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CHEMICAL STRUCTURAL AGING EFFECTS

LOCKHEED PROPULSION COMPANY
REDLANDS, CALIFORNIA

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TECHNICAL REPORT AFRPL-TR-72-64

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SECTION II

SUMMARY

The following summarizes the work completed, and the results obtained during the initial program period 14 June 1971 to 15 April 1972.

1. PHASE I, PROPELLANT AND SAMPLE PREPARATION

To assure that the ANB-3066 propellant to be used as the test vehicle would be representative of Minuteman III production, propellant originating from a Thiokol 300-gallon Minuteman 3rd Stage production line mix was procured, and the material was processed into ½- and 1-gallon specimens for storage at 30°F (propellant bank), and 70, 115, and 145°F (Phase II Surveillance). Analysis of randomly selected specimens showed that the propellant was uniform within the limits of analytical errors.

A ten-gallon mix of KCl analog propellant was prepared at LPC using Minuteman specification ingredients in order to elaborate upon the effect of AP upon ANB-3066 propellant aging.

A ten-gallon mix using a special aziridine curative analog propellant failed to cure, and its preparation will be repeated.

All specimens prepared for surveillance purposes were sealed in cans under dry nitrogen atmosphere. Elapsed time between propellant processing (Thiokol) and canning was ten weeks.

2. PHASE II, PILOT EXPERIMENTS

Aging was initiated upon bulk samples (½-1-gallon) at 70, 115, and 145°F, and using both unstrained and strained (3 and 5%) specimens for determining both thermally and stress induced aging events. Results and conclusions to date are as follows:

(1) Uniaxial tensile and crosslink density measurements show that ANB-3066 propellant undergoes significant hardening during early storage at moderate temperatures (approximately three weeks at 115°F or two weeks at 145°F). Storage under three percent strain appears to counteract this effect. Changes in gel and degree of swell also occur but their meaning relative to the crosslink density effects is not as yet clear.

(2) Multiple internal reflectance infrared analysis promises to be a suitable analytical technique for determining changes in cure linkage concentration in propellant. Using a new Perkin-Elmer Model 180 spectrophotometer, sufficiently well defined bands for the ester, carboxyl, amide I (carbonyl) and amide II (NH deformation) moieties are obtained to enable the determination of cure linkage participation in post cure and degradation processes. By comparing this information with the measured rate

FOREWORD

This is the first Interim report issued under Contract No. FO4611-71-C-0025, "Chemical Structural Aging Effects", covering the period 14 June 1971 through 1 April 1972. This contract is assigned to Lockheed Propulsion Company, Redlands, California, and is monitored by Robert Biggers, Air Force Rocket Propulsion Laboratory, Edwards, California.

Technical effort under the program is under the supervision of Drs. W. E. Baumgartner (Manager, Chemistry Department), G. E. Myers (Program Manager), and A. B. Tipton (Project Engineer). Contributing to the program are W. G. Stapleton, W. E. Heikkila, J. D. Leggett, and J. A. Hammond. Dr. Harold Leeming of Leeming Associates is participating on the program on a consulting basis to aid in the definition of interaction between chemical states and mechanical behavior. A specific aspect of the problem, namely the definition of the physico-chemical parameters that control propellant tear behavior, has been assigned (subcontract) to Dr. W. G. Knauss, California Institute of Technology.

Publication of this report does not constitute Air Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas

Robert A. Biggers (MKPB)
Project Engineer

ABSTRACT

This program is determining the individual chemical rate processes that govern the aging of ANB-3066 propellant, and it is attempting to establish the effect of chemical (compositional) changes upon the system's mechanical response to enable better utilization of accelerated surveillance test data.

Chemical changes, as they occur in the propellant under the influence of time, temperature and stress are determined by reflectance infrared techniques, measurement of sol content and crosslink density, off-gas analysis, and analysis (CPC/infrared) of sol extracts. The system's changes in chemical composition, as evidenced by these measurements, are then related to corresponding changes in mechanical response as determined by uniaxial tensile measurements and measurement of creep compliance and tear propagation.

The report outlines the experimental matrix to be followed, and it quotes initial data obtained with ANB-3066 propellant and an analog propellant containing KCl in substitution for ammonium perchlorate.

TABLE OF CONTENTS

Section		Page
I	INTRODUCTION	1
	1. THE GENERAL PROBLEM IN MOTOR SERVICE LIFE PREDICTION	1
	2. ACCELERATED SURVEILLANCE TESTING	3
	3. PROGRAM OBJECTIVES AND SCOPE	5
	4. PROGRAM APPROACH	5
	a. Phase I, Propellant and Sample Preparation	5
	b. Phase II, Pilot Experiments	7
	c. Phase III, Detailed Aging Studies	7
	d. Phase IV, Data Analysis and Correlations	7
	e. Restrictions	8
	5. GENERAL APPROACH	8
	6. CHEMISTRY OF AGING IN ANB-3066 PROPELLANT	8
	a. Aging Reactions	8
	b. Methods of Measurement	10
	c. Use of Model Systems	11
	7. CHARACTERIZATION OF CHANGES IN PROPELLANT MICROSTRUCTURE AND MACRO BEHAVIOR	12
	8. AGING CONDITIONS AND SCHEDULE	12
II	SUMMARY	14
	1. PHASE I, PROPELLANT AND SAMPLE PREPARATION	14
	2. PHASE II, PILOT EXPERIMENTS	14
III	RESULTS AND DISCUSSION	16
	1. PHASE I, PROPELLANT AND SAMPLE PREPARATION	16
	2. PHASE II, PILOT EXPERIMENTS	16

TABLE OF CONTENTS (Continued)

Section		Page
	a. Phase II Test Schedule	16
	b. Analytical Methods and Results	16
	c. Mechanical Property Changes	29
APPENDIX		36
1.	PREPARATION OF PROPELLANT FOR AGING AND TESTING	36
2.	CHEMICAL ANALYSIS METHODS	36
	a. Multiple Internal Reflectance Infrared Analysis (MIR)	36
	b. Off-Gas Analysis	36
	c. Sol/Gel and Swell	39
	d. Crosslink Density	39
3.	MECHANICAL PROPERTIES MEASUREMENT	40
	a. Creep Compliance	40
	b. Tear Rate Measurement	43
	c. Uniaxial Tensile Measurements	43
REFERENCES		45

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ILLUSTRATIONS

Figure		Page
1	Elements of Service Life Prediction	2
2	Schematic Illustration of Complexity of Reactions in Propellant	4
3	Schematic Illustration of Dependence of Mechanical Parameters upon Various Reactions in Propellant	4
4	Service Life Prediction	6
5	Underlying Processes/Parameters for Service Life Prediction from Accelerated Surveillance	9
6	Reflectance Infrared Spectra of Unaged and Aged KCl Analog Propellant	19
7	Effect of Aging upon Percent Gel, Swell and Crosslink Density for ANB-3066	24
8	Analytical GPC for Binder Ingredients (0.5% concentration)	27
9	Analytical GPC for Extract from ANB-3066 Propellant	27
10	Analytical GPC for Extract from KCl Analog Propellant	28
11	Creep Behavior of Zero Time KCl Analog Propellant (5 psi load)	30
12	Creep Behavior of Zero Time KCl Analog Propellant (30 psi load)	30
13	Creep Behavior of Zero Time ANB-3066 Propellant (5 psi load)	31
14	Creep Behavior of Zero Time ANB-3066 Propellant (60 psi load)	31
15	Tear Propagation of Zero Time ANB-3066 (0.75" initial end cut in 3" x 1" x 0.1" strip)	32
16	True Stress vs Strain for Zero Time ANB-3066 (Minithin specimens. Note stress scale displacement for upper two sets of curves.)	33
17	True Stress vs Strain for Aged ANB-3066 (Minithin specimens. Note stress scale displacement for upper two sets of curves.)	34

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ILLUSTRATIONS (Continued)

Figure		Page
18	ANB-3066 Aging Blocks	37
19	OGA Samples	37
20	OGA Demountable Cell	38
21	Schematic Diagram of Perkin-Elmer TMS-1 Thermo-mechanical Analyzer	41
22	Typical Compression Modulus Curve for Swollen ANB-3066	42
23	Creep Measurement Apparatus	42
24	Tear Rate Apparatus	44
25	Minithin Tensile Specimen	44

TABLES

Table		Page
I	PHASE II SCHEDULE	17
II	PHASE II TEST FREQUENCY	18
III	OFF-GAS ANALYSIS CELLS FOR FIRST TEST POINT	21
IV	AVERAGE GAS EVOLUTION RATE	21
V	SOL/GEL, SWELL, AND CROSSLINK DENSITY	22
VI	EFFECT OF STRAIN UPON SOL/GEL, SWELL AND CROSSLINK DENSITY OF ANB-3066	25
VII	GPC MOLECULAR WEIGHTS OF SOL EXTRACTS	28
VIII	UNIAXIAL TENSILE PARAMETERS OF ANB-3066	35

GLOSSARY

$D(t)$	Creep compliance
E_o	Initial tensile modulus
$E(t)$	Stress relaxation modulus
f_s	Sol fraction of binder
$G(t)$	Shear modulus
GPC	Gel Permeation Chromatography
MIR	Multiple Reflectance Infrared
OGA	Off-Gas Analysis
RSD	Relative standard deviation
TMA	Thermo Mechanical Analyzer
γ_c, γ_a	Cohesive and adhesive fracture energy at a finite rate of crack growth
Γ_c, Γ_a	Cohesive and adhesive fracture energy at equilibrium
σ_b/ϵ_b	Uniaxial tensile stress/strain at rupture
σ_m/ϵ_m	Uniaxial tensile stress/strain at maximum stress
$\sigma_y/\ _y$	Uniaxial tensile stress/strain at yield
ν/V	Crosslink density (moles of network chains/cc)

SECTION I

INTRODUCTION

1. THE GENERAL PROBLEM IN MOTOR SERVICE LIFE PREDICTION

A problem that continues to face the solid propulsion community rests with the continuing difficulties in making accurate long range predictions of solid rocket motor service life. The problem impacts the assessment of the reliability of the operational systems and the forecasting of replacement requirements, and it is therefore of large concern to the services. It equally impacts the projected assessment of service life capability of new systems under development, a problem that affects the propulsion systems developers and manufacturers.

At present the methods of service life prediction which are given most credence are those based upon actual testing of aging motors. This includes the Navy "Type-Life" procedure with its exposure of motors to somewhat accelerated surveillance conditions, and it includes the combined cumulative damage and statistical procedures developed for Minuteman. Although these approaches continue to undergo refinements (instrumented motors, cut-away motors, improved statistical analyses) in an effort to enable reliable predictions beyond a two year time span, they inherently constitute empirical approaches, and as such carry inherent limitations.

On the more chemical side, the propellant developers continue to rely heavily upon accelerated surveillance testing involving both propellant itself, or analog motors, to arrive at shelflife predictions on the basis of temperature extrapolations. This approach too was found to be quite limited in its usefulness as repeated experience revealed serious discrepancies between predicted (by extrapolation) and experienced (under field conditions) service life.

The difficulties rest with the fact that the propellant under varying time/temperature/stress histories undergoes complex chemical changes that translate into changes in mechanical response resulting in a feed-back situation that frustrates any effort toward arriving at long term service life predictions on the basis of linear data extrapolation.

To arrive at significantly improved means of motor service life prediction numerous elements must be considered in their mutual interaction (Figure 1). These elements may be grouped into three major areas.

(1) The motor specific failure criteria.

(2) The stress history that will be experienced by critical propellant volume fractions within the motor, taking into account that the stress/strain behavior of the propellant will change non-uniformly as a function of time-temperature and local stress levels (feed-back situation).

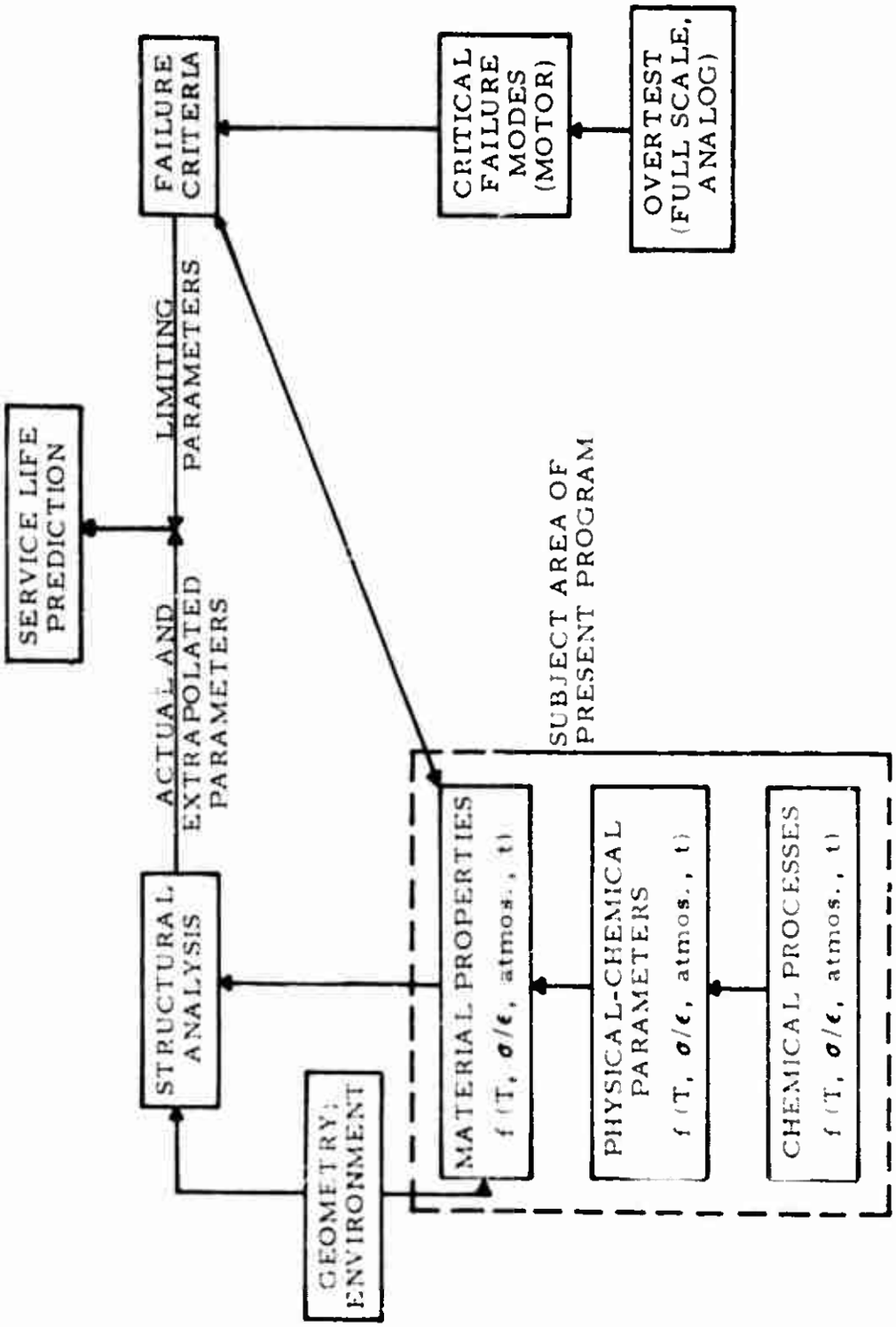

Figure 1 Elements of Service Life Prediction

(3) The chemical and physical rate processes (aging, fatigue) that underly and control the rate of change in the propellant's (unit volumes) mechanical response.

This program deals exclusively with the third element, namely the isolation and definition of the critical chemical rate processes that constitute "aging", and the definition of the interrelation between changes in the propellants' (notably the binders') chemical structure and resulting changes in mechanical response. In doing so, the program is expected to provide a better theoretical and experimental basis for conducting accelerated surveillance tests.

2. ACCELERATED SURVEILLANCE TESTING

Accelerated surveillance testing, as practiced to-day, suffers from the following major shortcomings:

(1) The complexity of the chemical changes taking place in propellant makes it highly unlikely that a single activation energy would be applicable over the temperature range of interest. Thus, a simple linear temperature extrapolation would be invalid, as illustrated in Figure 2.

(2) Each chemical process may be expected a priori to exert a different quantitative effect upon a given propellant mechanical parameter. This is illustrated schematically in Figure 3.

