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## LINER TECHNOLOGY

### Liner Development Methodology Manual

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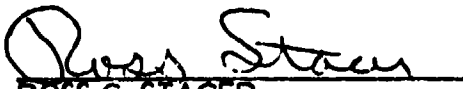
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><br>This manual provides a systematic methodology for formulating, evaluating,<br>and developing liners to fit various propellant/insulation and solid<br>rocket motor environment requirements. |                       |                                                                                      |

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## LINER METHODOLOGY MANUAL

### 1.0 INTRODUCTION

This manual has been designed to provide a sound, systematic methodology for developing and characterizing structurally-reliable, age-stable propellant/liner/insulation bond systems for solid rocket motors. There has in the past been a general lack of guidelines for the development and tailoring of liners for specific propellant insulation applications. Approaches to liner development have generally been empirical in nature and frequently the tailoring of an existing liner to a new application has been the route dictated by time constraints and the lack of definitive development techniques.

To overcome these shortcomings a systematic procedure is presented which identifies the critical requirements imposed in each bonding system by the selected propellant and insulation, and by the motor environment processing and design constraints. This is followed by a procedure for selecting the approaches for meeting these identified limits which permits a systematic and rapid development of the appropriate liner. This methodology streamlines the development operation by providing for the selection of only those materials and approaches which are relevant to the particular liner application, thereby forcing the formulator to take a systematic approach to liner development. Included in the manual are procedures for the screening and characterization tests necessary for development of the liner and verification of its adequacy.

It is recognized that, in general, liner development is initiated prior to finalization of the propellant formulation. Minor, late changes in motor design, ballistic requirements and processing may alter the composition of the propellant sufficiently to affect its bondability and bond age life. Thus, the program must provide for some liner tailoring late in the development program. A flow diagram showing the various system interactions in the systematic evolution of a liner is presented in Figure 1.

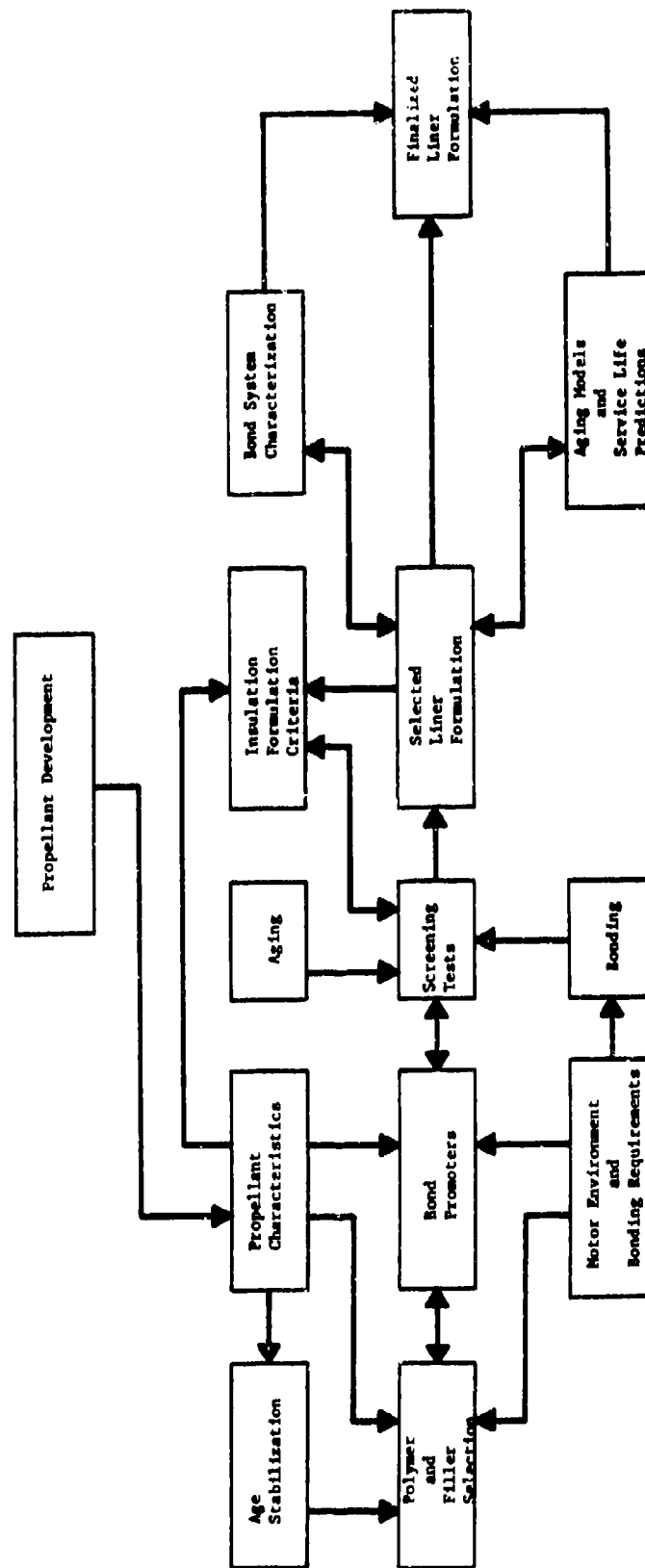


Figure 1. Liner Bond System Methodology Flow Diagram

This manual requires periodic updating as new and more definitive testing techniques become available, as new polymer systems with liner applications are developed and as advances in solid rocketry create changes in propellants, insulators and operational environments.

## 2.0 ORGANIZATION

The organization of the manual is directed toward simplifying and systematizing the selection of liner ingredients and formulation approaches. The desired result should be a more rapid development of a liner system that more than adequately meets all the structural, processing and aging requirements imposed by the particular rocket motor application.

To achieve this simplification the formulator turns first to the Liner Formulation Guide (Section 3.0) and from this guide selects the liner ingredients and the approaches for most efficiently meeting the bonding, processing and aging requirements. Test methods recommended for determining structural data requirements which are not common to the propellant industry have been included in Section 7.

## 3.0 LINER FORMULATION GUIDE

In order to simplify the task of establishing the liner development criteria and for identifying the most efficient approach, the table shown in Figure 2 was prepared. The first column to the left presents the various possible constraints introduced by the interaction of propellant, insulation, motor environment, motor design and processing considerations. The critical considerations associated with these constraints are listed in the third column. The fourth column lists the possible formulation approaches for developing a good bonding system with adequate age life as well as the special techniques which may be used to overcome some of the problems introduced by some of the limiting constraints.

| <u>CONSTRAINTS</u>                        | <u>APPLICABLE APPROACHES</u>                                                                                                                                          | <u>CRITICAL FACTORS</u>                                                           |
|-------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| A. Propellant Formulation Impact          |                                                                                                                                                                       |                                                                                   |
| 1. Propellant Cure and Excitose System    | 4.1, 4.2                                                                                                                                                              | Compatibility.                                                                    |
| 2. Propellant Migrants                    | 4.1.2, 4.1.3, 4.2<br>4.1.2, 4.1.4 or 4.1.5, 4.2, 4.3.2<br>4.1.2, 4.1.5, 4.1.6, 4.2, 4.3.2<br>4.1.2, 4.1.3, 4.1.4 or 4.1.5, 4.3.2<br>4.1.2, 4.1.4 or 4.1.5, 4.2, 4.3.2 | Effect of migrants on bond and on insulation and propellant ballistic properties. |
| B. Insulation Composition Impact          |                                                                                                                                                                       |                                                                                   |
| 1. Structural effects on bond             | 4.1, 4.2                                                                                                                                                              | Bond compatibility.                                                               |
| 2. Migrants                               | 4.1.2, 4.1.4 or 4.1.5, 4.2, 4.3.2<br>4.1.2, 4.1.4, 4.2, 4.3.2<br>4.1.2, 4.2, 4.3.1                                                                                    | Influence of migrants on bond, and propellant and liner age life.                 |
| C. Water Environment Impact               |                                                                                                                                                                       |                                                                                   |
| 1. Humidity Limits                        | 4.1.2, 4.2<br>4.1.2, 4.2, 4.3.1<br>4.4.1, 4.4.2                                                                                                                       | Influence on propellant/liner/insulation bond and system age life.                |
| 2. Temperature                            | 4.1.2, 4.2<br>4.1.2, 4.1.5, 4.1.7, 4.1.8, 4.2<br>4.1.1, 4.1.2, 4.1.3, 4.2, 4.4<br>4.1.1, 4.1.2, 4.1.3, 4.1.5, 4.2, 4.4                                                | Effect on bond integrity.                                                         |
| D. Design Constraints                     |                                                                                                                                                                       |                                                                                   |
| 1. High rate bond requirements (ignition) | 4.2.1, 4.2.2, 4.2.3                                                                                                                                                   | Effect on bond integrity.                                                         |
| 2. Low rate bond requirements (storage)   | 4.2.1, 4.2.2, 4.2.3                                                                                                                                                   |                                                                                   |
| E. Processing Constraints                 |                                                                                                                                                                       |                                                                                   |
| 1. Application Method                     |                                                                                                                                                                       |                                                                                   |
| (a) Trowel                                | 4.5.1, 4.5.2, 4.5.3                                                                                                                                                   | Viscosity, thixotropy, pot life.                                                  |
| (b) Spray                                 | 4.3.1, 4.5.2                                                                                                                                                          |                                                                                   |
| (c) Electrostatic spray                   | 4.5.1                                                                                                                                                                 |                                                                                   |
| (d) Sling                                 | 4.5.1, 4.5.2, 4.5.3                                                                                                                                                   |                                                                                   |
| (e) Spin                                  | 4.5.1, 4.5.2, 4.5.3                                                                                                                                                   |                                                                                   |
| (f) Spin/Trowel                           | 4.5.1, 4.5.2, 4.5.3                                                                                                                                                   |                                                                                   |
| (g) Powder Substant                       | 4.5.1, 4.5.2                                                                                                                                                          |                                                                                   |

Figure 2. Liner Formulation Guide

To use the table to best systematically develop a liner to fit a particular propellant/insulation/motor system, Column 1 is reviewed and the pertinent constraints checked. These are based on the particular propellant and insulation being used and on the required motor thermal and humidity limits. The design constraints should also be noted and the desired processing technique and associated minimum pot life recorded. In Column 2, opposite each of the particular items checked, are given the paragraph numbers associated with the various development approaches and techniques listed in Column 4. Details of these approach methods are presented in Section 4.0, and two hypothetical examples using this procedure are given in Section 9.0. A flow diagram describing the formulation selection steps is presented in Figure 3.

#### 4.0 FORMULATION APPROACHES

The various techniques for formulating a liner with specific characteristics suitable for use in a particular motor system are presented in this section. This technology is gathered under general classifications such as Polymer Structures or Bond Promotion, etc. The specific approach to a particular set of conditions is identified by the related subheading.

Each of these techniques is discussed in some detail and references to source material listed whenever available.

##### 4.1 POLYMER STRUCTURES

A wide variety of curative systems and prepolymers are available to the liner formulator. These systems vary significantly in thermal stability, oxidative and hydrolytic stability, and high temperature properties and resistance to chemical attack. Specific motor applications require differing combinations of these properties and an optimum liner for a particular application is best prepared from the polymer/curative combination that is best suited

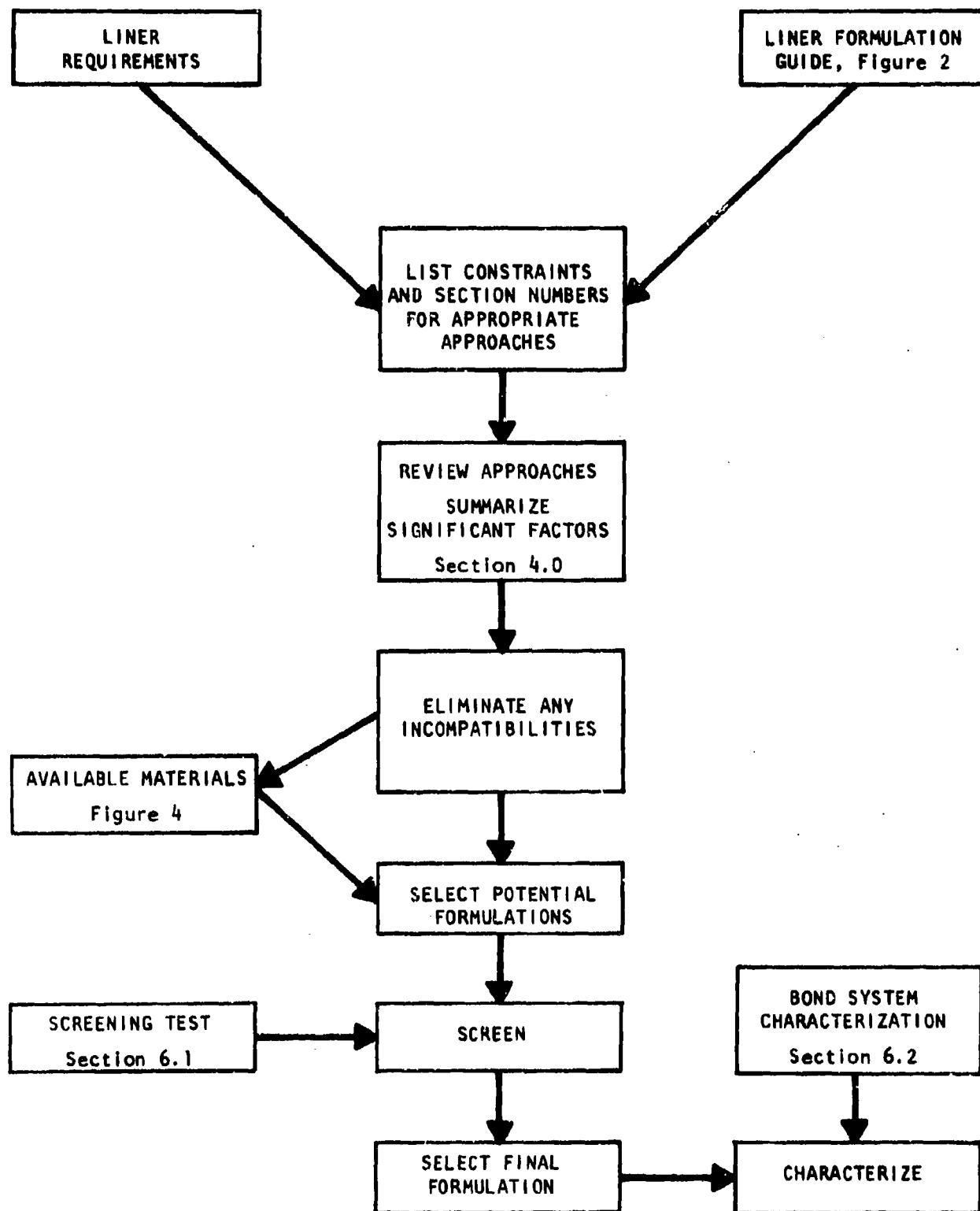


Figure 3. Liner Candidate Selection Logic Flow Diagram

for meeting the particular constraints imposed. A listing of polymer and cure systems available to the formulator with some of their characteristics is given in Figure 4.

#### 4.1.1 Thermally-Stable Polymers

The most likely site for thermal degradative cleavage of polymer networks is that of the cure linkage. The thermal stability in decreasing order for cure linkages which find employment in liners are listed as follows:

- imide/epoxy
- acid/imide/epoxy
- acid/epoxy
- alcohol/isocyanate
- acid/aziridine

Although the polymer backbone is usually not the site for thermal degradation, it may be generally stated that hydrocarbon structures are more thermally-stable than polyethers. Of the hydrocarbon types the unsaturated polybutadienes (CTPB and HTPB) are slightly more thermally-stable than the saturated chains (saturated HTPB or saturated CTPB), however, if oxidative attack at high temperature is a consideration the saturated hydrocarbon backbone should be considered. Nitrile modification of hydrocarbon chains (PBAN or BNO) tends to reinforce the polymer network because of increased interchain association.

#### 4.1.2 Structurally-Compatible Polymers

It is important from a bonding consideration that the cured liner have a low enough modulus so that when propellant is cast against it, and it undergoes cure shrinkage, the stresses are not concentrated at the

# Polymer and Cure Systems for Liner Formulation

| <u>Carboxyl-Terminated Polymers</u> | <u>Pertinent Polymer Characteristics</u>                              | <u>Carboxyl-Terminated Polymer Cure Systems</u>                                                    | <u>Pertinent Cure Characteristics</u>                                                                      |
|-------------------------------------|-----------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| CTPB                                | Low polarity, unsaturated, little branching.                          | Aziridines (TEAT, TMAT, MAPO, BITA, etc); no catalyst required.                                    | Low hydrolytic stability                                                                                   |
| PBAN                                | Medium polarity, high stability, little branching.                    | Epoxies (Epon-828, EPL-4221, 9500, 0510, MY-720, etc); catalyst required (FeAA, FeOctoate, AWC-2). | Aromatic types have high hydrolytic stability.<br>Aliphatic types = ERL-4221, butanediol diglycidyl ether. |
| Dimer Acid                          | Low polarity, highly branched, chemically stable. Oxidatively stable. |                                                                                                    |                                                                                                            |
| Trimer Acid                         | Low polarity, highly branched, chemically stable. Oxidatively stable. |                                                                                                    |                                                                                                            |

Figure 4. Polymer and Cure Systems  
Sheet 1 of 3

# Polymers and Cure Systems for Liner Formulation

| <u>Hydroxy-Terminated<br/>Polymers</u> | <u>Pertinent Polymer<br/>Characteristics</u>                                  | <u>Hydroxy-Terminated<br/>Polymer Cure Systems</u>                                                                                | <u>Pertinent<br/>Cure Characteristics</u>                 |
|----------------------------------------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|
| HFPB - Unsaturated                     | Low polarity, little branching, thermally stable, subject to oxidative attack | Isocyanates (HDI, TDI, DDI, IPDI, etc)<br>No catalyst required if primary hydroxyl, otherwise use FeAA, triphenyl bismuth or T-12 | Aromatic types.<br>Aliphatic types -<br>HDI, DDI and IPDI |
| - Saturated                            | Low polarity, little branching, thermally stable, oxidatively stable          |                                                                                                                                   | DDI and IPDI branched                                     |
| Polyethylene Glycol                    | High polarity, linear, oxidatively and thermally stable                       |                                                                                                                                   | Binder has high hydrolytic stability                      |
| Polypropylene Glycol                   | High polarity, short branches, oxidatively and thermally stable               |                                                                                                                                   |                                                           |
| Polyisobutylene Glycol                 | High polarity, branched, oxidatively and thermally stable                     |                                                                                                                                   |                                                           |
| CTRO                                   | Low polarity, highly branched, oxidatively and thermally stable               |                                                                                                                                   |                                                           |

Figure 4. Polymer and Cure Systems  
Sheet 2 of 3

# Polymers and Cure Systems for Liner Formulation

| <u>Imide-Terminated Polymer</u>                                                       | <u>Pertinent Polymer Characteristics</u>                                                                                                                       | <u>Imide-Terminated Polymer Cure Systems</u>     | <u>Pertinent Cure Characteristics</u>               |
|---------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------|
| (No commercially available materials at this time)                                    | Low polarity, high thermal and oxidative stability                                                                                                             | Epoxies, cure catalyst required (AMC-2)          | See pertinent characteristics, carboxy cure systems |
| <u>Anhydride-Terminated Polymers</u>                                                  | <u>Pertinent Polymer Characteristics</u>                                                                                                                       | <u>Anhydride-Terminated Polymer Cure Systems</u> | <u>Pertinent Cure Characteristics</u>               |
| <u>Linear:</u>                                                                        |                                                                                                                                                                |                                                  |                                                     |
| Polyazeleic Anhydride                                                                 | Low polarity, linear, oxidatively and thermally stable                                                                                                         | Epoxies, cure catalyst required (ATC-3)          | See pertinent characteristics, carboxy cure systems |
| Polysebacic Anhydride                                                                 | Low polarity, linear, oxidatively and thermally stable                                                                                                         |                                                  |                                                     |
| <u>Cyclic</u>                                                                         |                                                                                                                                                                |                                                  |                                                     |
| MVA, hexahydro and tetrahydro phthalic anhydrides, dodecenyl succinic anhydrides, etc | MVA and phthalic anhydrides cyclic backbone, poor low temperature properties. In general, structures listed are low polarity, stable thermally and oxidatively |                                                  |                                                     |

Figure 4. Polymer and Cure Systems  
Sheet 3 of 3

interface. In some cases where migrants are present this must be achieved while still maintaining a low permeation profile. The use of highly branched polymers or polymers with pendant side chains of varying bulk or size provide an answer to those conflicting requirements. The branching may arise from the use of a branched backbone polymer or the use of a branched curing agent. As a backbone system, alkylsubstituted diacids such as alkenylsuccinic acids or anhydrides are available. As branched curing agents, DDI and GTRO are among the candidates.

#### 4.1.3 Oxidatively-Stable System

Propellant hardening, particularly at the bore surface, is frequently age life limiting. This usually is the result of the oxidation of unsaturated polymer backbone structures. Because of its location away from the surface, severe oxidative attack on the liner system is not generally a problem. However, if the motor is to be exposed to extreme high temperatures such as for heat sterilization for space missions, or some unusual aerodynamic heating conditions where the liner system sees periodic high temperatures, oxidative attack from dissolved oxygen should be guarded against. From a structural standpoint both the saturated hydrocarbons and the polyethers have inherent oxidative resistance. For all systems, even for normal motor storage, the use of antioxidants is a necessity (see Section 4.4.1).

#### 4.1.4 High Polarity Polymers

High polarity polymers can be utilized in liner formulations to (1) act as a barrier to nonpolar migrating species by providing low-solubility and (2) to increase the bonding to a polar propellant by increasing the associative or Van der Waals type interaction at the interface. Polyether and polybutadiene acrylonitrile polymer backbones are materials of this type. For low temperature applications, only branched polyethers are suitable because of the tendency for these highly polar materials to form highly associated (crystalline) areas.

#### 4.1.5 Low Polarity Polymers

Low polarity polymers are final applications in liner formulations to provide (1) barriers which reduce the migration of polar migrants, and (2) low and high temperature and thermal cycling capabilities. Typical low polarity polymers are carboxyl- or hydroxyl-terminated hydrocarbon systems cured with isocyanates or epoxides. The use of imide epoxy-cured systems can be used to provide increased higher temperature capability.

#### 4.1.6 Chemically Stable Polymers

Certain aging processes such as hydrolysis which can seriously limit the life of the liner bond can be avoided by the judicious selection of hydrolytically resistant cure systems and fillers which do not catalyze hydrolysis. Moisture migration from the atmosphere through boots to the insulation/liner/propellant bond is always a potential problem during environmentally uncontrolled storage of rocket motors. Aziridine cure systems are particularly susceptible and the hydrolysis of the B-amino ester linkages is catalyzed by basic systems. The presence of basic fillers such as potassium titanate, used to control viscosity of the liner during processing, should be avoided. Basic fillers can also catalyze the hydrolysis of urethane and ester linkages. Nitric acid generated by the reaction of moisture with the decomposition products of energetic plasticizers can also serve as a catalyst for hydrolytic degradation. The imide linkage and the ester linkages produced by the epoxy cure are the least subject to hydrolytic attack.

