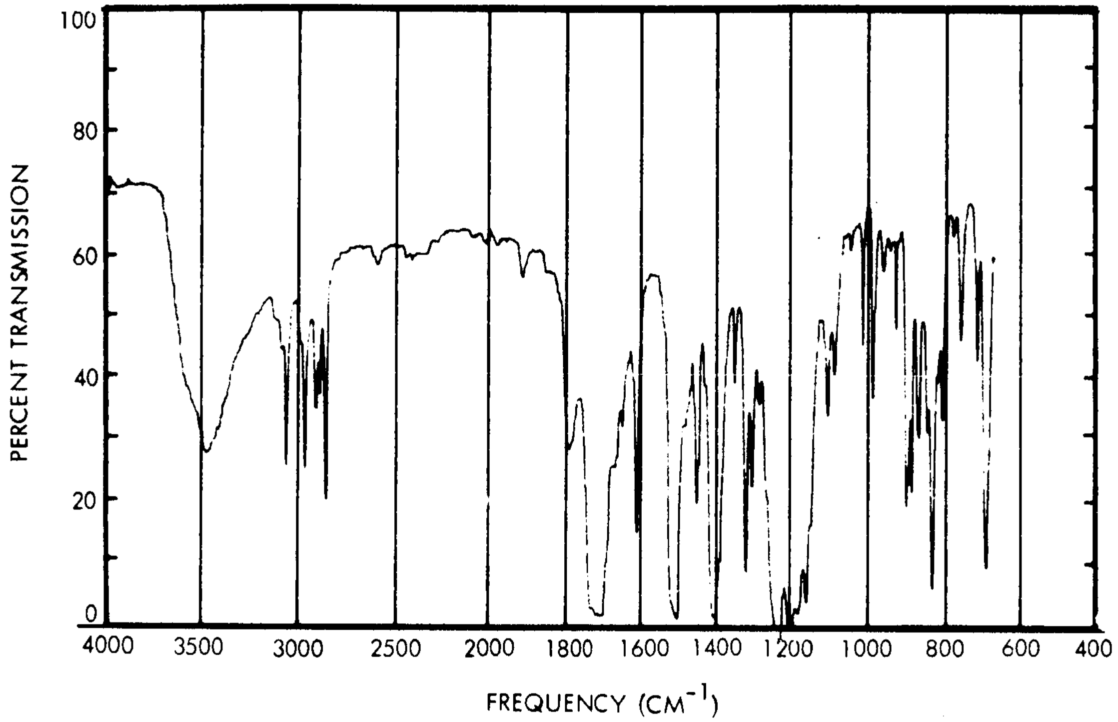
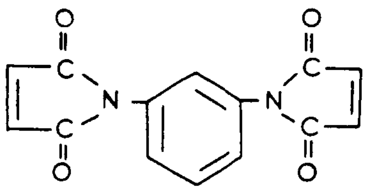


Figure A-9. Infrared Spectrum of p, p'-Diphenyl Ether-di(1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 9.0 mg/g KBr

A. 6 m-Phenylene dimaleimide



Procedure A. 6

Dissolve 5.4 g (0.5 mole) of m-phenylene diamine in 50 ml of acetone and add slowly to a stirred solution of 9.8 g (0.1 mole) of maleic anhydride in 100 ml of acetone. Treat generally as in Procedure A. 1.

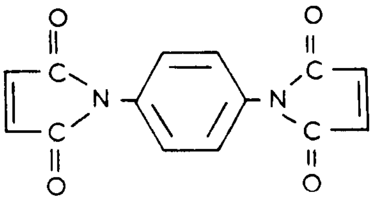
Observed Results A. 6

The reaction solution turned yellow and began to reflux gently. After a short time a precipitate began to form. The reaction mixture was stirred for one half hour after the addition of diamine was completed. The yellow precipitate was collected and washed with fresh acetone and dried on a sintered glass Buchner funnel (mp > 300°C). This material was dissolved in hot acetic anhydride and stirred at 90°C for one-half hour. At the end of the stirring period the reaction mixture was poured into crushed ice. A dark precipitate formed as the ice melted. The water was decanted and the precipitate was washed with distilled water and then with a water-acetone mixture. Filtration left 3 g of yellow crystals which were rewashed with acetone and dried on the filter.

Characterization of Product A. 6

Melting Point: 201 -202°C (Literature: 198 -199°C)
Form: Yellow crystals
Infrared Spectrum: See Figure A-10

A. 7 p-Phenylene dimaleimide



Procedure A. 7

Add 9.8 g (0.1 mole) of maleic anhydride to 5.4 g (0.05 mole) of p-phenylene diamine and 1 g of anhydrous sodium acetate. Add 50 ml of acetic anhydride and heat to 85°C with stirring. Stir for 30 minutes, dump onto crushed ice, decant the water, and wash precipitate with water and then with water/acetone. Recrystalize from DMF and wash with acetone.

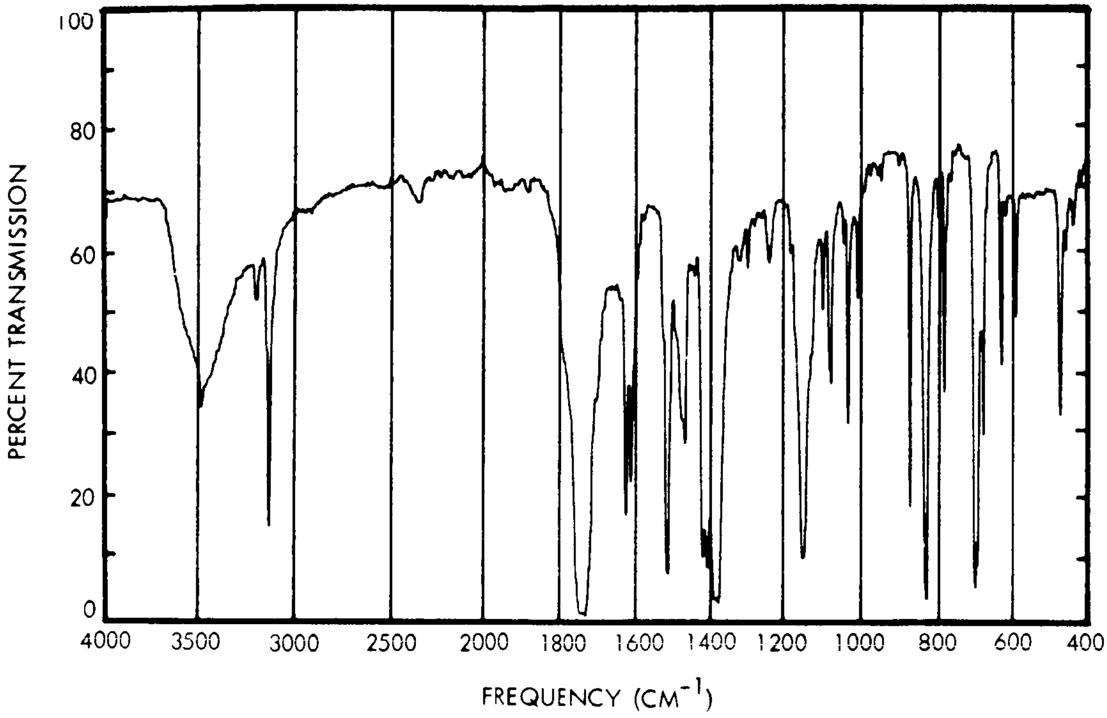


Figure A-10. Infrared Spectrum of m-Phenylene-Dimaleimide
Concentration: 4.4 mg/g KBr

Observed Results A.7

The heating was ended in 30 minutes, but the temperature rose to approximately 92°C. The reaction mixture was stirred for an additional half hour and then dumped onto crushed ice. After the ice melted the water was decanted from the dark oily precipitate which formed and then the precipitate was washed with water and a water-acetone mixture. The resultant green solid was collected and washed with acetone and dried on the filter (mp>300°C). The green solid was recrystalized from DMF and washed with acetone.

Characterization of Product A.7

Melting Point: 302°C

Form: Green solid

Infrared Spectrum: See Figure A-11

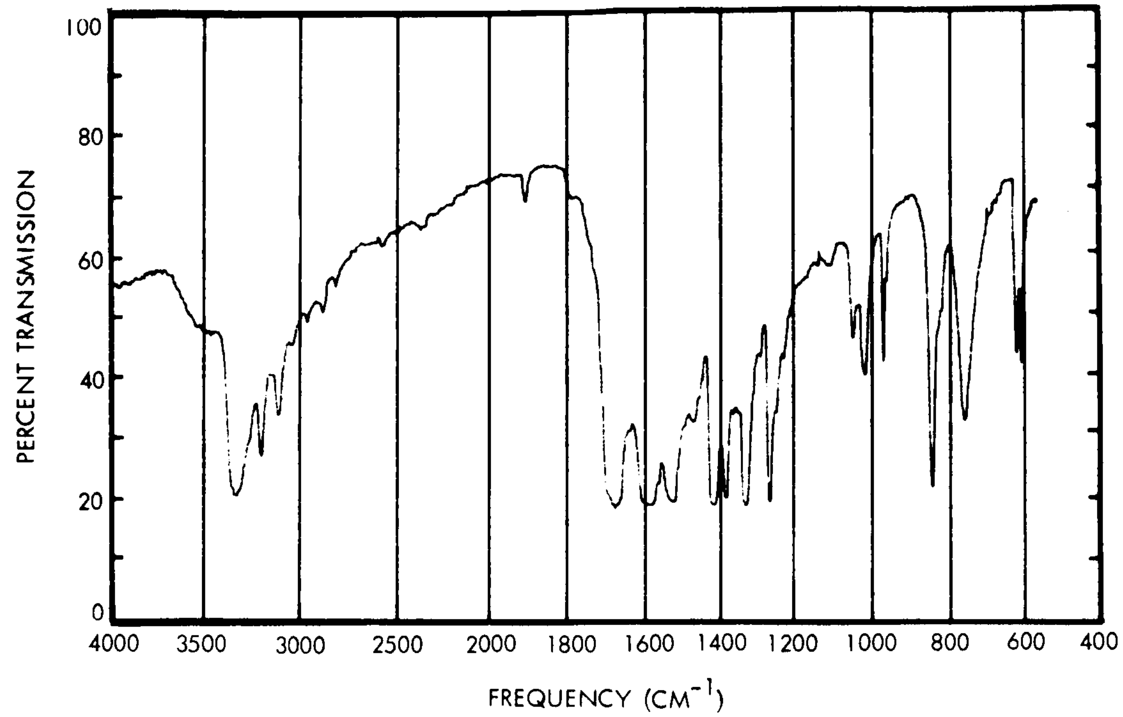
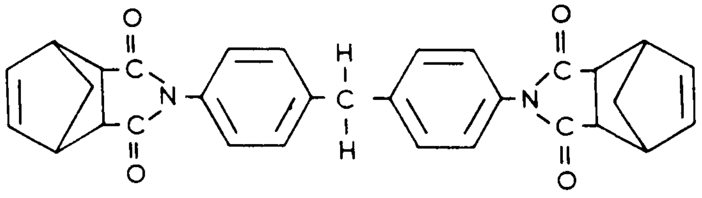


Figure A-11. Infrared Spectrum of p-Phenylene-Dimaleimide
Concentration: 4.9 mg/g KBr

A. 8 p, p'Diphenylmethane-di(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)



Procedure A. 8

Dissolve 49.5 g (0.25 mole) of p, p'-methylene dianiline in 50 ml of DMF and add to 81.0 g (0.5 mole) of nadic anhydride in toluene in the manner described in Procedure A.1. Reflux for 7 hours, cool, and wash precipitate with toluene. Recrystalize from toluene/DMF and wash again with toluene. Dry under vacuum.