(3) It is recognized further that the chemical rate processes accelerate not only with temperature, but that rate acceleration can also be caused by mechanical energy input. This equality between thermal and mechanical energy input has been demonstrated for numerous polymer systems. For example, Zhurkov showed that the time to failure of polymer samples under constant stress can be stated by Equation 1

$$t_f = t_o \exp \frac{E - \gamma\sigma}{RT} \qquad (1)$$

where t_f is the observed time to failure, t_o a constant relating to vibration frequencies, E the activation energy for the purely thermal process of bond breakage, σ the applied stress and γ an energy concentration factor. The statement implies that in order to extrapolate accelerated surveillance test data and to apply them toward motor service life predictions, one must account not only for likely differences in the activation energy for the purely thermal processes, but that one must additionally make corrections for the stress enhancement. This stress enhancement will vary throughout a motor grain, and it will vary with the motor's environmental history.

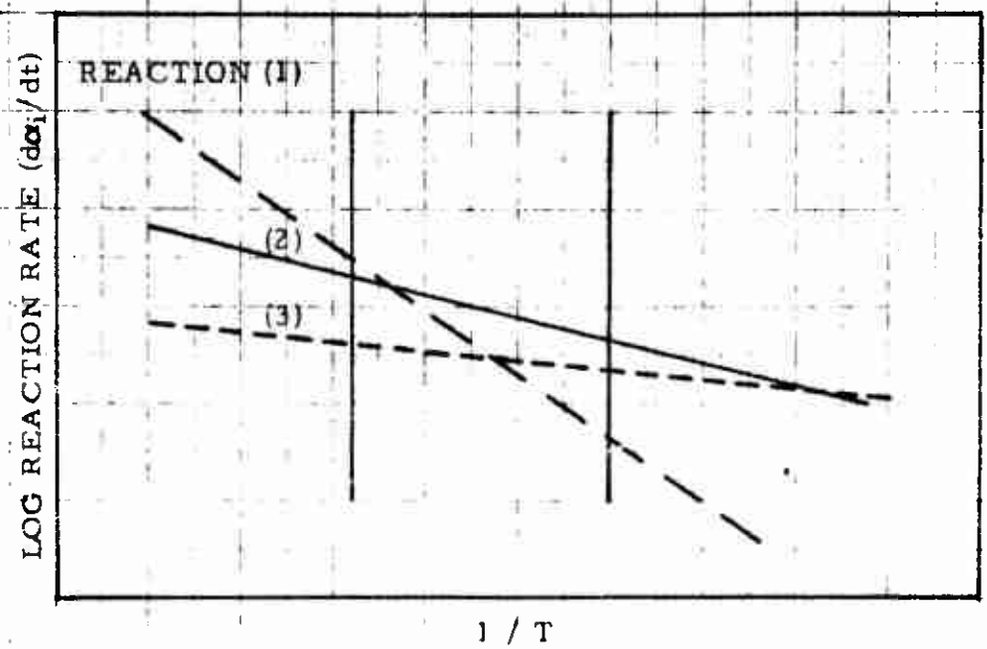

Figure 2 Schematic Illustration of Complexity of Reactions in Propellant

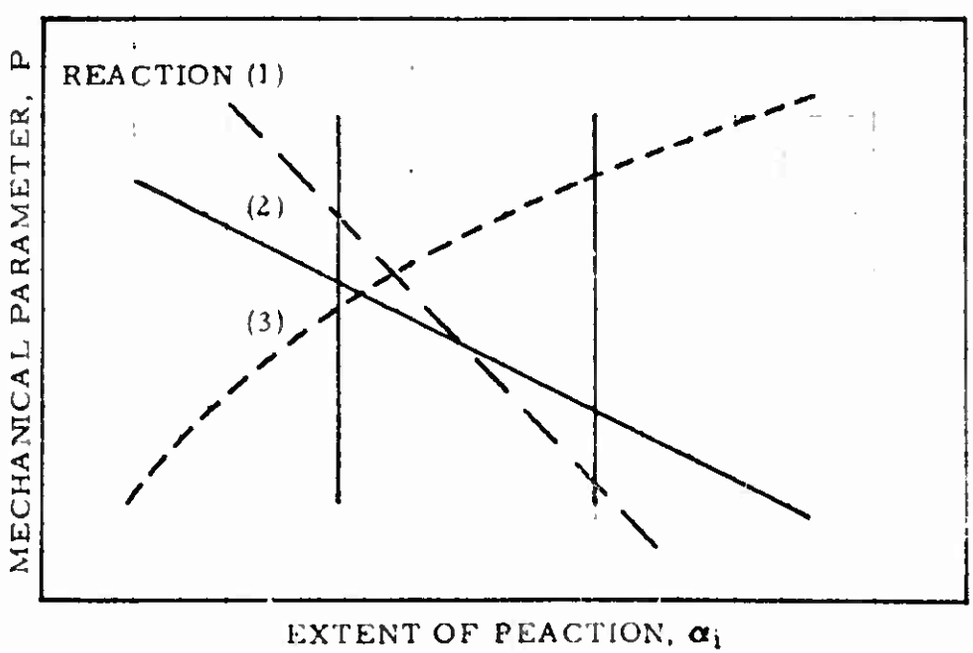

Figure 3 Schematic Illustration of Dependence of Mechanical Parameters Upon Various Reactions in Propellant

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(4) Finally it is necessary to account in the experimental design for the fact that service life prediction involves the element of statistics, and that small errors, for example, in defining activation energies, can result in large errors in time prediction (Figure 4). This produces an additional paradox in that measurement performed over a relatively narrow temperature range (surveillance) will produce relatively large errors in determining activation energies (thus the temperature extrapolation), while increasing the temperature range will render the mechanistic definition of the critical aging process considerably more complex.

3. PROGRAM OBJECTIVES AND SCOPE

The immediate objective of this program is to determine the relationship between the chemical state, especially within the binder, and the mechanical properties of ANB-3066 propellant as the propellant undergoes aging both under ambient and elevated temperature, and under varying conditions of mechanical loading. To accomplish its purpose the program will perform the following:

(1) ANB-3066 propellant will be stored in an inert atmosphere over a range of temperatures and at strain levels from zero to five percent.

(2) Chemical analysis will be used to define the changes in the chemical state of bulk propellant as they occur as a consequence of different temperature storage, and as a consequence of strain level. This analysis will be performed in sufficient depth to isolate and kinetically define the critical rate processes.

(3) Concurrent with the chemical analyses the changes in the bulk propellant's mechanical response will be determined, and the program will seek to relate the rate of change in mechanical response to chemical rate processes.

(4) Analog propellants will be used as necessary to elaborate upon the chemical mechanisms.

Although the program will use ANB-3066 Minuteman III propellant as the specific test vehicle, its ultimate purpose is to establish in a broad sense an improved technology for conducting accelerated surveillance tests as a basis for motor service life prediction.

4. PROGRAM APPROACH

The program is divided into three phases as follows:

a. Phase I, Propellant and Sample Preparation

Necessary quantities of ANB-3066 propellant, representative of Minuteman III production, are to be prepared and processed into surveillance

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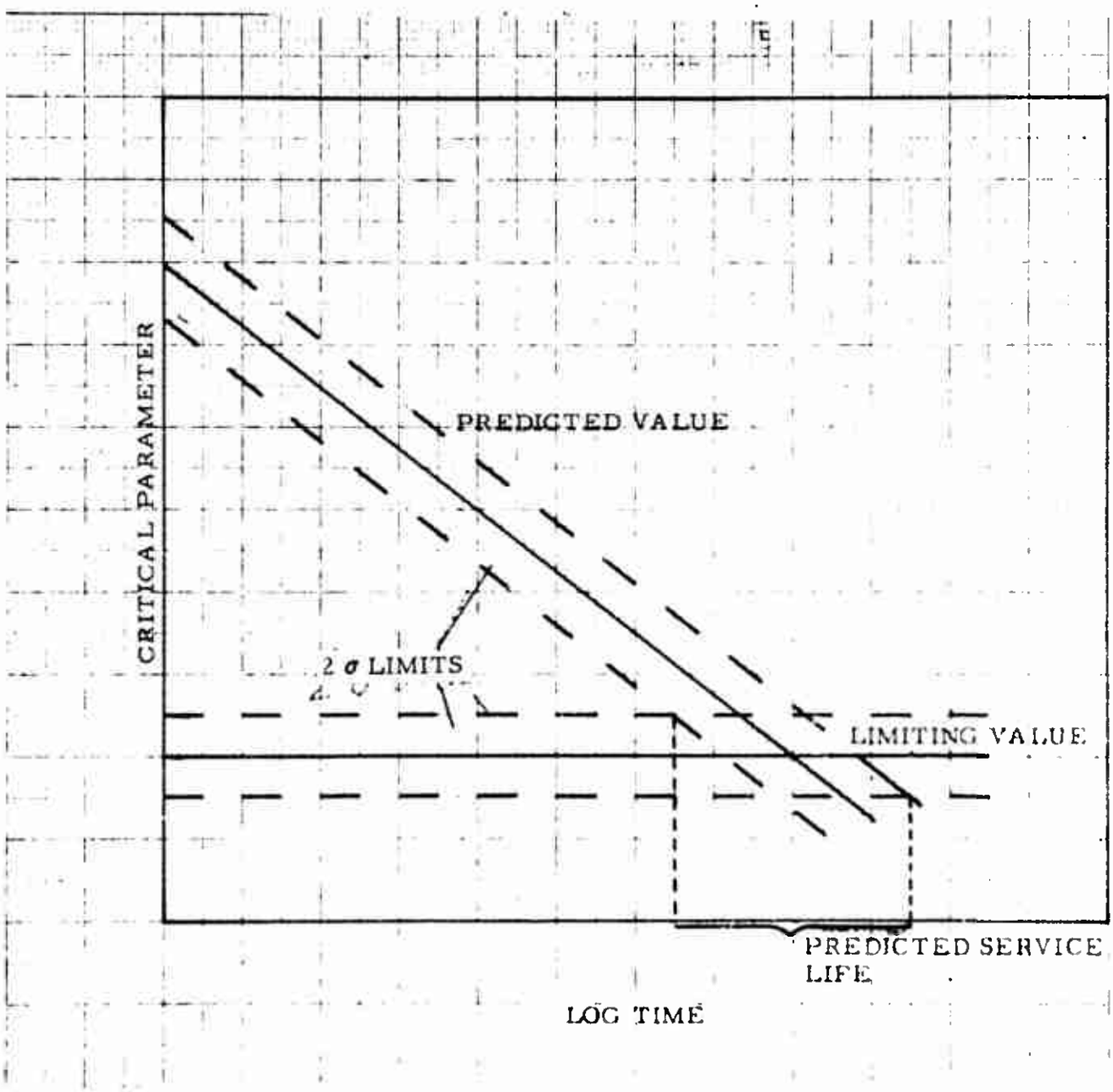


Figure 4 Service Life Prediction

specimens for storage at 30, 70, 115 and 145°F under inert atmospheric environment. Concurrently an analog propellant (KCl replacing ammonium perchlorate) and a propellant matching ANB-3066 but utilizing a new aziridine curative are to be prepared and processed in suitable specimens for surveillance.

b. Phase II, Pilot Experiments

An initial surveillance test program with necessary analytical back-up is to be performed to evidence the suitability of the experimental techniques to be used. This initial surveillance is to extend over a six months time period.

(1) Analytical Methods

The chemical changes occurring within the binder phase as a function of time-temperature-strain will be determined by measuring changes in crosslink density, sol/gel content, and composition of the sol fraction. Multiple reflection infrared analysis will provide a more detailed description of the chemical mechanisms and off-gas analysis will be used as a sensitive means of detecting changes in mechanism as a function of temperature and stress levels.

(2) Mechanical Response and Failure Processes

The changes in the propellants' mechanical response that accompany the measurable chemical changes will be determined relying upon uniaxial tensile property measurements, and measurement of creep compliance and tear behavior. This will be accompanied by a more thorough analysis of the parameters that control propellant tear behavior.

c. Phase III, Detailed Aging Studies

Upon completion of the Phase II Pilot Experiments, propellant held in a 30°F propellant bank will be placed into 70, 115 and 145°F storage for the performance of a more detailed analytical surveillance study. The sampling schedule to be used, and the detailed analytical, physical and mechanical test procedures to be employed, will be determined on the basis of the Phase II results.

d. Phase IV, Data Analysis and Correlations

The Phase IV efforts will encompass the following:

(1) A statistical analysis of the analytical results.

(2) A correlational analysis of the interaction between measurable changes in the systems' chemical state, and measurable changes in the systems' mechanical response.

(3) A definition of the chemical rate processes, and their temperature-stress dependency, that must be considered in translating accelerated surveillance test data into terms of long term motor mechanical behavior.

e. Restrictions

The program is to concentrate upon the analysis and rationalization of aging in bulk propellant, with emphasis upon binder aging effects. The program will not elaborate upon surface (inner bore) aging phenomena or phenomena involving the propellant-liner-case bond region.

5. GENERAL APPROACH

The essential elements contributing to a prediction of motor service life were summarized in Figure 1, which also denoted the particular area of direct concern under this program. That area is extracted and expanded in Figure 5 to include a listing of

(1) The more likely chemical processes underlying aging

(2) The microstructural and physico-chemical parameters which may be affected by the chemical processes

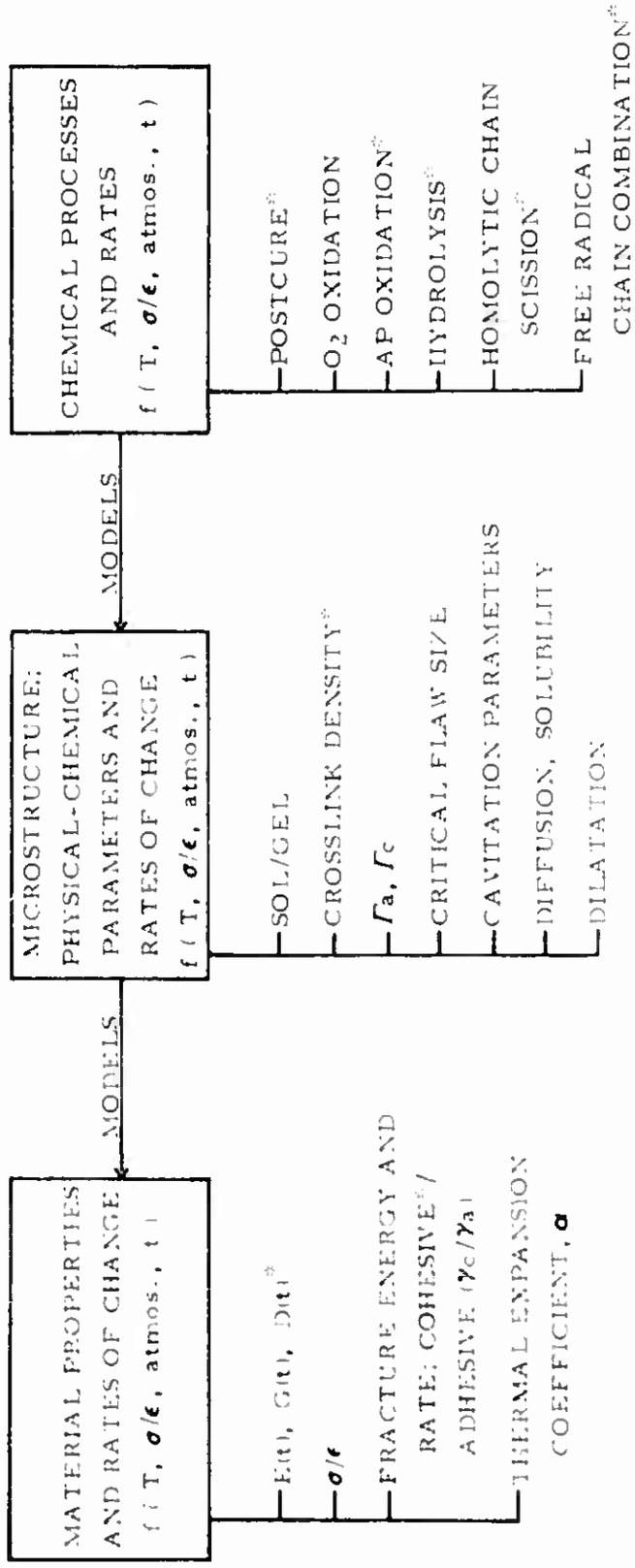
(3) Propellant macroscopic properties which may be altered as a consequence of (1) and (2).