#### 4.1.7 Branched Chain Systems

Polymers containing branched structures provide bond enhancement and improved low temperature capability. Techniques for increasing the amount of branched structure include the use of cure systems containing

branched substituents such as trimer acid in CTPB/epoxide polymer networks, or the modification of the polymer backbone through incorporation of such structures as, for example, alkenylsuccinic acid.

#### 4.1.8 Unsaturated Chains

(Carboxyl- or hydroxyl-terminated polybutadienes cured with any of the appropriate curing agents provide polymer networks having good low temperature properties.

### 4.2 BOND PROMOTION

Three types of bonds are possible between insulation, liner and propellant. These are (1) associative-type bonds resulting from Van der Waals forces, (2) chain entanglements across the bond interface and (3) chemical bonds that bridge the interface. From both a bond strength and age life consideration the latter two are superior with chemical bonds being the most desirable. The various techniques for enhancing each of these bond contributions are presented in this subsection.

#### 4.2.1 Branched Chains

Significant enhancement of the bond strength between insulation and liner, and liner and propellant, can be realized through the use of liner polymer systems containing multiple chain branches<sup>(1)</sup>. The pendant structures (branches) occurring at the interface may then become entangled with the branches from the neighboring polymer network. Branched structures may be provided as a constituent of the backbone polymer by the introduction of difunctional branched chains or may be introduced by the use of curing agents having branched structures.

(1) Liner Technology Final Report, Volume II - Liner Development, Characterization and Aging, Report AFRPL-TR-81-98.

#### 4.2.2 Functional or Reactive Sites

A very effective technique for improving bondability, particularly between the liner and propellant, is to employ a liner using a polymer matrix which, after cure, contains residual reactive sites. These may be the result of a nonstoichiometric combination of the reactive species used in preparing the liner or may be secondary sites which react by a different cure mechanism. In either case, the particular reactive site species should be selected that will react with functional constituents in the propellant. For example, a CTB/epoxy-cured propellant will contain hydroxyl groups formed by the cure reaction. Excess isocyanate groups in the liner can react with these sites to form strong urethane bridges.

#### 4.2.3 Low Contact Angle with Liquid Propellant

In order to establish a good bond across any interface it is essential that close contact between the surfaces is achieved. The introduction of wetting agents in the propellant and liner to promote low contact angles is a preferred method for ensuring this intimacy of contact. The best type of wetting agent is a liner curing or bonding agent which also lowers the surface tension. These are generally highly polar functional structures that can react with the polymer network to give pendant groups with high wetting capability. Among the structures providing these characteristics are aziridine curing agents and filler bonding agents.

#### 4.3 BARRIER TECHNIQUES

In most rocket motors, unless a positive seal is provided against the atmosphere, the migration of moisture to bond interfaces from booted areas can shorten the life of the bond. This bond strength loss results from the mechanical changes due to swelling; the destruction of interfacial associative

bonds and the hydrolysis of cure linkages. The migration of propellant plasticizers, even the nonenergetic types, can cause swelling of the liner and modification of the insulation mechanical properties. Migrating energetic plasticizers can change the ballistic properties of the insulation and deplete the plasticizer concentration at the propellant/liner interface. Energetic plasticizers which migrate into the liner may decompose to produce reactive species capable of attacking the bond structure. Liquid or soluble cure and burning rate catalysts can migrate to change the ballistic and mechanical properties of neighboring systems.

In those instances where these migrating species are components of either the propellant or insulation, it is desirable to use a liner which provides some barrier to migration. Because the difference in molecular size is such a factor in stopping migration, the barrier techniques for moisture and for liquid migrants have been treated separately.

#### 4.3.1 Moisture

Of the migrating species present in insulation/liner/propellant systems, moisture is the most difficult to stop. Because of its small cross section, it will permeate all existing polymer systems. The only absolute barrier to moisture is a metallic film. However, there are certain techniques and basic principles which may be employed to lower the solubility of moisture in a polymer system and to reduce its permeability. These techniques and principles are presented in the following paragraphs.

#### 4.3.1.1 Low Polarity

The solubility coefficient for moisture in a liner is lowered through the use of a polymer network of low polarity.<sup>(1)</sup> This must, of course, also require the use of a nonhygroscopic filler, if a filler is used as a processing aid. Polymer networks incorporating hydrocarbon chains and curing agents such as isocyanates which yield cured linkages having minimum association for moisture are recommended.

#### 4.3.1.2 High Density

Moisture permeability through a polymer network is inversely proportional to its density. High density polymers such as Saran (polyvinylidene chloride) have far lower moisture permeabilities than polyethylene or polypropylene.<sup>(1)</sup> Certain fillers also can reduce permeability through a liner network. Fillers such as iron oxide reduce the permeability by a considerably greater degree than would be calculated from the blocking resulting from cross-sectional area considerations.

#### 4.3.1.3 High Crosslinking (if density increases)

Highly crosslinked polymers tend to have lower moisture permeabilities if the crosslinking results in an increased density.<sup>(1)</sup> This reduction in permeability is related to the reduction in the interstitial path cross-section.

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(1) Liner Technology Final Report, Volume II - Liner Development, Characterizing and Aging, Report AFRPL-TR-81-98.

#### 4.3.2 Liquid Migrants

In general, it is less difficult to reduce the permeability and solubility of liquid migrants than moisture. However, linear plasticizers having small cross-sectional areas, such as Arneel OD, are considerably more difficult to control than branched or condensed ring structures. Several techniques, listed in the following paragraphs, have proved particularly effective.

##### 4.3.2.1 High Crosslink Level

Increasing the crosslink density of the liner polymer network is an effective method of reducing its permeability to such migrants as catocene, energetic plasticizers and branched chain moities. This technique has little effect on the liner permeability to linear polymers with small cross-sectional areas. Again, fillers can be used to introduce a more tortuous path, thus reducing the permeability of the liner.

##### 4.3.2.2 Polarity Adjustment

The solubility of the various liquid migrants in the liner can be reduced by the use of a polymer network having a polarity opposite to that of the migrant. For example, a nonpolar plasticizer will have a low solubility in a highly polar liner system. Conversely a highly polar plasticizer such as a nitrate plasticizer will demonstrate low solubility in a nonpolar liner polymer network. Again, the selection of fillers used for processing considerations must also be based on these principles.

#### 4.3.2.3 High Density

As in the case of moisture permeability, the density of the polymer is inversely proportional to the permeability of the system to liquid migrants. Polymers having substituents such as halogens, which increase the density of the network, tend to have lower permeabilities. Fillers again can be used to reduce the cross-sectional area of the permeation path.

### 4.4 AGE STABILIZATION

The susceptibility of polymeric systems to such aging processes as hydrolytic cleavage or oxidative crosslinking varies considerably and is a function of chemical nature of the cure linkage and the degree of unsaturation of the polymer chains. As with other propellant polymer components the use of antioxidants to inhibit oxidation and the selection of chemical linkages resistant to hydrolytic attack are basic approaches to meeting age life requirements.

#### 4.4.1 Antioxidants

To best stabilize a polymer against oxidative degradation reactions, two types of antioxidants should be employed. The first, which functions as a reducing agent, acts to destroy the hydroperoxide formed in the first oxidative step. The second type which should be considered is a resonating structure such as a hindered phenol or a phenylene diamine which can act as a free radical trap and a chain growth limiter.

#### 4.4.2 Structural Factors

Structural considerations for reducing oxidative attack have been previously described under polymer structures (see Subsection 4.1.3.). Similarly the approaches to hydrolytic stability from a structural standpoint are addressed in Subsection 4.1.6.

#### 4.5 PROCESSING

The particular technique selected to apply the liner in the motor determines the physical properties of the uncured liner, the method of initiating cure, the temperature limits during application and the pot life. A variety of application techniques are employed which range from manually troweling the liner onto the insulation or by a fully automated system spraying or slinging the liner onto the surface. Each of these techniques calls for differing physical and cure characteristics. The general approaches to modify viscosity, thixotropy or pot life as required for these differing methods are presented in the following subsections.

##### 4.5.1 Pot Life Modification

Significant differences in pot life are required by various application techniques. In general, if the liner is applied by troweling a relatively long polymer pot life is needed, this same requirement applies to powder imbedment techniques where the resin system must not gel before the powder has been applied. Pot life is controlled by catalyst level and type. However, if the liner is to be applied by spray or a sling method, gelation must occur almost immediately on contact with the insulation. Two methods of pot life adjustment have been used in this latter case. If the two cure components of the liner system are mixed in the spray head, a highly catalyzed cure is used so that the two systems are very fluid for pumping but cure rapidly on mixing. If a fully mixed liner is fed to the spray or slinging head a long pot life with a rapid cure is the desired property. This may be achieved by the use of such selected catalysts as triphenyl bismuth.

#### 4.5.2 Viscosity Modification

Viscosity modification to control the flow properties of liners during application is usually accomplished by the addition of fillers such as silica. Other considerations such as moisture solubility which may be an undesirable factor from environmental or propellant compositional constraints should be taken into account in selecting the filler material.

#### 4.5.3 Thixotropy

Thixotropic behavior is a highly desirable feature in uncured liners when applied to the insulation by trowelling, or spin/trowel techniques. Thixotropic properties are usually obtained by the addition of special agents such as Thixin E, a castor oil derivative.

### 5.0 INSULATION FORMULA CRITERIA

Only those insulation formulation criteria which relate to the formation of good liner bonds or to the problem associated with migration are subject matter for this section of the manual. These are dealt with briefly with the purpose of stressing the importance of the proper matching of the insulation to liner and propellant.

The first consideration is that the insulation be formulated with the same consideration for bondability as for insulating characteristics. The insulation material should be selected or formulated, so that it will not adversely affect the integrity of the bond or the properties of the other two motor components (liner and propellant).

If migrating species are present in the propellant, it is desirable that the polymer selected for the insulation have a low solubility coefficient for these materials. It is desirable to set up, if possible, an unfavorable partition coefficient between propellant and insulation.

Because booted areas in motors subjected to high humidity storage conditions form the short distance paths for moisture migration to the insulation/liner/propellant bond line, it is desirable that low moisture permeability be a factor in the development of the insulation formulation.

Finally, if migration of a nonenergetic plasticizer is a consideration, the use of the same plasticizer in the insulation to equilibrate the total insulation/liner/propellant system is one way to prevent the development of high modulus, low plasticizer level areas adjacent to bond interfaces with a possible inherent reduction in high rate shear capability.

## 6.0 TEST METHODOLOGY

This portion of the Methodology Manual presents the various testing methods available for screening during the liner development phase, fully characterizing the bond system of the developed liner, and finally predicting the service life of the bond.

The procedures for conducting these tests not already common to the industry are presented in Section 7.

### 6.1 SCREENING TESTS

Screening tests employed to guide the development of a liner are made up of those standard tests which apply to all motor systems and a limited number of specific tests related to the particular constraints imposed by the specific propellant composition, motor environment, and design

criteria and the liner processing method selected. Thus, certain tests which are listed would only be conducted if the pertinent propellant compositional or environmental, etc, constraint was predicted.

The following are the screening tests that are performed to guide liner development and to provide some measure of assurance that the end product will prove adequate:

#### Propellant/Liner and Insulation/Liner Bond Strength

- (1) Double plate bond tensile (either at several rates or at several temperatures).
- (2) Spot checks of double plate bond shear.
- (3) Examination of test failure modes.

A typical test matrix for preliminary and final screening of bond strength of developing liner candidates is shown in Figure 5. This matrix shows the progression to more complete testing as the liner candidates are reduced in number and the tailoring becomes finalized.

#### Interfacial Effects - Propellant/Liner

- (1) Mini tensile strength profile specimens cut at 1/10 in. intervals parallel to propellant/liner interface.
- (2) Migration - Extraction and analysis of mini profile tensile strength specimens for migrant concentration.

#### Gel Time - Shawbury Curometer

#### Slump Test (for Trowelable Liners)

FIGURE 5. TYPICAL EVALUATION SCHEME FOR PROPELLANT-LINER-INSULATION BOND

| Sequence                                         | Test                            | Test Conditions |                           |                | Purpose                                                                                              |
|--------------------------------------------------|---------------------------------|-----------------|---------------------------|----------------|------------------------------------------------------------------------------------------------------|
|                                                  |                                 | Temp, °F        | Crosshead, in./min        | Pressure, psig |                                                                                                      |
| Preliminary                                      | Double Plate Tensile            | 77              | 1.0                       | 0              | Compare with strength of propellant; evaluate mode of failure.                                       |
| Screening (Δ to preliminary testing)             | Double Plate Tensile            | { 150<br>-40    | { 0.2<br>0.2 }<br>or      | 0              | Evaluate bond strength over a range of times-to-failure (or reduced times-to-failure).               |
|                                                  |                                 | { 77<br>77      |                           | { 0<br>20.0 }  |                                                                                                      |
| Supplemental (Δ to screening)                    | High Rate Shear with Pressure   | Low operational | 20.0                      | Meop           | Evaluate strength and mode of failure for operational firing. (Bracket expected to to max pressure.) |
|                                                  |                                 |                 | 200.0<br>200.0            |                |                                                                                                      |
| Structural Evaluation Static (Δ to supplemental) | Constant Load Tensile and Shear | 77              | ≥4 loads;<br>(~20-70 psi) | 0              | Evaluate bond strength for long-term storage.                                                        |
|                                                  |                                 | or TBD          |                           |                |                                                                                                      |
| Dynamic                                          | Fatigue                         | TBD             |                           | 0              | Evaluate bond strength for operational conditions at required temperature.                           |

### Preliminary Age Life Stability Testing

Six weeks aging at upper limit of predicted motor operation and storage temperature if a controlled storage environment is anticipated for the motor (135 to 165°F).

- (1) Measure changes in bond tensile and shear before and after aging.
- (2) Examine for interfacial effects - mini tensile profile and migrant analysis before and after aging.

## 6.2 BOND SYSTEM CHARACTERIZATION

Once the liner screening and early development is completed a full characterization of the bonding system is required to validate the ability of the bond to meet the design and processing limits. These data also provide the basis for any final tailoring of the system to meet these limits or to adjust for any final changes in propellant composition. The testing required is listed below. Details of the test procedures are presented in Section 8.

### 6.2.1 Mechanical and Physical Properties - Standard Procedure

#### Bond Characterization

Effect of loading rate on <sup>(2)</sup> bond tensile and shear.

- (1) Loading rates 0.021 to 2000 in./min., testing with and without imposed pressurization.
- (2) Testing must be performed over the entire operational temperature range of the motor.

(2) A typical test matrix is shown in Figure 5.

### Liner Properties

- (1) Mechanical properties S & E and stress relaxation.
- (2) Coefficient of thermal expansion.
- (3) Density.
- (4) Viscosity build-up.
- (5) Flow range (to establish specifications).
- (6) Shelf life of components (particularly important for two component systems).
- (7) Shelf-life of lined chamber.
- (8) Repair procedures (should areas of inadequate thickness be found).

#### 6.2.2 Tear Energy

A method for measuring the J integral fracture energy criterion has been developed as a part of the AFRLP Liner Technology Program conducted by Aerojet Strategic Propulsion Company.<sup>(3)</sup> This fracture energy can be mathematically converted by the following equation to other well known fracture energy criteria for structural analysis purposes:

$$J_{Ic} = G_{Ic} = \frac{(1 - \nu^2)K_{Ic}^2}{E} = 2\gamma \quad (1)$$

This new, more accurate and convenient analytical procedure is presented in Section 7.

(3) Liner Technology, Final Report, Volume I - Fracture Energy Method Development, Report AFRLP-TR-81-97.

### 6.2.3 Transport Coefficients

An important measurement of the effectiveness of the selected liner composition is a determination of the transport coefficients of the cured material for the various migrant species derived from the propellant and insulation or moisture from the environment. These data are also required for bond system service life prediction. A new and more accurate method for determining the permeability and diffusivity coefficients of any membrane, the Dual Reservoir Method for Permeability Measurement, was discovered and developed by ASPC while conducting the AFRPL Liner Technology Program.<sup>(1)</sup> The details of the method are presented in Section 7.

### 6.3 BOND SYSTEM AGING MODELS AND SERVICE LIFE PREDICTION

The final validation of the liner system is the determination of its adequacy in providing a bonding system which meets the motor age life requirements. The recommended procedure for developing this service life prediction is the structural chemical aging kinetic method developed by ASPC as part of the Minuteman LRSLA Program and used for the age life analysis in the AFRPL Liner Technology Program.<sup>(4)</sup> This method involves the aging of representative insulation/liner/propellant analogs at various humidity levels and at three elevated temperatures. From the data obtained and the application of chemical kinetic methodology the activation of the critical degradation processes are calculated and the effect of humidity exposure determined as a function of RH. The critical bonding parameters for structural analysis are established by correlative methods. Using the transport data for migrants described in subsection 6.2.3 mathematical models are developed to handle the concurrent diffusion and degradation processes and a projection is made of the aging changes in critical bond parameters with time as a function of operational environment. Applying the limits for bond properties established through structural analyses the service life can be estimated. Details of the methodology are presented in Section 8.

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(4) LRSLA Minuteman Age Life Projection Report.

## 7.0 TEST METHODOLOGY

The test methods presented in this section are for test methods recommended in the Liner Methodology Manual which are either new or are not generally used in the industry. The test methods presented are: the screening and migrant transport methods developed in the Liner Technology Program, a flow test for use as a processing aid, and the test procedure for measuring tear energy.

### 7.1 PERMEABILITY TESTS

#### 7.1.1 Cup-Swelling Screening Test

The cup-swelling test methods has as its basis the variations in swelling of liner and insulation materials on exposure to liquid migrating species. In conducting the test, a 1/16-inch thick disc of liner is cast into the base of a 1-inch-diameter open-ended aluminum tube. After cure, a layer of the liquid migrant is poured into the tube on top of the liner and the liner behavior is observed. The appearance of the test samples as a function of time is pictured in Figure 6. The tubes are stored in a polyethylene test tube rack in such a way that the bottom of the tube makes no contact with the rack. The bulk of each sample is therefore free to distort; the extent of this distortion can be measured as the distance from the bottom edge of the aluminum tube to the bottom of the distortion. The distortion or deformation of the test specimen is thus used to measure the relative resistance of the liner or insulation to penetration of migrant chemicals.

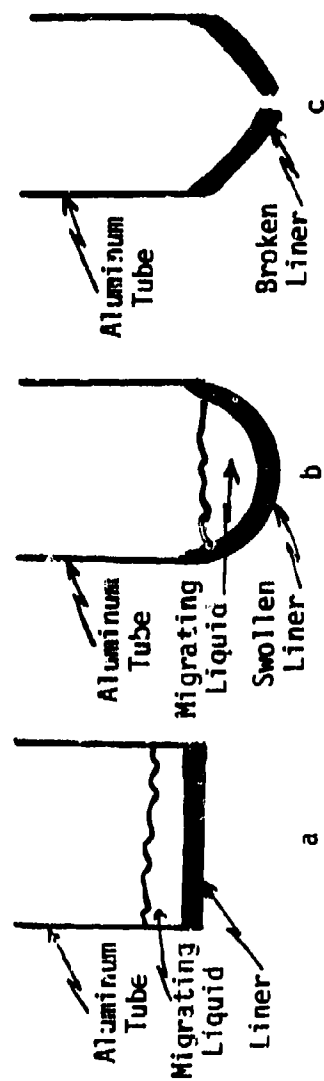


Figure 6. Cup-Swelling Test Method. Appearance of Test Specimens at Various Times

### 7.1.2 Dual Reservoir Diffusion Test

The Dual Reservoir Diffusion Device (DRDD) allows the investigator to determine in one test not only the permeability and diffusivity coefficients but also the solubility coefficient of a polymeric film for any liquid migrating species. The device, shown in Figure 7, is composed of two commercially available 1-inch-diameter glass 90° flanged "L's." The liner or insulation specimen to be studied is secured between the two L's by tightening the flanges finger-tight. The first reservoir, the delivering reservoir, contains the migrating species diluted in a high molecular weight prepolymer such as TP-4040. (Preliminary experiments show that some polar migrating chemical species, such as FEFO and TMETN, have a tendency to self-associate when neat, thus giving distorted transport coefficients.) On the other side of the liner or insulation specimen is the receiving reservoir which also contains a high molecular weight prepolymer. (Migrating liquids required a continuous liquid polymer phase adjacent to the liner or insulation in order to facilitate migration.) The receiving reservoir is continuously stirred by a small air-driven stirrer to ensure a uniform concentration of the migrant species throughout the prepolymer. The entire device is placed inside an oven set at constant temperature during the test period to ensure accurate temperature control.

Several analytical techniques can be used to determine the concentration of migrating species as they permeate through the test samples. These include infrared spectroscopy, refractive index, and ultraviolet/visible spectrophotometry.