Observed Results A. 8

13 ml of liquid were collected in trap after 7 hours refluxing. The product weighed 69. 7 g, which is 57 percent of theoretical yield.

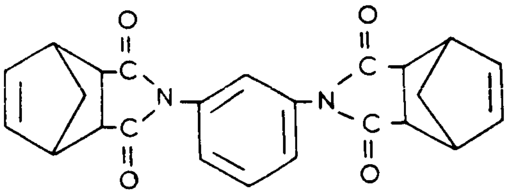
Characterization of Product A. 8

Melting Point: 254 - 257 °C

Form: Crystaline

Infrared Spectrum: See Figure A-12

A. 9 m-Phenylene di-(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)



Procedure A. 9

Dissolve 54. 0 g (0. 5 mole) of m-phenylene diamine in 50 ml of DMF and add to 170. 5 g (1. 04 mole) of 3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalic anhydride in the manner described in Procedure A. 1. Reflux for 18 hours. Filter, cool, and wash precipitate with toluene. Dry under vacuum.

Observed Results A. 9

19 ml of liquid were collected in the trap. The product weighed 106. 8 g, which is 53. 4 percent of theoretical yield.

Characterization of Product A. 9

Melting Point: 243 - 247 °C

Form: Crystaline

Infrared Spectrum: See Figure A-13

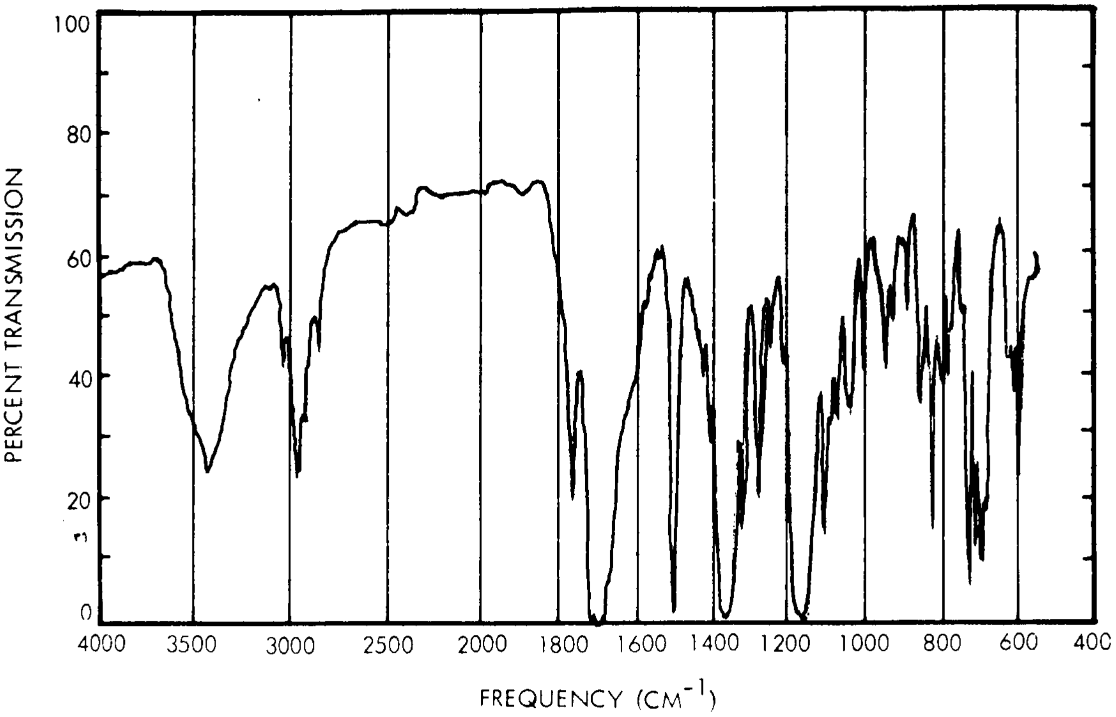


Figure A-12. Infrared Spectrum of p, p'-Diphenylmethane-di(3, 6-Endomethylene-1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 7.8 mg/g KBr

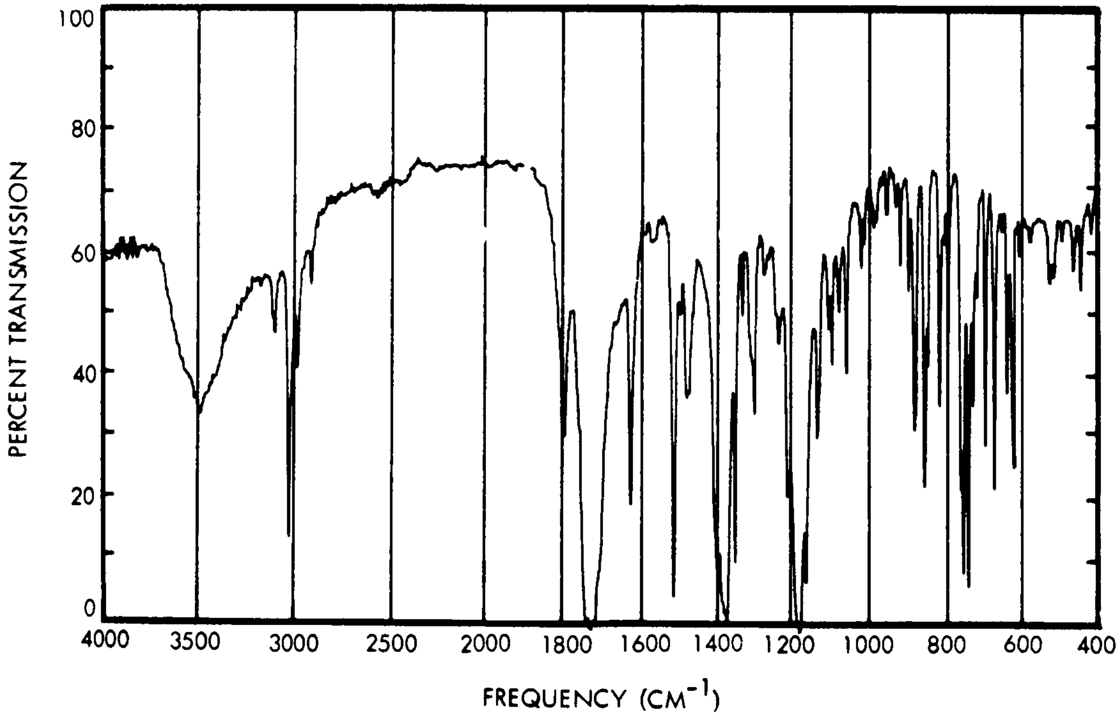
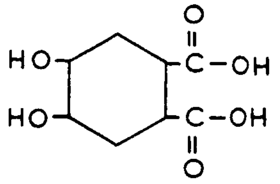


Figure A-13. Infrared Spectrum of m-Phenylene di-(3, 6-Endomethylene-1, 2, 3, 6-Tetrahydrophthalimide)
Concentration: 4.6 mg/g KBr

A. 10 4, 5-Dihydroxy-cyclohexane-1, 2-dicarboxylic acid



Procedure A. 10

Add 15.2 g (0.1 mole) of 1, 2, 3, 6-tetrahydrophthalic anhydride in one portion to a solution of 8.4 g (0.21 mole) of sodium hydroxide in 100 ml of water. When solution is complete, cool to 0°C by means of dry ice-acetone bath. Add 15.8 g (0.1 mole) of $KMnO_4$ in 300 ml of H_2O slowly over a period of one hour while the temperature is maintained at 0°C.

Observed Results A. 10

MnO_2 began to precipitate immediately from the reaction mixture. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was filtered. The yellow filtrate was acidified with HCl but no precipitate formed. $CaCl_2$ solution was added and a white precipitate settled out. This was collected, washed with water and then reslurried in water and acidified to pH3 with H_2SO_4. The $CaSO_4$ was removed by filtration and the clear solution was allowed to stand overnight. The next morning, colorless crystals were found in the solution. These were collected, washed with distilled water and dried under vacuum to yield 3 g which is 14.7 percent of theoretical yield.