The program therefore takes a stepwise, cause/effect approach from underlying chemical changes to microstructural changes to macroscopic property changes. Furthermore, it makes the very explicit assumption that in order to arrive at a quantitative understanding of relations between rates of chemical and rates of macroscopic property change an essential intermediate step is an understanding of the simultaneous changes in propellant microstructure. Prediction of propellant useful life will thus be made using existing and newly developed models describing the cause/effect relations between the three areas. Contributing primarily to this aspect of the program will be studies under subcontracts to Dr. W.G. Knauss of Cal Tech and Dr. H. Leeming of Leeming Associates.

6. CHEMISTRY OF AGING IN ANB-3066 PROPELLANT

a. Aging Reactions

Aziridine/carboxyl chemistry in the propellant environment is undoubtedly quite complex and is complicated further in materials such as HX-868 by a tendency towards homopolymer and oxazoline formation. While studies of aziridine/carboxyl reactions have been conducted in non-propellant and in simulated propellant (e.g., low AP levels) environments (Ref 1 and 2), evidence is mounting that such data cannot be applied to highly solids loaded systems without explicit verification.



*Process/parameter being studied in this program

Figure 5 Underlying Processes/Parameters for Service Life Prediction from Accelerated Surveillance

It is apparently generally assumed that ANB-3066 is in an "undercured" state at termination of its standard cure cycle and that the subsequent hardening observed is due primarily to continued reaction between residual aziridine (and oxazoline?) and carboxyl groups. It is far from clear at present, however, to what extent additional crosslinking may be produced by the influence of AP (catalytic or oxidative) upon the polybutadiene or plasticizer backbone double bonds.

There is likewise little information available upon the possible reactions which could lead to a reduction in network crosslinking in bulk ANB-3066. This includes processes, for example, such as chain cleavage by AP attack, by hydrolysis (through residual water or water produced by AP oxidative reactions) or by homolytic scission under the influence of grain stresses.

Finally, the possibility of stress enhancement of reactions other than chain scission must be considered, as noted earlier. There seems every reason to anticipate, for example, that the chemical bonds within short network chains will exist in a highly strained condition even at low bulk propellant extensions and will thus be highly susceptible to attack by AP, $HClO_4$, and H_2O.

b. Methods of Measurement

In sum there are a variety of reactions which may be contributing to aging changes in ANB-3066 and present ability to separate their rates and temperature coefficients is extremely limited. The primary reason for this situation is the previous lack of analytical methods with sufficient sensitivity and versatility to follow the very small changes (and rates) in the concentration of critical moieties in aging propellant. By way of illustration, we can estimate the order of magnitude of such changes in the following manner. The modulus of ANB-3066 may increase by something like thirty percent during its first year of storage. If we assume that modulus is directly proportional to binder crosslink density (network chains/cc) and that a gain of one cure linkage results in a gain of one network chain, then the thirty percent modulus change corresponds approximately to a gain of 1×10^{-5} network chains/cc. Thus, analytical methods must be able to measure the rate of change of carboxyl, ester, amide groups at a level of about 1×10^{-5} groups/cc/year, and this should preferably be done in situ upon real propellant.

Studies at LPC have indicated that the method having greatest potential for direct in situ measurement of propellant aging chemistry is multiple reflectance infrared, particularly if multiple scan averaging is employed using digitized spectra (Ref. 3). Less direct information is also being obtained by examining the GPC elution chromatograms for sol extracts and by infrared measurements upon the GPC fractions.

As noted earlier, both thermal and mechanical energy have been observed to cause gas evolution from propellant, apparently as a consequence of both homolytic chain scission and AP/binder oxidative reactions (Ref. 4). Measurement of such gaseous products thus provides sensitive

means to follow those types of chemical changes during aging. Three experimental techniques are being employed for this purpose (see Appendix for experimental details):

(1) The effect of mechanical energy input is determined using Dynamic Tensile Mass Spectrometry (DMS) which immediately observes the primary gaseous species evolved during ambient temperature straining of a propellant sample within the high vacuum of a time-of-flight (TOF) mass spectrometer.

(2) These data are contrasted with measurements of primary gaseous species produced by thermal degradation alone, using Mass Thermal Analysis (MTA) in the TOF high vacuum.

(3) The long term effects of both mechanical and thermal energy under accelerated aging conditions and under conditions approaching actual use are determined using Static Off-Gas Analysis (OGA), in which samples are held at constant strain in sealed containers. After aging at various temperatures the gas composition is measured by mass spectrometry (Perkin-Elmer 270). By monitoring a small free volume to sample volume sensitivity may be increased to the point where mechanisms under accelerated conditions may be verified under actual use conditions.

In addition to the information gained about chemical aging per se from these three gas analysis techniques, they also enable judging the importance of internal gas pressure to ANB-3066 propellant failure. While this is an aspect of failure which has generally been regarded as pertinent only for high energy propellant it is quite possible that enhancement of gas evolution by stress/strain may result in a gas pressure contribution to local cracking rates.

c. Use of Model Systems

As an aid in clarifying the aging chemistry the program will make use of two analog propellants. This first of these is one in which the AP has been replaced by KCl, the advantage here being severalfold: (1) elimination of the effects of AP upon the aziridine and upon its reaction with carboxyl, (2) elimination of the acidic environment and effects upon hydrolytic processes, (3) elimination of oxidative processes. The second analog is one in which the HX-868 in ANB-3066 is replaced by pure di and tri aziridines whose reactions with carboxyl appear to be freer of complicating side reactions, e.g., homopolymerization and oxazoline formation (Ref. 2).[1]

1. 1,3-Benzene-dicarbonyl-trans-2,3-dimethyl aziridine and 1,3,5-benzene-tris carbonyl-trans-2,3-dimethyl aziridine.

7. CHARACTERIZATION OF CHANGES IN PROPELLANT MICRO-STRUCTURE AND MACRO BEHAVIOR

Parameters chosen to be followed are indicated by asterisk in Figure 5. While information on other parameters undoubtedly would be desirable, funding limitations necessitate that selectivity be excerised. Criteria applied in that selection were: importance of the parameter to behavior of propellant-in-motor, presumed sensitivity to aging, ease of measuring by sensitive/reproducible procedure, presumed correlatibility with aging processes. The following provides some additional rationale for that selection and briefly describes methods employed. Where deemed desirable, further details are given in the Appendix.

Gel content and crosslink density are the obvious parameters of choice to characterize the binder network structure. As described in the Appendix, gel content is measured by a simple extraction procedure while crosslink density is determined from compression modulus measurements upon solvent-swollen propellant using Perkin-Elmer's Thermomechanical Analyzer (TMA). Other parameters listed in Figure 5 were eliminated, from initial studies at least, on the basis primarily of difficulty in obtaining accurate/reproducible values.

Program emphasis for propellant mechanical property characterization is upon measurement of creep compliance and tear rate/energy, with lesser emphasis upon uniaxial tensile properties. Since initiation and growth of cracks constitutes a major failure mode for propellant grains, tear energy and rate are increasingly recognized as important parameters characterizing propellant mechanical performance. Creep compliance was selected because of its (or stress relaxation modulus) importance to grain stress analysis and to propellant tear behavior (Ref. 5 and 6). On the other hand, uniaxial tensile properties are given less attention since their value for characterizing grain performance has become less evident in recent years; this is particularly the case when only a single parameter set, such as stress and strain at maximum stress, is employed to represent the complete stress/strain behavior.

To enhance reproducibility and preclude effects of water and oxygen, both creep compliance and tear measurements are performed within a purged glove box. Compliance is measured over the time range from 1 to 600 seconds at two load levels in order hopefully to observe the behavior in an essentially undamaged state and in a state of moderate dilatation. Tear behavior is determined at several constant loads, with measurement of strain and of time to achieve various degrees of crack growth. In all cases measurements are performed at 75 ± 3°F.

8. AGING CONDITIONS AND SCHEDULE

The program is divided into three phases: Phase I - Preparation, Phase II - Pilot Experiments, Phase III - Detailed Aging Studies. Phase II is of six months duration and its purpose is to establish the applicability/reproducibility of the experimental procedures and to define a rational test schedule for the long term aging to be conducted in Phase III.

During Phase II only a small fraction of the available propellant blocks are kept at the three aging temperatures, 70, 115 and 145°F. The remaining blocks are stored at 30°F to minimize any chemical processes and thus permit the introduction of additional "zero time" samples at initiation of Phase III or at any time during Phase III. This cold storage bank therefore provides considerable flexibility to the testing and allows for a certain amount of duplication of test points if questions should arise or refinement in methods should occur.

Sample blocks ($\frac{1}{2}$- or 1-gallon) are stored under nitrogen in hermetically sealed cans. To establish the influence of mechanical energy upon aging processes, similar blocks (approximately 3" x 4" x 3") are bonded to metal plates which are then separated by set screws to produce overall strains of three or five percent (see Appendix). Those samples are then also stored under N_2 in cans. Specimens for actual test/analysis are in the form of 0.1-inch slabs microtomed from the center portion of propellant blocks; with the strained blocks the 0.1-inch slabs are cut parallel to the strain direction. All microtoming is performed under dry N_2 to preclude oxidative damage to specimen surfaces.

SECTION II

SUMMARY

The following summarizes the work completed, and the results obtained during the initial program period 14 June 1971 to 15 April 1972.

1. PHASE I, PROPELLANT AND SAMPLE PREPARATION

To assure that the ANB-3066 propellant to be used as the test vehicle would be representative of Minuteman III production, propellant originating from a Thiokol 300-gallon Minuteman 3rd Stage production line mix was procured, and the material was processed into ½- and 1-gallon specimens for storage at 30°F (propellant bank), and 70, 115, and 145°F (Phase II Surveillance). Analysis of randomly selected specimens showed that the propellant was uniform within the limits of analytical errors.

A ten-gallon mix of KCl analog propellant was prepared at LPC using Minuteman specification ingredients in order to elaborate upon the effect of AP upon ANB-3066 propellant aging.

A ten-gallon mix using a special aziridine curative analog propellant failed to cure, and its preparation will be repeated.

All specimens prepared for surveillance purposes were sealed in cans under dry nitrogen atmosphere. Elapsed time between propellant processing (Thiokol) and canning was ten weeks.

2. PHASE II, PILOT EXPERIMENTS

Aging was initiated upon bulk samples (½-1-gallon) at 70, 115, and 145°F, and using both unstrained and strained (3 and 5%) specimens for determining both thermally and stress induced aging events. Results and conclusions to date are as follows:

(1) Uniaxial tensile and crosslink density measurements show that ANB-3066 propellant undergoes significant hardening during early storage at moderate temperatures (approximately three weeks at 115°F or two weeks at 145°F). Storage under three percent strain appears to counteract this effect. Changes in gel and degree of swell also occur but their meaning relative to the crosslink density effects is not as yet clear.

(2) Multiple internal reflectance infrared analysis promises to be a suitable analytical technique for determining changes in cure linkage concentration in propellant. Using a new Perkin-Elmer Model 180 spectrophotometer, sufficiently well defined bands for the ester, carboxyl, amide I (carbonyl) and amide II (NH deformation) moieties are obtained to enable the determination of cure linkage participation in post cure and degradation processes. By comparing this information with the measured rate

of change in crosslink density, the relative importance of $-CH=CH-CH_2-$ group interaction (AP catalyzed?) can be deduced.

(3) Off-gas analysis performed on ANB-3066 and KCl analog propellant stored for 40-50 days at 70, 115 and 145°F evidence CO_2 and N_2 as the major species. The gas generation rates during this initial storage period are in the range of 10^{-5} to 10^{-6} cc/gram propellant/hour, with the ANB-3066 propellant showing higher rates than the KCl analog system. Stress effects, if any, are masked by data scatter.

(4) Zero time data on creep compliance and tear rate have been obtained, and standardized operating procedures were established for using these tests under Phases II and III.

SECTION III

RESULTS AND DISCUSSION

1. PHASE I, PROPELLANT AND SAMPLE PREPARATION

The ANB-3066 propellant samples, and the KCl propellant analog samples were processed as summarized under Section II. Additional information on the preparation of samples to be stored under strain, as well as on the method of preparation of test samples from aging blocks, is given in the Appendix. Analytical data evidencing uniformity of the ANB-3066 propellant batch will be quoted below.

2. PHASE II, PILOT EXPERIMENTS

The pilot experiments, Phase II, are designed to test the experimental procedures so that all experimental work to be performed under Phase III and to extend into 1974 will be based on fully standardized techniques offering necessary sensitivity and precision.

a. Phase II Test Schedule

The Phase II test schedule is outlined in Tables I and II. Table I gives the sample surveillance conditions and the withdrawal schedule. Table II lists the test methods and frequency.

b. Analytical Methods and Results

(1) Multiple Internal Reflection Infrared Analysis

Multiple internal reflectance infrared analysis is one of the few chemical analysis techniques that can be used directly with highly solids loaded composites while concurrently offering high sensitivity. A particular benefit in applying this technique for the purpose of this program is that it will enable distinction between different chemical rate processes (rate processes involving the cure linkage as opposed to rate processes involving the polymer's carbon skeleton) affecting changes in polymer crosslink density. There is reason to suspect that some of these processes operate with largely different activation energies, rendering such distinction necessary if more meaningful temperature extrapolation is to be achieved.

Duplicate reflectance spectra have been obtained upon the KCl analog propellant using a Perkin-Elmer Model 180 infrared spectrophotometer. Traces of the 3500 to 2500 cm^{-1} and the 1800 to 1300 cm^{-1} regions for propellant unaged and aged 15-days at 145°F are given in Figure 6. The traces show that the bands indicative of the ester carbonyl, carboxyl carbonyl and amide groups (CO stretch and NH deformation) are sufficiently well defined to enable determination of group concentration changes. Comparison of the standardized (2920 cm^{-1} CH absorbance used as an internal standard to correct for differences in contact area) spectra for the aged (15-days at 145°F) and unaged KCl analog propellant does not as yet reveal a

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TABLE I

PHASE II SCHEDULE

Temp, °F	Strain, %	System[1]	No. of Cartons[2]	Schedule[3] January	February	March	April	May	June
30	0	A	105	▼(1/7)					
		B	14	▼(1/26)					
70	0	A	30[4] + 7	▼$_1$(1	▼$_2$(2/4)	▼$_3$(3/7)		∇$_4$(5/15)	
	3, 5		6	▼(1/20)	▼$_2$(2/21)			∇$_3$(5/31)	
	0	B	2	▼$_1$(1/4)	▼$_2$(2/4)			∇$_3$(5/15)	
	3		1		▼(2/4)			∇$_2$(5/31)	
115	0	A	4	▼(1/4) ▼$_2$(1/24)		▼$_3$(3/7)	∇$_4$(4/11)		
	3, 5		6	▼(1/23)	▼$_2$(2/14)		∇$_3$(4/27)		
145	0	A	4	▼(1/4) ▼$_2$ 1/17)	▼$_3$(2/10)	▼$_4$(3/14)			
	3, 5		6	▼(1/20)	▼$_2$(2/4)	▼$_3$(3/30)			
	0	B	1	▼(1/4) ▼$_2$(1/13)		▼$_3$(3/14)			

(1) A = ANP-3041, B = EC1 analog
(2) For A, prepared from legal cartons; for B, prepared from legal cartons. Stored in nitrogen-purged, sealed cans
(3) [illegible] date as month/day. ▼ represents initiation of storage. ∇1 represent initiation of storage and initial test point (non-fire testing). ∇2, 3, 4 represents subsequent test points. Open ▽ for planned events. Solid ▼ for completed events
(4) Thirty cartons to be retained at [illegible] for entire period for gear and material failure. Air Force at program conclusion.