A permeability coefficient is obtained from a plot of the amount of transported material versus time as typified by the plot shown in Figure 8. The coefficient is represented by the slope and is expressed as:

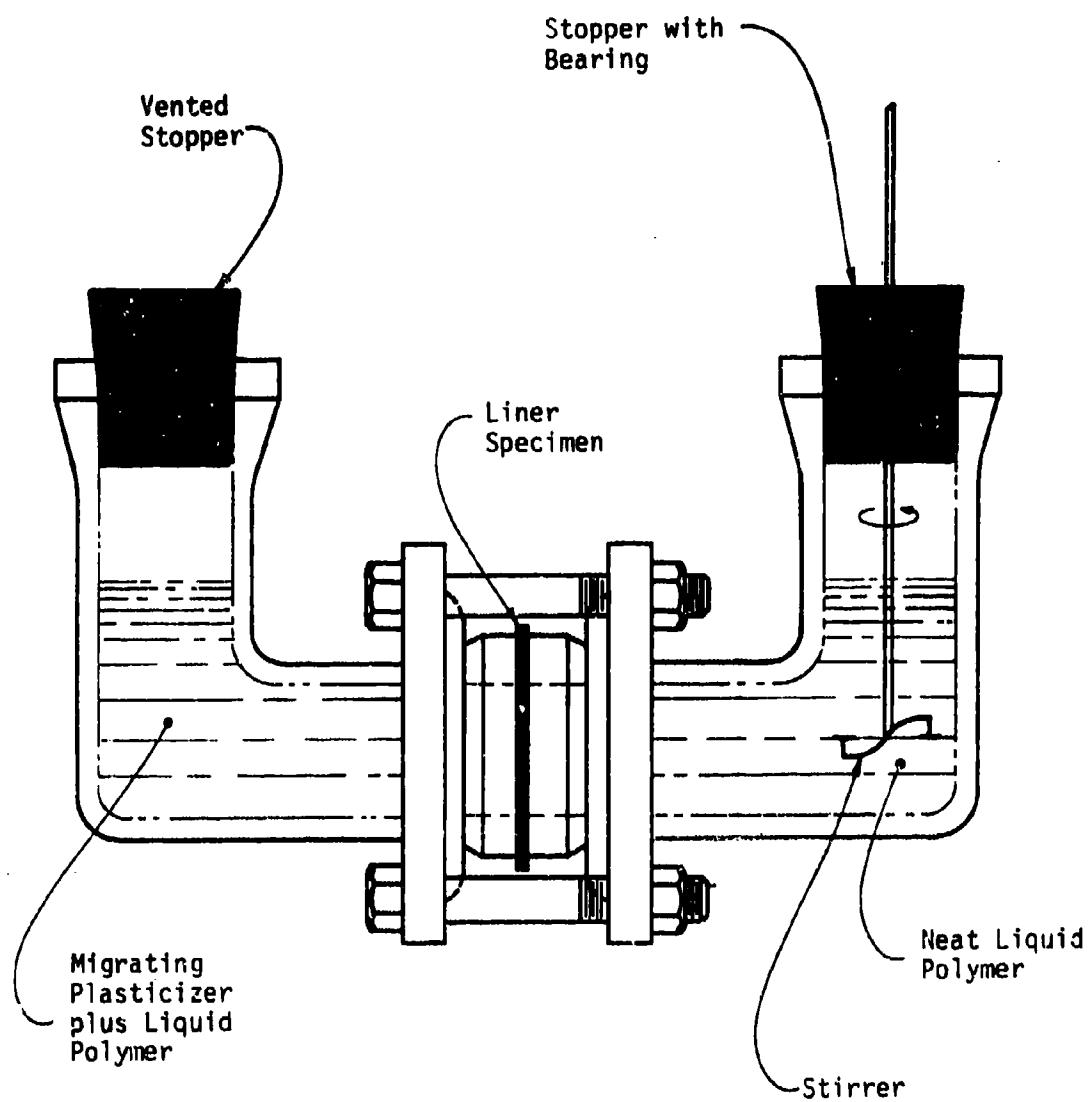


Figure 7. Dual Reservoir Diffusion Device for Measuring Transport Coefficients

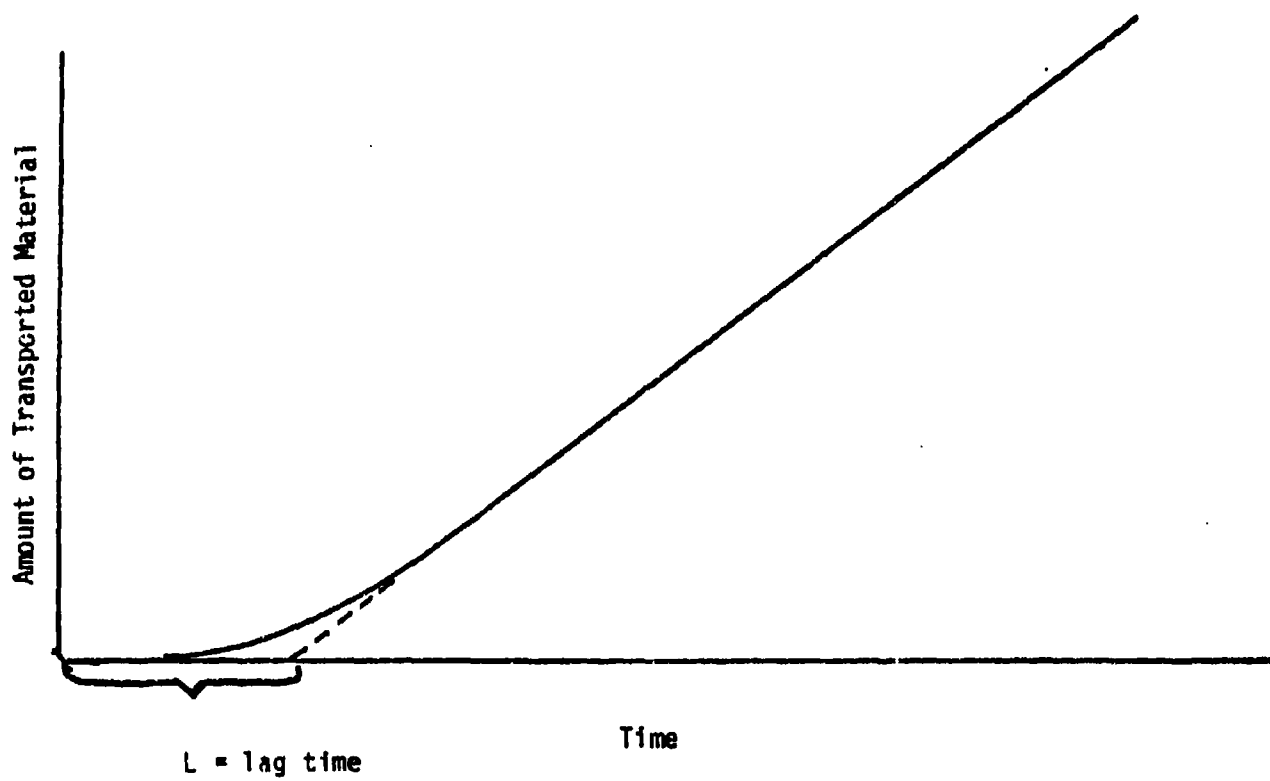


Figure 8. Determination of Diffusion and Solubility Constants  
from Permeability Curve

$$\text{Permeability} = \frac{\text{weight transported} \times \text{thickness of membrane}}{\text{time in days} \times \text{cross-sectional area} \times \text{concentration gradient}} \quad (2)$$

The diffusivity coefficient can also be determined from these data plot by using the equation

$$\text{Diffusivity} = \frac{(\text{thickness})^2}{6 \times \text{lag time}} \quad (3)$$

and from the relationship  $D = P/S$ , the solubility coefficient can then be calculated. According to the work of Barrer, as presented in Jost<sup>(6)</sup>, it is possible to determine diffusivity,  $D$ , and solubility,  $S$ , directly from permeation data provided these permeation measurements cover a period necessary to achieve a steady-state permeation. Although Barrer's work dealt with the permeation of gases through organic polymer membranes, it was found to be applicable to the permeation of organic and inorganic liquids through the same kind of membranes. Experiments were performed to verify this relationship.

The standard procedure for calculating diffusivities is to experimentally determine permeability and solubility coefficients and use the relationship

$$D = \frac{P}{S} \quad (4)$$

As previously stated, Barrer's work indicates that diffusivities can also be determined directly from permeability data using the relationship

$$\text{Diffusivity} = \frac{(\text{thickness})^2}{6 \times \text{lag time}} \quad (5)$$

(6) Jost, W., Diffusion, Academic Press, Inc., New York, 1960, pp 42-45.

## 7.2 FLOW MEASUREMENT

This test procedure is presented as an example of a method which may be adapted to any liner system where slump characteristics during application are important. It is taken from Weapon Specification 1091A, Test Method 4.6.4., used for qualifying adhesive/potting material used in the Polaris motor.

The test is a simple determination of the flow distance versus time for a standard specimen of the adhesive held on a flat vertical surface.

A standard Semco sealant gun cartridge shall be filled with freshly mixed liner. The gun and material shall be maintained at standard conditions throughout the test. The test shall be conducted with a flow-test jig, as shown in Figure 9, and the material shall exhibit a flow, as specified for the particular application when a cylindrical section, formed in the flow-test jig, is allowed to flow under its own weight on a vertical surface. Depth of plunger tolerance is critical and shall be controlled within the tolerance during all tests. The flow-test jig shall be placed on a table with the front face upward and the plunger depressed to the limit of its travel. Within 15 minutes after the beginning of mixing, enough of the mixed liner material shall be extruded from the application gun to fill the recessed cavity of the jig and leveled off even with the block. The test at this interval shall be considered the initial flow of the liner material. Within 10 seconds after the leveling operation, the jig shall be placed on its end and the plunger immediately advanced to the limit of its forward travel. The flow measurement shall be taken exactly 30 minutes after the liner has been applied to the test jig. The flow shall be measured from tangent to the lower edge of the plunger to the farthest point to which flow has advanced.

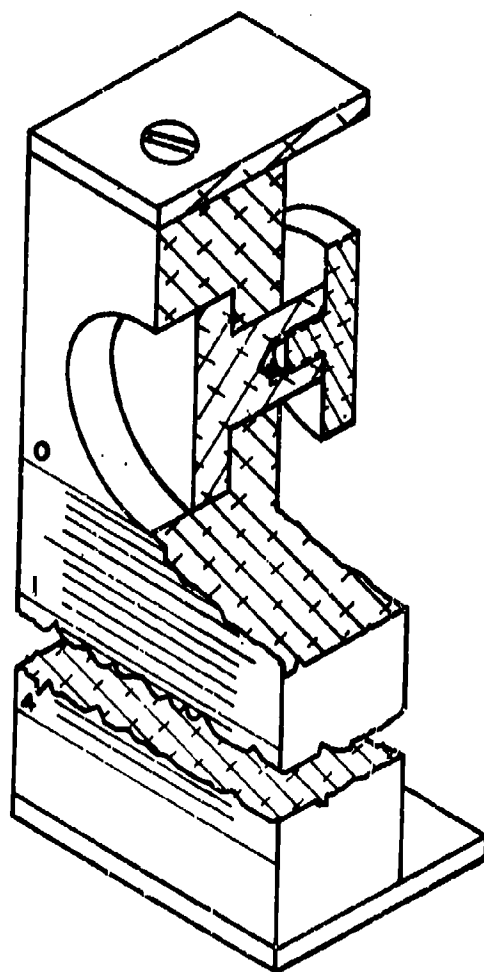


Figure 9. Flow-Test Jig

### 7.3 TEAR ENERGY MEASUREMENT (J-INTEGRAL METHOD)

The information presented on this test method is limited to a presentation of the test procedure and data reduction techniques. A full description of the methodology, its theoretical basis and application, is presented in Volume I of the final report of the Liner Technology Program (Report No. AFRPL-TR-81-97).

#### 7.3.1 Preparation and Testing Procedures for the Scarf-Joint Specimen

Procedures are described for the preparation and testing of propellant/liner bonds in the scarf-joint specimens. Test specimens will contain piezoelectric crack sensors for monitoring tear propagation. Calculations are made from a combination of parameters including those of force, time, deflection, temperature and the ultrasonic transit time,  $\Delta t$ , measurements from the PZT crystals. A DAR data recording and analysis system is employed to monitor these parameters.

##### 7.3.1.1 Equipment and Materials

The following equipment and materials are needed to prepare and test the scarf-joint specimens (Figure 10):

- a. Measuring rule (0.01 in. graduations).
- b. Double-backed tape (Permacel or equivalent).
- c. X-acto knife with 2-1/2 in. blade No. 226.
- d. Adhesive (Ren 6405) Ren Plastics.
- e. Adhesive (EA 901-R1) Hysol-Dexter Corp.
- f. Paint or acid brush approximately 1/2 in. wide.
- g. Ball point (fine) or fine felt-tipped pen.

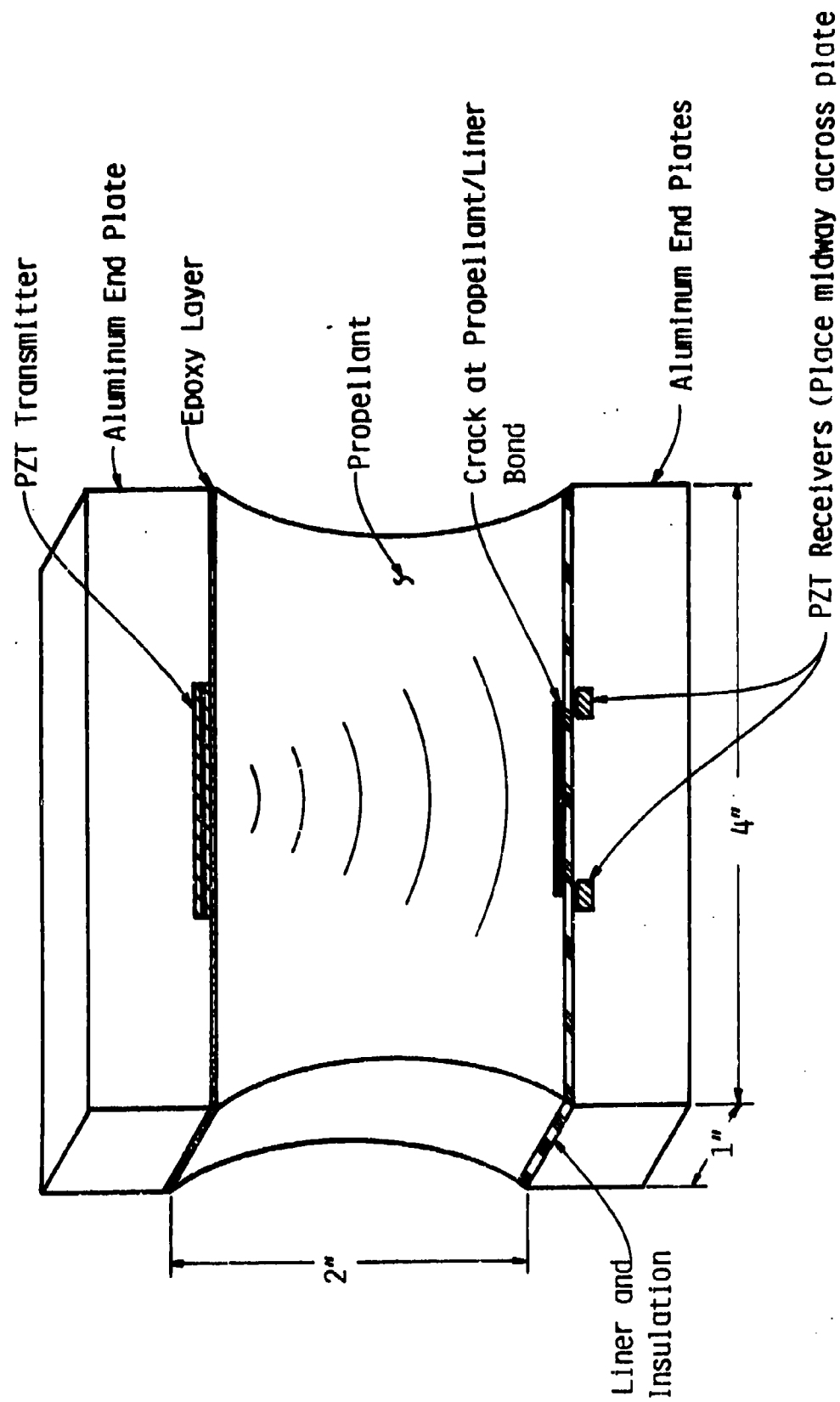


Figure 10. Scarf-Joint Specimen with Acoustic Profilography

- h. Prepared aluminum end-plates measuring 1 x 1 x 4 in. (with embedded PZT crystal transducers suitable for attachment to tester hardware).
- i. ASPC-developed bonding support (Figure 11), flaw-inducing fixture (Figure 12), and cutting blades (Figure 13).
- j. Specimen preparation saw or milling machine capable of producing uniform 4 x 2 x 1 in. propellant specimens (Figure 14).
- k. Instron tensile tester with temperature environment chamber.
- l. Multi-channel variable gain and zero control junction for extensometer calibration and balance.
- m. DAR data recording and analysis system (Figure 15).
- n. Multi-channel time y - MV strip recorder plus 5 to minus 5 MV full-scale range.
- o. Piezoelectric crystal transducers - transmitters and receivers (Figure 10).
- p. High frequency signal conditioning system (pulse generator) for PZT crystals (Figure 15).
- q. Oscilloscope Tektronik Mod 77048 or equivalent.
- r. Multimeter (VOM) Kiethley Mod 178 or equivalent.
- s. Stop watch accurate to within 0.01 sec.
- t. Video recording system with closed circuit TV.
- u. Preston Mod DK variable gain amplifiers or equivalent - 1 each per channel of recording.
- v. Copper - Constantan temperature reference junction.
- w. Copper - Constantan thermocouple.
- x. Shear component extensometer with attachment hardware (Figure 16).
- y. Axial displacement fixture with four extensometers and attachment hardware (Figure 17).
- z. Digital clock and frequency counter.
- aa. ASPC-developed programmable temperature rate controller (P.T.R.C.) (Figure 18).

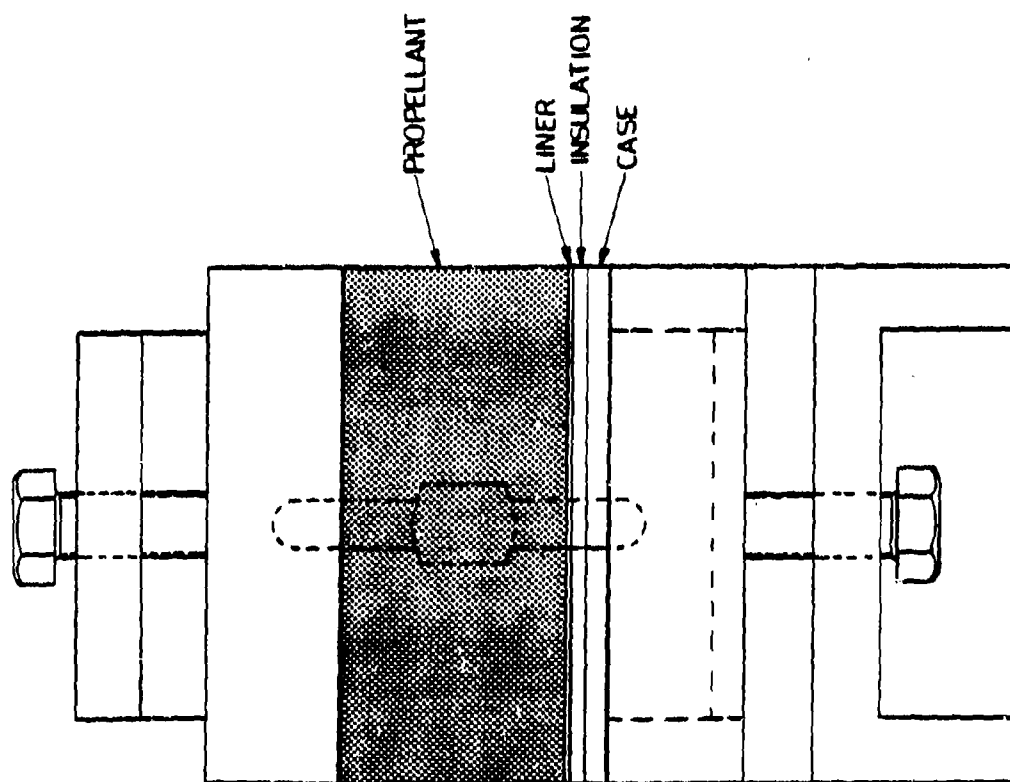
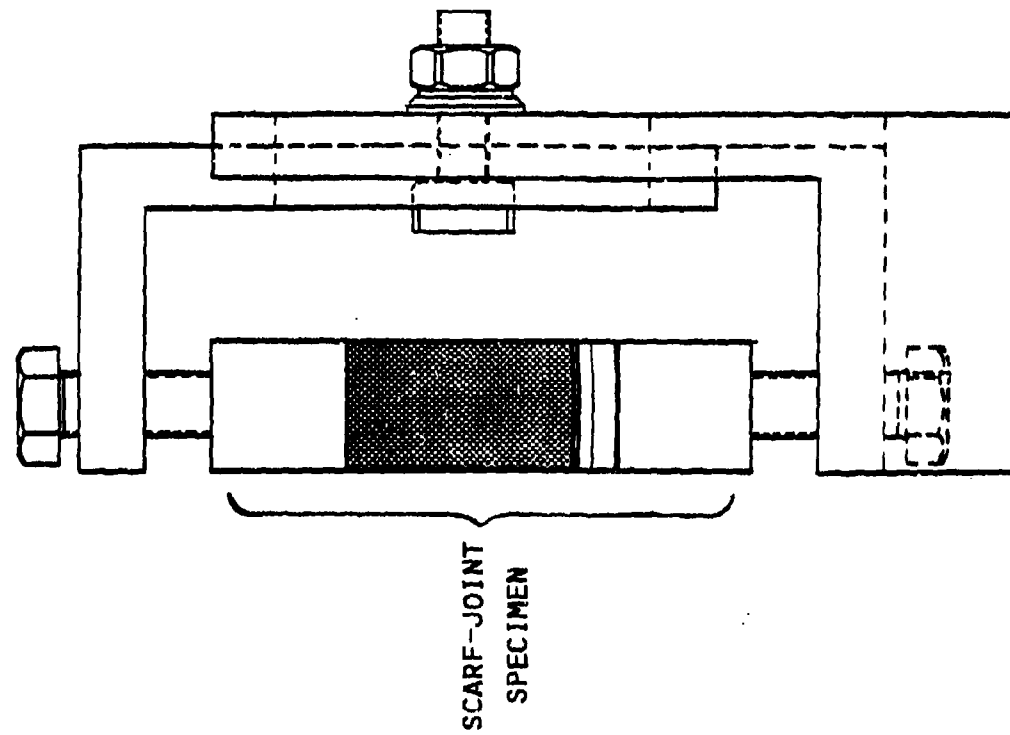