Characterization of Product A. 10

Melting Poing: 230 -232°C

Form: Colorless Crystals

Infrared Spectrum: See Figure A-14

Carbon, Hydrogen Analysis:	Theoretical (percent)	Found (percent)
	C - 47.06	47.37
	H - 5.92	5.87

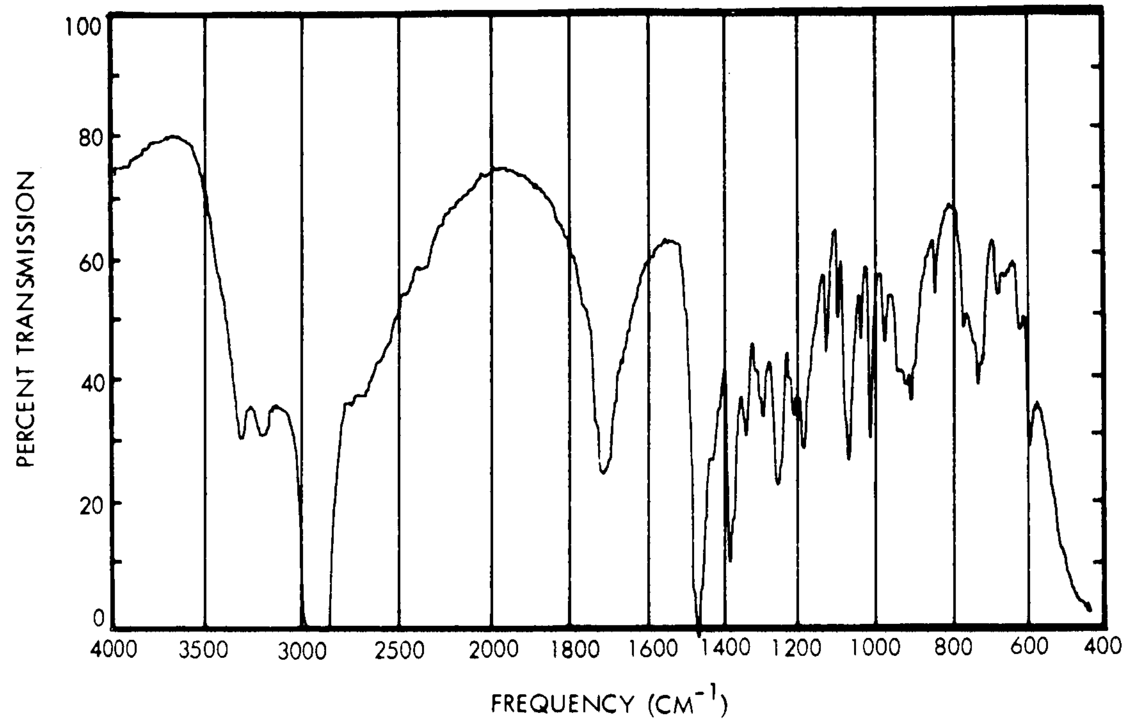
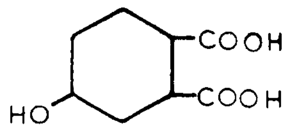


Figure A-14. Infrared Spectrum of 4, 5-Dihydroxy-Cyclohexane-1, 2-Dicarboxylic Acid
Concentration: Film

A. 11 4-Hydroxy-cyclohexane-1, 2-dicarboxylic acid



Procedure A. 11

Slurry 20. 0 g (0. 13 mole) of 1, 2, 3, 6-tetrahydrophthalic anhydride in 50 ml of 50 percent H_2SO_4 in a 100-ml, single necked, round bottom flask, fitted with a reflux condenser. Stir the reaction mixture and heat to refluxing temperatures (125 ^{o}C). Continue refluxing for 20 hours. Cool, and allow white crystals to precipitate. Collect the precipitate and wash with H_2O and dry. Reslurry the crystals in H_2O and then add 15 ml of 10 percent w/v NaOH. Stir the clear solution for one hour and then reacidify with HCl to pH3. Extract the solution with three 50-ml portions of ethyl ether. Combine the extracts and wash with H_2O and dry over Na_2SO_4.

Observed Results A. 11

Approximately 5.0 g of the white sulfonic acid crystals precipitated after cooling the reaction mixture. A total of 2.0 g of white crystalline product was obtained.

Characterization of Product A. 11

Melting Point: 215 - 217 °C

Form: White crystals

Infrared Spectrum: See Figure A-15

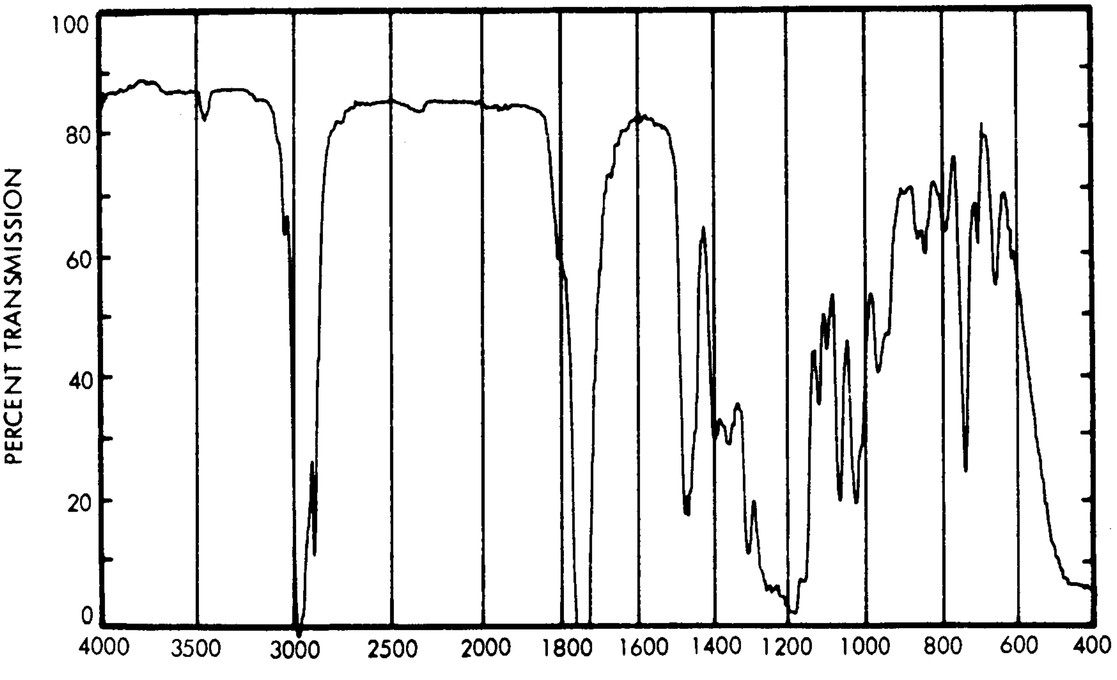
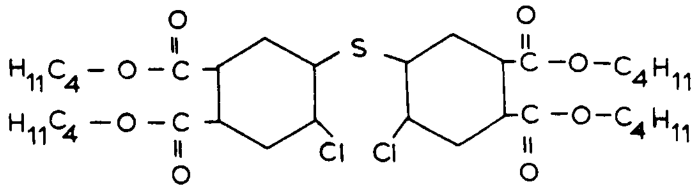


Figure A-15. Infrared Spectrum of bis(2-Chloro-4, 5-di-n-Carboxy Cyclohexyl) Sulfide
Concentration: Film

A. 12 bis(2-Chloro-4, 5-di-n-butyl carboxy cyclohexyl) sulfide



Procedure A. 12. 1

Add 5.6 g (0.5 mole) of sulfur monochloride drop-wise to 28.2 g (0.1 mole) of neat di-n-butyl-1, 2, 3, 6-tetrahydrophthalate with stirring. After stirring for 18 hours at ambient temperature, pour the reaction mixture into 600 ml of cold water and stir for 15 minutes.

Observed Results A. 12. 1

The oil which separated was dissolved in methylene chloride and washed with water. The solution was dried over Drierite and filtered. After stripping of the solvent, 27.8 g of yellow oil remained.

Characterization of Product A. 12. 1

Thin Layer Chromatogram: Shows small amount of elemental sulfur, but no starting materials.

Infrared Spectrum: Figure A-16 shows no vinyl C-H nor C=C absorption.

Elemental Analysis:

Theory (percent)	Found (percent)
S - 4.79	8.12*
Cl - 10.64	10.18

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*Excess percent due to elemental sulfur.

Procedure A. 12. 2

Transfer 141.0 g (0.5 mole) of di-n-butyl-1, 2, 3, 6-tetrahydrophthalate into a 250-ml, single neck, round bottom flask. Add 33.5 g (0.25 mole) of sulfur monochloride to the flask. Stir the reaction mixture for 18 hours at room temperature, then transfer the contents of the flask to a vessel containing approximately one liter of cold, distilled water (not iced). Stir this mixture rapidly for 30 minutes, then add 200 ml of methylene chloride and continue stirring for an additional 30 minutes. Allow the organic layer to separate from the aqueous layer, remove the organic layer and then repeat the washing and separation steps. Dry the product over anhydrous $CaSO_4$ (Drierite) and then remove the solvent by evacuation.

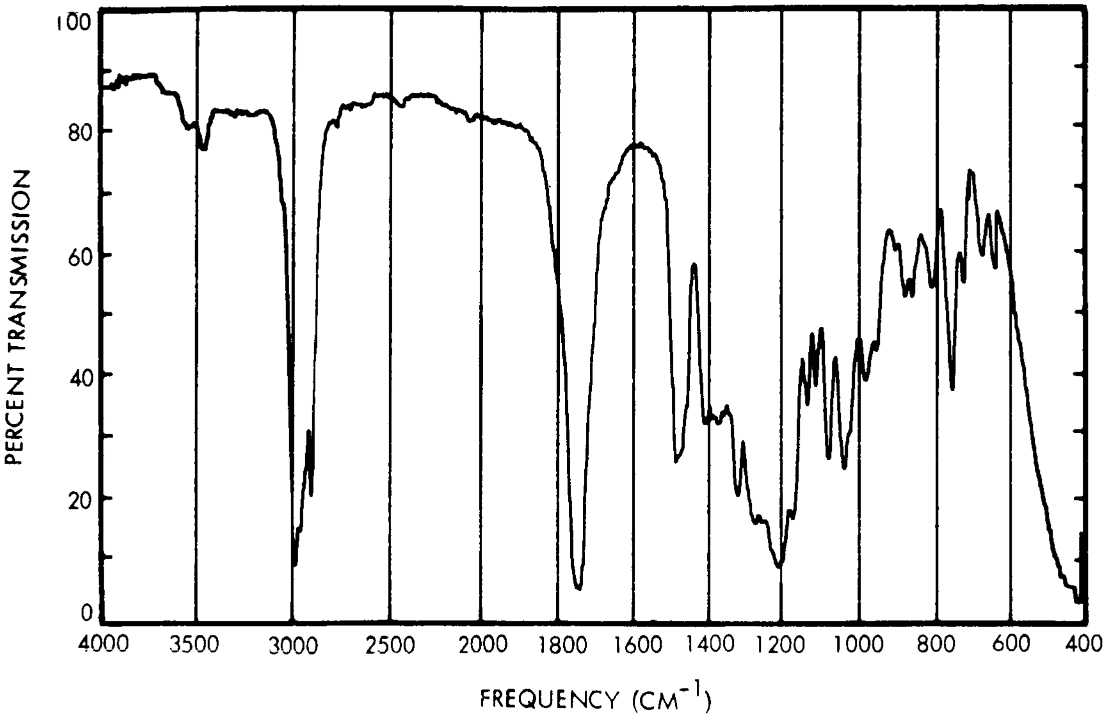


Figure A-16. Infrared Spectrum of bis(2-Chloro-4, 5-di-n-Butyl Carboxy Cyclohexyl) Sulfide
Concentration: Film