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TABLE II

PHASE II TEST FREQUENCY

Test	Storage Strain %	Test Points at Storage Temperature, °F[1] ANB-3066 70°	ANB-3066 115°	ANB-3066 145°	KCl Analog 70°	KCl Analog 115°	KCl Analog 145°
1. Chemical							
MIR[2]	0	3	3	3	2		2
	3				1		
	5	2	2	2			
ν and f_s[3]	0	3	3	3	2		2
	3	2	2	2	1		
	5	2	2	2			
Sol/Analytical GPC	0	2		3	2		2
Sol/Preparative GPC + IR	0	2		2			
Off-Gas Analysis-Static	0	2	2	2	2	2	2
	5	2	2	2	2	2	2
Dynamic Tensile Mass Spec	-	-------7-------			-------4-------		
2. Mechanical							
Crack Propagation	0	[illegible]	3	3	2		2
	3	2	2	2	1		
	5	2	2	2			
Creep	0	3	3	3	2		2
	3	2	2	2	1		
	5	2	2	2			
Uniaxial Tensile	0	2	2	2			
	5	2	2	2			

(1) In addition to zero time tests.
(2) MIR = Multiple Internal Reflectance Infrared
(3) ν = crosslink density and f_s = sol content

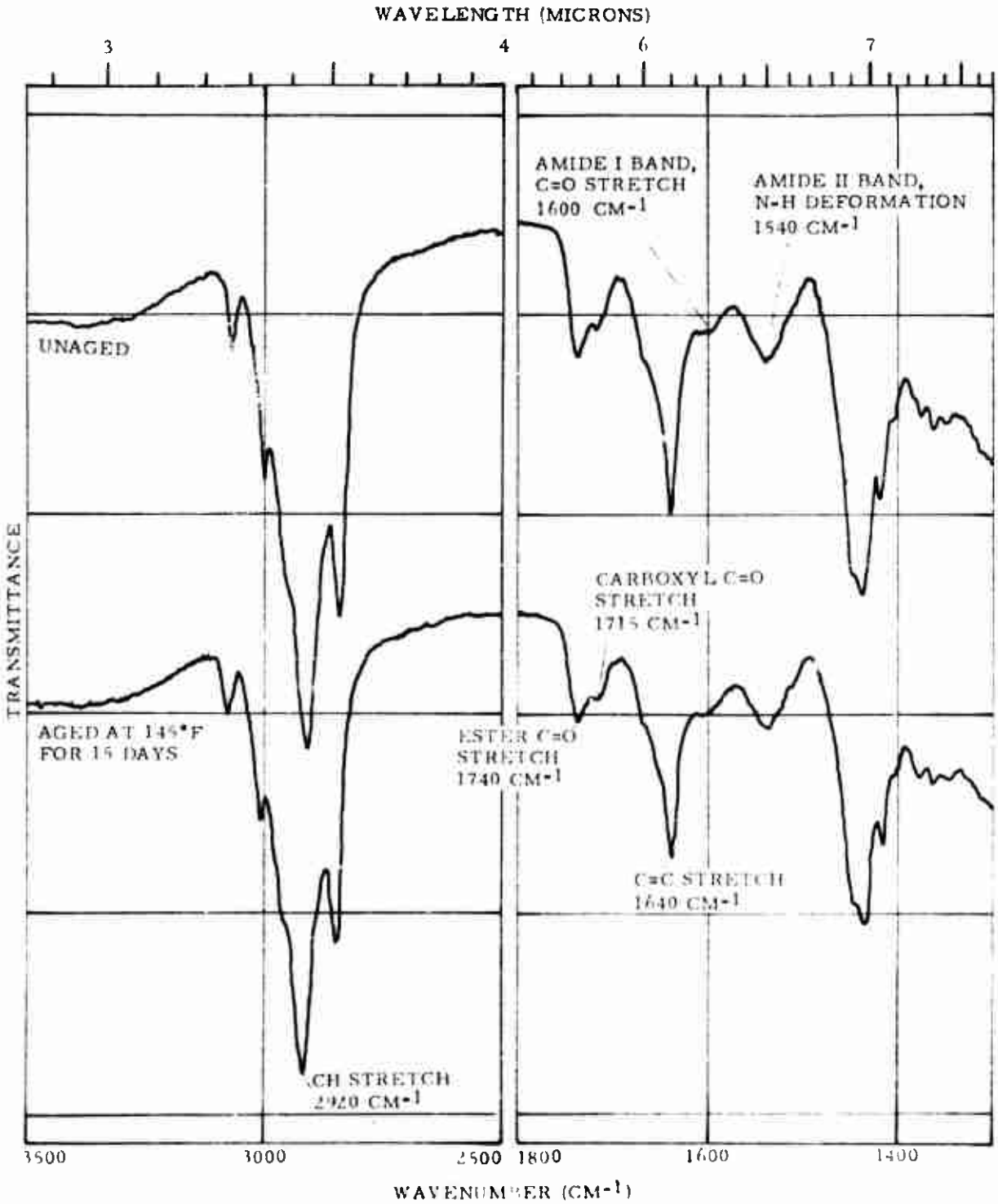

Figure 6 Reflectance Infrared Spectra of Unaged and Aged KCl Analog Propellant

significant change. This is in agreement with the crosslink density measurements (Section II, (3)) that equally show a very minor change for the analog propellant after 15-days at 145°F.

(2) Off-Gas Analysis

Since off-gas analysis, either by gas chromatographic or mass spectrometric techniques, can be performed at high sensitivity, and since changes in degradation mechanism are likely to be reflected in a change in off-gas composition, off-gas analysis provides one means of verifying the validity of temperature-time and temperature-stress-time extrapolations.

The experimental conditions that are being used are summarized in the Appendix. Tables III and IV summarize off-gas analysis data that have been obtained with ANB-3066 and KCl analog propellant stored for six weeks at 70, 115 and 145°F. Conclusions at this time are as follows:

- The only species consistently observed were CO_2 (mass 44) and N_2 (mass 28). Designation of mass 28 as N_2 rather than CO is supported by the appearance of mass 14 and absence of mass 12.
- Because of the comparatively mild surveillance conditions, the total quantity of gas produced to-date by all samples was small, causing true differences to be masked by normal data scatter. This situation will improve as the surveillance period is extended.
- Total gas evolution rates are in the range of 1×10^{-6} to 1×10^{-5} cc/g/hour. This approaches the level found to be shelflife limiting for certain high energy systems (Ref. 7).
- Gas evolution rates are higher for the ANB-3066 than for the KCl analog. Moreover, the ANB-3066 seems to produce more CO_2 relative to N_2.
- Changes in gas composition as a result of placing the samples under strain are within experimental error.

(3) Sol/Gel, Swell and Crosslink Density Measurements

The data accumulated to-date on sol/gel, swell and crosslink density changes for both ANB-3066 and the KCl analog propellant are summarized in Table V. The F-ratio significance test (ratio of between-carton mean squares to the within-carton mean square) was used for evaluating the results, and Table V includes pertinent data. The percentage values that are quoted represent the probability that the observed difference between aged value and the pooled zero-time value is due to chance, i.e., the significance level. At a one percent level the difference is judged significant, at five percent probable, and a greater than five percent a significant difference is considered not proven. A graphic presentation with the pooled "zero time"

TABLE III

OFF-GAS ANALYSIS CELLS FOR FIRST TEST POINT[1]

% Strain	ANB-3066			KCl Analog			Control (Ar/10% He)		
	70°F	115°F	145°F	70°F	115°F	145°F	70°F	115°F	145°F
0	2/2[2]	2/1	2/1	2/2	2/1	2/1	2/1	2	2
5	2/2	2[3]	2	2/2	2	2			

(1) 70°F after 46 days, 115°F after 44 days, 145°F after 42 days.
(2) Number of Demountable Cells/Sealed Cells (Demountable cells are jointed cells which can be dis-assembled and have a valve for gas sampling. Sealed cells are completely sealed glass cells with a break seal for sampling.)
(3) Demountable Cells only.

TABLE IV

AVERAGE GAS EVOLUTION RATE[1]

Sample	cc/g/hr x 10^6					
	CO_2			N_2		
	70°F	115°F	145°F	70°F	115°F	145°F
ANB-3066						
0% strain	2 ± 1	3 ± 2	15 ± 5	<1	<1	7 ± 2
5% strain	5 ± 3	11 ± 4	14 ± 6	<1	<1	10 ± 3
KCl Analog						
0% strain	1 ± 1	3 ± 1	3 ± 3	<1	<1	4 ± 1
5% strain	1 ± 1	3 ± 2	5 ± 3	7 ± 2	<1	4 ± 1

(1) Average over the time period for the cells noted in Table III. Indicated errors arise primarily from electronic noise level.

TABLE V

SOL/GEL, SWELL, AND CROSSLINK DENSITY

Test Point	% Gel(1)	Swell(2)	$\nu_e/V \times 10^4$(3)
1. ANB-3066			
• Zero Time			
Carton No. 001	64.53±0.43(4)	12.17±0.60	2.17 ±0.34
Carton No. 049	62.94±0.55	12.08±0.20	2.27 ±0.31
Carton No. 099	62.55±2.21	12.25±0.20	2.28 ±0.27
Pooled	63.34±1.47	12.17±0.34	2.24 ±0.27
• 13 Days at 145°F	66.27±0.72 1%(5)	13.49±0.33 1%	2.91 ±0.08 1%
• 15 Days at 145°F and 3% Strain	67.17±0.60 1%	11.93±0.19 >5%	2.30 ±0.27 >5%
• 20 Days at 115°F	69.49±0.58 1%	11.53±0.39 5%	2.59 ±0.19 >5%
• 25 Days at 115°F and 3% Strain	65.34±0.89 >5%	12.40±0.29 >5%	2.15 ±0.17 >5%
• 31 Days at 70°F	61.82±0.62 >5%	14.48±0.30 1%	2.06 ±0.15 >5%
• 32 Days at 70°F and 3% Strain	62.64±0.28 >5%	12.67±0.26 5%	1.88 ±0.02 >5%
2. KCl Analog			
• Zero Time			
Carton No. 01B	88.12±0.45	11.40±0.61	0.275±0.035
Carton No. 21T	88.21±0.34	11.88±0.41	0.321±0.022
Pooled	88.17±0.40	11.64±0.53	0.298±0.028
• 15 Days at 145°F	90.77±1.48 1%	10.68±0.13 5%	0.340±0.014 >5%
• 31 Days at 70°F	89.99±0.46 1%	12.32±0.26 >5%	0.265±0.025 >5%

(1) Percent of original prepolymer plus curative which is insoluble.
(2) In units of g (toluene)/g (gel).
(3) In units of mole/cm^3. Calculated from Eq. (1), Table XVI, Report No. E26-69, Thiokol Chemical Corporation, February 1969.
(4) Errors reported are standard deviations (each sample in triplicate).
(5) Probability that the difference between the pooled "zero time" value and the aged value is due to chance.

95 percent (2 standard deviations) and 99 percent (3 standard deviations) confidence limits inidcated is given in Figure 7.

The following may be noted:

(1) There is no significant carton effect on the zero time values with either the ANB-3066 or the KCl propellant, implying that the mixes were uniform; this is confirmed further by the tensile values (Section III, 2, c).

(2) Crosslink density of ANB-3066 shows an increase after 13-15 days storage at 145°F if the sample is under zero strain, but no change from zero time if the sample is under three percent strain (see Table VI for direct comparison).

(3) A comparison of sol/gel, degree of swell and crosslink values between the ANB-3066 and the KCl analog propellant evidences considerable complexity:

- Based upon the gel content it is apparent that the cure reaction was able to proceed to a much greater extent in the presence of KCl than in the presence of AP, presumably as a consequence of AP catalysis of aziridine homopolymer and oxazoline formation. This is consistent with infrared spectra in Figure 6 which show the free carboxyl in the KCl analog propellant as only a shoulder on the ester peak and no significant change upon aging for 15 days at 145°F.

- The apparent crosslink density observed for the AP system however is about ten-fold greater than for the KCl system. This is very likely due to one or both of the following: (1) a very high crosslink density (primarily HX-868 homopolymer?) in the AP interfacial region (which of course accounts for a significant fraction of the binder volume), (2) incomplete dewetting of the AP/binder bonds by the swelling solvent (toluene) with consequent contributions to compression modulus by those bonds and by the solid AP itself.

- Degree of swell, as measured by weight of solvent sorbed, will be affected oppositely by dewetting (increased due to filling of open pore volume) and by extent of cure (true crosslink density of binder itself). Hence the nearly equal degree of swell observed for the two systems is perhaps not surprising.

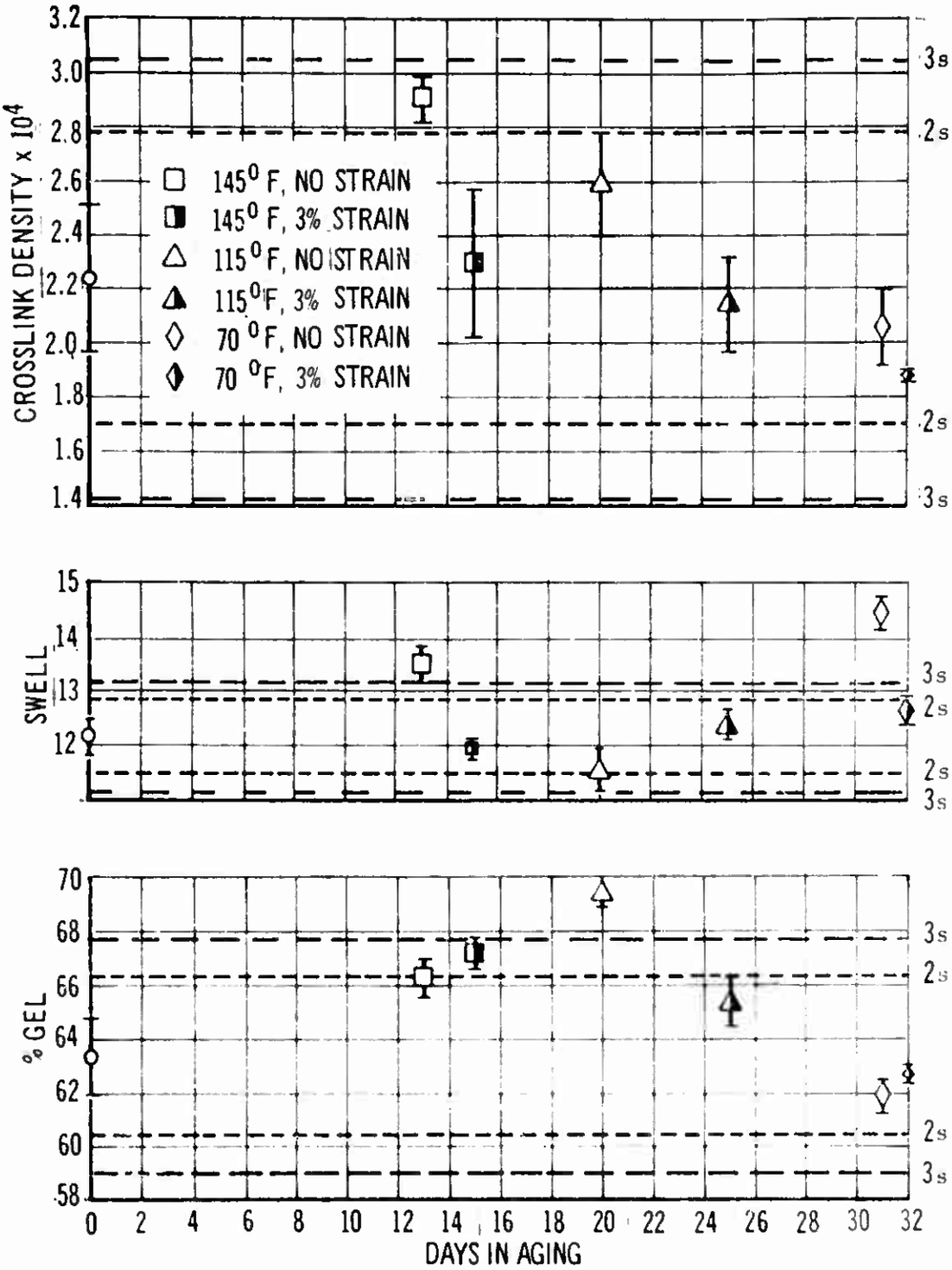

Figure 7 Effect of Aging Upon Percent Gel, Swell and Crosslink Density for ANB-3066

TABLE VI

EFFECT OF STRAIN UPON SOL/GEL, SWELL, AND CROSSLINK DENSITY OF ANB-3066

Temperature	% Gel	Swell	ν_e/V
70°F	61.8/62.6(1) >5%(2)	14.5/12.7 1%	2.06/1.88 >5%
115°F	69.5/65.3 1%	11.5/12.4 5%	2.59/2.15 5%
145°F	66.3/67.2 >5%	13.5/11.9 1%	2.91/2.30 5%

(1) Aged unstrained/aged under 3% strain for approximately the same time period.
(2) Probability that the difference is due to chance.