Figure 11. Bonding Support Fixture

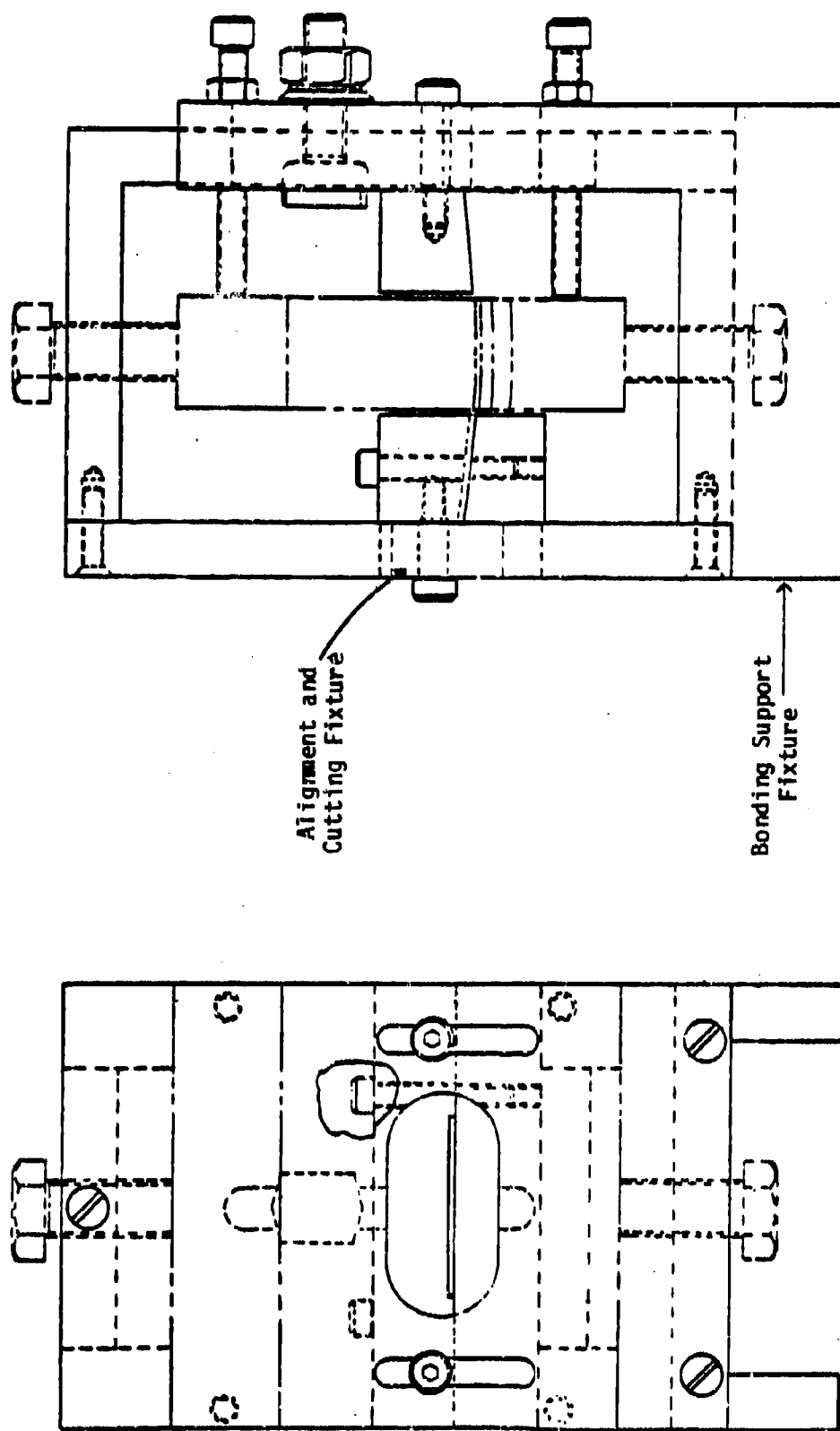
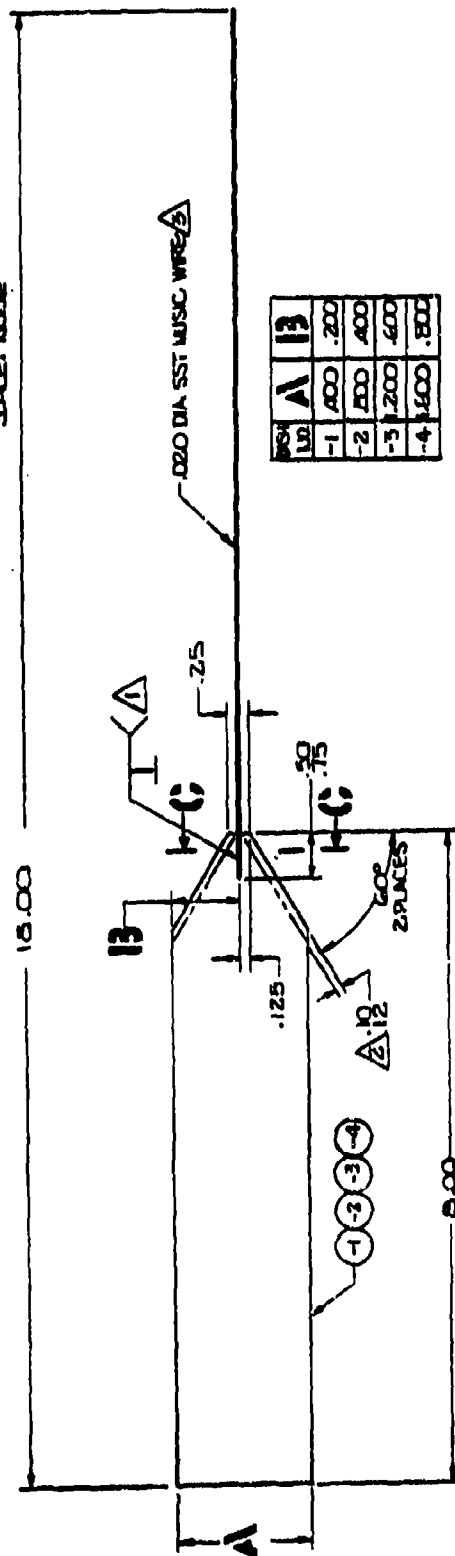


Figure 12. Bonding Support, Alignment and Cutting Fixture for Motor Specimens

- 



| Test | A   | B   |
|------|-----|-----|
| 1    | 100 | 200 |
| 2    | 100 | 400 |
| 3    | 200 | 600 |
| 4    | 100 | 800 |

|    |            |                               |                  |
|----|------------|-------------------------------|------------------|
| AP |            | STAINLESS STEEL WIRE .020 DIA | 3                |
| AP | -1-2-3 4-4 | STAINLESS STEEL SAW STICK     | TYPE 302 620 THK |

**Figure 13. Cutting Blade for Scarf-Joint Specimen Preparation**

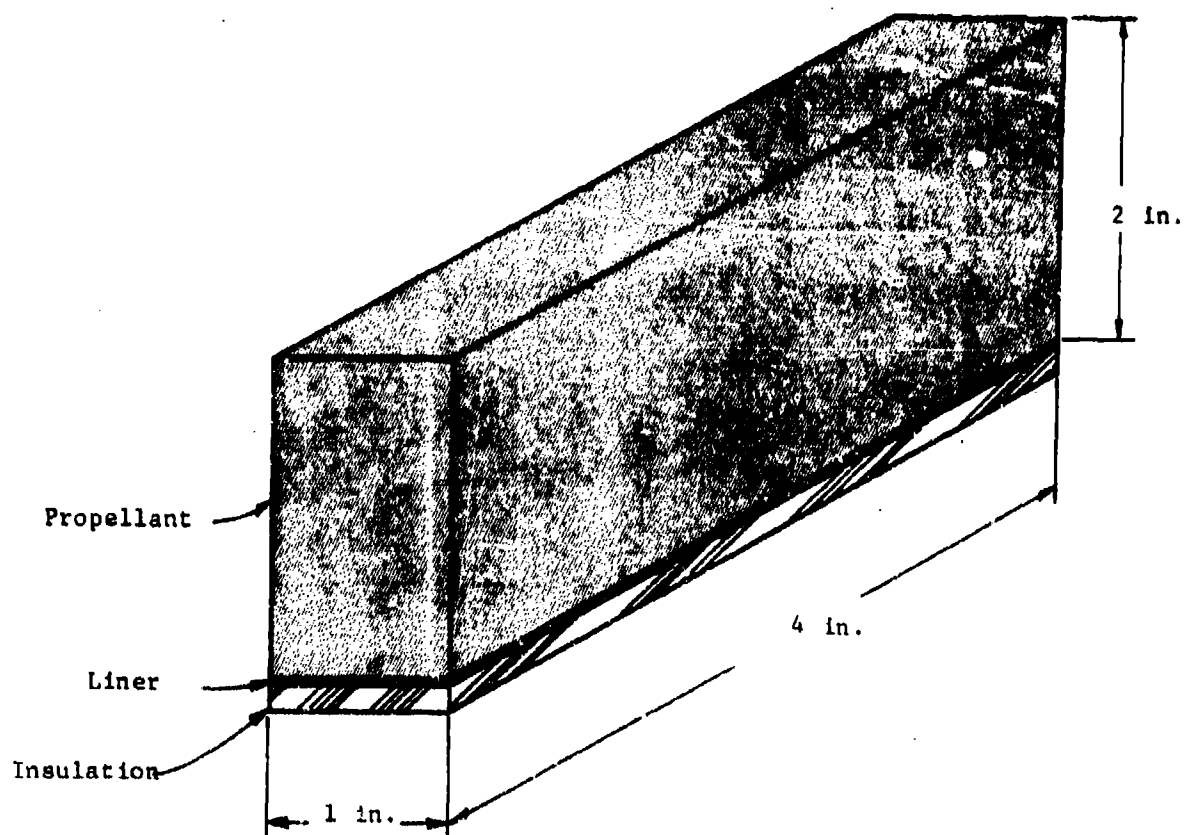


Figure 14. Milled or Saw-Cut Scarf-Joint Specimen

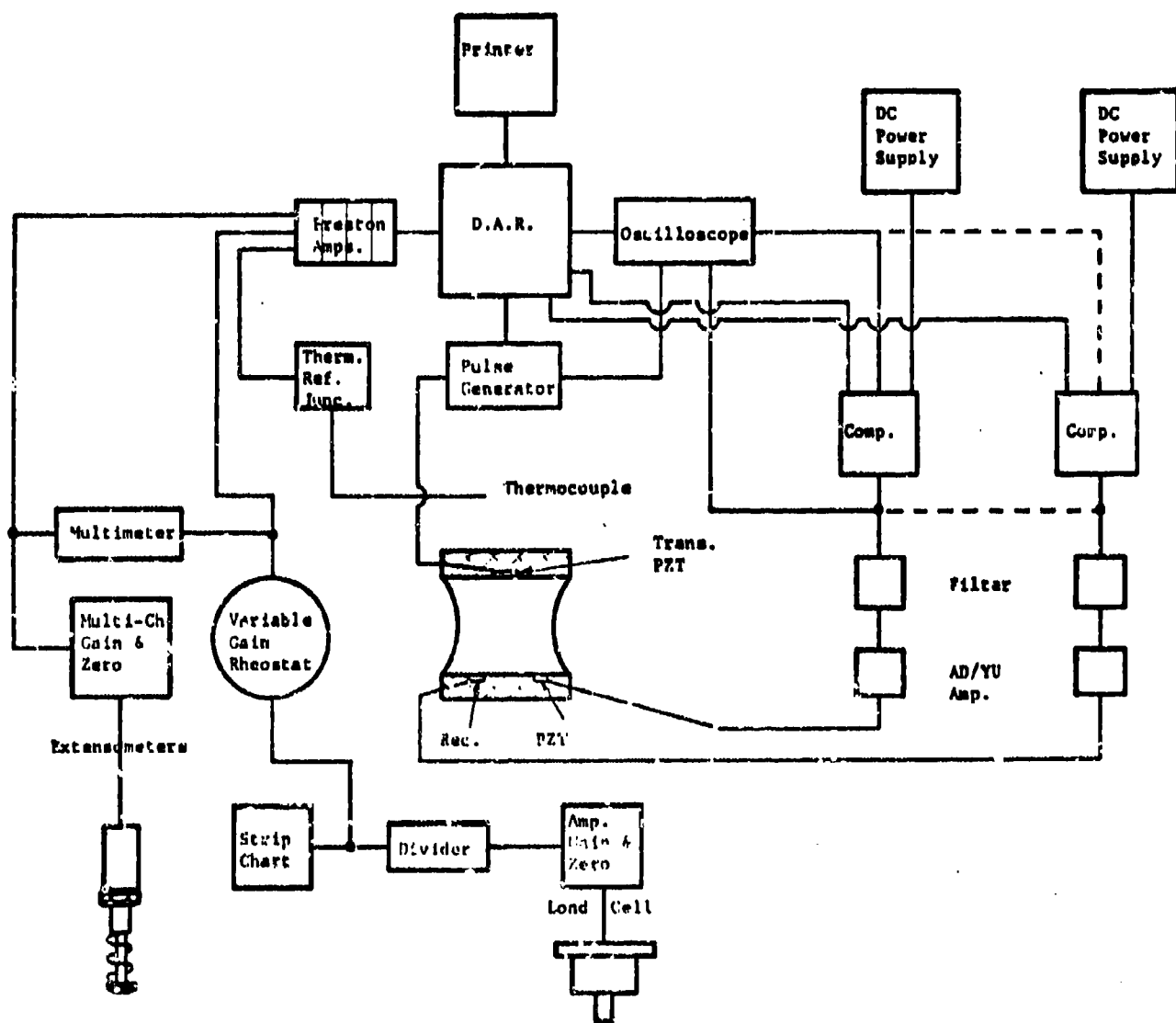


Figure 15. D.A.R. Data Recording and Analysis System

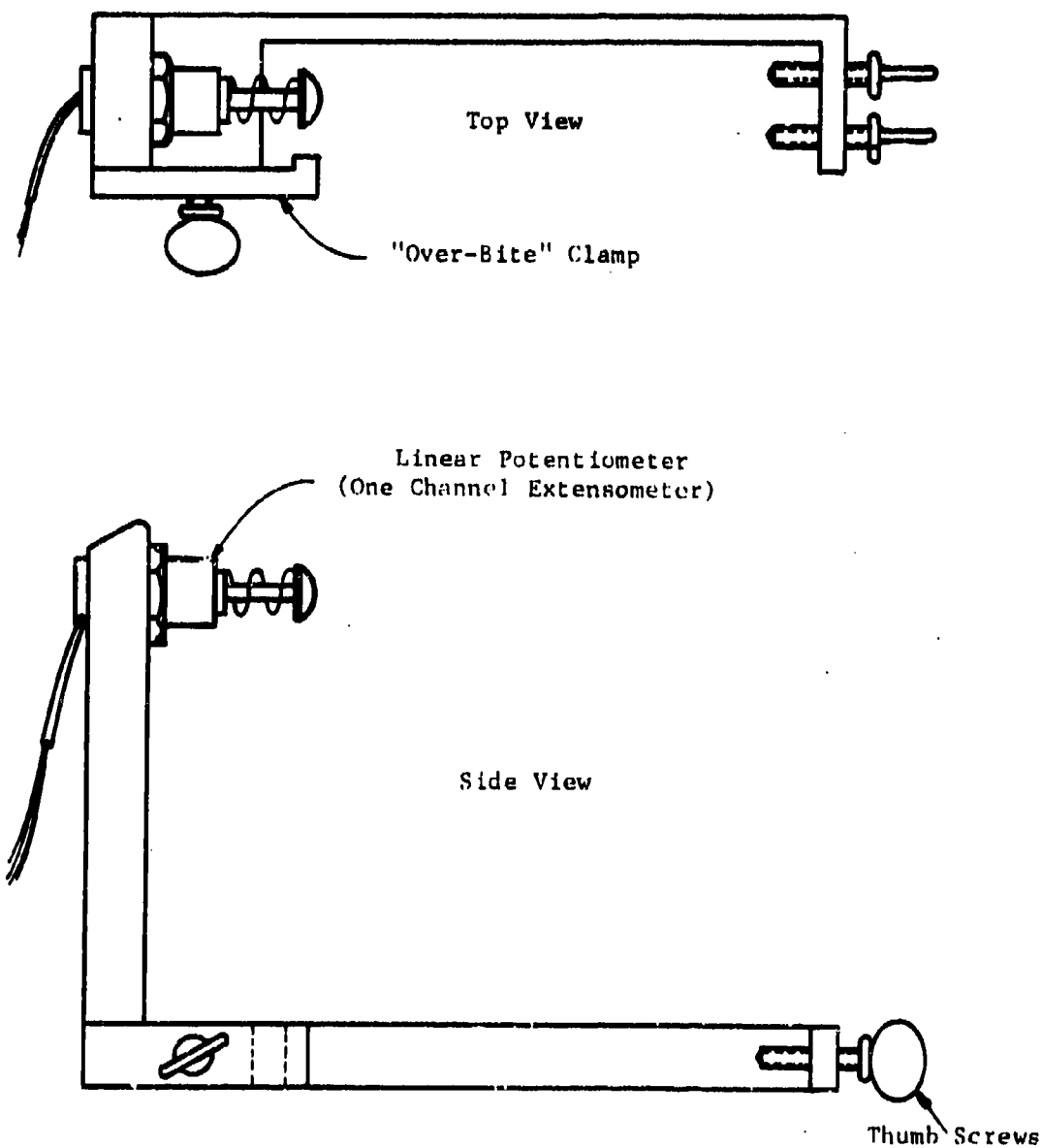


Figure 16. Shear Component Extensometer  
(Used in measuring shear deformation in combined  
tension/shear test configuration)

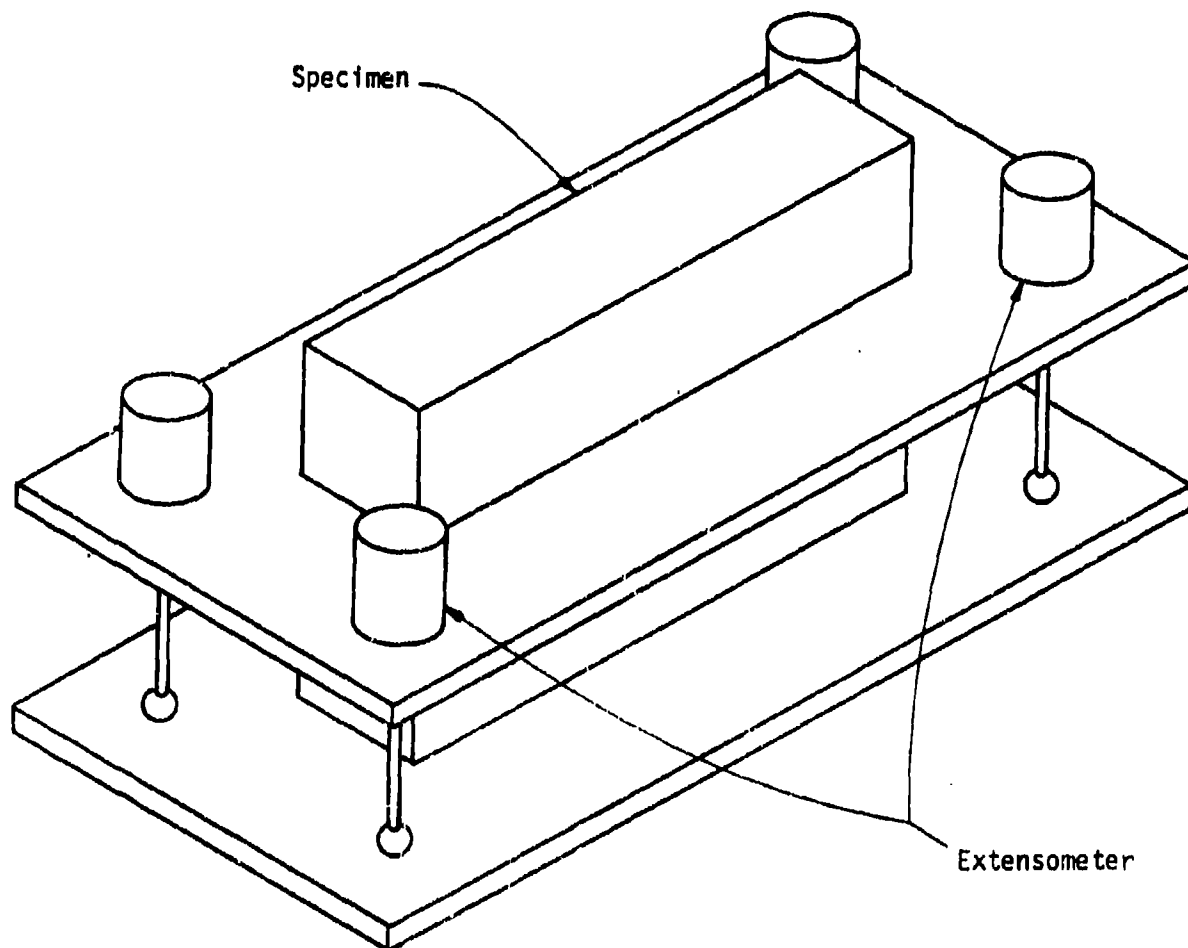


Figure 17. Parallel Displacement Monitoring Fixture for the Scarf-Joint Specimen

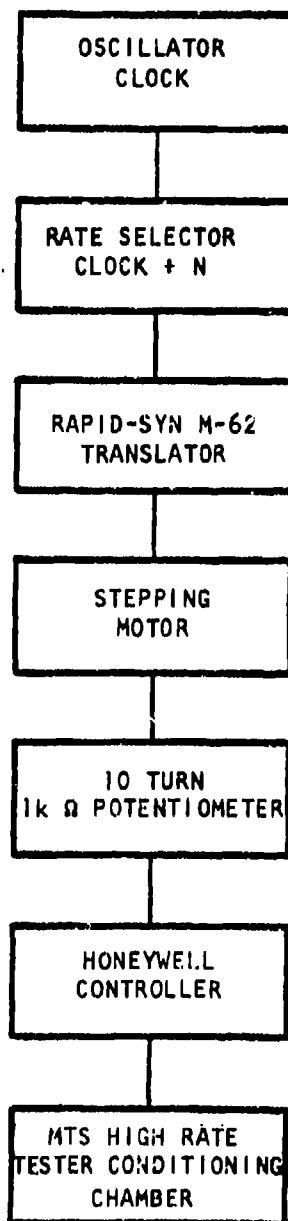


Figure 18. Programmable Temperature Rate Controller

### 7.3.1.2 Procedures

#### 7.3.1.2.1 Specimen Preparation

Machine-saw scarf-joint specimens from liner box measuring 4 x 2 x 1 inch. All sides must be parallel and 90 degrees from the adjacent side (Figure 14).

- a. Brush loose particles from all specimen surfaces.
- b. Place strips of double-backed tape on a flat surface. Press the surfaces to be bonded to the exposed adhesive face to remove the remaining loose material. Repeat until no new material transfer is detected.
- c. Mix EA 901-B1 per manufacturer's instructions.
- d. Apply a thin layer of EA 901-B1 adhesive to the sand-blasted and degreased (with embedded PZT crystal) aluminum end plate.
- e. Apply layer of EA 901-B1 to insulator of specimen.
- f. Place end-plate and specimen on a flat nonstick (waxed paper) surface in preparation for bonding.
- g. With the adhesive-painted surfaces opposite one another, push the end plate to the insulator of the specimen with sufficient force to produce an epoxy bead at the interface edge.
- h. Cure the bond for 24 hours at 77°F.
- i. Mix Ren 6405 adhesive per manufacturer's instructions and allow 10-15 minutes before application.

- j. Bolt sand-blasted and degreased, aluminum end-plate (with embedded PZT crystal transducer) to bonding support fixture (Figure 11).
- k. Apply Ren 6405 adhesive to end-plate propellant surfaces.
- l. Push bonding surfaces together and bolt EA 901-B1 bonded end-plate to bonding fixture to ensure proper contact and alignment (Figure 11).
- m. Cure the bond for 24 hours at 77°F.
- n. Remove bonded specimen from fixture.
- o. Mark the flaw locations at the propellant-liner interface on the specimen and then carefully drill a 0.2-inch hole at the midpoint of the proposed flaw.
- p. Reinstall specimen in the bonding support flaw-inducing fixture (Figure 11) and align the flaw-inducing guide slots at the propellant liner interface (Figure 12).
- q. Feed the flaw-inducer blade guide tab (Figure 13) through the guide slot at one side of the fixture, through the predrilled hole in the specimen and through the guide slot on the opposite side of the fixture. Using a firm, continuous motion, pull the guide tab and attached blade through the fixture and specimen.
- r. Remove the specimen from the fixture.
- s. Map and cut the stress relief configuration in the propellant (Figure 19).
- t. Measure and record all specimen dimensions.
- u. Attach extensometer hardware to the specimen end plates.