Observed Results A. 12. 2

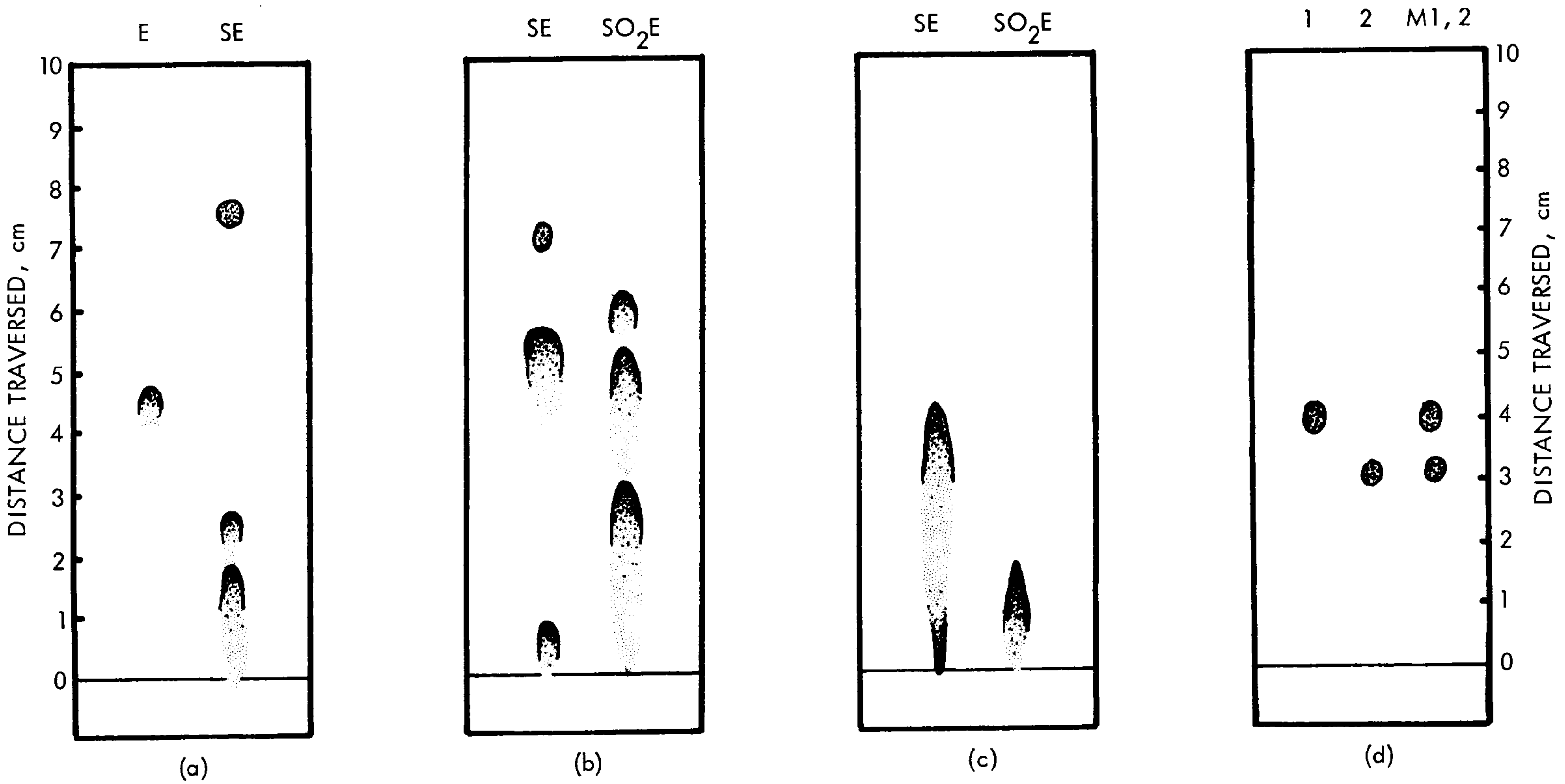
The mixture became quite viscous during the stirring period. A total of 172. 6 g of the viscous yellow oil product was obtained (104% yield).

Characterization of Product A. 12. 2

Thin Layer Chromatogram:	Figure A-17 (a) shows this material to be a mixture consisting of mainly a new compound and small quantities of the starting ester and sulfur byproduct.
Infrared Spectrum:	The infrared spectrum was essentially identical to that obtained from the product prepared by procedure A. 12. 1.

Procedure A. 12. 3

Transfer 56. 4 g (0. 2 mole) of di-n-butyl-1, 2, 3, 6-tetrahydrophthalate into a 100-ml, three-neck, round bottom flask which is equipped with a thermometer, dropping funnel and magnetic stirrer. While stirring the contents of the flask, add drop-wise 10. 3 g (0. 10 mole) of sulfur dichloride. With the aid of an ice bath, maintain the temperature of the



(a)

		R_f Value
Solvent:	Benzene	
E:	Starting Ester	0.46
SE:	Sulfide Ester	0.26
	Sulfur	0.75
	Unknown	0.17

See Preparation A. 12. 1

(b)

		R_f Value
Solvent:	70% v/v Chloroform; 30% v/v Benzene	
SE:	Sulfide Ester	0.53
	Sulfur	0.75
	Unknown	0.09

See Preparation A. 12. 2

SO$_2$E:	Sulfone Ester	0.28
	Sulfide Ester	0.53
	Sulfoxide Ester (?)	0.60

Made using A. 12. 2 as Starting Product

(c)

		R_f Value
Solvent:	70% v/v Chloroform; 30% v/v Benzene	
SE:	Sulfide Ester Preparation A. 12. 3	0.43
SO$_2$E:	Sulfone Ester Preparation A. 13	0.29

(d)

		R_f Value
Solvent:	50% v/v Methylene Chloride; 50% v/v Toluene	
1:	bis(chloro phenyl) sulfone	0.40
2:	Crystallized product Compound A. 14	0.30
M1, 2:	Brown product (unpurified)	
	Product	0.30
	Starting sulfone	0.40

Figure A-17. Thin Layer Chromatograms of Anhydride Precursors reaction flask below 30 °C throughout the duration of sulfur dichloride addition (approximately one hour). Remove the cooling bath when the addition is complete. Allow the reaction mixture to stir overnight and then transfer the contents of the flask to a vessel containing 400 ml of distilled water. Stir this mixture for 30 minutes, then add 75 ml of methylene chloride and continue stirring for 30 minutes. Allow the organic layer to separate, remove it from the aqueous phase, and repeat the washing step. Dry the organic layer over anhydrous $CaSO_4$ (Drierite) and then strip the solvent by evacuation.

Observed Results A. 12. 3

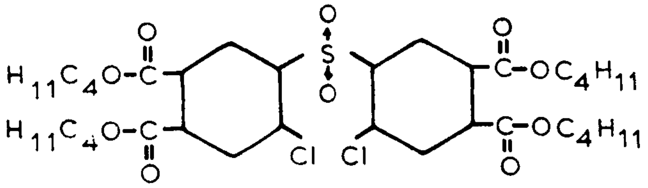
The synthesis reaction was very exothermic. The mixture became viscous during the reaction period. The product, weighing 55. 6 g (83% yield), was a viscous yellow oil.

Characterization of Product A. 12. 3

Thin Layer Chromatogram: Figure A-17 (c) shows the product to be quite pure. Comparison with Figure (b) for Compound A. 12. 2 in the same solvent shows sulfur has been removed and the impurity has been practically eliminated.

Infrared Spectrum: The infrared spectrum was essentially identical to that obtained from the product prepared by procedure A. 12. 1.

A. 13 bis(2-Chloro-4, 5-Di-n-Butyl Carboxy Cyclohexyl) Sulfone



Procedure A. 13

Dissolve 55. 6 g (0. 083 mole) of bis(2-chloro-4, 5-di-n-butyl carboxy cyclohexyl) sulfide (made by procedure A. 12. 3) in 200 ml of glacial acetic acid contained in a 500-ml, three-neck, round bottom flask which is equipped with a thermometer, dropping funnel, heating bath and magnetic stirrer. Elevate the temperature of the reaction mixture to

60-65 °C, and while maintaining it at that temperature and stirring it, add 37.0 g (0.34 mole) of 30% H_2O_2 drop-wise to the flask over a period of one hour. When the addition is complete, maintain the reaction mixture at 60 °C for 24 hours. At the end of the heating period, transfer the contents of the flask to a vessel containing 500 ml of distilled water. Stir the resulting mixture for 15 minutes, then add 100 ml of methylene chloride. Separate the organic phase from the aqueous phase and wash it with dilute $NaHCO_3$ solution. Remove the solvent by stripping.

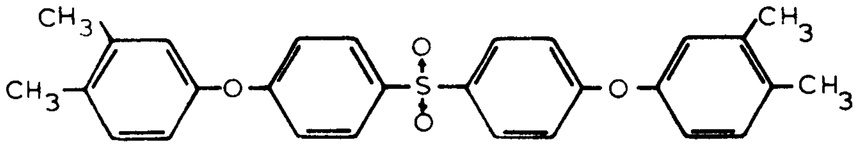
Observed Results A. 13

During the 24-hour heating period the reaction mixture decolorized. Stripping of the solvent yielded 30.8 g (53%) of colorless oil.

Characterization of Product A. 13

Thin Layer Chromatogram:	Figure A-17 (c) shows that the product has essentially no impurities.
Infrared Spectrum:	Figure A-18 shows new absorptions at 1135 cm^{-1} and 1325 cm^{-1} which are characteristic of sulfone.