(4) Chemical Analysis of Sol Extracts

Sol extracts from both propellant systems were analyzed by gel permeation chromatography (GPC), and selected GPC fractions (preparative mode) were analyzed further by infrared spectroscopy.

In all cases the propellant was treated with dichloroethane at ambient temperature, and the resulting extract was vacuum stripped at 25°C (rotovap) to approximately one percent residual solvent. The resulting material thus contains the plasticizer plus the "sol" as the term is used in this report.

Figure 8 shows the GPC curves for the raw materials. Figures 9 and 10 show the GPC curves for the extracts obtained with zero time and aged ANB-3066 and KCl analog propellant. The following may be noted:

(1) In the unreacted prepolymer fraction (Butarez), the prepolymer's bimodal distribution is retained in both the ANB-3066 and the KCl analog system (peaks a and b), however, at a reduced concentration of the lower molecular weight fraction (peak b). Molecular weights were calculated for that region (elution volumes 17-27) and the resulting values are summarized in Table VII. Both $\bar{M}_n$ and $\bar{M}_w$ for the extracts are above the original prepolymer values. Behavior during initial aging is qualitatively consistent with the lower degree of cure for ANB-3066 relative to the KCl analog and extensive postcure of the former. In either case, aging at 145°F causes selective incorporation of the largest molecules into the gel network with consequently more rapid reduction in $\bar{M}_w$ of the sol.

(2) HX-868 is no longer present as a soluble entity. This is not unexpected in view of the material's tendency to undergo homopolymerization, and in view of the lower than unity aziridine/carboxyl ratio that was used in both systems.

(3) Peak c of the zero time extracts contains primarily non-functional, unsaturated low molecular weight hydrocarbon (prepolymer + plasticizer?) and antioxidant. No change is apparent upon aging.

(4) Peak d of the zero time extracts consists of very volatile aromatic hydrocarbon. Observed differences upon aging may reflect volatilization during aging but more likely are due to losses during solvent stripping of the sol itself and the GPC fraction.

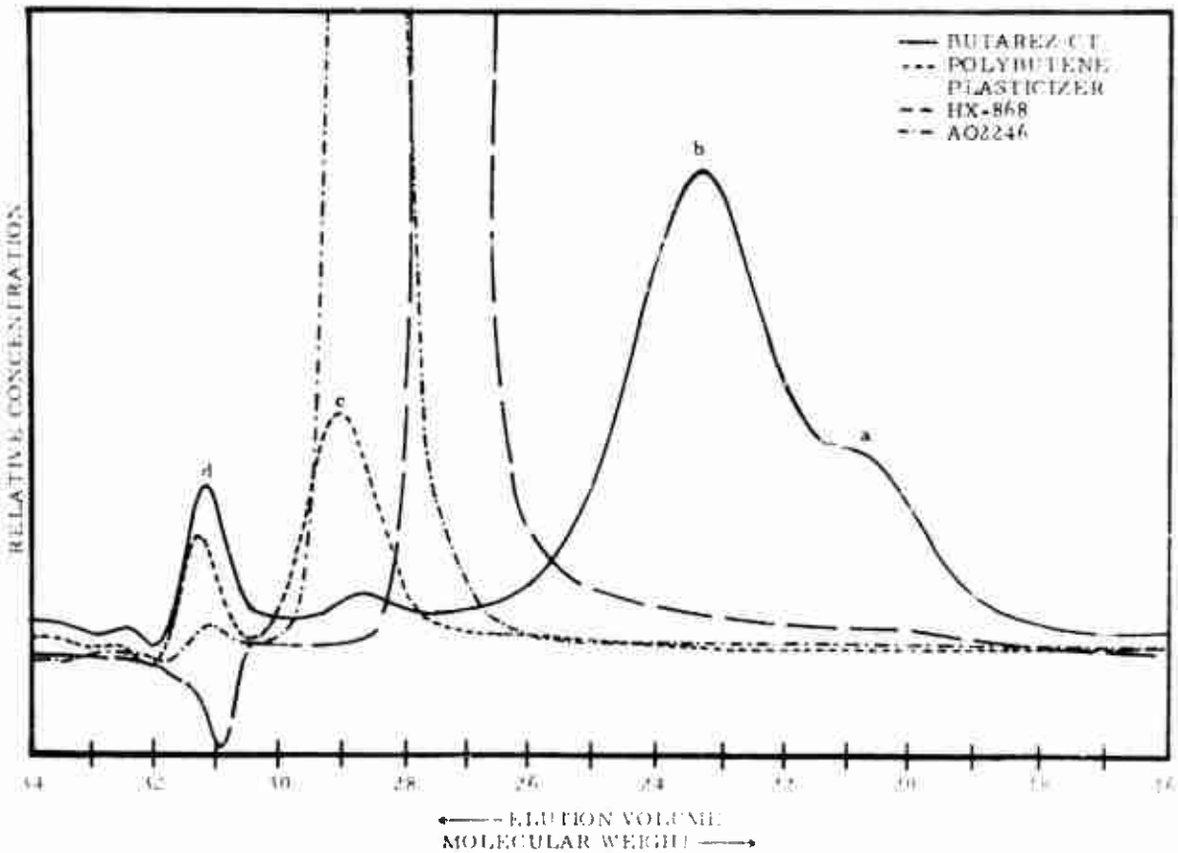

Figure 8 Analytical GPC for Binder Ingredients (0.5% concentration)

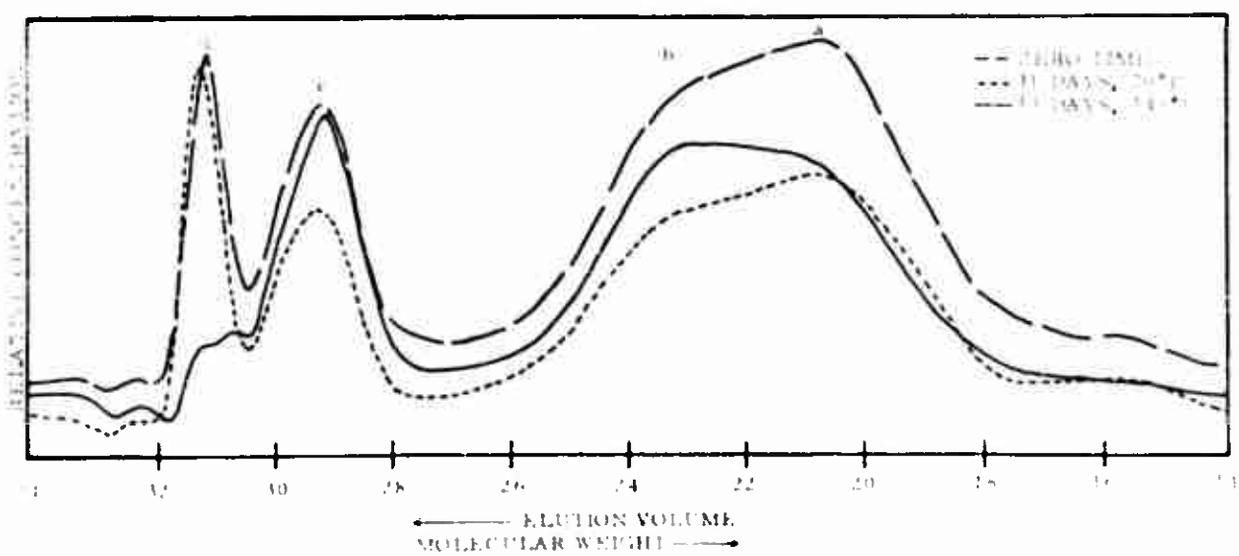

Figure 9 Analytical GPC for Extract from ANB-3066 Propellant

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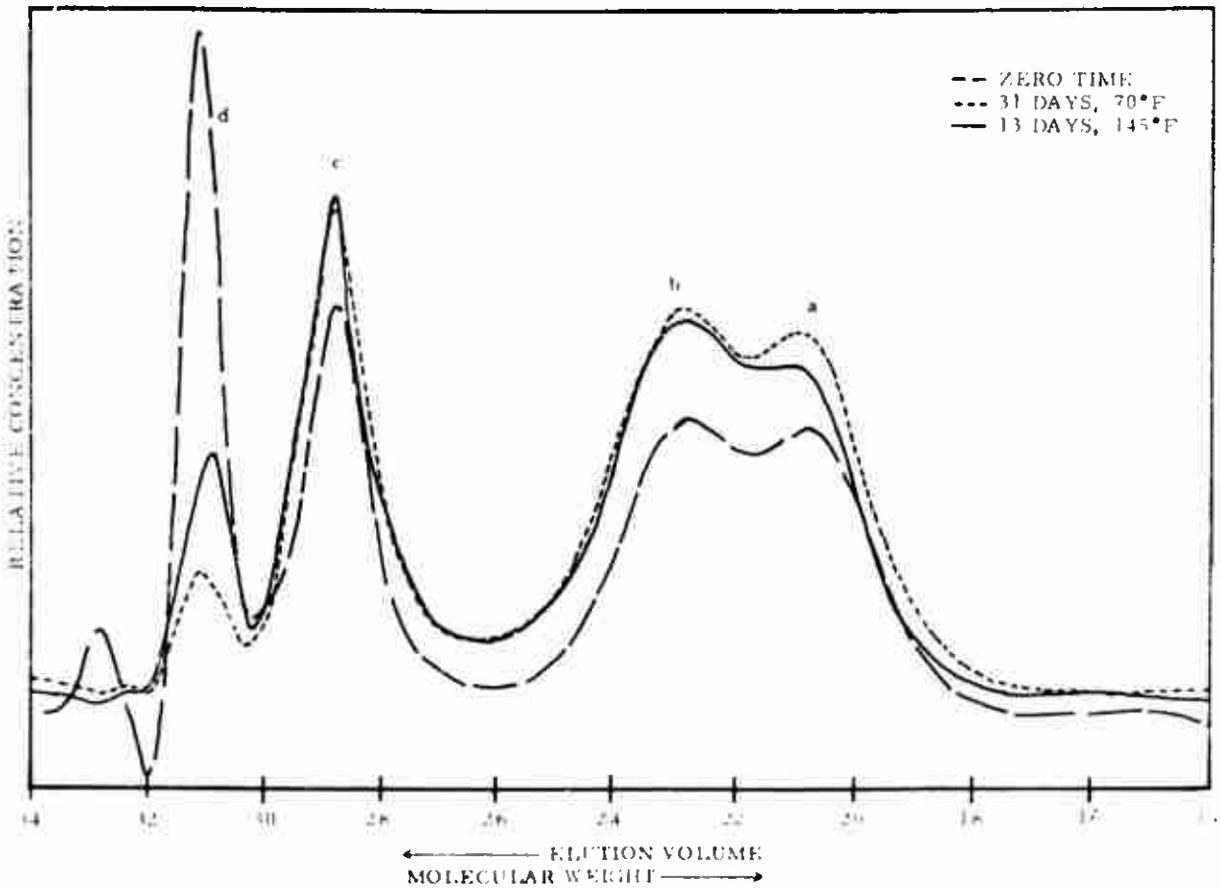

Figure 10 Analytical GPC for Extract from KCI Analog Propellant

TABLE VII

GPC MOLECULAR WEIGHTS OF SOL EXTRACTS[1]

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1. Butarez CTL-II, Lot 24RI	4320	7,710	1.78
2. Sol Extracts			
ANB-3066			
"Zero Time"	6250	19,000	3.05
31 Days, 70°F	6690	21,400	3.19
13 Days, 145°F	6070	15,700	2.58
KCI Analog			
"Zero Time"	6440	11,400	1.77
31 Days, 70°F	5920	11,200	1.89
13 Days, 145°F	5880	9,620	1.64

(1) Peaks a, b region of Figures 9 and 10.

c. Mechanical Property Changes

(1) Creep Compliance

Creep measurements have been completed upon both ANB-3066 and the KCl analog at zero time and at several aging points. Data reduction is completed upon the zero time systems and those data are presented here by way of illustration. Measurements were performed at 73 ± 3°F in an inert environment using two loads for each specimen, without allowing any recovery between the two loads. For the ANB-3066 the two stresses and the maximum strains were approximately 5 psi/1.5 percent and 60 psi/12 percent; for the KCl analog these values were 5 psi/0.5 percent and 30 psi/4 percent.

Plots of inverse creep compliance versus time are given in Figures 11 and 12 for the zero time KCl analog and in Figures 13 and 14 for ANB-3066 (each curve is the average of two specimens). The KCl data indicate that significant damage (dilatation) is occurring at the higher load (drop-off in "modulus" in Figure 11 vs Figure 12); this is to be expected since the 30 psi stress approaches σ_m for this very weak system. In contrast, no obvious damage is exhibited at the high load with the stronger ANB-3066 system (Figures 13 and 14); in fact the modulus is significantly greater at the higher load due to the greater strain rate.

(2) Tear Behavior

Tear behavior is being measured at several constant loads at 73 ± 3°F in an inert environment. Experiments have been performed upon a number of samples and data reduction is in progress. By way of illustration Figure 15 presents data for several specimens of zero time ANB-3066.

(3) Uniaxial Tensile Measurements

Uniaxial tensile measurements have been performed upon ANB-3066 propellant at zero time and at three aging points (31 days at 70°F, 20 days at 115°F, 13 days at 145°F). The true stress-strain curves are shown in Figures 16 and 17. No obvious differences in curve shape occur upon aging. To provide more quantitative criteria for changes in the entire stress/strain curves, values of stress and strain at "yield", at maximum stress and at failure are tabulated in Table VIII along with initial modulus values. The degree of reproducibility in σ_m and ϵ_m noted here is consistent with general LPC experience, i.e., approximately three percent RSD for σ_m and eight percent RSD for ϵ_m; E_o is notoriously difficult to define reproducibly. As noted previously, no significant carton effect was observed at zero time.

Within the rather large errors in E_o and strain parameters no aging effect can be established. In contrast all the stress parameters are significantly increased by aging and these changes are qualitatively in accord with crosslink density changes (c.f., Table V).