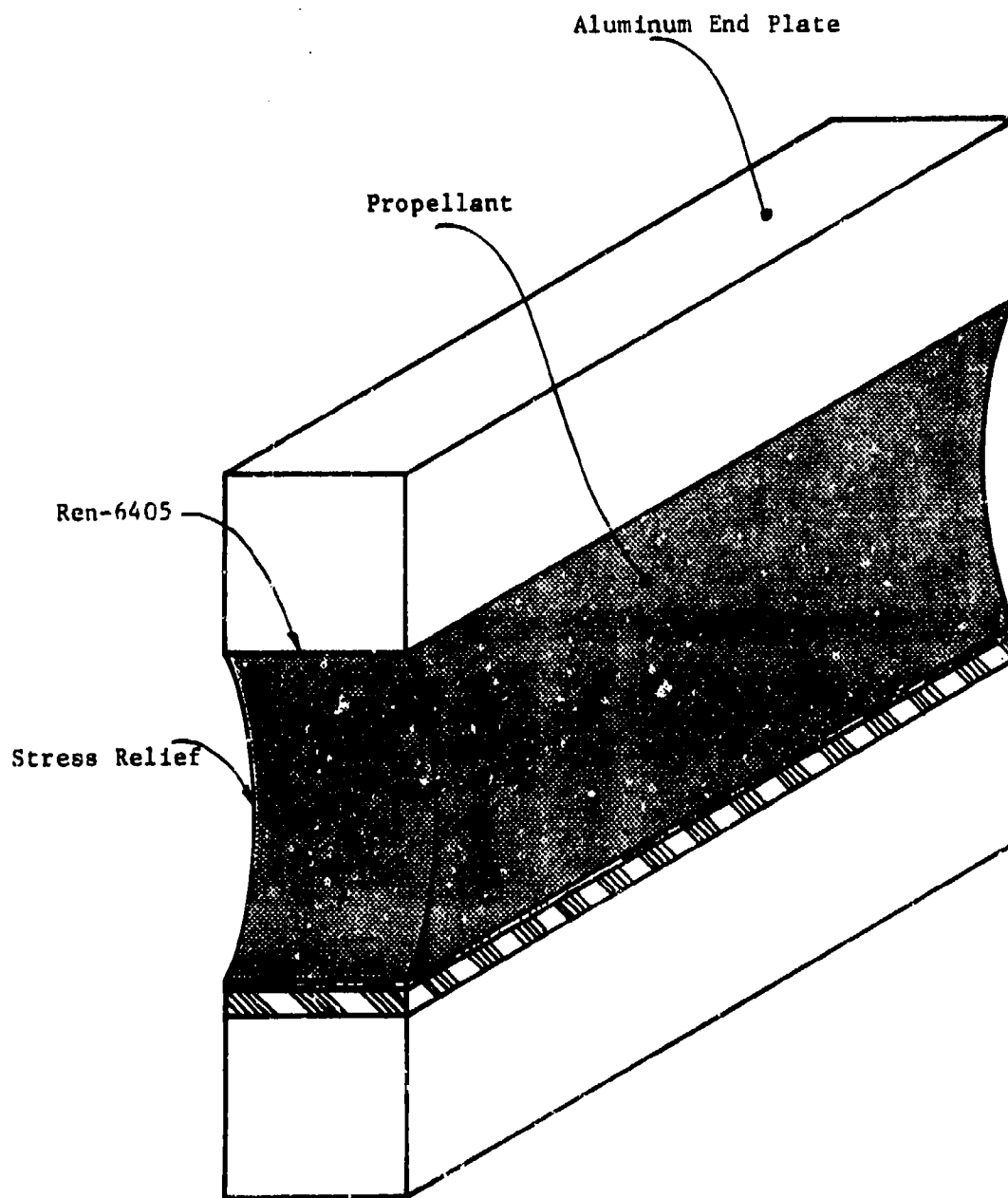


Figure 19. Cutting End Stress Relief

#### 7.3.1.2.2 Temperature Conditioning

Prior to testing, condition specimen at the prescribed test temperature as follows:

| <u>Test Temperature, °F</u> | <u>Conditioning Time, hours</u> |                |
|-----------------------------|---------------------------------|----------------|
|                             | <u>Minimum</u>                  | <u>Maximum</u> |
| a. -75 to +60               | 1                               | 24             |
| b. +60 to +80               | 1                               | -              |
| c. +80 to +110              | 1                               | 8              |

#### 7.3.1.2.3 Testing Procedure

- a. Secure predrilled 1000-pound capacity load cell in place. Particular care should be taken to ensure that the cell is level and aligned with the cross-head shaft (Figure 20).
- b. Calibrate tensile tester according to Section 5.30 of the "Operating Instructions for the Instron Tensile Testing Instruments" Manual, 10-29-1.
- c. Calibrate the load voltage input to the DAR system using a VOM hook-up with a variable output rheostat control. Calibrate 5 volts full scale regardless of load cell or amplifier output.
- d. Balance individual specimen tare weight before each test.
- e. Secure specimen with jam nut to lower cross-head shaft. Remove slack with manual cross-head adjustment control while taking care not to preload specimen (watch VOM for zero, not the chart pen). Lock jam nut at the upper load cell shaft and recheck the zero manipulating the cross-head adjustment control as necessary.

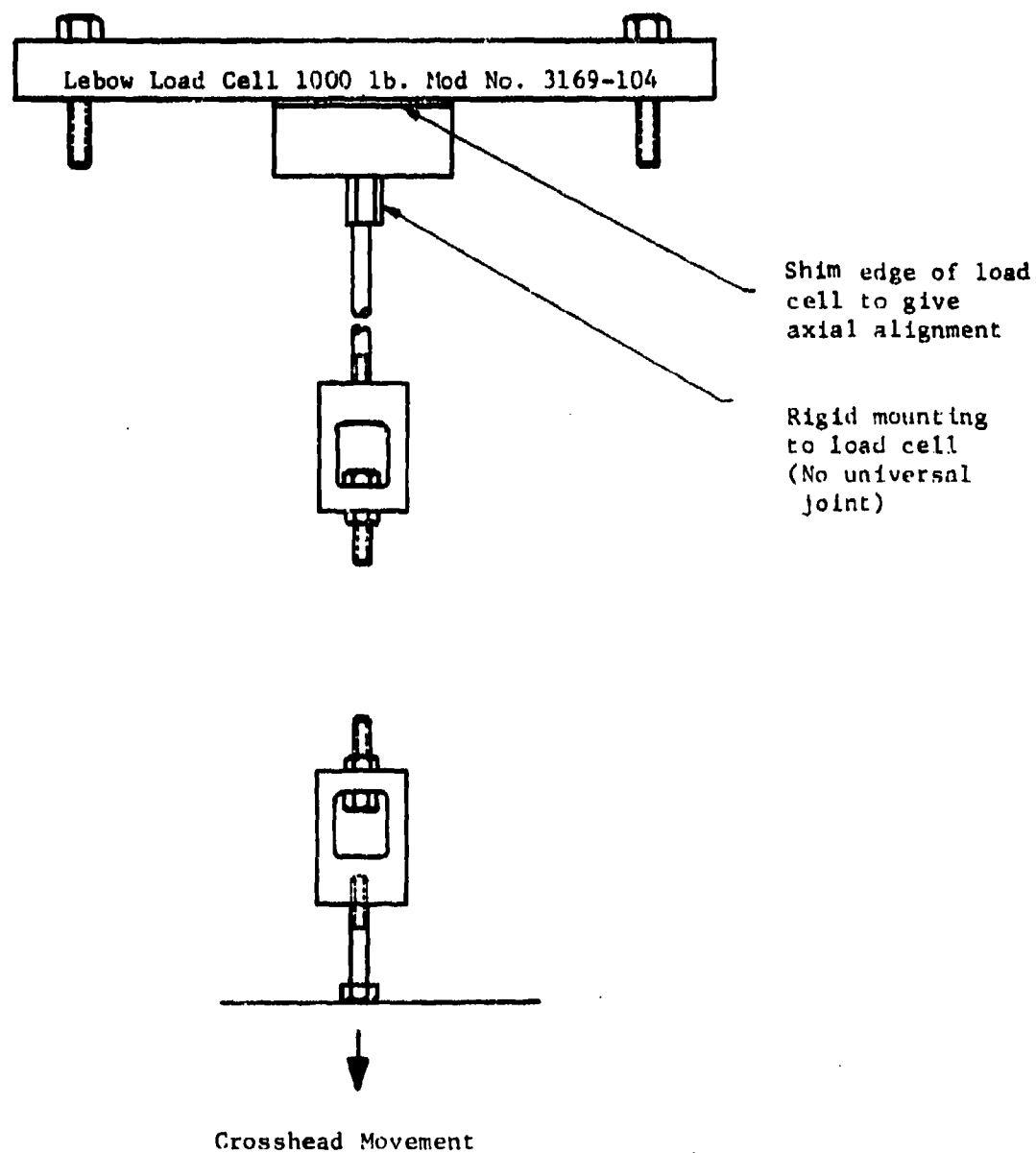


Figure 20. Instron Tester - Typical Test Setup

f. Connect PZT and extensometer cables to DAR monitoring system.

g. Calibrate extensometers output to 5 volt DAR system using VOM hook-up with variable gain controls:

- (1) Set zeros for each extensometer in turn.
- (2) Insert spacing block of known thickness, i.e., 0.075 in. represents half-scale of 0.15 in. total displacement.
- (3) Adjust variable gain controls to represent the percentage of mechanical displacement in volts, i.e., using half-scale displacement adjust the VOM readout to 50% of 5 volts full-scale - 2.5 volts.

h. Switch trigger mode at pulse generator to "internal." Adjust comparator controls and amplifier settings to correct value for the test, i.e., using the oscilloscope, set the trigger level at the comparator controls to a level above the random noise of the setup and adjust the amplitude of the receiver PZT crystals to matching levels (Figure 21).

i. Switch the trigger mode at the pulse generator back to the "external" position.

j. Address DAR and call for operator options.

k. Set test duration and time interval.

l. Calibrate analog channels.

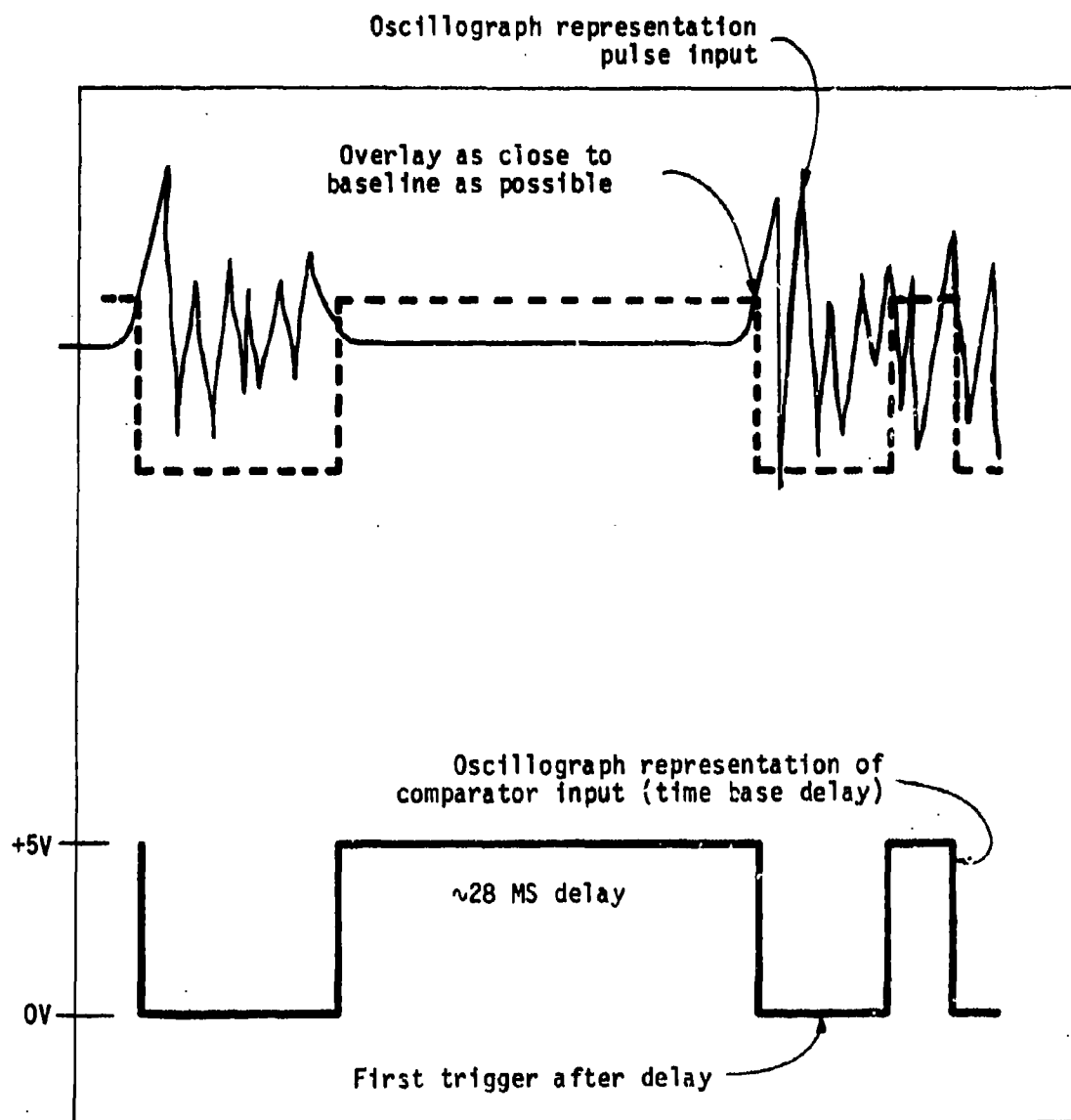


Figure 21. Amplitude Adjustment of PZT Crystals

m. Recheck settings and record test temperature for each specimen.

n. Set up video recording equipment and position TV camera in such a manner that the specimens and the digital counter can both be seen on the monitor.

o. Record the test conditions and the video recorder counter number on the specimen information sheet.

p. Start the test in the following sequence as rapidly as possible:

- (1) Video recorder on
- (2) DAR on
- (3) Tensile tester and Recorder chart on

q. Observe test and record all relevant events on the strip chart.

- (1) Location of fracture initiation
- (2) Location of fracture propagation
- (3) Flaws at tip of original crack
- (4) Rotation or distortion of specimen prior to fracture initiation
- (5) Separation at bondline along edge of specimen
- (6) Description of failure sequence

r. When test is complete, reverse order to "p" above.

s. Address DAR to print-out data.

### 7.3.2 Data Reduction Methods

There are two methods worth considering. The first is a general method that allows for highly nonlinear behavior. The second is a relatively easier method to use and is based upon the power law relationship. These data reduction methods, together with laboratory observations, lead to a recommended pattern for the testing.

#### 7.3.2.1 General Method of Data Reduction

This method permits the use of both linear and nonlinear behaviors, as described in Section 2. The J integral is derived from the test data using the following equations:

$$J = -2t^{-m} \frac{\partial}{\partial 2a'} \int_0^{-U} c(a,U) U^m dU \quad (6)$$

where: U is the point load tensile displacement of the test specimen  
t is the testing time.

The values of  $c(a,U)$  and m are obtained from crossplots at constant a and U according to the following relationship:

$$f = c(a,U) R^m \quad (7)$$

where f is a normalized pulling force and R is the crosshead speed

$$f = F/2B \quad (8)$$

The values of  $m$  and  $c(a,U)$  were obtained from linear regression analyses of  $\log f$  versus  $\log R$ , where  $R$  is limited to a narrow range (a factor of 25). Then, integration at constant time is followed by partial differentiation with respect to crack size to obtain  $J$ .

Hand-trimmed specimens of ANB-3066/SD-851-2 propellant-liner bond (numbered J-71 through J-82) were used to evaluate this method early in the program. These specimens were tested at 77°F at three crosshead speeds and five crack sizes.

Figure 22 contains a tabulation of the integral

$$\int_0^U c(a,U) U^m dU$$

as a function of  $U$  for the five test crack lengths. The partial derivative of that integral is also tabulated in Figure 22 along with the calculated  $J$  integral values.

To complete the analyses of these specimens, the observed critical displacements,  $U_c$ , are provided in Figure 23 along with the corresponding values of  $J_c$ . The test results are consistent, but are not considered to be accurate considering the preliminary nature of the specimen preparation and testing procedures.

#### 7.3.2.2 Power-Law Approach

This approach is more convenient to use and may be treated graphically or on a computer. It is an extension of Equation (7) and assumes a further separation of the variables to give the following power-law relation:

$$f = K(a) R^m U^n \quad (9)$$

FIGURE 22. J-INTEGRAL VALUES FOLLOWING THE GENERAL METHOD OF ANALYSIS\*

| U, in. | $\int_0^U c(a,U) U^m dU$ , in.-lb/in. |       |       |       |       | $-\frac{2a}{32a'} \int_0^U c(a,U) U^m dU$ |       | $J$ in. - lb/in. <sup>2</sup> |            |
|--------|---------------------------------------|-------|-------|-------|-------|-------------------------------------------|-------|-------------------------------|------------|
|        | $2a' = \text{inches}$                 |       |       |       |       |                                           |       | $R = 0.02$                    | $K = 0.50$ |
|        | 0.00                                  | 0.32  | 0.60  | 1.2   | 2.0   |                                           |       | $R = 0.10$                    | $K = 0.50$ |
| 0      | 0                                     | 0     | 0     | 0     | 0     | 0                                         | 0     | 0                             | 0          |
| 0.01   | 0.032                                 | 0.033 | 0.031 | 0.028 | 0.021 | 0.018                                     | 0.020 | 0.022                         | 0.026      |
| 0.02   | 0.135                                 | 0.134 | 0.128 | 0.117 | 0.083 | 0.080                                     | 0.080 | 0.090                         | 0.104      |
| 0.03   | 0.316                                 | 0.311 | 0.297 | 0.270 | 0.185 | 0.190                                     | 0.184 | 0.210                         | 0.242      |
| 0.04   | 0.579                                 | 0.566 | 0.542 | 0.489 | 0.334 | 0.354                                     | 0.334 | 0.382                         | 0.442      |
| 0.05   | 0.927                                 | 0.901 | 0.864 | 0.775 | 0.529 | 0.574                                     | 0.530 | 0.610                         | 0.702      |
| 0.06   | 1.363                                 | 1.317 | 1.265 | 1.131 | 0.777 | 0.854                                     | 0.776 | 0.892                         | 1.024      |
| 0.07   | 1.889                                 | 1.817 | 1.747 | 1.557 | 1.078 | 1.194                                     | 1.072 | 1.232                         | 1.418      |
| 0.08   | 2.506                                 | 2.400 | 2.310 | 2.054 | 1.430 | 1.596                                     | 1.416 | 1.626                         | 1.879      |
| 0.09   | 3.216                                 | 3.069 | 2.957 | 2.622 | 1.834 | 2.052                                     | 1.810 | 2.080                         | 2.392      |
| 0.10   | 4.019                                 | 3.823 | 3.687 | 3.253 | 2.283 | 2.592                                     | 2.256 | 2.592                         | 2.978      |
| 0.11   | 4.915                                 | 4.664 | 4.502 | 3.976 | 2.783 | 3.188                                     | 2.752 | 3.162                         | 3.634      |

\*  $m = 0.163$

FIGURE 23. CRITICAL VALUES OF THE J-INTEGRAL

| Specimen No. | Crosshead Speed, R, in./min | Crack Length, 2a', in. | U <sub>c</sub> , in. | J <sub>Ic</sub> , * lb/in. |
|--------------|-----------------------------|------------------------|----------------------|----------------------------|
| J-75         | 0.02                        | 0.32                   | 0.107                | 2.3                        |
| J-74         | 0.10                        | 0.32                   | 0.116                | 3.5                        |
| J-76         | 0.50                        | 0.32                   | 0.108                | 3.1                        |
|              |                             |                        | mean                 | 3.0                        |
| J-71         | 0.02                        | 0.60                   | 0.123                | 3.5                        |
| J-72         | 0.10                        | 0.60                   | 0.108                | 2.7                        |
| J-73         | 0.50                        | 0.60                   | 0.109                | 3.1                        |
|              |                             |                        | mean                 | 3.1                        |
| J-77         | 0.02                        | 1.2                    | 0.098                | 2.2                        |
| J-78         | 0.10                        | 1.2                    | 0.118                | 3.7                        |
| J-79         | 0.50                        | 1.2                    | 0.107                | 3.1                        |
|              |                             |                        | mean                 | 3.0                        |
| J-80         | 0.02                        | 2.0                    | 0.110                | 2.8                        |
| J-81         | 0.10                        | 2.0                    | 0.093                | 2.6                        |
| J-82         | 0.50                        | 2.0                    | 0.089                | 2.3                        |
|              |                             |                        | mean                 | 2.6                        |

where  $K(a)$  is constant for any given test, but is a function of crack size,  $a$ , while  $n$  is an empirical constant. The parameters,  $R$ ,  $U$  and  $M$  are defined as above.

The  $J$  integral derived from the power-law relation can be of either of the following forms:

$$J = \psi t^{-m} U^{1+m+n} \quad (10)$$

or

$$J = \psi R^m U^{1+n} \quad (11)$$

where

$$\psi = - \frac{2}{1+m+n} \left( \frac{\partial K(a)}{\partial 2a} \right)_{U,t} \quad (12)$$

Figures 24 through 27 illustrate this data reduction procedure for a set of tests conducted at 0°F. In this illustration there were 13 specimens tested at five different crack sizes and three cross-head speeds. With this number of specimens the results are reasonable.