A. 14 bis [p-(3,4-Dimethyl phenoxy) phenyl] Sulfone



Procedure A. 14

Transfer 8.30 g (0.058 mole) of the sodium salt of 3,4-dimethylphenol and 8.33 g (0.29 mole) of bis(p-chlorophenyl) sulfone into a 100-ml flask containing a mixture of 50 ml of dimethyl sulfoxide and 10 ml of chlorobenzene. Heat the contents of the flask to 50 °C, maintain them at that temperature and stir them by means of a magnetic stirrer for 72 hours. At the end of this period, transfer the contents to a vessel containing 400 ml of distilled water and stir the resultant mixture for one hour. Filter the mixture through a sintered glass funnel and wash the solid residue with

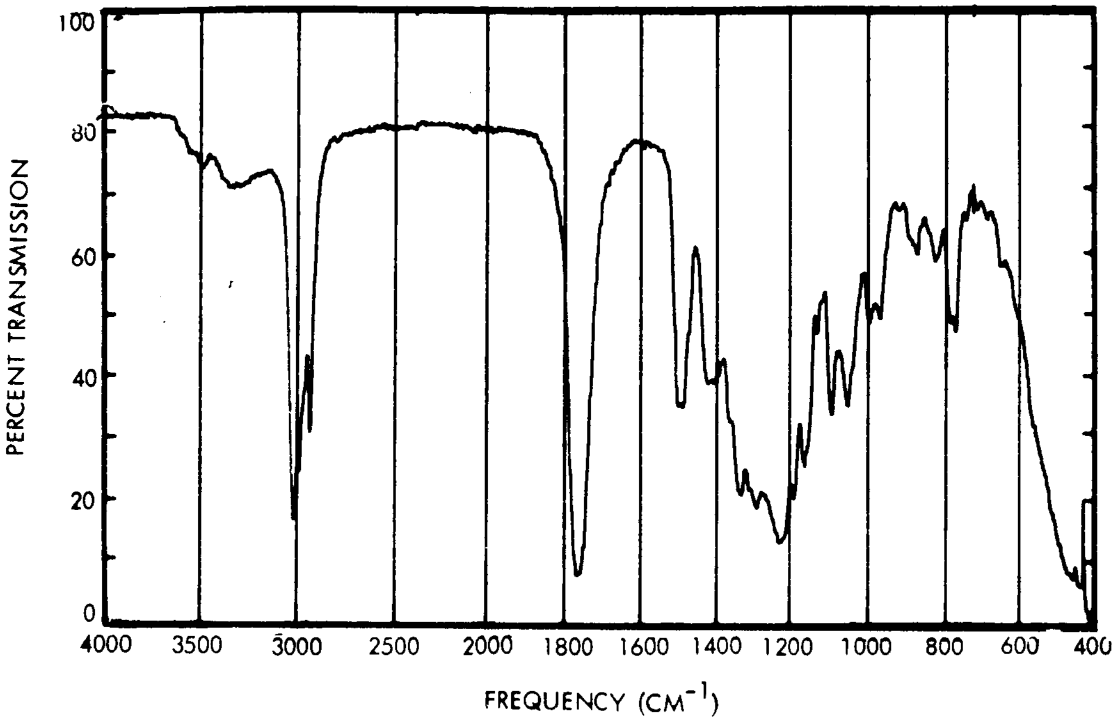


Figure A-18. Infrared Spectrum of bis(2-Chloro-4, 5-di-n-Butyl Carboxy Cyclohexyl) Sulfone

fresh distilled water. Remove the residue from the filter, slurry it in a small amount of 2-propanol and refilter the product. Recrystallize the product from 2-propanol and dry it in an oven maintained at 105 °C.

Observed Results A. 14

The reaction mixture turned very dark. An oily precipitate in the bottom of the flask was found to be water soluble (NaCl). The residue collected on the filter was brown. A white solid was obtained from the washing of the brown solid with 2-propanol which melted at 114-117 °C. The recrystallized solid melted at 118-120 °C. The yield was 5. 5 g (41%).

Characterization of Product A. 14

Thin Layer Chromatogram: Figure A-17 (d) shows that the crystallized product has an Rf value that is different than that of the starting product. The brown, impure product is a mixture of the crystalline product and the bis(chlorophenyl) sulfone starting material.

Infrared Spectrum: See Figure A-19. The absorption at 800 cm^{-1} confirms that a phenyl ether linkage was formed.

Melting Point: 118 - 120 °C.

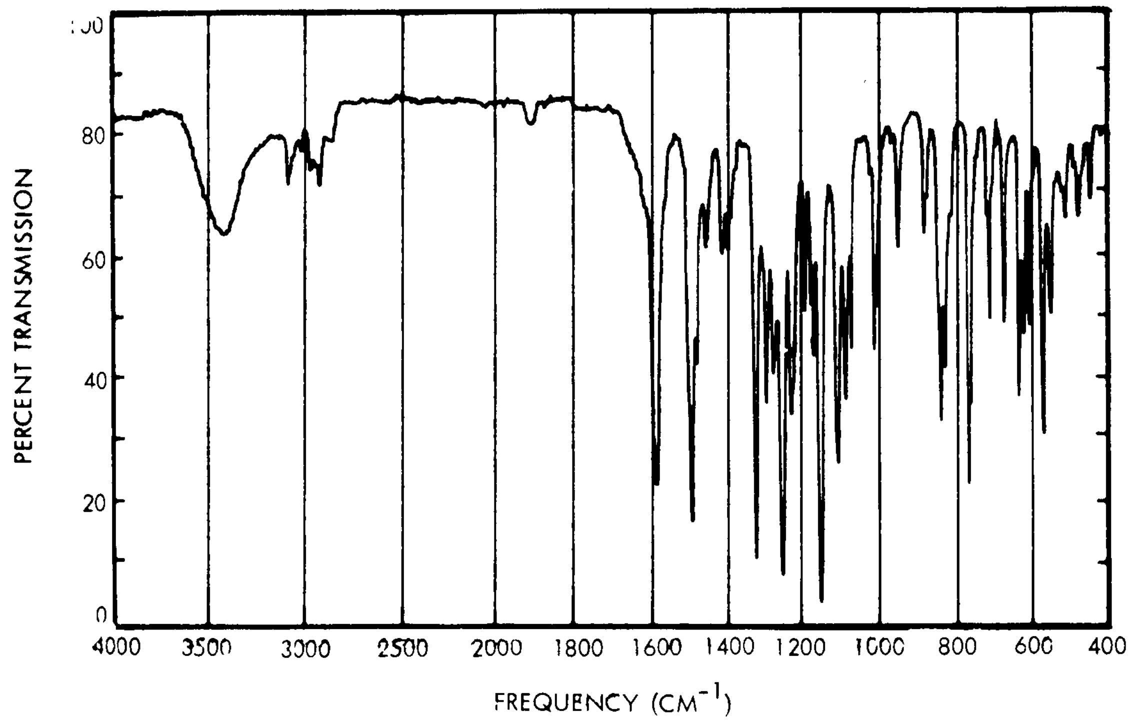


Figure A-19. Infrared Spectrum of bis(p-3,4-Dimethylphenoxy Phenyl) Sulfone

APPENDIX B

THERMOGRAMS OF CANDIDATE ABLATIVE RESINS

Thermograms of ablative resin systems recommended in Contract NAS3-4188 are given in Figures B-1 through B-4. These curves were obtained using an American Instruments Company Thermograv in an air environment at a scan rate of 3 °C/minute.

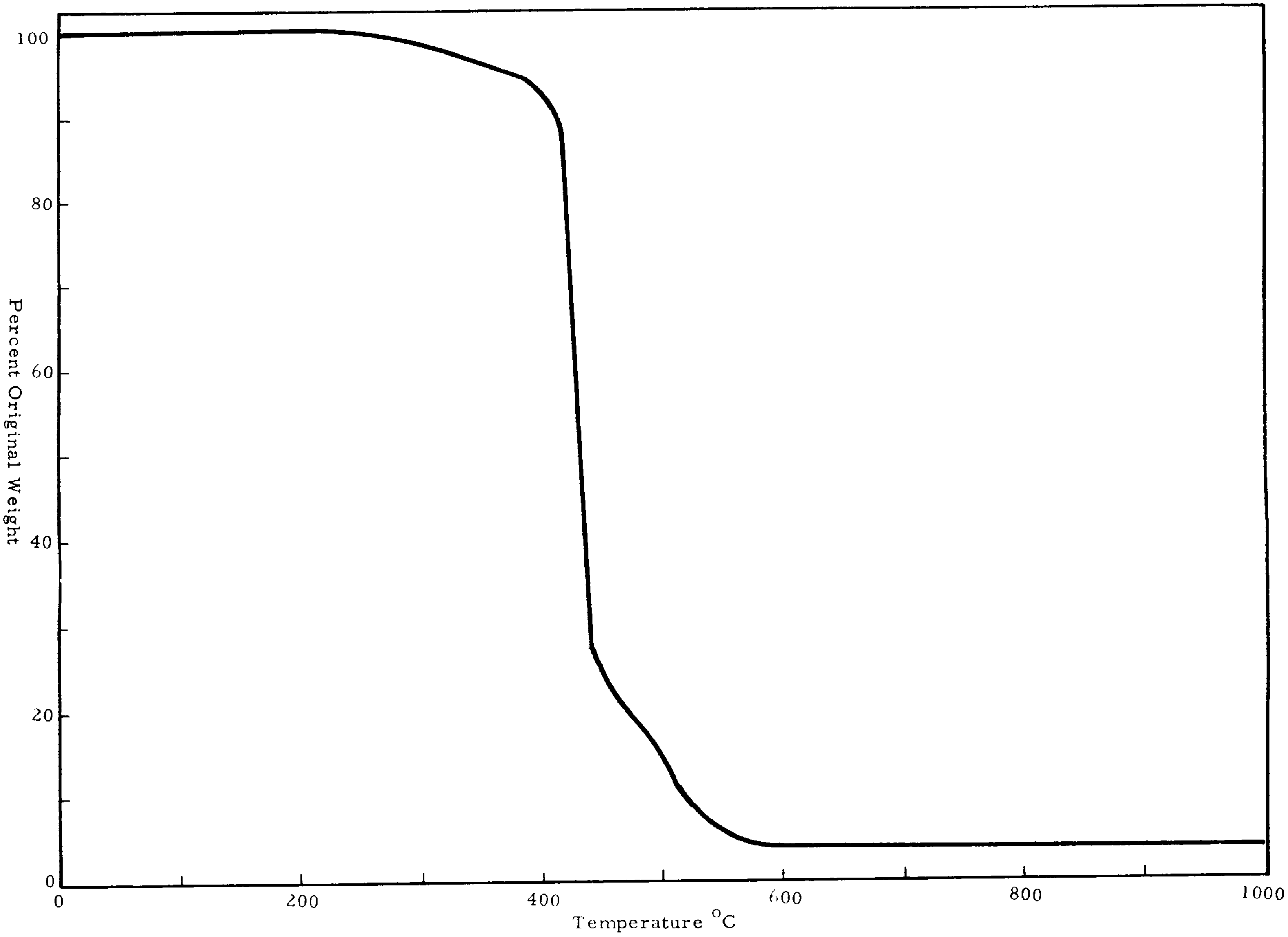


Figure B-1. Thermogram of Poly(Cyclized 1, 2-Polybutadiene) Tolyl Urethane
Environment: Air Scan Rate: 3°C/min