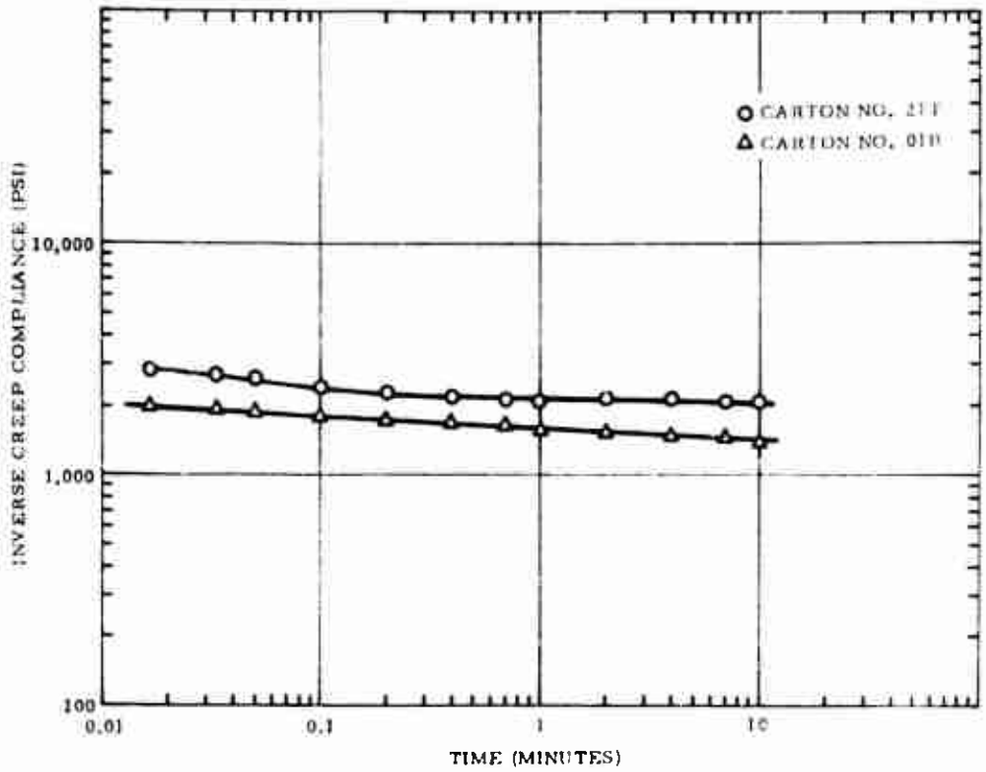

Figure 11 Creep Behavior of Zero Time KCl Analog Propellant (5 psi load)

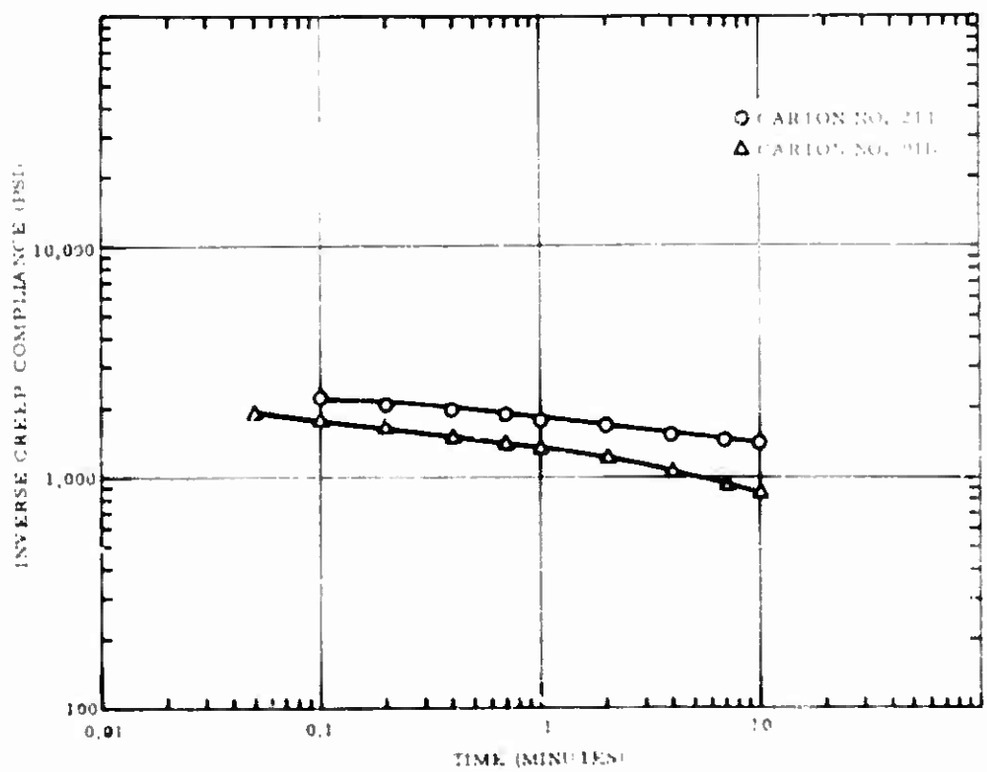

Figure 12 Creep Behavior of Zero Time KCl Analog Propellant (30 psi load)

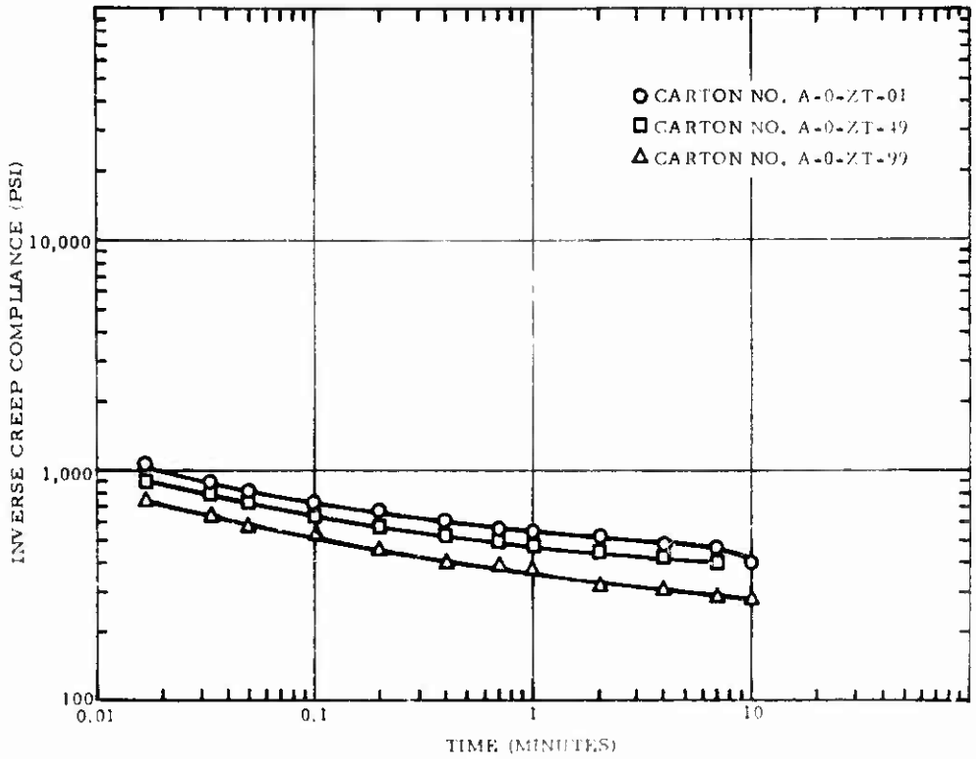

Figure 13 Creep Behavior of Zero Time ANB-3066 (5 psi load)

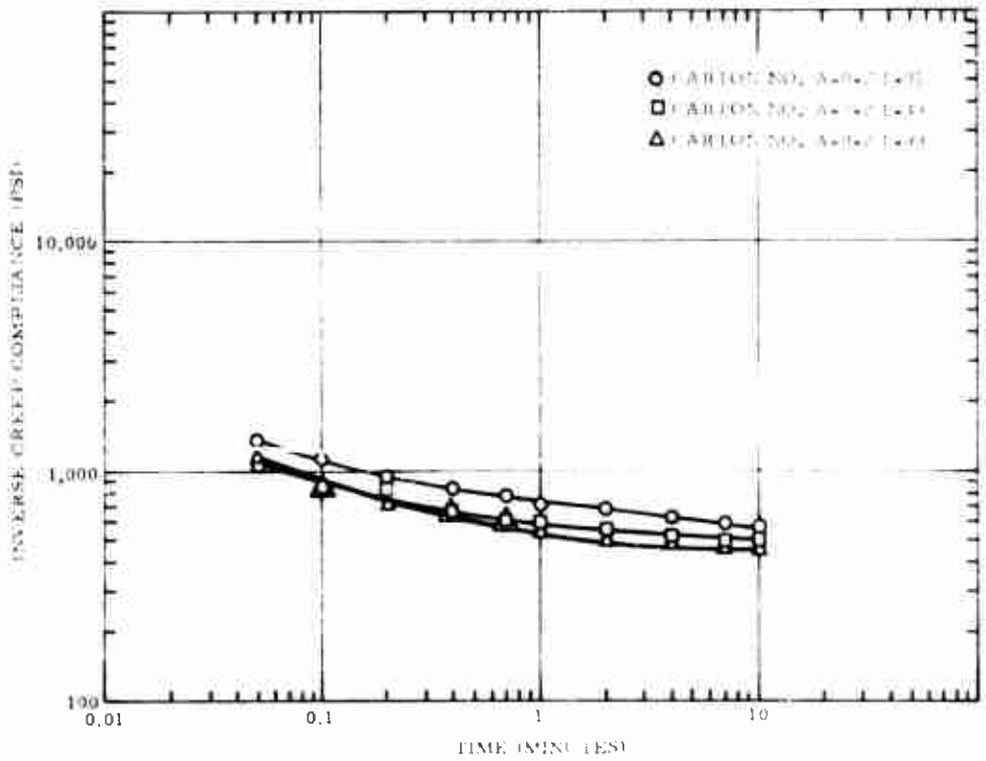

Figure 14 Creep Behavior of Zero Time ANB-3066 (60 psi load)

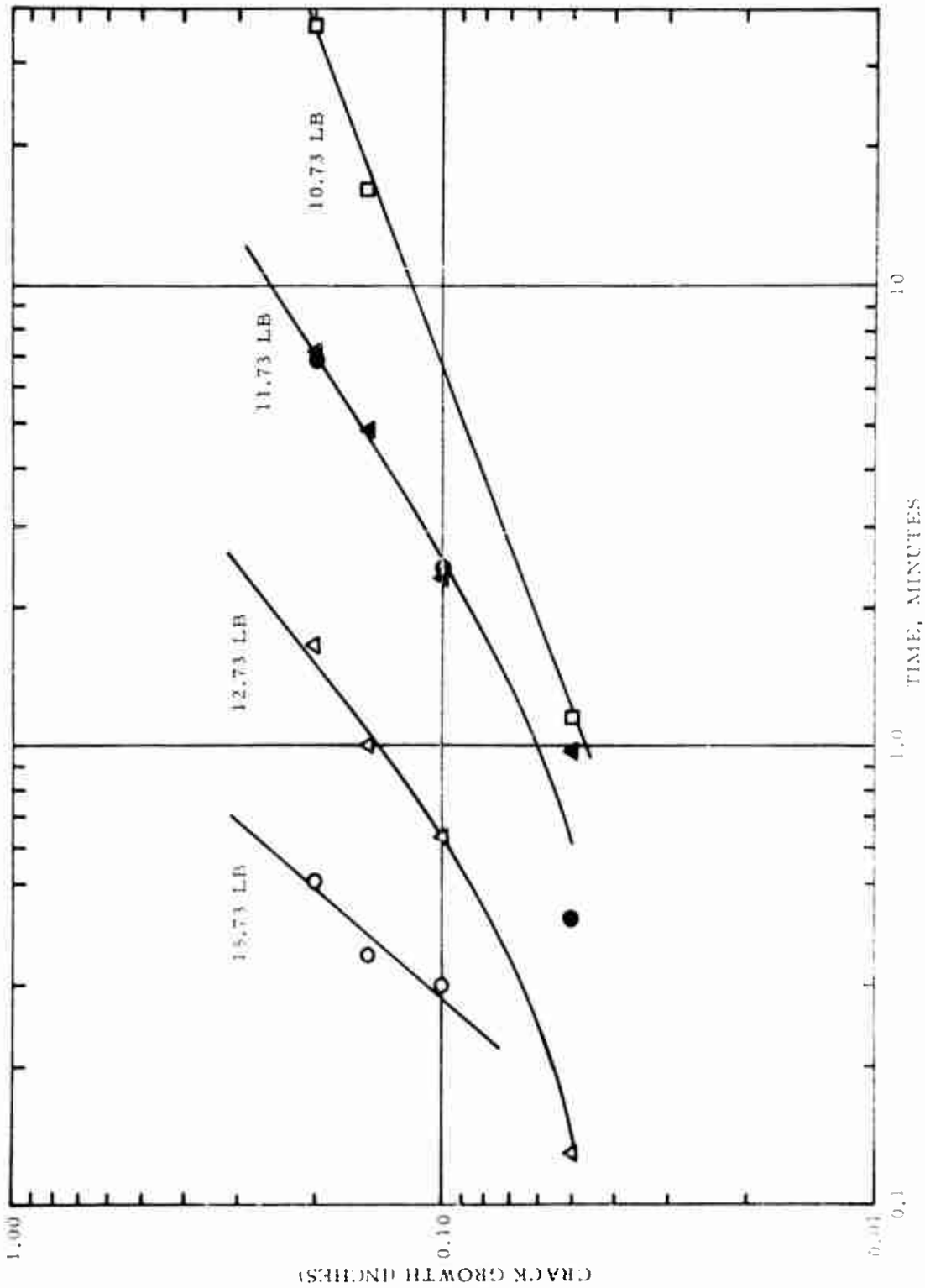

Figure 15 Tear Propagation of Zero Time ANB-3066 (0.75" initial end cut in 3" x 1" x 0.1" strip)

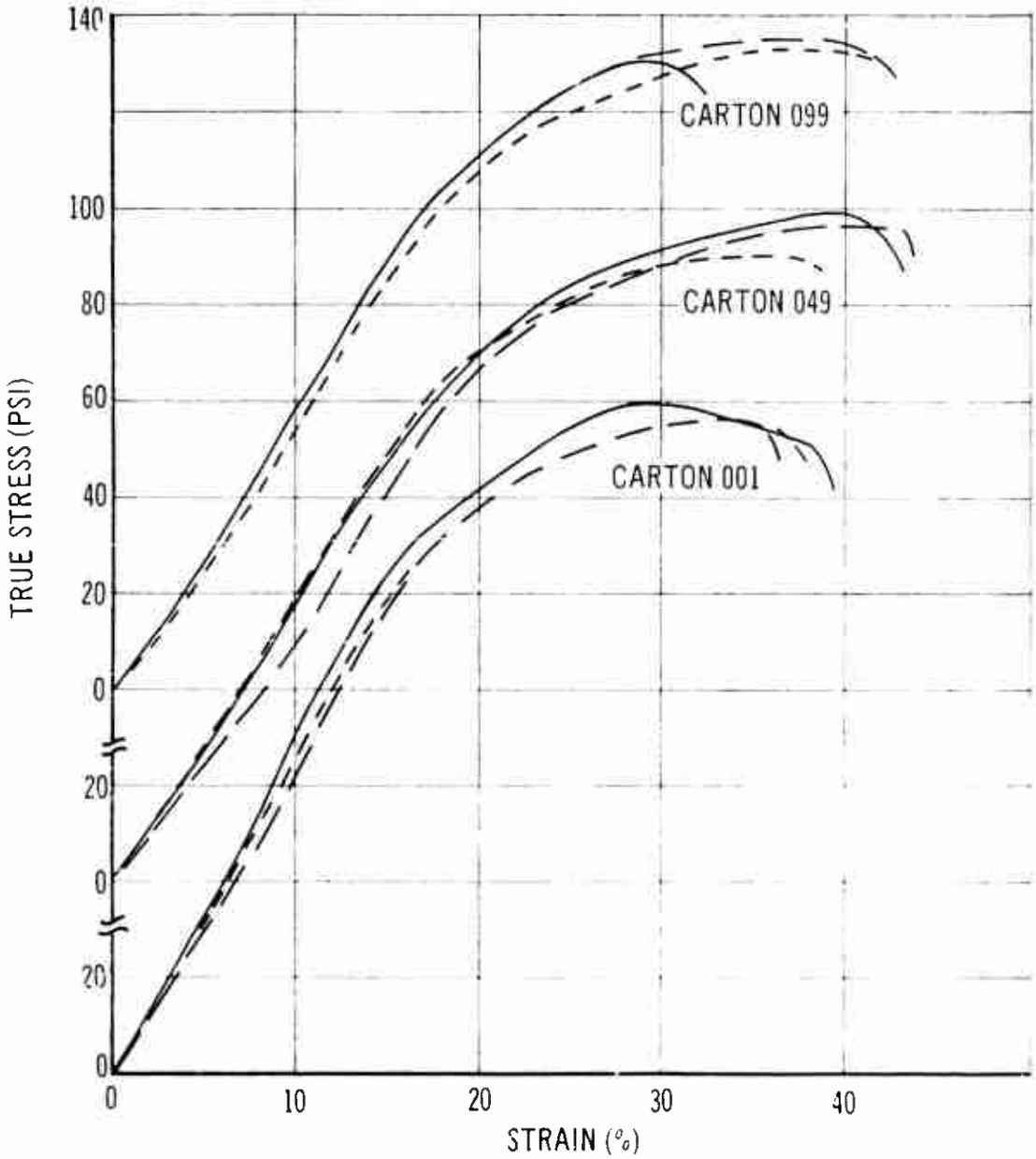

Figure 16 True Stress vs Strain for Zero Time ANB-3066 (Minithin specimens. Note stress scale displacement for upper two sets of curves.)