The individual values of  $n$  were obtained from separate regression analyses of  $\log f$  versus  $\log U$ , which usually has correlation coefficients between 0.999 and 0.9999. Typical data are given in Figure 24. These values are averaged (a mean of 0.787 is illustrated) then used to force parallel curves through the data to obtain the individual  $A_0$  values. The quantity  $A_0$  is obtained from the relation

$$f = A_0 U^n \quad (13)$$

FIGURE 24. DETERMINATION OF (n) FROM SPECIMENS TESTED  
AT 0°F AT ATMOSPHERIC PRESSURE

| <u>Specimen</u> | <u>2a', inch</u> | <u>R, in./min</u> | <u>n</u> |
|-----------------|------------------|-------------------|----------|
| 5-10            | 0.2              | 0.10              | 0.817    |
| 5-12            | 0.4              | 0.02              | 0.773    |
| 5-12            | 0.4              | 0.10              | 0.838    |
| 5-50            | 0.4              | 0.50              | 0.905    |
| 5-30            | 0.8              | 0.02              | 0.840    |
| 5-11            | 0.8              | 0.10              | 0.781    |
| 5-29            | 0.8              | 0.50              | 0.784    |
| 5-31            | 1.2              | 0.02              | 0.772    |
| 5-26            | 1.2              | 0.10              | 0.780    |
| 5-28            | 1.2              | 0.50              | 0.770    |
| 5-49            | 1.6              | 0.02              | 0.740    |
| 5-27            | 1.6              | 0.10              | 0.776    |
| 5-56            | 1.6              | 0.50              | 0.758    |
| mean            |                  |                   | 0.787    |

FIGURE 25. DETERMINATION OF (m) FROM  $A_0$  VALUES TAKEN ON SPECIMENS  
TESTED AT 0°F AT ATMOSPHERIC PRESSURE

| <u>Specimen</u> | <u>2a', inch</u> | <u>R, in./min</u> | <u><math>A_0</math></u> | <u>m</u> |
|-----------------|------------------|-------------------|-------------------------|----------|
| 5-52            | 0.4              | 0.02              | 1108.0                  | 0.136    |
| 5-12            | 0.4              | 0.10              | 1436.0                  |          |
| 5-50            | 0.4              | 0.50              | 1715.0                  |          |
| 5-30            | 0.8              | 0.02              | 913.7                   | 0.157    |
| 5-11            | 0.8              | 0.10              | 1195.0                  |          |
| 5-29            | 0.8              | 0.50              | 1513.0                  |          |
| 5-31            | 1.2              | 0.02              | 872.5                   | 0.157    |
| 5-26            | 1.2              | 0.10              | 1070.0                  |          |
| 5-28            | 1.2              | 0.50              | 1448.0                  |          |
| 5-49            | 1.6              | 0.02              | 659.3                   | 0.203    |
| 5-27            | 1.6              | 0.10              | 940.8                   |          |
| 5-56            | 1.6              | 0.50              | 1267.0                  |          |
| mean            |                  |                   |                         | 0.163    |

FIGURE 26. DETERMINATION OF  $(\partial K(a)/\partial 2a')_{R,U}$  FROM SPECIMENS TESTED AT 0°F AT ATMOSPHERIC PRESSURE

| <u>Specimen</u> | <u>R, in./min</u> | <u>2a', inch</u> | <u>K(a)</u> | <u><math>(\partial K(a)/\partial 2a')</math></u> <sub>R,U</sub> |
|-----------------|-------------------|------------------|-------------|-----------------------------------------------------------------|
| 5-52            | 0.02              | 0.4              | 2099        | -657.5                                                          |
| 5-30            | 0.02              | 0.8              | 1729        |                                                                 |
| 5-31            | 0.02              | 1.2              | 1652        |                                                                 |
| 5-49            | 0.02              | 1.6              | 1248        |                                                                 |
| 5-10            | 0.10              | 0.2              | 2293        | -652.0                                                          |
| 5-12            | 0.10              | 0.4              | 2091        |                                                                 |
| 5-11            | 0.10              | 0.8              | 1739        |                                                                 |
| 5-26            | 0.10              | 1.2              | 1557        |                                                                 |
| 5-27            | 0.10              | 1.6              | 1370        |                                                                 |
| 5-50            | 0.50              | 0.4              | 1920        | -393.8                                                          |
| 5-29            | 0.50              | 0.8              | 1694        |                                                                 |
| 5-28            | 0.50              | 1.2              | 1622        |                                                                 |
| 5-56            | 0.50              | 1.6              | 1419        |                                                                 |
| Overall value = |                   |                  |             | -590.0                                                          |

FIGURE 27. DETERMINATION OF J-CRITICAL FROM SPECIMENS TESTED AT 0°F AT ATMOSPHERIC PRESSURE

| <u>Specimen</u> | <u>R, in./min</u> | <u>2a, inch</u> | <u><math>U_c</math>, inch</u> | <u><math>J_{Ic} = 605 \frac{-0.163 U_c^{1.95}}{t}</math></u> |
|-----------------|-------------------|-----------------|-------------------------------|--------------------------------------------------------------|
| 5-52            | 0.02              | 0.4             | -                             | mean = 3.82                                                  |
| 5-30            | 0.02              | 0.8             | 0.093                         |                                                              |
| 5-31            | 0.02              | 1.2             | 0.087                         |                                                              |
| 5-49            | 0.02              | 1.6             | <u>0.073</u>                  |                                                              |
| 5-10            | 0.10              | 0.2             | -                             | mean = 3.59                                                  |
| 5-12            | 0.10              | 0.4             | -                             |                                                              |
| 5-11            | 0.10              | 0.8             | 0.073                         |                                                              |
| 5-26            | 0.10              | 1.2             | 0.073                         |                                                              |
| 5-27            | 0.10              | 1.6             | <u>0.063</u>                  |                                                              |
| 5-50            | 0.50              | 0.4             | -                             | mean = 3.23                                                  |
| 5-59            | 0.50              | 0.8             | 0.050                         |                                                              |
| 5-28            | 0.50              | 1.2             | 0.068                         |                                                              |
| 5-56            | 0.50              | 1.6             | <u>0.053</u>                  |                                                              |
| Overall mean =  |                   |                 |                               | 3.56                                                         |

Thus, from Equation (9) we have

$$A_0 = K(a)R^m \quad (14)$$

The  $A_0$  values given in Figure 25 are used in regression analyses at constant crack size to obtain the separate values of  $m$ , which are also listed in Figure 25. These values of  $m$  are averaged (a mean of 0.163 is shown), then used to give parallel curves to obtain the individual values of  $K(a)$ . Then, all of the  $K(a)$  values reported in Figure 26 are used in a further regression analysis versus crack size ( $2a'$ ) to obtain the

$$\left( \frac{\partial K(a)}{\partial 2a'} \right)_{R,U}$$

value which equals -590 in this case.

Inserting the constants obtained above into Equation (10) gives

$$J = 605t^{-0.163}U^{1.95} \quad (15)$$

The exponent on  $U$  is very close to the ideal value of 2, which theoretically applies to elastic materials.

The constant rate form of the  $J$  integral is

$$J = 605R^{0.163}U^{1.79} \quad (16)$$

As in the general method,  $J$ -critical is obtained from  $U_c$ . The  $J$  values of this test are given in Figure 27, and yield an overall average value of 3.56 in.-lb/in.<sup>2</sup>.

### 7.3.2.3 Fracture Approach

Combining Equations (9) and (11) and taking the values at the critical point gives the following interesting relation for  $J_{IC}$ :

$$J_{IC} = \Psi \left[ \frac{f_c U_c}{K(a)} \right] \quad (17)$$

Within experimental error the quantity inside the bracket is a constant over the test matrix. Since  $\Psi$  is a constant, then  $J_{IC}$  is, also.

The constancy of  $f_c U_c / K(a)$  is illustrated in Figure 28. There the mean value is  $5.96 \times 10^{-3}$ . Inserting this quantity into Equation (17) and taking the previously used value of  $\Psi = 605$ , gave  $J_{IC} = 3.61 \text{ in.-lb/in.}^2$ . This value is almost identical to that given in Figure 27.

The real value of Equation (17) is that it provides an internal check on the critical value determinations.

### 7.3.3 Preferred Test Matrix

Analyses of various test results using the power-law method have demonstrated the need for:

- Test replications sufficient to eliminate or minimize the effects of bad data
- As wide a range as possible for the crack sizes (an upper limit of 1.6-in. was previously established)
- At least three deformation rates.

FIGURE 28. DETERMINATION OF THE CONSTANCY OF CRITICAL RATIO  
 $f_c U_c / K(a)$  FROM SPECIMENS TESTED AT  
 0°F AT ATMOSPHERIC PRESSURE

| Specimen | $2a'$ , in. | $R$ , in./min | $K(a)$ | $f_c$ | $U_c$    | $f_c U_c / K(a)$      |
|----------|-------------|---------------|--------|-------|----------|-----------------------|
| 5-10     | 0.2         | 0.10          | 2293   | ----- | SBF----- | -----                 |
| 5-52     | 0.4         | 0.02          | 2099   | ----- | SBF----- | -----                 |
| 5-12     | 0.4         | 0.10          | 2091   | ----- | SBF----- | -----                 |
| 5-50     | 0.4         | 0.50          | 1921   | ----- | SBF----- | -----                 |
| 5-30     | 0.8         | 0.02          | 1729   | 142.4 | 0.093    | $7.66 \times 10^{-3}$ |
| 5-11     | 0.8         | 0.10          | 1739   | 153.1 | 0.073    | $6.43 \times 10^{-3}$ |
| 5-29     | 0.8         | 0.50          | 1694   | 151.4 | 0.05     | $4.47 \times 10^{-3}$ |
| 5-31     | 1.2         | 0.02          | 1652   | 123.5 | 0.087    | $6.50 \times 10^{-3}$ |
| 5-26     | 1.2         | 0.10          | 1557   | 135.1 | 0.073    | $6.33 \times 10^{-3}$ |
| 5-28     | 1.2         | 0.50          | 1622   | 173.4 | 0.068    | $7.27 \times 10^{-3}$ |
| 5-49     | 1.6         | 0.02          | 1248   | 81.8  | 0.073    | $4.78 \times 10^{-3}$ |
| 5-27     | 1.6         | 0.10          | 1370   | 107.8 | 0.063    | $5.35 \times 10^{-3}$ |
| 5-56     | 1.6         | 0.50          | 1419   | 130.0 | 0.053    | $4.86 \times 10^{-3}$ |
|          |             |               |        | mean  |          | $5.96 \times 10^{-3}$ |

SBF - secondary bond failure

A test pattern like the following is recommended as a minimum effort. A reduced test matrix with half this number of tests was followed on this program.

| Crosshead Speed<br>in./min | Tests at Crack Size $2a'$ , in. |     |     |     |
|----------------------------|---------------------------------|-----|-----|-----|
|                            | 0.4                             | 0.8 | 1.2 | 1.6 |
| 0.01                       | x                               | xx  | xx  | x   |
| 0.10                       | x                               | xx  | xx  | x   |
| 1.00                       | x                               | xx  | xx  | x   |

x indicates a single test to be performed under the indicated conditions.

#### 8.0 BOND AGE-LIFE ASSESSMENT (CHEMICAL KINETIC METHOD)

The description of the chemical kinetic method for propellant/liner/insulation age-life prediction is taken directly from the paper presented by ASPC at the AIAA/SAE/ASME Fifteenth Joint Propulsion Conference, June 1979, at Las Vegas, Nevada.<sup>(7)</sup>

The kinetics of the chemical and diffusion processes that lead to grain (and motor) age-out are discussed below. These processes can be followed experimentally and in sufficient detail to define a chemical model of the aging process. A kinetic treatment of this model is then used to make long range predictions of the chemical changes that will occur in the grain and its adhesive interfaces.

(7) K. W. Bills, D. O. DePree, R. K. McCamey and R. M. Smith, "The Chemical Kinetic Approach to Service Life Prediction of Propellant Systems," Paper 79-1243 AIAA/SAE/ASME Fifteenth Joint Propulsion Conference, June 19-20, 1979, Las Vegas, Nevada.

## 8.1 KINETICS OF THE AGING PROCESSES

The various possible failure modes of a propellant/liner/insulation system are determined by the complex interplay of the chemical and physical changes which occur during aging. Our experience has shown that a predictive age life approach based on chemical kinetics can deal with a wide range of failure modes, some straightforward and some more subtle.

The chemical and physical changes which occur during aging dictate the degradation modes of the bonding system, as well as the propellant and insulation, and the particular failure mode of the motor can be affected by the changes occurring during aging. Current examples involving age-out of the bonding systems are found in the Minuteman motors.

In the case of the Minuteman III Stage II and III motors, the liner and propellant are subject to post-cure, so that the bond system appears to improve in the early stages of storage life, while the propellant hardening due to oxidative crosslinking (in propellant containing Phillips CTPB) makes the grain more subject to crack initiation. On continued aging, the liner softens due to hydrolytic attack, and the weakened liner is now the critical area of concern.

A more subtle life-limiting failure mode arises from the combination of liner degradation with a shrinkage of the boot caused by plasticizer loss. The failure mechanism is the lifting of the boot nipple due to a combination of boot shrinkage and the weakening of the liner bond. On ignition, a pressure differential between the cavity under the raised nipple and the volume behind the boot causes the boot to unbond further, exposing additional propellant surface to ignition.

A key factor in establishing both the mechanism and rate of the boot shrinkage process is the recognition of the migration processes occurring in the total propellant/liner/insulation system. The boot shrinkage is not caused by evaporation of dioctyl phthalate, the V-45 plasticizer, because under Minuteman operational conditions it is essentially nonvolatile. What actually occurs is the equilibration of the DOP plasticizer (from the insulation) with the Oronite 5 plasticizer (from the propellant), by crossmigration. Because of the far greater quantity of propellant than insulation, the plasticizer mix in the insulation becomes predominantly Oronite 6. This plasticizer, which has a wide boiling range, contains a high concentration of volatile fractions. These evaporate from the insulation at a rate higher than the diffusion rate replacing the loss. The overall effect is a net loss of plasticizer and a volumetric shrinkage of the boot which can be as great as 7%.

Although motor failure modes, as exemplified by Minuteman, can result from the complex interplay of several individual processes, it is important to note that the Minuteman experience shows that a predictive aging model can be developed by combining kinetic data from all the pertinent individual processes.

A flow diagram showing the various steps necessary for age rate evaluation prediction by the kinetic method is shown in Figure 29.

## 8.2 EVALUATION OF FAILURE MECHANISMS

The specific mechanisms of the associated physical and chemical changes, and the failure modes associated with them, must first be established.

This definition for each component is made through a review of the chemistry of the particular system, and in preliminary laboratory experimentation and aging studies, to identify the significant aging processes. The

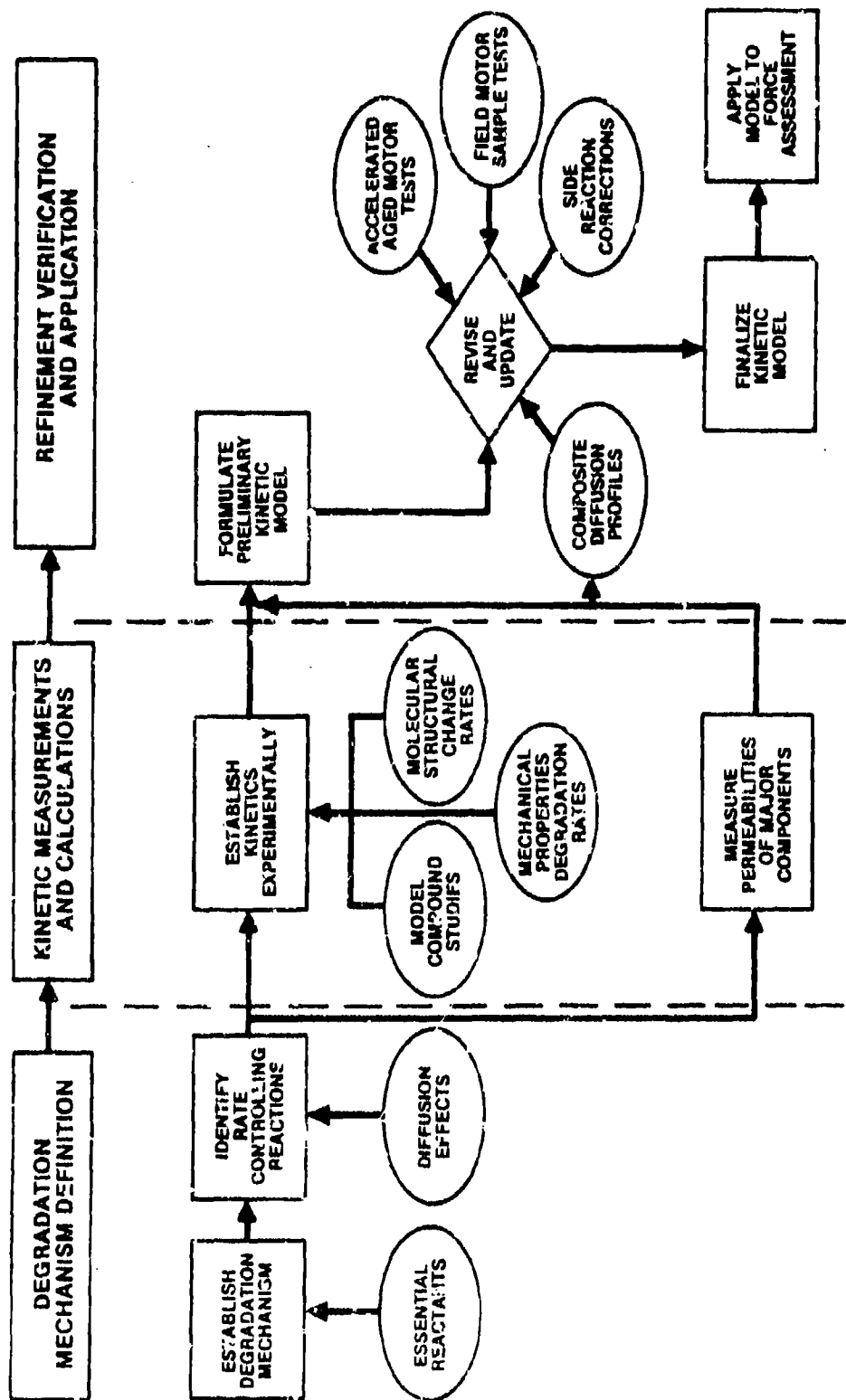


Figure 29. Logic Flow Diagram

significant aging processes may be chemical in nature, or may result from physical changes, such as the loss of a critical component by diffusion or evaporation. As previously indicated, in the case of the Minuteman III Stages II and III, the degradation of the liner was found to be the dominant degradation process which, when combined with a second process, the shrinkage of the boot, represented the primary life-limiting failure mechanism. The rates of both of these processes were measured and extrapolated using kinetic methods. The liner degradation mechanism was identified, by laboratory experimentation and IR and NMR analysis of specimens subjected to various aging environments, to be caused by hydrolytic attack on the amide linkages. The boot shrinkage mechanism was found by determining the plasticizer compositional changes in composite specimens with storage time.

### 8.3 KINETIC MEASUREMENTS

Once the various possible mechanisms have been identified by the preliminary studies, the kinetics of the processes may now be measured in storage tests over a range of temperatures. The kinetic measurements include the determination of the permeabilities of any diffusible rate controlling reagents as well as the use of independent studies including model compounds, molecular structural change rates and mechanical property change rates. These studies provide data for determination of the individual rate constants, activation energy data, and diffusion profiles that are necessary for calculation of the overall degradation rate and its extrapolation to operational conditions.

Model compound kinetic measurements provide a necessary confirmation of the degradation mechanism and the proper identification of the rate controlling reactions. A vital feature in proving the validity of the method is that the activation energies calculated from the model compound studies were verified by two additional kinetic measurements using techniques closely related to the critical parameters of component performance. These are,

(1) molecular structural analysis in which the rate of change of the polymeric backbones crosslink density, calculated from swelling ratios using the Flory-Rehner equation, is determined as a function of temperature, and  
 (2) the rate of change of the previously established critical mechanical property as a function of temperature. This comparison proved that in the Minuteman case, the latter, simpler techniques could then be used to follow the aging changes and establish the overall kinetics. The determination of the reaction order and the rate constant using the appropriate rate equation for the reaction order obtained at two storage temperatures provides the basis for calculation of the activation energy. The activation energy is calculated using the following integrated form of the Arrhenius equation:

$$\ln \frac{k_2}{k_1} = \frac{\Delta H_a (T_2 - T_1)}{R T_2 T_1} \quad (18)$$

$k_1$  = Rate constant at absolute temperature  $T_1$

$k_2$  = Rate constant at absolute temperature  $T_2$

$R$  = Ideal gas constant per mole or per unit concentration

$\Delta H_a$  = Activation energy per mole or unit concentration of reactant

In practice, a minimum of three temperatures are used in the accelerated aging studies with lowest temperature as close as practicable to the operational conditions. This permits determination of activation energies from a variety of temperature pairs to identify any changes in activation energy with temperature, should they exist.

In the Minuteman study, storage conditions comprised temperatures from 110 to 210°F at relative humidities of 0 to 100%. A total of 95 separate rate constants were calculated from model compound studies, from changes in crosslink density, and changes in bond tensile strengths of liner specimens

(nent and composite). Activation energies calculated from all the combinations were in general agreement. The first order rate data obtained from crosslink density measurements and bond tensile at standard rates were found to be essentially identical up to a storage time of two half-lives. This important finding validates the use of mechanical properties as well as changes in crosslink density in determining the kinetics of aging. A typical example is the first-order plot shown in Figure 30 of the logarithm of crosslink density ( $\rho$ ) and bond tensile ( $\sigma_m$ ) versus storage time at 150°F.

#### 8.4 SELECTION OF ACCELERATED AGING CONDITIONS

It is essential to select aging conditions of temperature and humidity which can be directly related to the motor operational environment. Our experience shows that our predictive age life approach can deal not only with the thermal environment, but also with changes caused by diffusion of atmospheric moisture and oxygen through the propellant/liner/insulation bond system.

Aging conditions must be selected with care to provide test data which can be accurately correlated to motor behavior in the operational environment. In the Minuteman LRSLA work we found that specific requirements are to select the aging conditions to provide (1) early indications of degradation trends, (2) a broad enough temperature range to identify reaction thresholds or rate crossovers and provide confidence in extrapolation of the data to ambient conditions, (3) the effect of diffusion and concentration of moisture on reaction rate, and (4) a high level of confidence in the activation energy.