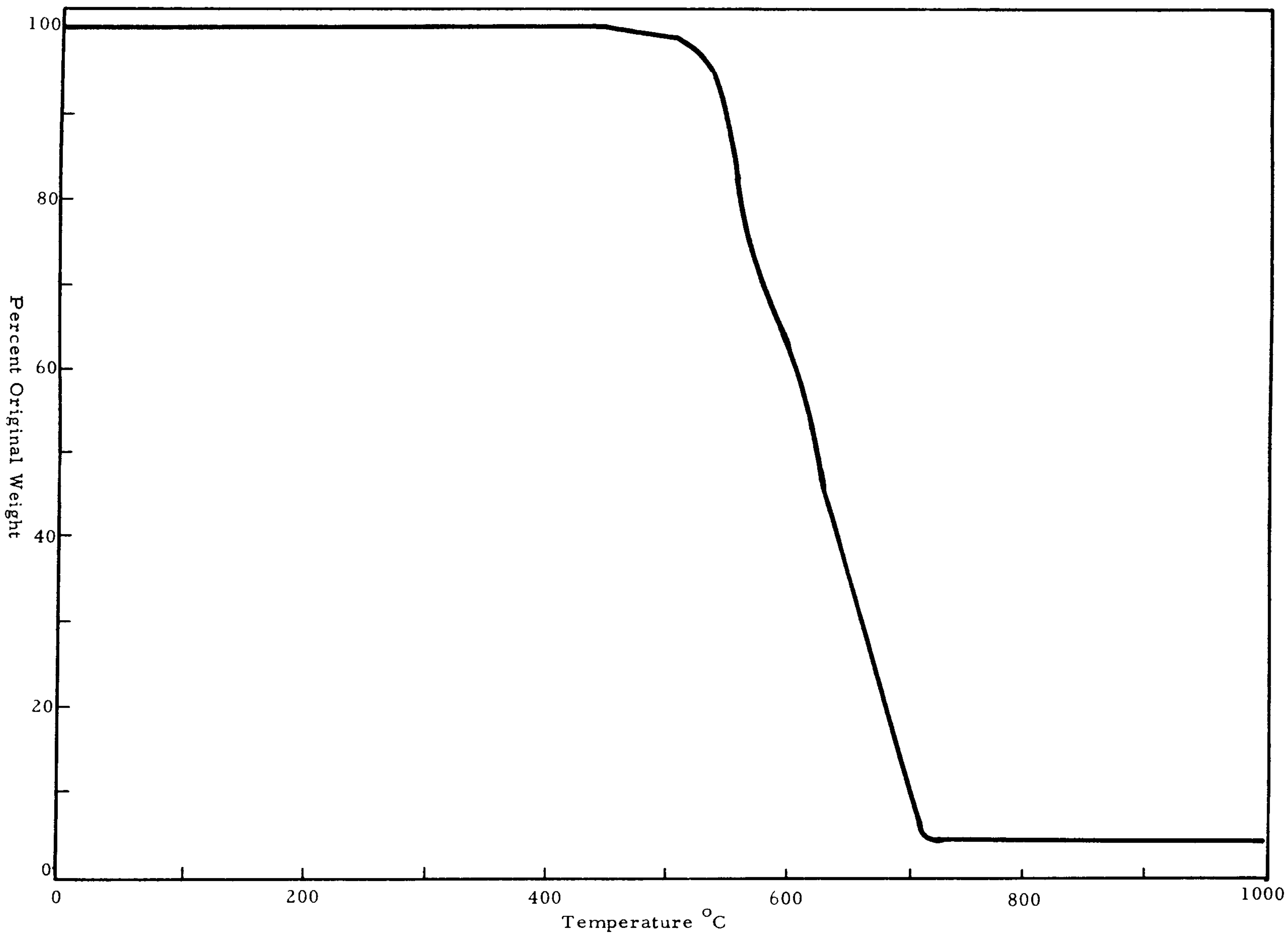


Figure B-2. Thermogram of DuPont's SP-1 (Poly pyromellitimide)
Environment: Air Scan Rate: 3°C/min

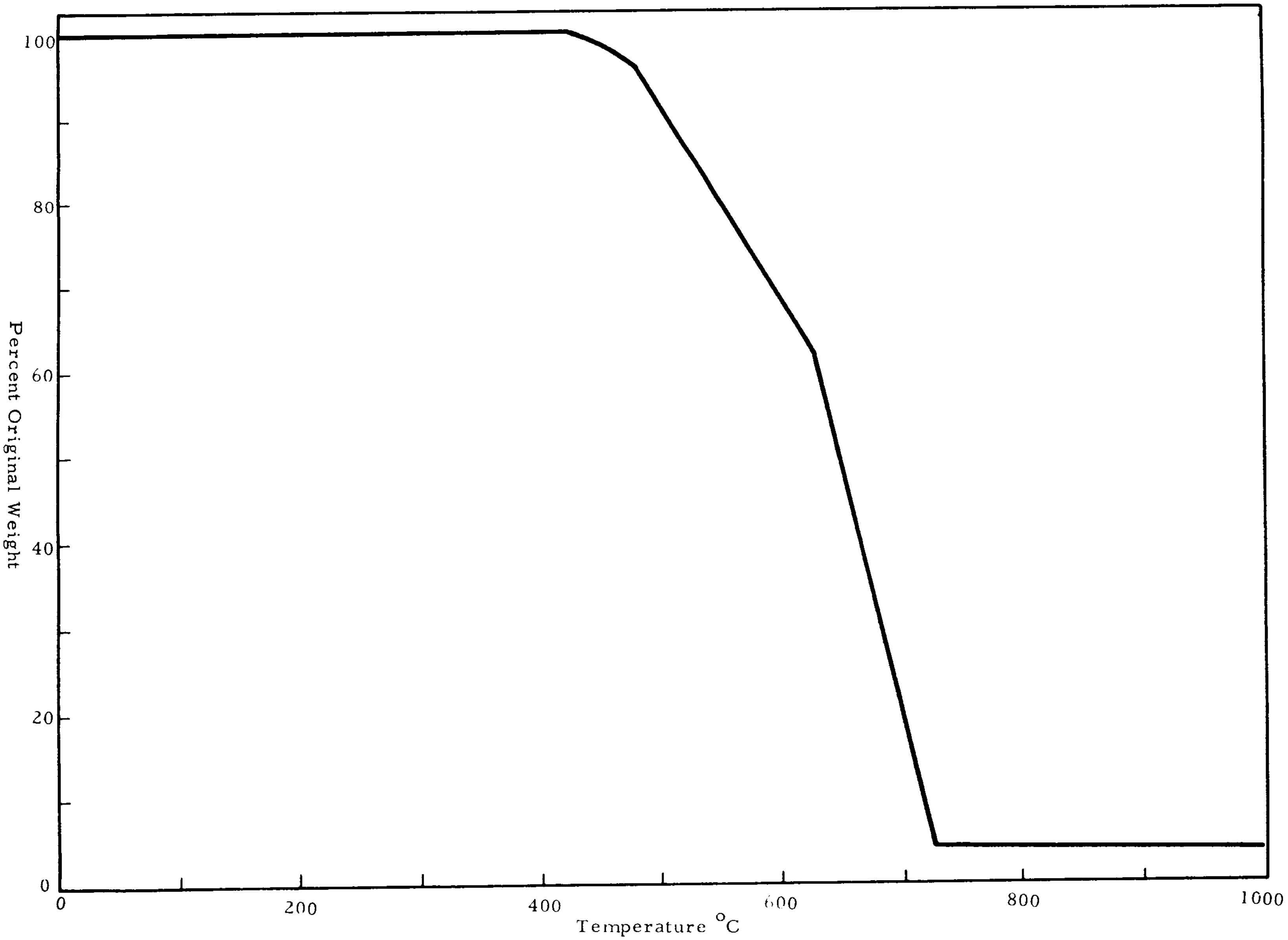


Figure B-3. Thermogram of Amoco's Polyimide-amide
Environment: Air Scan Rate: $3^{o}C/min$