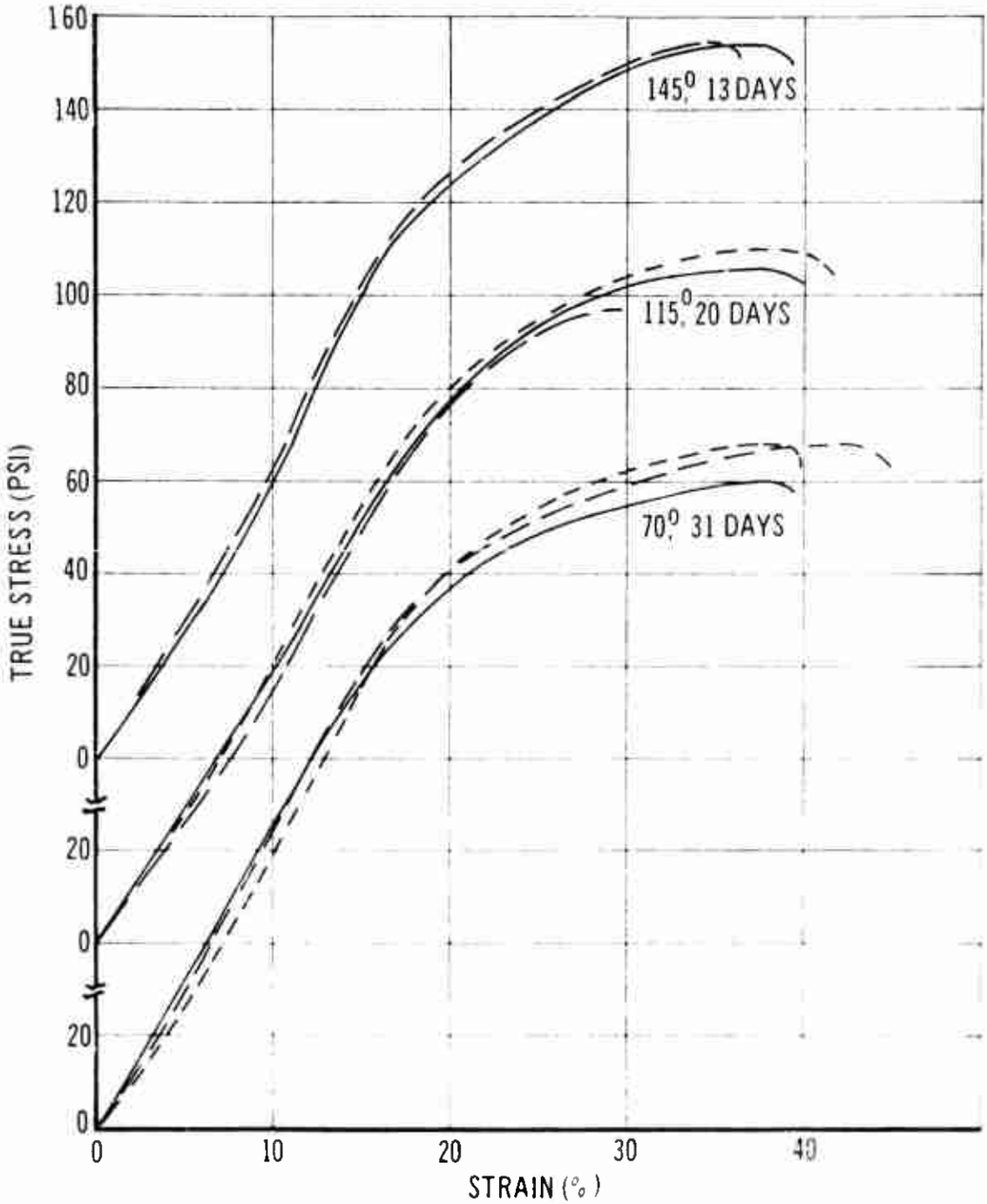

Figure 17 True Stress vs Strain for Aged ANB-3066 (Minithin specimens. Note stress scale displacement for upper two sets of curves.)

TABLE VIII

UNIAXIAL TENSILE PARAMETERS OF ANB-3066(1)

Aging Condition	Parameters(2)						
	E_o (psi)	σ_y (psi)	ϵ_y (%)	σ_m (psi)	ϵ_m (%)	σ_b (psi)	ϵ_b (%)
• Zero Time							
Carton No. 001	640±32(3)	107±1	16±1	137±3	32±3	128±3	37±2
Carton No. 049	551±69	105±4	18±1	135±5	38±2	131±4	41±3
Carton No. 099	561±23	106±1	18±1	133±3	34±5	128±3	39±6
Pooled	584±58	106±2	17±1	135±3	35±3	129±3	39±3
• 70°F, 31 Days	604±49	121±2	18±1	145±4	39±2	136±2	40±2
	>5%(4)	1%	>5%	1%	>5%	1%	>5%
• 115°F, 20 Days	545±17	118±4	19±1	144±6	34±4	141±3	40±1
	>5%	1%	5%	1%	>5%	1%	>5%
• 145°F, 13 Days	582±45	121±1	18±1	154±1	36±1	151±1	37±2
	>5%	1%	>5%	1%	>5%	1%	>5%

(1) Minithin tensiles at 75±3°F. Stress and strain values from true stress vs strain curve.
(2) E_o = initial modulus, σ_y/ϵ_y at "yield" point, σ_m/ϵ_m at maximum true stress, σ_b/ϵ_b at rupture.
(3) The reported errors are the standard deviations for triplicate specimens.
(4) Probability that the difference in the pooled "zero time" value and the aged value are due to chance.

APPENDIX

EXPERIMENTAL TECHNIQUES SUMMARY

1. PREPARATION OF PROPELLANT FOR AGING AND TESTING

Figure 18 illustrates the configuration of ANB-3066 aging blocks, which are wrapped in foil and canned under nitrogen. The original propellant cartons were approximately 5" x 7" x 7" and were trimmed to the dimensions in Figure 18 to permit storage in standard one-gallon cans. For the blocks aged under strain the two 4" x 3" faces are bonded to steel plates which are then separated using metal studs/nuts to produce the desired gross strain. After aging, slices are microtomed from the center portion of the block in the plane perpendicular to the original casting direction, and the direction of straining for those slices as tear, creep, tensile specimens is kept constant.

The KCl analog blocks are treated in a similar fashion with the exception that block dimensions are somewhat different due to casting in one-half gallon cartons instead of one-gallon cartons.

2. CHEMICAL ANALYSIS METHODS

a. Multiple Internal Reflectance Infrared Analysis (MIR)

Development and standardization of the MIR method for use under Phase III has been delayed by a changeover from the Perkin-Elmer Model 221G to the Perkin-Elmer Model 180 instrument, the latter offering significantly higher sensitivity and resolution for this type of application.

To further enhance the usefulness of this method the IR spectrophotometer is being interfaced with a digital data acquisition/processing system to enable multiple scan data averaging.

b. Off-Gas Analysis

Propellant samples are shown in Figure 19. These are stamped from 0.1-inch thick slices and bonded to metal tabs with Torrseal (high vacuum epoxy sealer). Holes are located in the metal tabs such that the desired propellant strain is produced when the samples are stretched to fit on the support jig. Four specimens are placed on each jig, with one jig contained in each cell.

Two cells have been employed, a so-called demountable cell (Figure 20) and a completely sealed cell. The former is far easier to use but it was felt advisable to provide some replication with sealed cells which were unlikely to leak, particularly where long term storage would be required (e.g., 70°F).

Prior to being mounted on the jigs, the samples are held in an evacuated desiccator overnight to remove dissolved gases and the vacuum

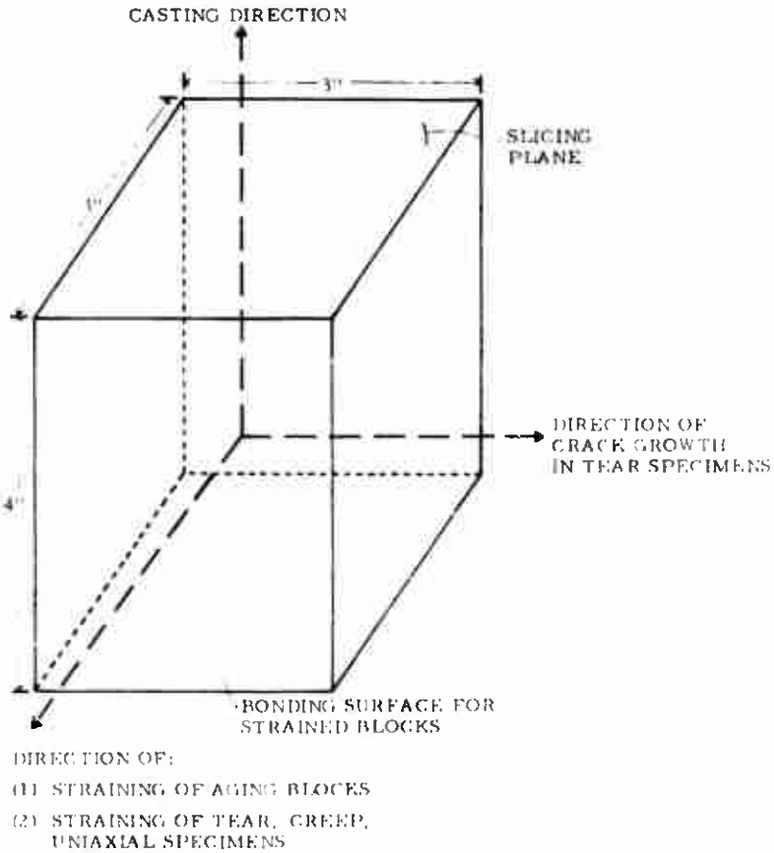

Figure 18 ANB-3066 Aging Blocks

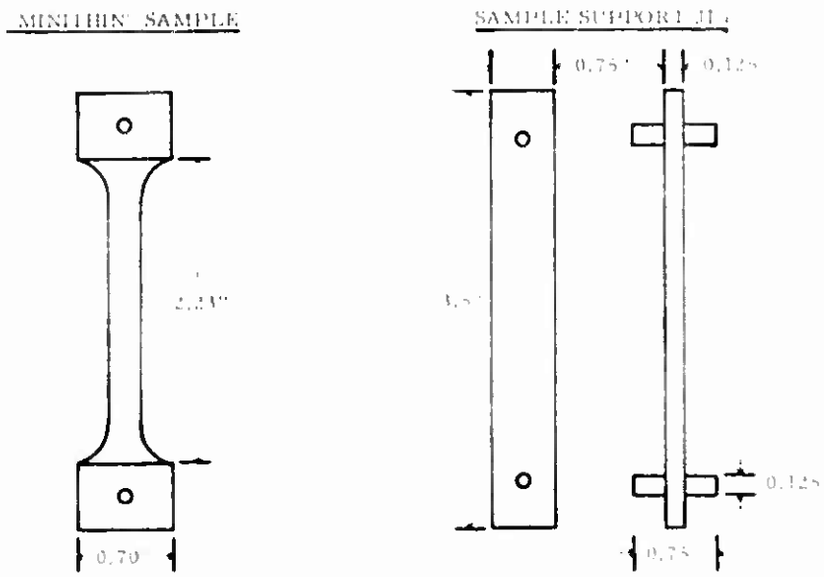

Figure 19 OGA Samples

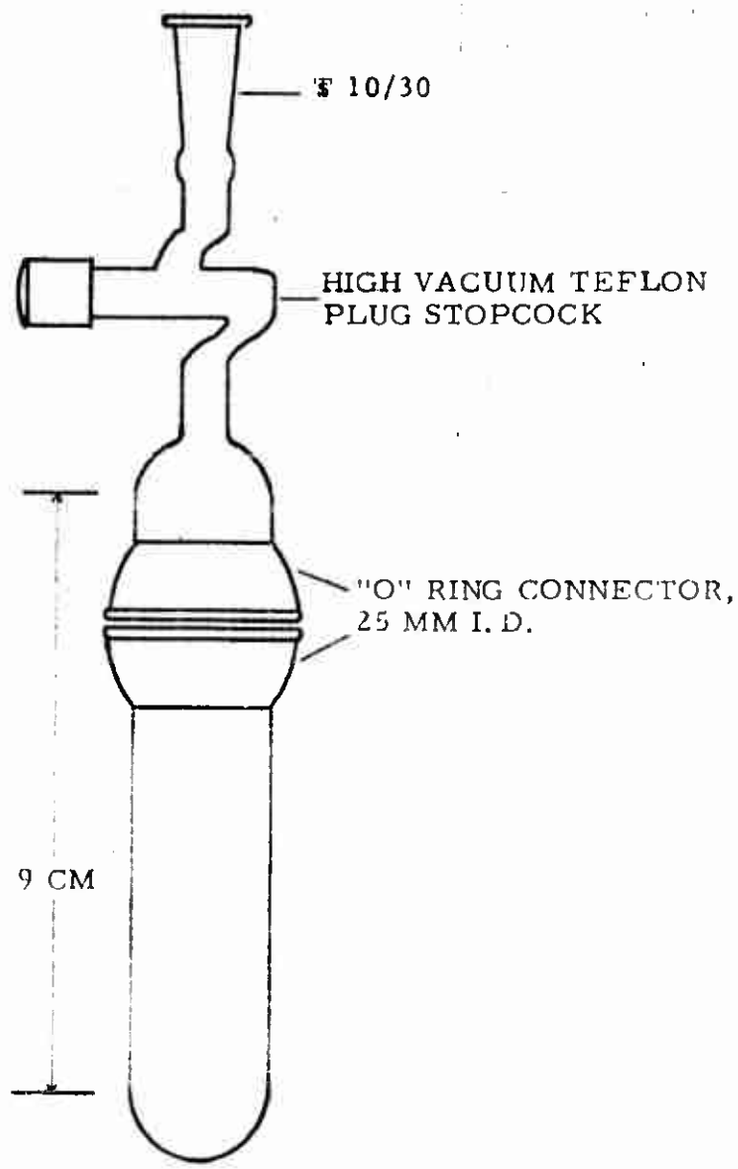

Figure 20 OGA Demountable Cell

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broken with Ar/He (90/10 mixture). Mounting on the jigs and insertion into cells is conducted rapidly in a dry box and followed by additional evacuation (two hours) and purging with Ar/He. The demountable cells are finally filled to slightly above atmospheric pressure and sealed cells slightly below atmospheric pressure. In all cases the actual cell pressure is measured by means of a Baratron and is similarly measured at the time of analysis. As further insurance against leakage of air during aging, the cells are sealed in metal cans purged with Ar/He.

At analysis time the cells are cooled to ambient and opened under conditions such that the cell pressure can be accurately determined. The gas composition is then analyzed with the Perkin-Elmer 270 mass spectrometer using the 90/10 Ar/He as an internal standard.

c. Sol/Gel and Swell

Sol/gel and degree of swell are determined simultaneously upon cured gumstock or propellant by swelling/extracting the material in toluene (solvent to sample ratio of 100:1). A sample is swelled first in solvent vapor for 96 hours and then extracted for 96 hours, with solvent changed at 24-hour intervals during the initial 48 hours of extraction. Swell is calculated from the ratio of solvent taken up to gel content of material.

$$\text{Swell} = \frac{\text{Weight of Solvent}}{\text{Weight of Gel}}$$

Gel is determined from the ratio of weight for non-extractible binder to initial binder (prepolymer + curative) weight

$$\%\,\text{Gel} = \frac{\text{Weight of Insoluble Binder Gel}}{\text{Initial Weight of Binder}} \times 100$$

Sample size is approximately 0.5-gram of gumstock or five-gram of propellant, and in either case the sample is chopped into pieces <1 cm per side before extraction.

d. Crosslink Density

Crosslink density is calculated from the compression modulus for a swollen propellant specimen using the following expression:

$$\frac{\nu e}{V} = \frac{m\,h_c}{3\,R\,T\,A_c\,(1-\phi)} \left(\frac{1 - S\,(1-\phi)}{1-S}\right)^{\frac{2}{3}} \qquad \text{(Ref. 8)}$$

where: $\nu e/V$ = concentration of effective network chains, moles/cm^3

mh_c/A_c = compression modulus with h_c, the unswelled sample height; A_c, the unswelled cross sectional area; and m, slope of the linear portion of the force-deflection curve for swollen specimen, gm/cm^2

R = Universal gas constant, 0.846×10^5 gm-cm/°K-mole

T = test temperature, °K

S = sol fraction determined as specified in Sol/Gel and Swell Section of the Appendix

$1 - \phi$ = volume fraction of binder in propellant

ϕ = volume fraction of filler in propellant

Compression modulus is determined using the Perkin-Elmer Model TMS-1 Thermomechanical Analyzer (TMA). The instrument, shown schematically in Figure 21, consists of a quartz probe connected to the core of a linear variable differential transformer (LVDT). Samples to be tested are placed on the bottom of a tube that is stationary with respect to the LVDT core. Displacement of the sample results in displacement of the transducer core. The transducer signal output is directly proportional to the amount of displacement.