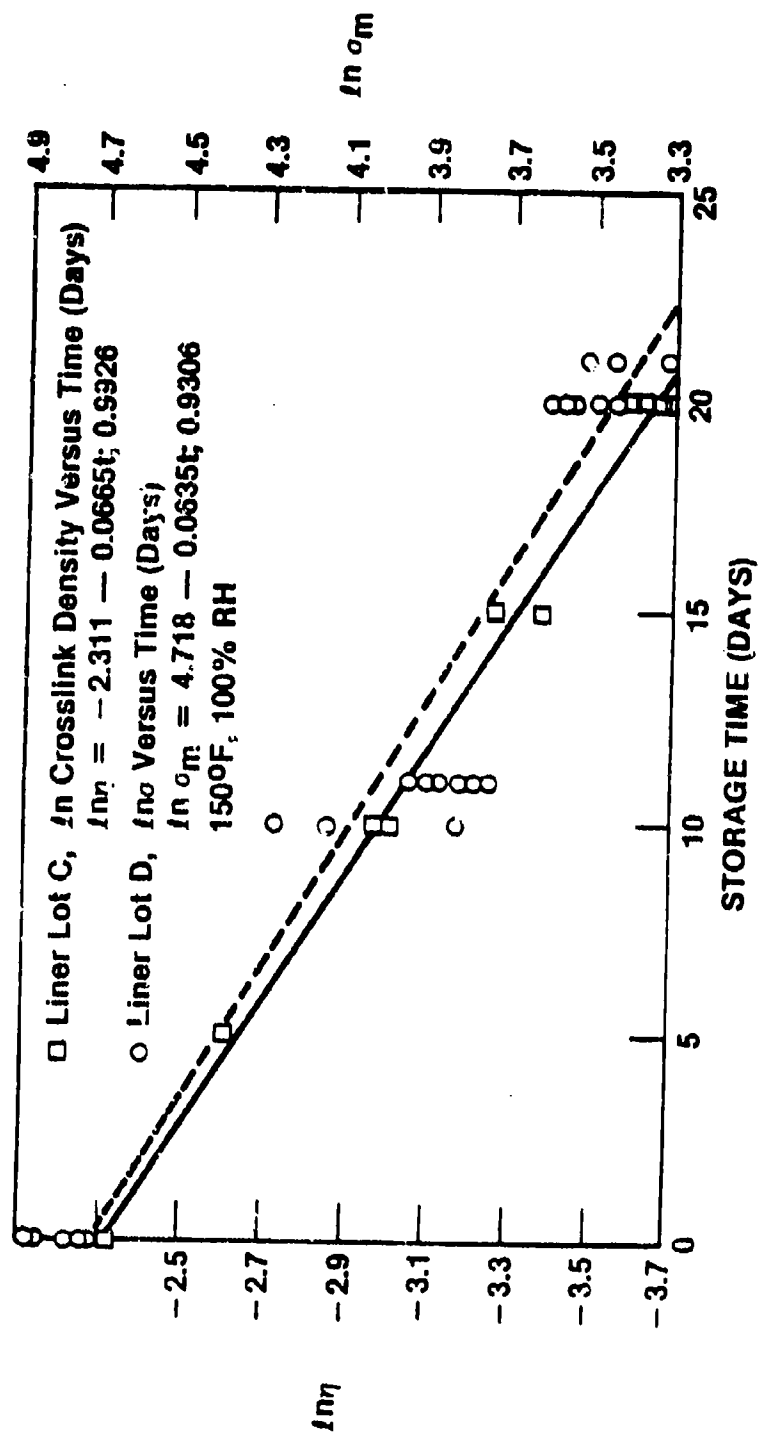


Figure 30. Kinetic Determination (First Order)

## 8.5 PREDICTIVE MODELING

As noted above, the kinetic treatment is capable of dealing with the effects of diffusion of atmospheric moisture (liner hydrolytic degradation), as well as the effects of temperature. This allows for the inclusion, in the predictive model, of a wide variety of kinetic relationships involving both chemical and physical changes.

The comprehensive predictive aging model which was developed for the LRSLA liner studies can be adapted to take into account (1) the thermal effect, (2) the diffusion of reactive ingredients (moisture or oxygen from the atmosphere and/or reactive migratory species from or into neighboring components), (3) the effect of the migration of plasticizers, and (4) any other modifying reactions such as post-cure.

The ultimate aging model for a particular propellant/liner/insulation system is obtained by combining all the measure rate constants and activation energies for the various processes into a computer program for making service life predictions. (In principle a set of nomographs could alternatively be devised.) This approach can encompass all degradation-related processes, including thermal, oxidative, hydrolytic, and diffusion-related effects.

The procedures used to develop individual parts of the model are described below with examples from the Minuteman study. Using these data obtained from the aging studies, the rate constant using the appropriate reaction order is determined. Plots of regression lines relating rate constant to relative humidity are drawn for each temperature. Typical regression plots obtained in the Minuteman study are presented in Figures 31 and 32.

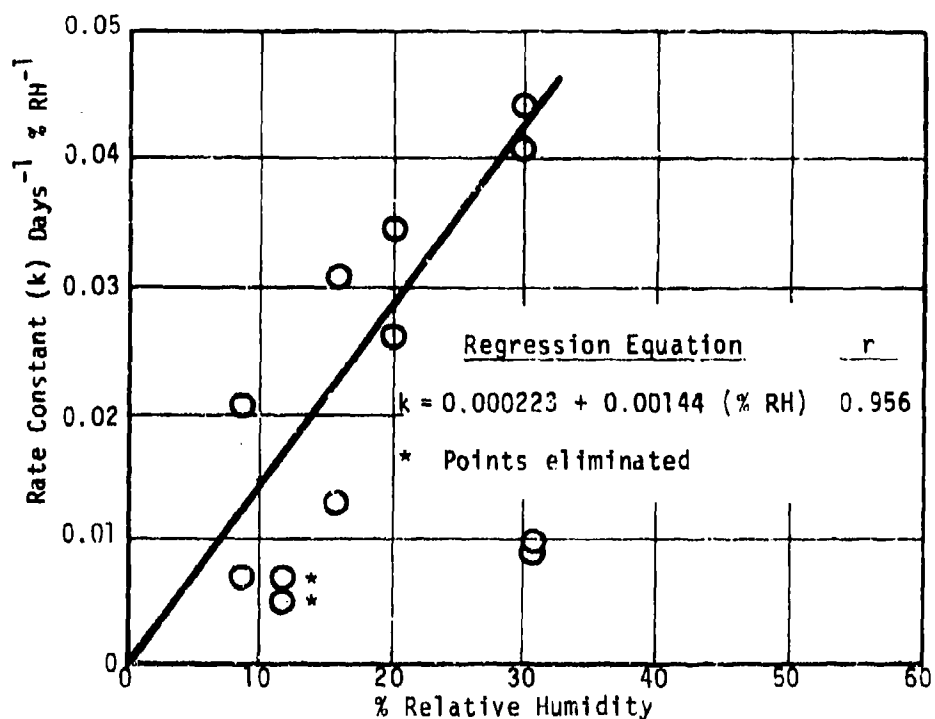


Figure 31. Liner Degradation Rate Constants (k) vs Humidity at 165°F for all Studies to Date

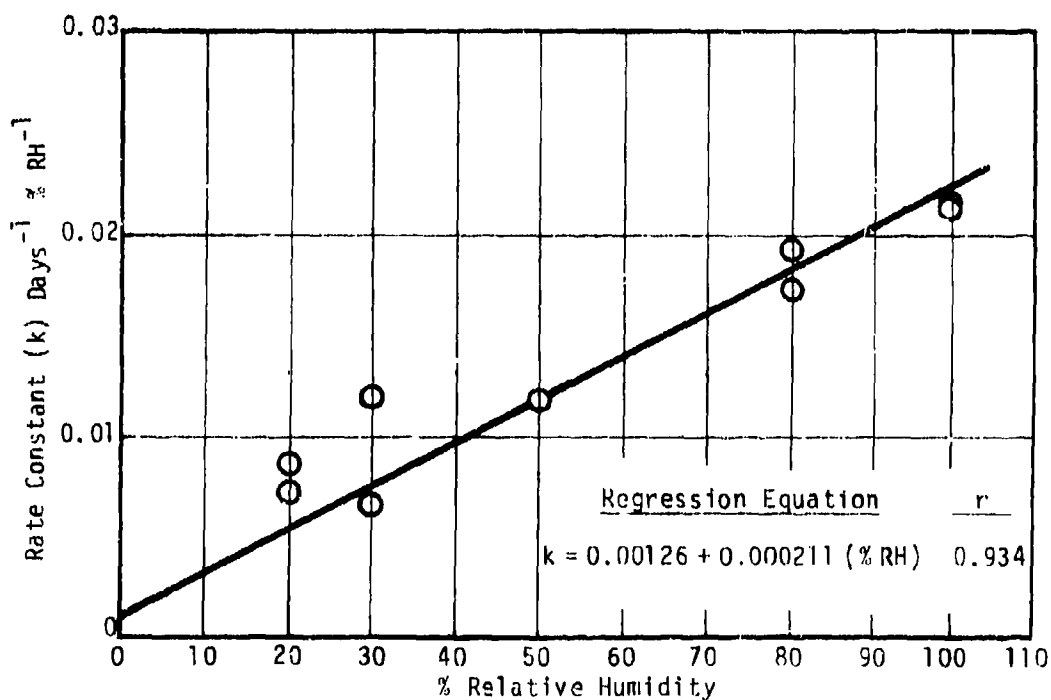


Figure 32. Liner Degradation Rate Constants (k) vs Humidity at 135°F for all Studies to Date

Figure 33 is a weighted Arrhenius plot of  $\ln k$  versus  $T^{-1}$  of all the data used to obtain a mean activation energy which in the Minuteman liner case is 19.29 kcal mole<sup>-1</sup>. The weighting at each temperature was proportional to the number of data points used in deriving the regression lines. As indicated, the points fall quite close to the regression line.

If diffusible reagents are involved in the degradation process, the effect of reagent concentration on the reaction rate must be determined. If the reagent concentration is rate-controlling, the change of concentration due to diffusion at operational conditions must be determined and a concentration profile established.

The permeability, solubility and diffusion constants of the various components of the motor through which the reagent must pass are determined by standard analytical techniques; for example, in the case of moisture, the cup method may be used. Using these constants and the thicknesses of the various components in the path, the reagent concentration profile is readily determined using the analogous computer program designed for heat transfer. Profiles of the change of migrating reagent concentration (in this case, moisture) in the Minuteman boot-liner interface, are shown in Figure 34.

#### 8.6 MATHEMATICAL TREATMENT FOR CONSECUTIVE COMPETING REACTIONS

Secondary processes such as post cure, chemical rearrangement or oxidative crosslinking, may modify the shape of the overall degradation curve. The three mentioned above are generally processes that occur either initially (post cure or chemical rearrangement) or at the end of the aging process (oxidation after the stabilizer has become exhausted). In these instances the projection to operational conditions can be modified to account for these competing reactions by treating the processes consecutively.

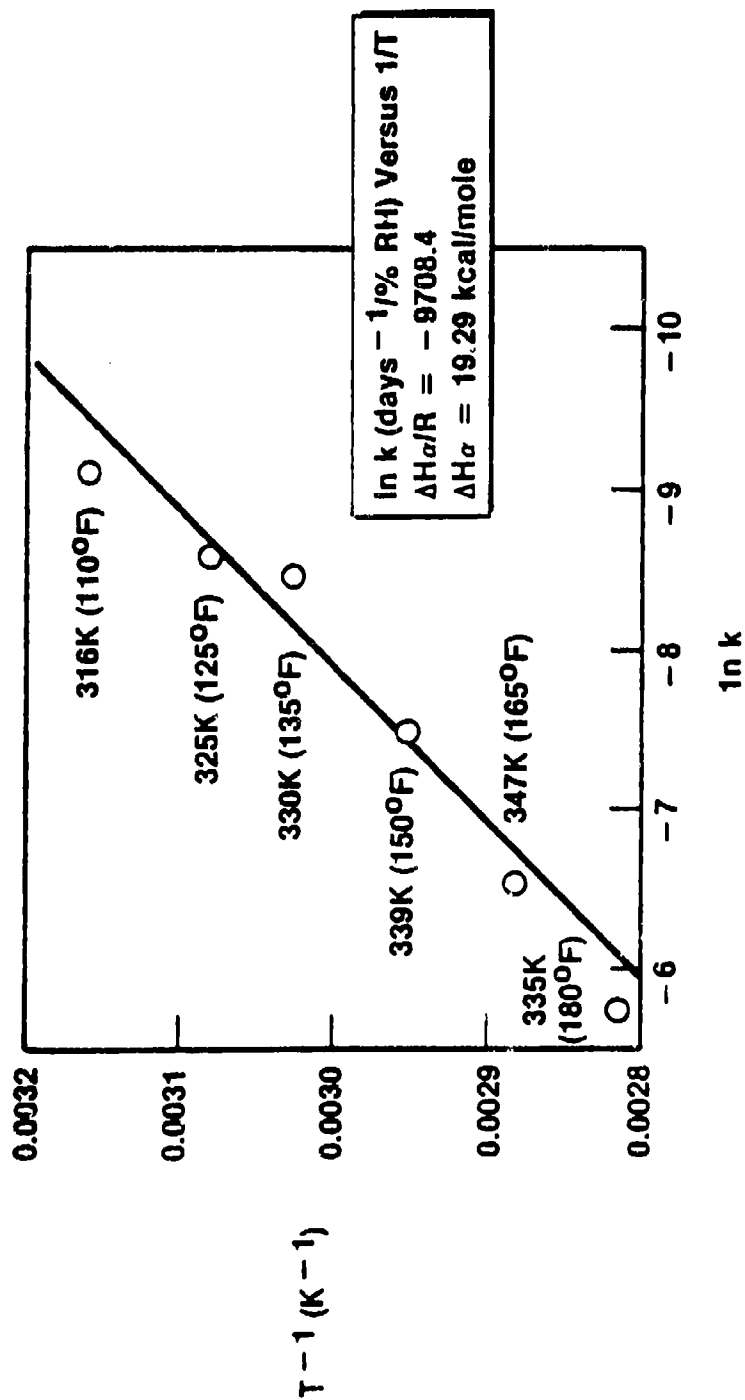
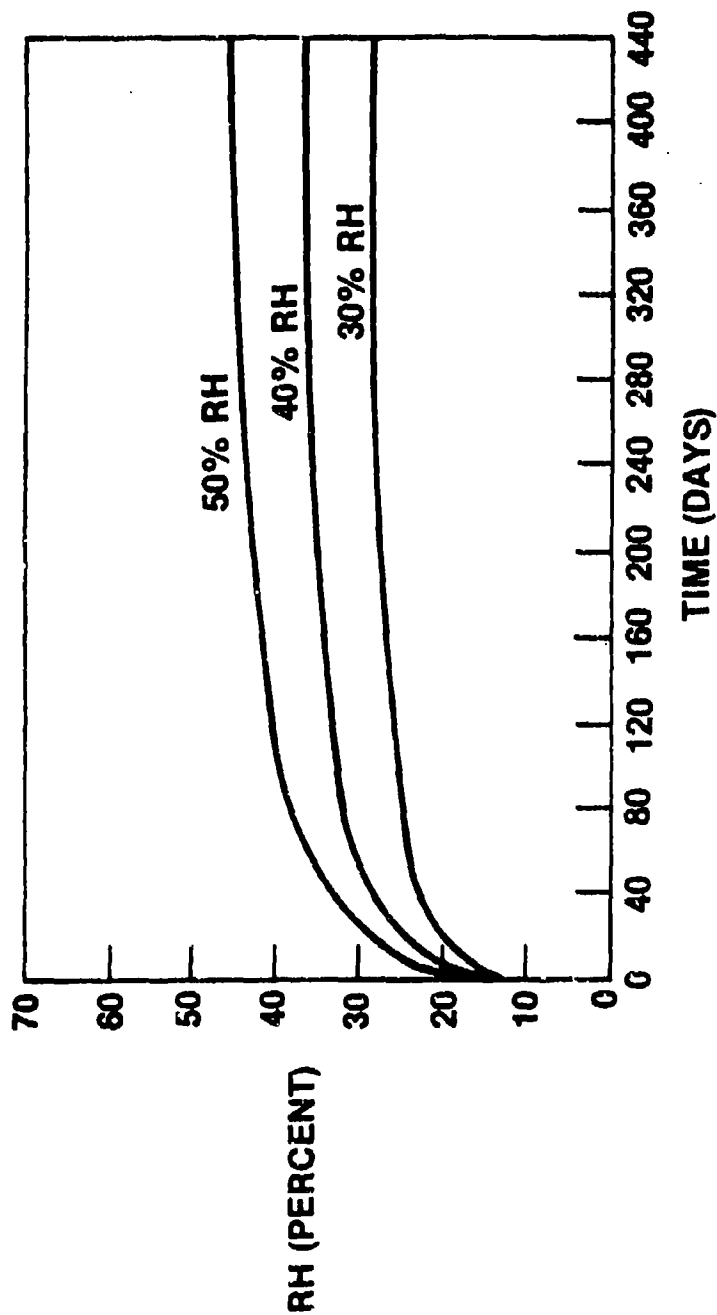


Figure 33. Activation Energy Determination (Arrhenius Relationship)



**Fully Developed Computer Programs Can Be Used To  
Develop Moisture Profiles For Any Surface**

Figure 34. Moisture Profiles

The post cure reaction found in the Minuteman liner study opposes the hydrolytic softening process and gives an overall projection curve with an initial increase in tensile stress (Figure 35).

The MAPO-cured propellant, ANB-3005, on the other hand, undergoes an initial softening due to thermal cleavage of aziridine linkages. This is followed by a rehardening of an oxazoline linkage.

The tensile strength at each storage temperature exhibited an initial decrease with time for ANB-3005 propellant. After reaching a certain minimum value the tensile strength began to increase and in fact at 180°F nearly returned to the initial value in 24 weeks.

An attempt was made to approximate the observed behavior with a chemical kinetic model which could be used to extrapolate to additional times and temperature. A proposed model is a consecutive-type chemical reaction as shown in Equation (19):



where [A] represents the concentration of the initially formed crosslinks, [B] represents the noncrosslinked degradation products, and [C] represents the concentration of new crosslinks formed from the noncrosslinked degradation products,  $k_1$ , represents the rate constant associated with the degradation of A and  $k_2$  represents the rate constant for the formation of C from B. The tensile strength at any time is assumed to be proportional to the sum of [A] and [C].

The simplest model is to assume that both reactions are first order. The solutions of the differential rate expressions have been solved and are shown in Equations (20) and (21):

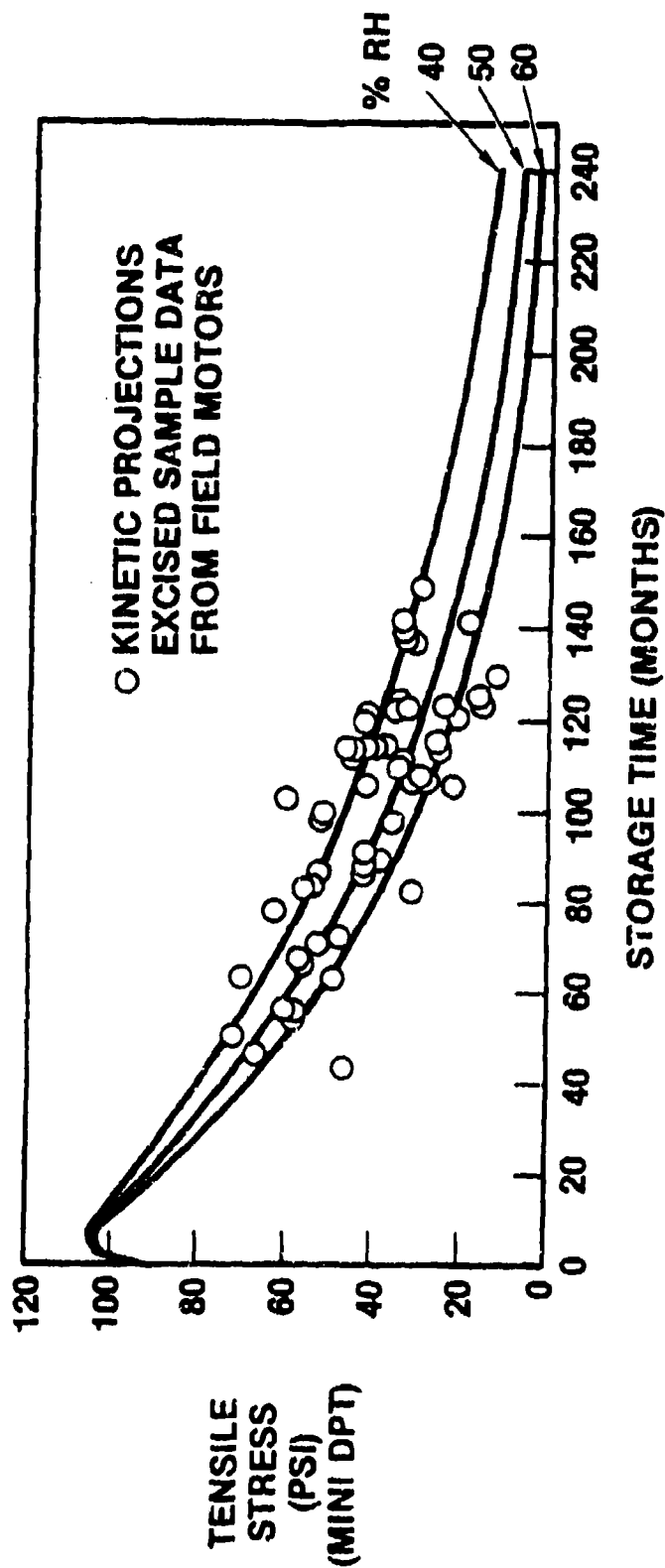


Figure 35. Projection Curve from Minuteman Operational Motors Validate the Kinetic Aging Projection (70°F)

$$[A] = [A]_0 e^{-k_1 t} \quad (20)$$

$$[C] = [A]_0 \left\{ 1 - \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right\} \quad (21)$$

The value of  $[A]_0$  can easily be read from the plots and the initial value of the rate of decrease of tensile strength with time yields a fairly good approximation for  $k_1$ . The value of  $k_2$  must then be found by successive approximation until the desired fit is obtained. The assumptions are, (1) that both  $A \rightarrow B$  and  $B \rightarrow C$  are strictly first order reactions and that no other reactions occur, and (2) that the tensile strength is linearly proportional to both types of crosslinks. For the 150°F data, the reaction forming new crosslinks "C" did not appear to be as complete as at 180°F. The approximate rate constants backed out from the plotted data are presented in Figure 36.

| <u>Temperature, °F</u> | <u><math>k_1</math> weeks<sup>-1</sup></u> | <u><math>k_2</math> weeks<sup>-1</sup></u> |
|------------------------|--------------------------------------------|--------------------------------------------|
| 180                    | 2.7                                        | 0.27                                       |
| 150                    | 2.27                                       | 0.10                                       |
| 110                    | 0.033                                      | 0.028                                      |
| 80                     | 0.010                                      | 0.020                                      |

Figure 36. First Order Rate Constants for Softening and Rehardening of ANB-3005 Propellant

Arrhenius plots of the above rate constants were made to determine the activation energies for the two reactions. The rate constant,  $k_1$ , has about double the activation energy as that for  $k_2$ . The activation energies enable extrapolation of the rate constants to other temperatures. The data were utilized to project aging behavior at 70°F, both with and without a third hydrolytic degradation reaction, i.e.,



Inclusion of this hydrolytic reaction results in a more complicated differential equation of [C] shown in Equation (23):

$$\frac{d[C]}{dt} = k_2 [B] - k_3 [C] \quad (23)$$

Since [B] may be expressed as a function of time only, the solution of [C] is most conveniently obtained by numerical methods such as the Runge-Kutta method.<sup>(8)</sup> First order equations of this type are easily performed by programmable calculators.

#### 8.7 MATHEMATICAL TREATMENT FOR SIMULTANEOUS COMPETING REACTIONS

Some processes such as the boot shrinkage in the second- and third-stage Minuteman motors are involved in the simultaneous interaction of more than one mechanism. The mathematical treatment shown below for a simultaneous process involving two mechanisms is illustrated in Figure 37. The excellent correlation between the mathematical model developed for boot shrinkage with the data obtained under accelerated aging conditions is shown in Figure 37. The sharp bend in the curve is typical of those processes in which the two simultaneous reactions are vastly different in activation energy.

$$\% \text{ Change} = [A]_0 (1 - e^{-k_1 t}) + [B]_0 (1 - e^{-k_2 t}) + \dots [N]_0 (1 - e^{-k_n t}) \quad (24)$$

(8) Techniques of Chemistry, Vol VI, Investigation of Rates and Mechanisms of Reactions, Ed. E. S. Lewis, John Wiley and Sons, New York, 1974.