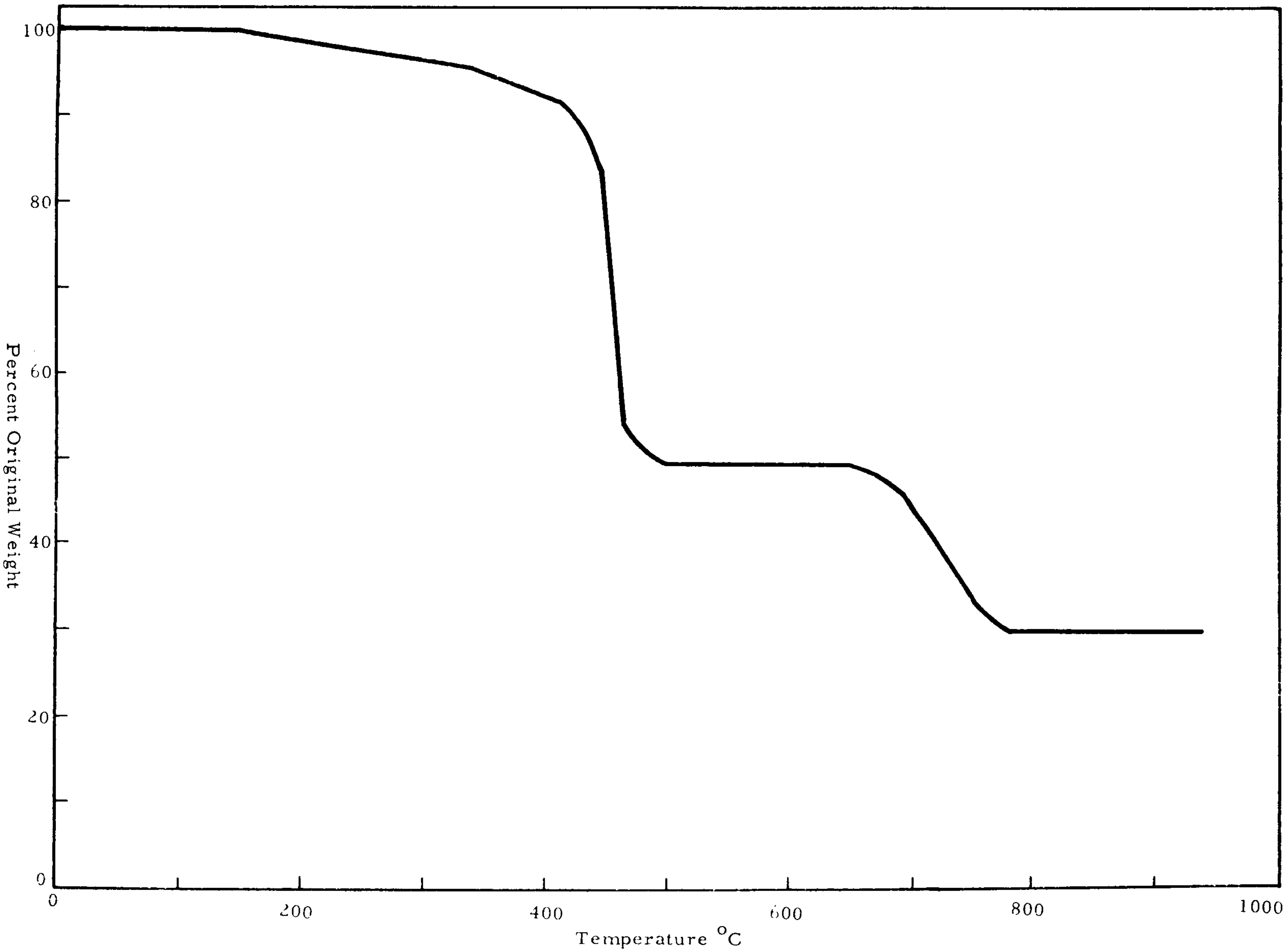


Figure B-4. Thermogram of Polycalcium Acrylate
Environment: Air Scan Rate: 3°C/min

APPENDIX C

OPERATING PROCEDURE FOR THE PROPELLANT EXHAUST ENVIRONMENT TEST APPARATUS

C.1 GENERAL DESCRIPTION

The propellant exhaust environment test (PEET) permits evaluation of the resistance of materials to exhaust species of advanced propellant combinations, such as fluorine-hydrogen, FLOX-hydrogen and FLOX-methane. This apparatus is designed to provide the chemical and thermal environment of rocket exhausts on a very small scale, e.g., the operational mass flow rate of fluorine is in the order of 0.06 g/sec (0.00013 lb/sec). The apparatus is controlled by explosion-proof, electrically operated solenoid valves during operation from outside of the Test Cell. The operating procedure presented here describes the specific steps for operation and maintenance of PEET, together with procedures for activation of the Hydrogen Fluoride Trap, passivation of hardware, preparation of FLOX mixtures and specific safety requirements for handling and use of fluorine, and is applicable for use of the small, 200-g size bottles of fluorine.

C.2 STANDARD OPERATING PROCEDURE

The operations described in this section refer to the components of the PEET apparatus shown diagramatically in Figure C-1.

C.2.1 Preliminary Operations

Examine the test cell to determine that all valves are turned off. Turn on the Coppus exhaust blower located in the hood. Turn on both nitrogen gas bottles (valve A) and adjust the reducing valves (valve B) to 50 psig. Turn on valve C_N. The lines up to solenoid valves 3, 4 and valve No. 7 are then pressurized for purging purposes.

Purge the fluorine side of the system by opening, in sequence, valves 4 and 6. Do not peg the flowmeter. After one minute, turn off,

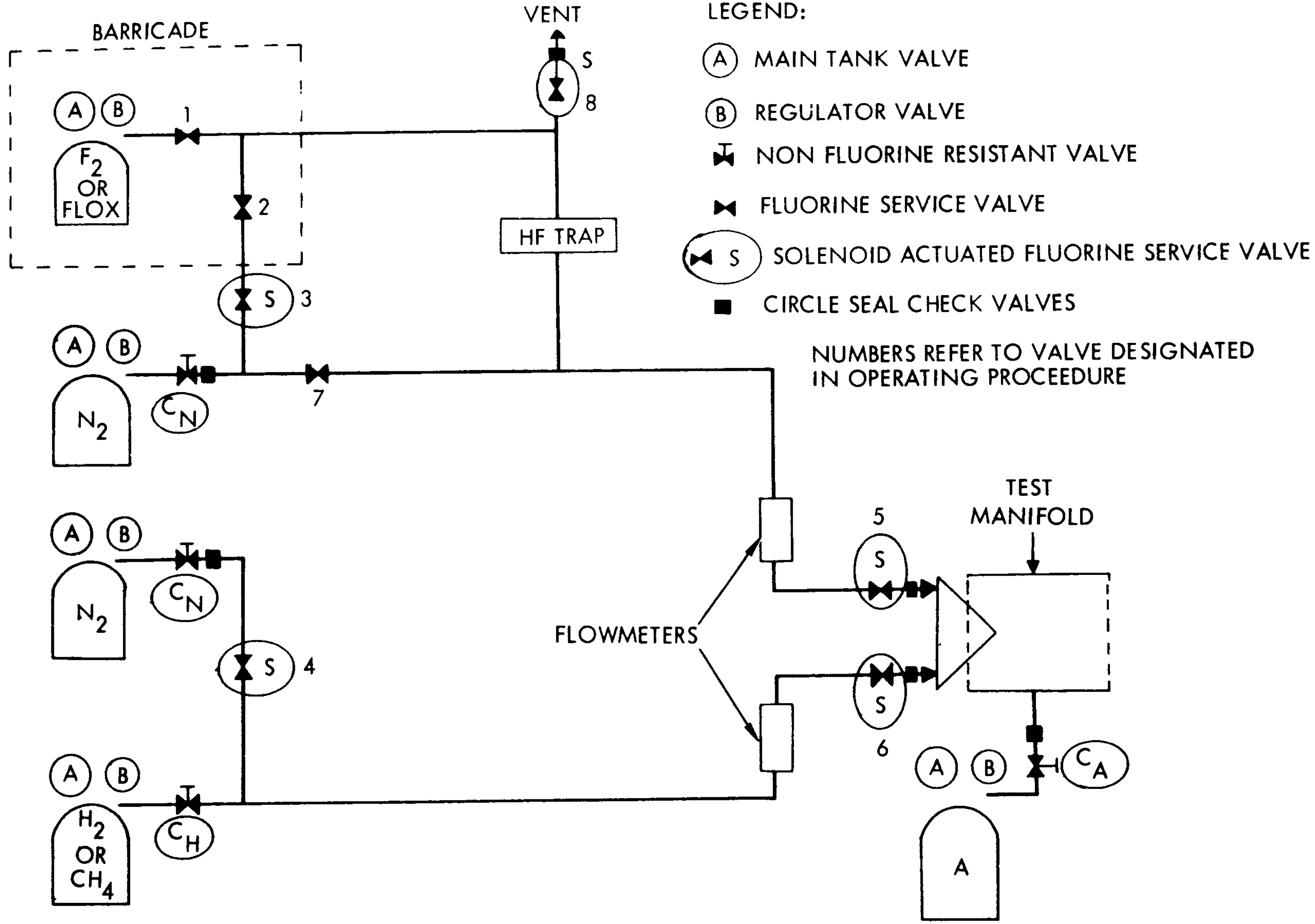


FIGURE C-1. SCHEMATIC DIAGRAM OF PROPELLANT EXHAUST ENVIRONMENTAL TEST (PEET) APPARATUS.

in sequence, valves 6 and 4. Examine fluorine barricade and regulator for irregularities (e.g., leak evidence by green fluoride salt formation). If irregularities are observed, do not proceed further with the PEET operation; report the situation to your supervisor who will initiate corrective action.

C.2.2 Calibration and Experimental Set-Up

Turn on main fluorine valve A. Determine that the system is leaktight by turning valve A off, and observing that the pressure does not change. A pressure drop of more than 20 psi indicates a leak between valves A and B. If there is a leak, stop operation and change regulator assembly on tank. If no leak is indicated, turn on valve A all the way. Turn the secondary fluorine regulation valve B to a specified pressure. Note to see if there is a pressure drop between regulator valve B and valve 1. If no pressure drop is observed, proceed to the next step. Slowly turn on the fluorine control valve 1 and determine that the fluorine pressure remains at the desired value. Turn on valve 2. Leave the cell and secure the area.

Turn on valve 5 by actuating the solenoid switch to an "on" position, and adjust the secondary fluorine regulation valve B by the remote handle to the specified flowmeter rate. Close valve 5 after the specified flowmeter rate has been obtained. Turn on hydrogen valve A, set valve B to a specified pressure, and turn on valve C_H. Turn on valve 6 by actuating the solenoid switch to an "on" position, and adjust the secondary hydrogen regulator valve B (which is located outside the Test Cell) to the specified flowmeter rate. Close valve 6 after the specified flowmeter rate has been obtained. If all operations are normal, testing may proceed.

C.2.3 Operation

Turn off valve C_H. Turn off valve 1 by remote handle. Add test specimens to test manifold. Turn on valve 1 by remote handle. Turn on valve C_H, and position operators at observation point. Turn on valve 6 by actuating the solenoid switch No. 6 to an "on" position. Specified flowrate of hydrogen will start. Turn on valve 5 by actuating solenoid switch No. 5 to an "on" position. Specified flowrate of fluorine will begin and flame from the ignition of fluorine/hydrogen will begin.

Expose the specimen for a specified duration. Turn off solenoid valve switch No. 6. Turn off solenoid valve switch No. 5. Turn off valve C_H. Turn on solenoid valve switch No. 4 and then No. 6. Purge for 2 minutes, then turn off, in sequence, valve switches No. 6 and No. 4. Turn off valve 1 by remote handle. Return to observation point and solenoid valve switch area.