The following procedure is used for compression testing of propellants:

A 3 mm diameter sample is cut from 2.5 mm thick propellant slab. The sample is swelled first in toluene vapor and then extracted for 96 hours (solvent to sample ratio of 100:1), with solvent changed at 24-hour intervals during initial 48 hours of extraction. The sample is placed on the tube support of the TMA, covered with a thin metal disc (6 mm diameter), and then immersed in solvent at room temperature. Weights are applied sequentially to the sample until a total 10-12 percent compression based on swollen height is attained. Sample displacement is measured at equilibrium compression under each load. A load-displacement curve as shown in Figure 22 is prepared from the resulting data. Compression modulus is determined from the least squares slope of the linear portion of the compression plot.

3. MECHANICAL PROPERTIES MEASUREMENT

a. Creep Compliance

The apparatus consists of a horizontal platform on which is mounted a fixed metal support and a carriage which travels on two guide rods (Figure 23) Ball bushings are used to reduce the coefficient of friction of the carriage on the rods to very low values. The carriage is caused to move by known weights suspended by the cable which passes over a block of nylon (the cable is stranded steel covered with nylon). Longitudinal translation of the carriage is detected and recorded by means of the electrical output of a linear variable differential transformer (LVDT). A micrometer is used for the calibration of the LVDT.

A propellant specimen (3" x 1" x 0.1" and bonded to wood tabs) is clamped in the position shown in Figure 23. The output of the LVDT is brought to electrical null and the recorder is started. A known weight is suspended from the weight cable and the displacement of the carriage (and

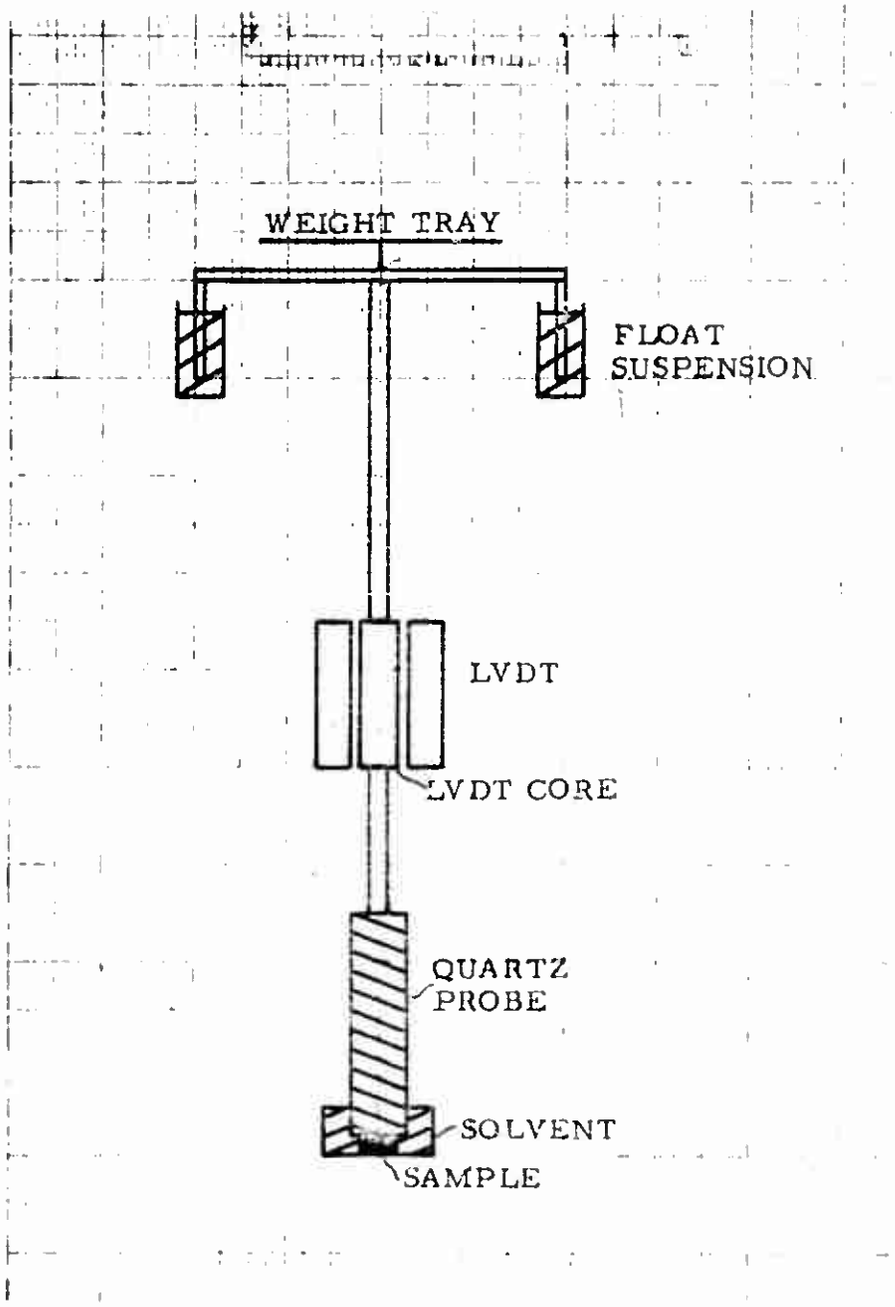

Figure 21 Schematic Diagram of Perkin-Elmer TMS-1 Thermomechanical Analyzer

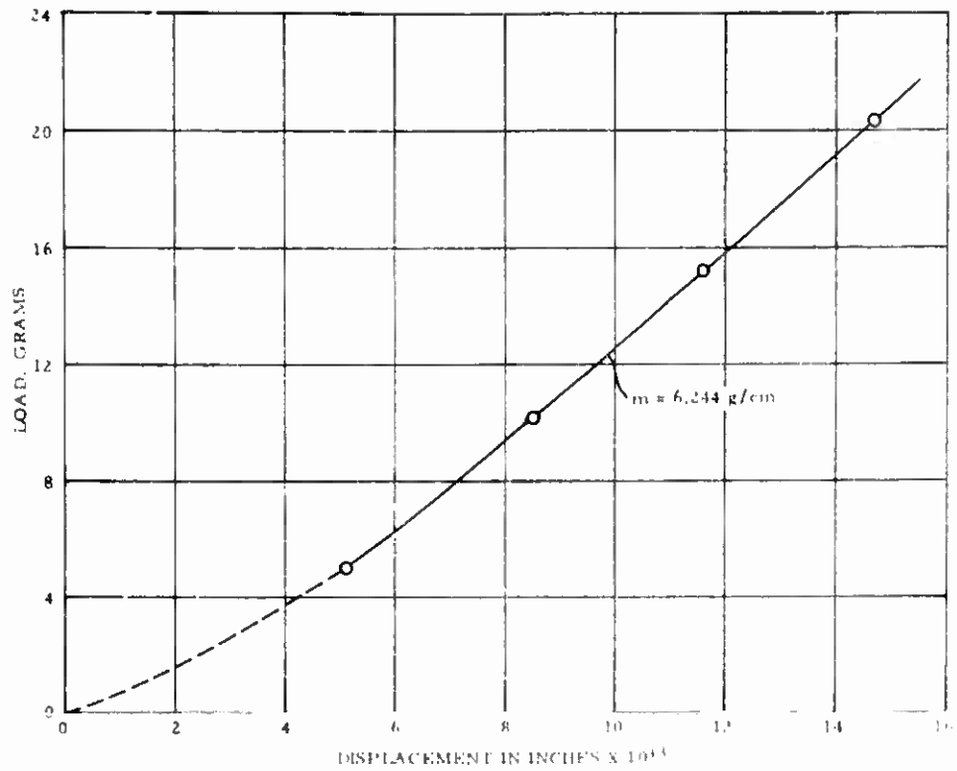

Figure 22 Typical Compression Modulus Curve for Swollen ANB-3066

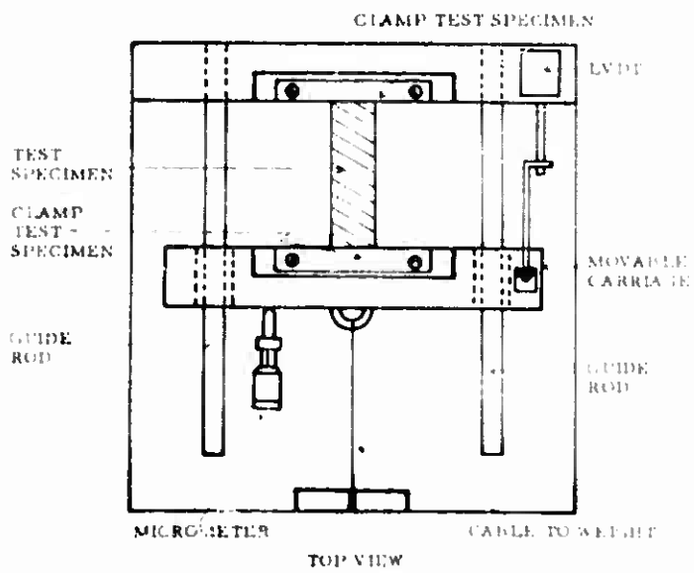

Figure 23 Creep Measurement Apparatus

thus the elongation of the sample) is detected and recorded with respect to time. Elongations of up to 17 percent (limit of the apparatus) are recorded. Inverse creep compliance for points in time are calculated according to

$$1 / D = \frac{W K l_o}{A C} \cdot 2.2 \times 10^{-3}$$

where:

W = force in grams

K = calibration constant

l_o = initial specimen length

A = initial cross-sectional area of test specimen

C = chart reading in inches

b. Tear Rate Measurement

The apparatus for tear rate measurement was adapted from the apparatus for creep compliance and is identical except in the following respects (see Figure 23):

- The fixed support plate is mounted so that the movable carriage travels vertically.
- A cam is used to support the movable carriage during the sample loading process. This cam is released to start the test.

A propellant specimen (3" x 1" x 0.1" and bonded to wooden tabs) which has a 3/4 inch slit at one edge, is mounted on the instrument in the position shown in Figure 24. A transparent reticle with 0.05 inch grid lines is mounted on the propellant surface with a small quantity of silicone grease. The proper weight is added to the weight hanger and the support cam is released. Simultaneously, a stop watch is started. Crack growth, which starts at the end of the slit, is timed at lengths of 0.050, 0.100, 0.150 and 0.200 inches. Extension of the sample during crack growth is recorded from the LVDT output. The data are plotted as log crack extension versus log time.

c. Uniaxial Tensile Measurements

Minithin tensile specimens are pulled on an Instron at 75 ± 3°F and a strain rate of 0.54 in/in/min. Figure 25 illustrates the minithin specimen which is stamped out of 0.1 inch thick propellant slices and bonded to wood tabs.

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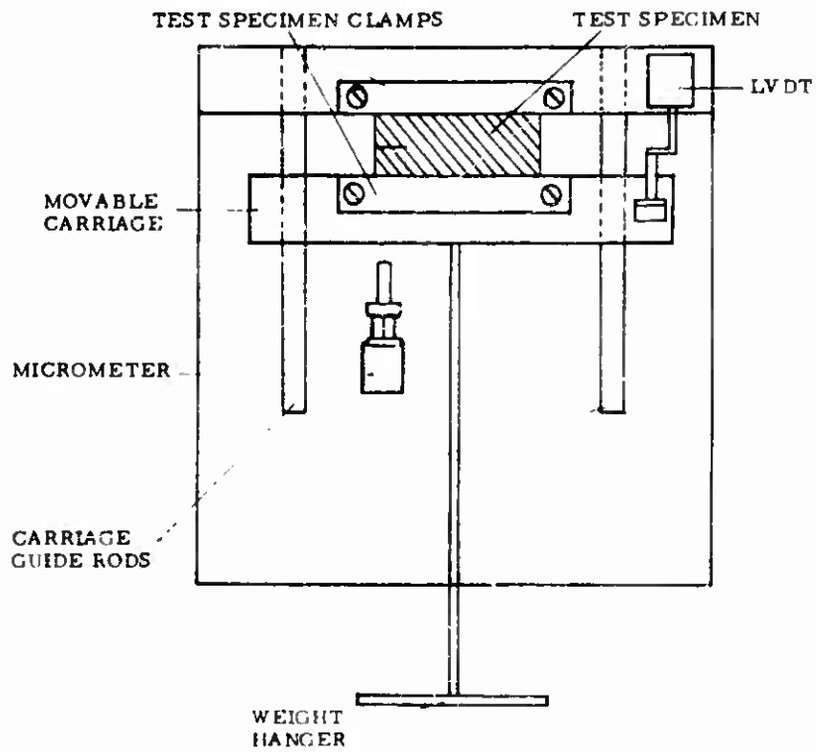

Figure 24 Tear Rate Apparatus

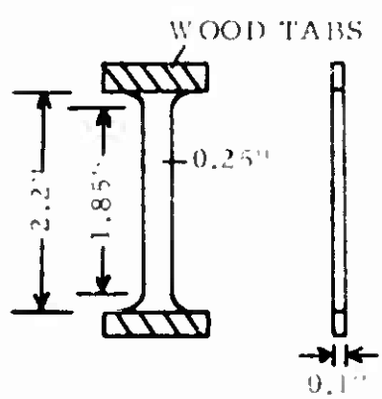

Figure 25 Minithin Tensile Specimen

REFERENCES

1. Minuteman Advanced Technology (Propellant) Production Support Program (U), Aerojet, Report No. 0162-041QAT-1, January 1965. CONFIDENTIAL

2. A.H. Muenker, C.A. Rowe, J. Linsk, and C. Gustavson, Synthesis and Evaluation of Curing Agents, Report No. AFRPL-TR-71-23, December 1970.

3. G.R. Cann, "Applications of Differential Internal Reflection Infrared Spectroscopy to the Study of Elastomer Cure and Aging", 9th Annual Meeting of the Society for Applied Spectroscopy, New Orleans, La., October 1970.

4. W.E. Baumgartner, J.A. Hammond, G.E. Myers, and W.G. Stapleton, "Stress Enhancement of Chemical Aging Process in Propellant", 1971 JANNAF Combined Propulsion Meeting, CPIA Publication No. 219, Vol II, October 1971.

5. S.J. Bennett, G.P. Anderson and M.L. Williams, "The Time Dependence of Surface Energy in Cohesive Fracture," J. Polymer Science, 14, 735 (1970).

6. W.G. Knauss, "Delayed Failure - The Griffith Problem for Linearly Viscoelastic Materials", Int. J. Fracture Mechanics, 6, 7 (1970).

7. G.E. Myers, Aluminum Hydride Propellant Shelflife, Report No. AFRPL-TR-71-12, March 1971.

8. Study of Characteristics and Standard Variability of Composite Solid Propellants, Thiokol Chemical Corporation, Elkton Division, Report No. E26-69, February 1969.

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13. ABSTRACT

This program is determining the individual chemical rate processes that govern the aging of ANB-3066 propellant, and it is attempting to establish the effect of chemical (compositional) changes upon the system's mechanical response to enable better utilization of accelerated surveillance test data.

Chemical changes, as they occur in the propellant under the influence of time, temperature and stress are determined by reflectance infrared techniques, measurement of sol content and crosslink density, off-gas analysis, and analysis (GPC/infrared) of sol extracts. The system's changes in chemical composition, as evidenced by these measurements, are then related to corresponding changes in mechanical response as determined by uniaxial tensile measurements and measurement of creep compliance and tear propagation.

The report outlines the experimental matrix to be followed, and it quotes initial data obtained with ANB-3066 propellant and an analog propellant containing KCl in substitution of ammonium perchlorate.

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