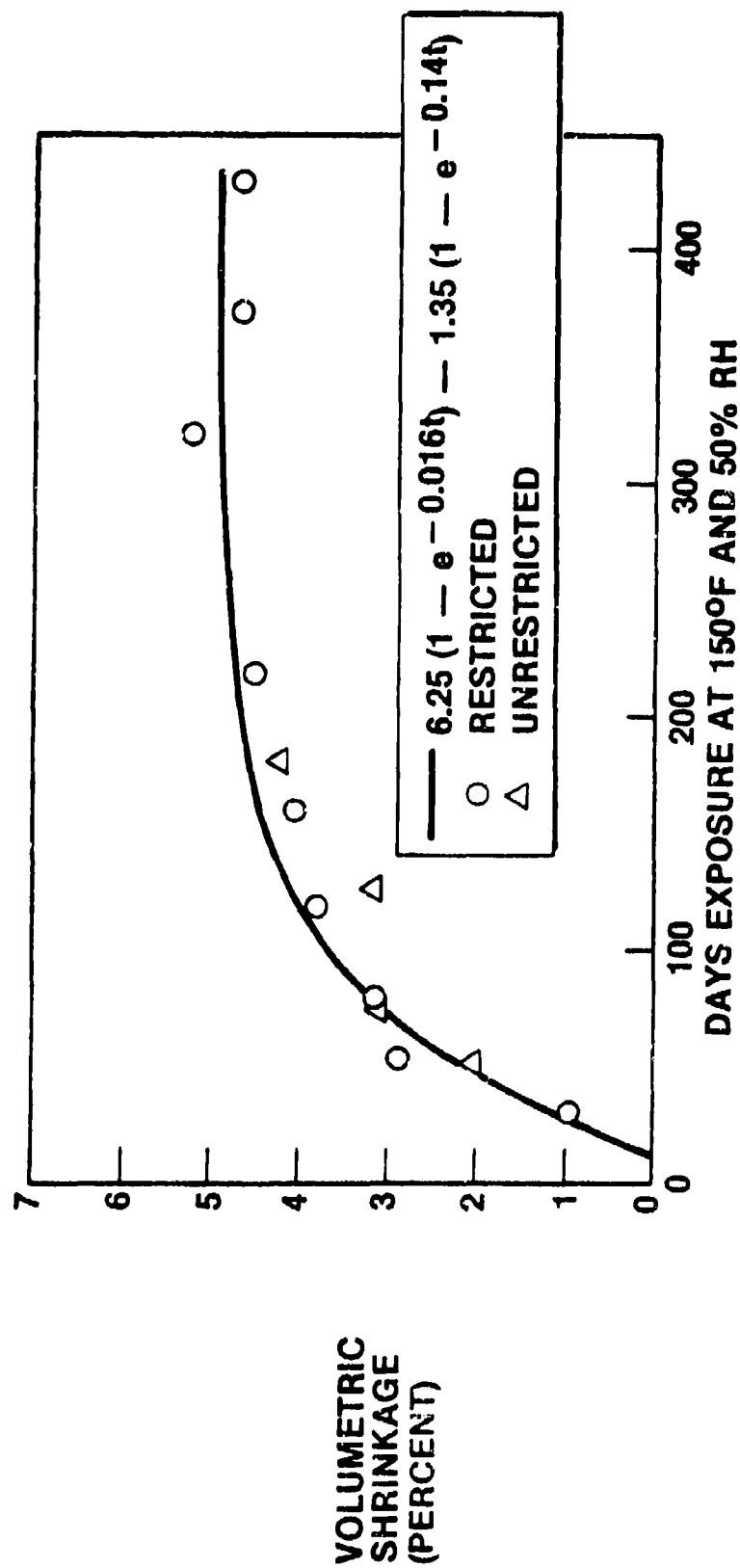


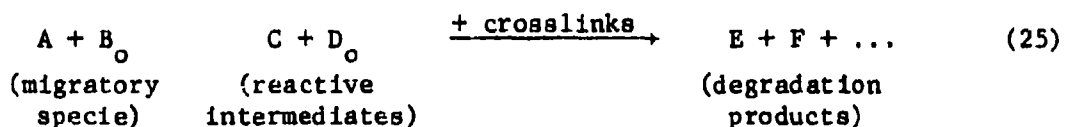
Figure 37. Kinetics - Two Simultaneous Processes

The final projection is made using a point-by-point calculation of the component condition based on the migrating reagent concentration, applying the concentration profile previously determined.

## 8.8 EXPANSION OF THE MODEL TO HANDLE REACTIVE MIGRANTS

The aging process may be further complicated by the introduction of additional diffusion processes, such as that of a diffusible oxidative degradation product from an energetic plasticizer.

The degradation of these components in the presence of such materials as water and oxygen must first be fully defined. An example of this type of process has been found to be responsible for case insulation separation in the Polaris A3 Stage I motor. In the Polaris motor the nitroplasticizer used in the propellant migrates to the insulator where it contacts oxygen and moisture from the atmosphere which has diffused into the insulator system through the fiberglass case. The hydrolytic and oxidative degradation of the plasticizer gives rise to a variety of products including acidic material such as nitric, formic, and acetic acids which have been shown to readily degrade the lightly crosslinked V-57 bond between the insulator and case. The logic diagram for dealing with the kinetics of these various influencing processes is shown in Figure 38. The overall kinetics can be handled mathematically by treating the process as a series of consecutive competing reactions:



The accuracy of the kinetic treatment may be verified by determining the accuracy in predicting the degradation in accelerated aged motors or analog motors. Comparison of predictions with the actual data in aged analog specimens

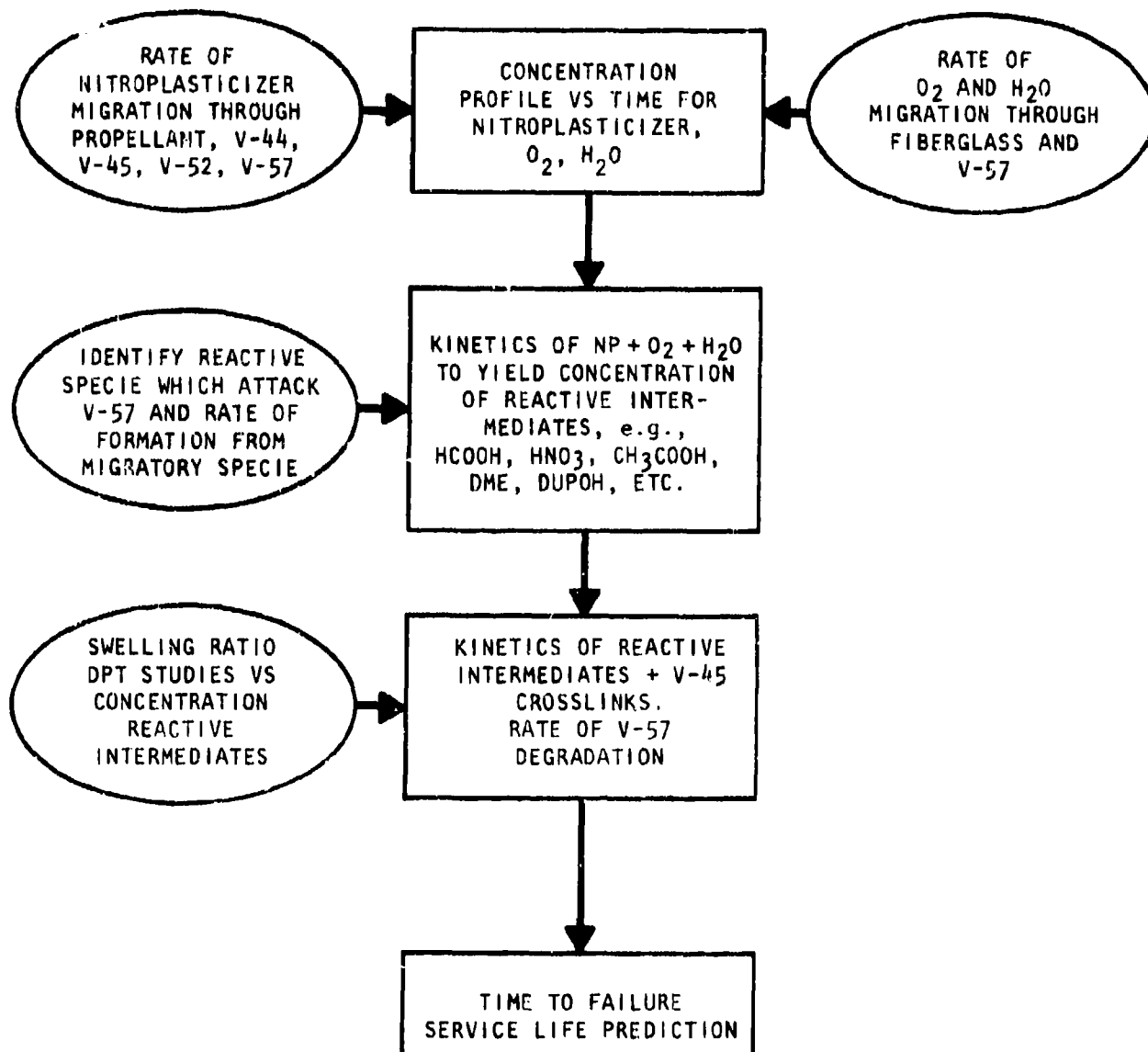


Figure 38. Logic Diagram for Case-Insulation Bond Age Prediction  
Polaris A3 Motor

from the aging program may also be made. The proper design of the analog to accurately represent the motor condition is essential for validation. The best verification, of course, is through comparison of the projection at operational conditions with field motor data, and this was done in the LRSLA work.

The accuracy of our method in predicting the condition of the liner in aged motors was confirmed in the Minuteman liner study by both the accurate prediction of the rate of liner degradation in accelerated aged motors, and by comparison of the prediction for operational conditions with data obtained from excised samples from motors in the field. In the former case, 94% degradation of the liner was predicted for a Stage III motor stored 92 days at 135°F, 80% relative humidity; the actual condition was found to be 96% degradation. A Stage II motor stored for 72 days under the same conditions was also predicted to be 94% degraded; analysis indicated 93% degradation. The excellent agreement between the predicted rate of degradation at the average silo environment of 70°F, 50% RH with the excised sample analysis, is shown in Figure 35.

Having established the critical degradation path and rate, the age limit for the motor, once the storage history is defined, is then determined by the point at which the component degrades to the limit established from structural and/or from ballistic analysis.

Although the discussion has dealt primarily with a chemical degradation process, we have shown that the same kinetic treatment is equally applicable to the rate of change induced by nonchemical processes such as hardening due to loss of plasticizer, or shrinkage due to the loss of a volatile constituent. In the Minuteman LRSLA program the kinetics of boot shrinkage was determined, as well as the kinetics of surface hardening. Again, projection of the rates of change to operational conditions can be made using the Arrhenius equation.

## 9.0 USE OF THE MANUAL--HYPOTHETICAL EXAMPLES

In order to aid the liner formulator in the use of this manual, two examples of its application in the development of a liner to meet a hypothetical set of conditions are presented. The first is a demanding set of conditions requiring the use of many special approaches, the second is an undemanding set of conditions requiring few special techniques.

### Example A

Step 1. We will assume for this hypothetical example that we are developing a liner for a tactical motor application. The first step is to set up a work sheet which lists the imposed constraints for the specific application, as shown in the first column in Figure 39. The order of listing follows that presented in the Liner Formulation Guide, Figure 2, page 4, of the manual.

Step 2. Having identified the specific constraints of this motor application, the next step is to turn to the Liner Formulation Guide, Figure 2, page 4, of the manual, and opposite the constraints we will list the section numbers for the specific approaches indicated.

Step 3. The selected approaches indicated are then reviewed, using the descriptions presented in the manual (Section 4.0, Formulation Approaches, pages 5-15). The possible specific approaches are then outlined in column three of the work sheet (Figure 39) and selections narrowed by elimination of nonapplicable techniques based on the total requirements. For example, the polymer selection may be narrowed by the low and high temperature requirements or by migration considerations. Certain bond enhancement techniques cannot be used because of the low temperature storage constraint.

| <u>Specific Constraints (Step 1)</u>              |                                                                            | <u>Section Numbers</u><br><u>Applicable Approaches (Step 2)</u> |  | <u>Summary and Review of Applicable Techniques (Step 3)</u>                                                                                                                                   |
|---------------------------------------------------|----------------------------------------------------------------------------|-----------------------------------------------------------------|--|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| A. PROPELLANT FORMULATION SELECTED                |                                                                            |                                                                 |  |                                                                                                                                                                                               |
| 1.                                                | PEG/IPDI Binder                                                            | 4.1, 4.2                                                        |  | General description of binder and bond types. Branched polymers, low polarity polymer, chemically-stable polymers, high crosslink level, low polarity, high density fillers and substituents. |
| 2.                                                | Energetic Plasticizer                                                      | 4.1.2, 4.1.5, 4.1.6, 4.3.2, 4.2                                 |  |                                                                                                                                                                                               |
| 3.                                                | Liquid Burning Rate Catalyst                                               | 4.1.2, 4.1.4 or 4.1.5, 4.3.2, 4.2                               |  |                                                                                                                                                                                               |
| B. INSULATION SELECTED                            |                                                                            |                                                                 |  |                                                                                                                                                                                               |
| 1.                                                | IEH-120 (EPDM Binder-Asbestos, Carbon Black, and Ammonium Sulfate Fillers) | 4.1, 4.2                                                        |  |                                                                                                                                                                                               |
| 2.                                                | Shell Flex-790 Plasticizer (Petroleum Fraction)                            | 4.1.2, 4.1.4 or 4.1.5, 4.3.2, 4.2                               |  | High polarity polymer.*                                                                                                                                                                       |
| 3.                                                | Tackifier - Wing Tack-95 (Natural Resin)                                   | 4.1.2, 4.1.4, 4.3.2, 4.2                                        |  |                                                                                                                                                                                               |
| 4.                                                | Moisture                                                                   | 4.1.2, 4.2.1, 4.3.1                                             |  | Low polarity polymer.                                                                                                                                                                         |
| C. MOTOR ENVIRONMENT                              |                                                                            |                                                                 |  |                                                                                                                                                                                               |
| 1.                                                | Uncontrolled Humidity                                                      | 4.1.2, 4.3.2, 4.2                                               |  | Antioxidants<br>Branched chain systems, unsaturated chains, antioxidants, oxidatively-resistant polymers, low aromaticity.                                                                    |
| 2.                                                | Ten-Year Service Life Minimum                                              | 4.4.1, 4.4.2                                                    |  |                                                                                                                                                                                               |
| 3.                                                | -65 to 145°F Operational Range                                             | 4.4.1, 4.1.2, 4.1.3, 4.1.5, 4.1.7, 4.1.8, 4.4                   |  |                                                                                                                                                                                               |
| 4.                                                | No Extreme Temperature: Air Carry Requirement                              | -                                                               |  |                                                                                                                                                                                               |
| 5.                                                | Cycling Capability                                                         | 4.1.1, 4.1.2, 4.1.3, 4.1.5, 4.2, 4.4                            |  |                                                                                                                                                                                               |
| D. DESIGN REQUIREMENTS                            |                                                                            |                                                                 |  |                                                                                                                                                                                               |
| 1.                                                | High Rate Bond<br>Shear >60 psi (at 1000 psi imposed pressure)             | 4.2.1, 4.2.2, 4.2.3                                             |  | Reactive sites, low contact angle with propellant.                                                                                                                                            |
| 2.                                                | Low Rate Bond<br>Tensile >100 psi at 0.2 in./min                           | 4.2.1, 4.2.2, 4.2.3                                             |  |                                                                                                                                                                                               |
| E. PROCESSING - SPIN/TROWEL METHOD OF APPLICATION |                                                                            |                                                                 |  |                                                                                                                                                                                               |
|                                                   |                                                                            | 4.5.1, 4.5.2, 4.5.3                                             |  | Pot life modification, viscosity modification, thixotropic agents.                                                                                                                            |

\* Not compatible with low temperature requirements.

Figure 39. Liner Development Work Sheet No. 1

Step 4. Using the approaches selected, the following outline then describes the binder systems, curatives, fillers, etc., to be tested in the liner development program. The polymer systems and curing agents meeting the approach requirements are selected from the listing in Section 4.1, Figure 4.

#### Approach Principles

#### Potential Candidates

##### 1. Binder Selection

Highly branched  
Low polarity  
Chemically stable  
High crosslink level  
Thermally stable  
Oxidatively stable  
Nonaromatic

- a. Combinations of dimer and trimer acids cured with ERL-4221 or butanediol diglycidylether or compatible aliphatic epoxide curing agents. Chromium (AMC-2) or iron octoate catalyst.
- b. GTRO/IPDI  
FeAA catalyst

##### 2. Plasticizer

None

##### 3. Filler

High density

Heavy metal oxides or metal silicates.\*

##### 4. Antioxidants

Dual system to eliminate hydroperoxides and also provide free radical traps.

Aromatic amine types and hindered phenols.\*\*

##### 5. Processing

Use of thixotropic filler

Clays or silicas.\*\*

\* All nonmetallic structures are low density.

\*\* State-of-the-art selections most commonly used.

### Example B

For Example B we will assume that we are developing a liner for a strategic missile which will operate under a narrowly controlled environment with a propellant containing no highly energetic or reactive species.

The steps again are the same. Steps 1 through 3 are summarized in the work sheet shown in Figure 40.

Step 4. As indicated from the work sheet, no migration barriers are required and the narrow operational temperature range makes it unnecessary to use many of the special technical approaches. Essentially all of the polymer systems, fillers, etc., can be used and only their inherent thermal, i.e., age stability, need be a consideration for selection and the use of a good dual antioxidant combination is desirable. The processing constraint indicates the need for viscosity control and close attention to catalysis for the proper viscosity build-up. The selection of polymer, crosslinking system, should be made on the basis of bond enhancement. Again, all of the bond enhancement techniques including the introduction of reactive sites may be used.

| <u>Specific Constraints (Step 1)</u>              | <u>Applicable Approaches (Step 2)</u> | <u>Summary and Review of Applicable Techniques (Step 3)</u>                                                    |
|---------------------------------------------------|---------------------------------------|----------------------------------------------------------------------------------------------------------------|
| A. PROPELLANT FORMULATION SELECTED                |                                       |                                                                                                                |
| 1. HTPB/IPDI                                      | 4.1, 4.2                              | General description of polymer and bond types.<br>Structurally compatible polymer, oxidatively stable polymer. |
| 2. No Potential Migrants                          | 4.1.2, 4.1.3, 4.2                     |                                                                                                                |
| B. INSULATION SELECTED                            |                                       |                                                                                                                |
| 1. V-45                                           | 4.1, 4.2                              | Low polarity polymer, high crosslink level, high density filler.                                               |
| 2. DOP Plasticizer                                | 4.1.2, 4.1.4 or 4.1.5, 4.3.2          |                                                                                                                |
| 3. Softening Agent                                | 4.1.2, 4.1.4, 4.3.2                   |                                                                                                                |
| C. MOTOR ENVIRONMENT                              |                                       |                                                                                                                |
| 1. Humidity Controlled<br>(Hermetic Weather Seal) | 4.1.2, 4.2                            | Antioxidants                                                                                                   |
| 2. Age Life, 10-year Minimum                      | 4.4.1, 4.4.2                          |                                                                                                                |
| 3. Temperature - Narrow Limits 60-110°F           | 4.1.2, 4.2                            |                                                                                                                |
| D. DESIGN CONSTRAINTS                             |                                       |                                                                                                                |
| 1. High Rate Bond                                 | 4.2.1, 4.2.2, 4.2.3                   | Branched chain systems, chemically-reactive sites, low constant angle with propellant                          |
| 2. Low Rate Bond                                  | 4.2.1, 4.2.2, 4.2.3                   |                                                                                                                |
| E. PROCESSING - ELECTRONIC SPRAY                  | 4.5.1                                 | Pot life modification.                                                                                         |

Figure 40. Liner Development Work Sheet No. 2

# GLOSSARY

|                   |                                                                                                  |
|-------------------|--------------------------------------------------------------------------------------------------|
| AMC-2             | Cordova Chemical proprietary epoxy catalyst                                                      |
| Arneel OD         | Oleyl nitrile                                                                                    |
| ATC-3             | Cordova Chemical proprietary epoxy-anhydride catalyst                                            |
| BITA              | Butylane imine derivative of trimesic acid, trimesoyl-1-(2-ethyl) aziridine                      |
| BNO               | Hydroxyl ethyl ester of carboxy-terminated polybutadiene acrylonitrile copolymer                 |
| Catocene          | Liquid ferrocene derivative                                                                      |
| CTPB              | Carboxy-terminated polybutadiene                                                                 |
| DDI               | Dimer diisocyanate                                                                               |
| Dimer Acid        | Dimerized 18 - carbon chain unsaturated fatty acid                                               |
| DOP               | Diocetyl phthalate                                                                               |
| Epon-828          | Epichlorohydrin/bisphenol A-type epoxy resin                                                     |
| ERL-4221          | Carboxylate bridged <u>bis</u> -cyclohexene oxide                                                |
| ERL-0500,<br>0510 | Tri-functional epoxide                                                                           |
| FeAA              | Ferric acetyl acetate                                                                            |
| FEFO              | Bis(2-fluoro-2,2-dinitroethyl)formal                                                             |
| GTRO              | Glycerol triricinoleate                                                                          |
| HDI               | Hexamethylene diisocyanate                                                                       |
| HTPB              | Hydroxy-terminated polybutadiene                                                                 |
| IPDI              | Isophorone diisocyanate                                                                          |
| MAPO              | Tris-1-(2-methyl) aziridinyl phosphine oxide                                                     |
| MNA               | Methyl nadic anhydride; methyl endo-cis-cyclo-2,2,1-5-heptene-2,3-dicarboxylic anhydride isomers |
| MY-720            | 4,4'-Tetraglycidyl diamino diphenyl sulfone                                                      |
| Oronite 5, 6      | Saturated polybutadiene                                                                          |
| PBAN              | Polybutadiene-acrylic acid-acrylonitrile terpolymer                                              |

# GLOSSARY (cont)

|             |                                                      |
|-------------|------------------------------------------------------|
| T-12        | Dibutyl tin dilaurate                                |
| TDI         | 2,4-Toluene diisocyanate                             |
| TEAT        | Tris-2-ethyl aziridinyl triazine                     |
| Thixin E    | Modified 1-hydroxy stearin                           |
| TMAT        | Tris-2,4,6-2-methyl-1-aziridinyl-1,3,5-triazine      |
| TMETN       | Trimethyolethane trinitrate                          |
| TP-4040     | Polyoxpropylene oxide adduct of trimethylol propane  |
| Trimer Acid | Trimierized 18 - carbon chain unsaturated fatty acid |
| V-44        | Nitrile rubber insulations                           |
| V-45        |                                                      |
| V-52        |                                                      |
| V-57        |                                                      |