Purge the fluorine side of the torch by turning on solenoid valve switch No. 3, and then switch No. 5. Purge for 4 minutes, then turn off, in sequence, switches No. 5 and No. 3. Turn off the fluorine at valve A. Go into the test cell and remove the sample assembly. "WARNING": This may be heavily coated with hydrogen fluoride and acidic fluoride products. Do not handle samples with bare hands until a thorough water wash and checks with pHydrone paper indicate that the hydrogen fluoride coating has been removed.

At the end of the test sequence, leave the fluorine valve A closed, open valve 1, open valve 5, wait until valve B reads zero, close valve B, close valve 1, and purge by opening valve 3 for 2 minutes. The minute amount of fluorine left is no hazard. Turn off valve 2 and valve 3 and secure the area.

C. 2. 4 Periodic Maintenance

Procedures for periodic maintenance of the PEET apparatus are given below.

- Decontamination

  Flush down all equipment with water to remove hydrogen fluoride film between each series of tests. Check with pHydrone indicator paper to determine that the hydrogen fluoride is removed.

- **Leak Test**

Pressure check all connections for leaks with 50 psig nitrogen pressure every month when system is not in use.

- **Hydrogen Fluoride Trap Activation**

Connect the heating coil (built in the trap) to a variable transformer and adjust the power to heat the system to 250-300 °C while purging the system with dry nitrogen. This is done by opening valve 7 and valve 8. Test the effluent gas for completion of the activation cycle periodically with blue litmus paper. When the paper no longer turns red, cool the absorber to room temperature and put into use. The activated trap is suitable for processing 18 to 24 pounds of fluorine before reactivation is necessary.

- **Passivation of System Hardware**

The system hardware will be passivated prior to each series of specimen testing by the following procedure: Place a swatch of cotton at the exit of the flow system. Turn on the main fluorine valve A. Carefully turn on fluorine regulator valve B with remote handle and slowly displace the inert gas in the system with fluorine. Continue the flow of fluorine until the cotton ignites. Close the system at solenoid valve 5. Apply fluorine working pressure to the system (e.g., 20 psig) for a period of 10 minutes. Close valve A. Vent the system by opening valve 8 and purge with nitrogen.

C.2.5 Emergency Procedures

The following procedures are given for handling emergencies such as leaking components, clogging and fire.

- Leaking Main Fluorine Valve

  Do not attempt to tighten the valve or packing unit. Open all valves in the system. Evacuate the area of all personnel before venting the fluorine. With a long handle wrench, cautiously open the main fluorine valve A and vent the entire contents of the tank (maximum quantity of 5 cu. ft.) through the reducing valve B, valve 1 and valve 8.

- Leaking Fluorine Regulator

  Close the main fluorine valve A. Relieve the pressure in the system through valves 1 and 8. Replace the fluorine regulator.

- Leaking Fluorine Valves

  Turn off the main fluorine valve A. Examine each valve and connection at 50 psig nitrogen. Replace the defective part or re-tighten the connection until no leaks are evident.

- Clogging of the System

  If during the start-up procedure, the fluorine side of the system is found to be clogged, relieve the pressure in the system by closing valve A and venting through valve 8. Purge the system with nitrogen by opening valves 3 and 7 for 2 minutes. Disassemble the apparatus and locate the clogged area and replace that section of the system.

- Fire

If a fire develops, immediately purge the lines by turning on solenoid valves 3 and 4. Turn off main hydrogen tank valve A. If the flame continues, activate the deluge switch and leave the area. Do not attempt to turn the main fluorine valve off under any circumstances. After the fire has expired, immediately flood the area with water in order to dilute any hydrogen fluoride produced.

C. 3 PREPARATION OF FLOX OXIDIZER MIXTURES

The operations described in this section refer to components of the mixing apparatus shown diagramatically in Figure C-2.

Check to insure that all valves are closed and then turn on the exhaust vent, hood, and vacuum pump. Turn on the nitrogen gas bottle (valve A) and adjust the reducing valve (valve B) to 50 psig. Turn on valve 2. The lines up to valves 1, 3, 4, 5 and 8 are then pressurized for purging purposes.

Purge the entire apparatus by opening valves 5, 7 and 8 for 2 minutes. After 2 minutes, turn off, in sequence, valves 8 and 7. Open valve 4 and pressurize the 3-liter cylinder to 50 psig. Close valve 2 and open valve 7 and bleed the system pressure to zero. Close valve 7. Add liquid nitrogen to the two cold traps and then open valve 6 and evacuate the system up to valves 1, 2 and 3. After the system has been evacuated, close valves 5 and 6. The apparatus is now ready for mixing of the two gases.

Open valve 4 with remote handle and then open valve 3 and pressurize the 3-liter cylinder to the desired oxygen pressure. After this pressure has been obtained, close valves 3 and 4. Open valve 8 and bleed the lines containing excess oxygen gas to zero pressure. Open valve 2 and purge the line for 2 minutes. Close valve 2. Close valve 8.

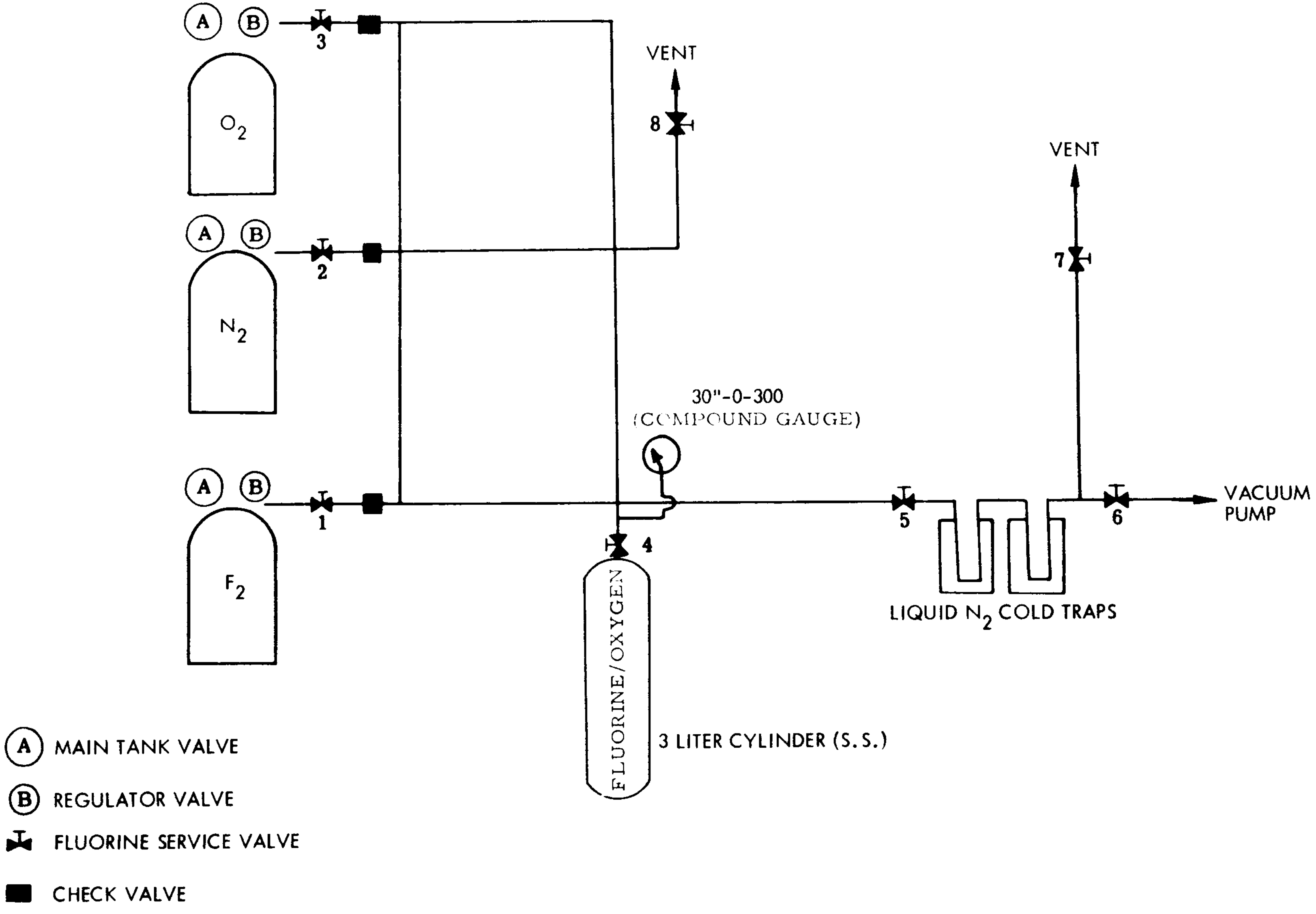


FIGURE C-2. FLOX (FLUORINE/OXYGEN) MIXING APPARATUS

Open valves 5 and 6 to remove residual nitrogen gas from the lines. Notice pressure reading on compound gauge. When the lines reach a vacuum of 30 inches, close valves 5 and 6.

Open valve 1 to pressurize the lines. Open valve 4 with remote handle and pressurize the 3-liter cylinder (containing oxygen gas) to the desired total pressure with fluorine gas. When this pressure has been obtained, close valves 4 and 1. Open valve 8 to vent excess fluorine gas from lines. Open valve 2 and purge the lines for 2 minutes. Close valve 2. Close valve 8, and open valves 5 and 6 to remove residual nitrogen gas from lines. When this last step has been completed, the mixing operation has been completed and the fluorine/oxygen (FLOX) mixture is ready to be used on the PEET apparatus. Let the mixture stand for 30 minutes to allow the two gases to mix uniformly.

Secure the mixing apparatus by removing liquid nitrogen cold traps, and by letting the traps warm up to room temperature. Open valves 2 and 5 and pressurize the mixing line up to 10 psig. Open valve 7 to purge the cold traps with nitrogen gas while the trapped fluorine gas and oxygen gas warm up to room temperature and vaporize through the vent. Close valve 7 only when the cold traps have reached room temperature and all of the fluorine and oxygen gas has vaporized. Close valve 2. Open valves 5 and 6 to remove residual nitrogen gas from the lines. The apparatus is now secure.

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