CHEMICAL STRUCTURE AGING EFFECTS

Lionel H. Layton

Thiokol Chemical Corporation

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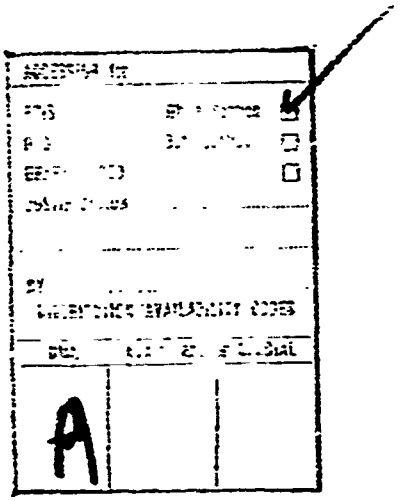
Department of the Air Force
Air Force Rocket Propulsion Laboratory
Edwards Air Force Base, California



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13. ABSTRACT

Aging and surveillance programs have been performed with solid propellants since their inception. To obtain some feel for the long term aging behavior in a short time, accelerated aging performed at elevated temperature has been used. It has been found that no comparison can be made between accelerated aging results converted to long time equivalent ambient aging and the actual long term ambient aging data. A study of the chemical changes occurring in TP-H1011 propellant with age at four temperatures has been made. It has been shown that the reaction responsible for the propellant cure is essentially complete in one week and contributes very little to the mechanical properties changes with age. Studies with NMR and EPR spectroscopy indicate that reactions are occurring at the sites of unsaturation along the polymer chain with a high percentage of the reaction at the pendant vinyl group. The reaction rate has been determined by following the change in gel found in the binder. A correlation of the mechanical properties and chemical changes has been made. A unique treatment of the data has been developed to define the behavior observed with strong indications of physical significance beyond the scope of aging behavior. The results of six months aging at 75, 110, 135, and 150° F have been used to predict equivalent 75° F aging to 10 years time. The predicted data have been very favorably compared to data obtained at OOAMA, Hill Air Force Base, for ten years with the same propellant type.

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CHEMICAL STRUCTURAL AGING EFFECTS

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FOREWORD

This Special Technical Report was prepared in compliance with line item B003 of DD Form 1423 "Contract Data Requirements List" to Contract F04611-71-C-0049. The work reported herein was done at the Wasatch Division of Thiokol Chemical Corporation at Brigham City, Utah, under the direction of Dr. Lionel H. Layton. Robert A. Biggers (MKPB) was the Air Force Project Engineer.

This document is identified by Thiokol Publications Number 73160.

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

Robert A. Biggers (MKPB)
Project Engineer

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I. INTRODUCTION

A. BACKGROUND

Aging and surveillance programs have been performed with solid propellants since their inception. The properties of all materials change with age and this change is sufficiently pronounced in materials containing organic molecular structures that a definition of the aging effects on materials properties and aging rates must be defined. To obtain some feel for the long term aging behavior in a short time, accelerated aging performed at elevated temperature has been used. It has been found, however, that no real comparison can be made between accelerated aging results converted to long term equivalent ambient aging and the actual long term ambient aging data. Many years of ambient aging have been performed on many solid propellant programs with the final conclusion being that no simple relationship exists between the aging behaviors observed at different temperatures.

In general, accelerated aging results have been converted to long term equivalent ambient aging predictions by means of the Arrhenius rate equation of the Eyring absolute rate theory. The basic theory for both of these methods requires the prediction be made for single chemical reaction or, at very best, simultaneous or competing reactions having very nearly the same reaction rates and the same activation energies. When the chemical reactions have a widely different temperature dependence, the Arrhenius equation and absolute reaction rate theory do not apply and the prediction of effects at one temperature from measurements at another temperature are no longer easily made.

Since the chemical reactions occurring during the cure and aging of solid propellants are varied and complex, it becomes necessary to study these reactions individually to understand the curing and aging mechanisms. It is apparent that some chemical reactions occur so slowly at room temperature that any effect on the material properties is insignificant in the times of interest. However, these same reactions can be accelerated at elevated temperature to become a major contributor to the mechanical property changes. A determination of the chemical

reactions occurring during cure and aging of a solid propellant will provide the understanding required to make a proper assessment of the mechanical properties measured as a function of age-time and a realistic treatment of the accelerated aging data feasible.

B. OBJECTIVES

The reactive groups chosen to cause a cure reaction in a crosslinked solid propellant binder are those which produce the best mechanical properties consistent with manufacturing requirements such as long pot life and short curing time. Additional reactions can, and very likely do, occur as a result of increasing the temperature to accelerate the aging process and these chemical changes generally have an adverse effect on the propellant mechanical behavior.

It is the objective of this program to develop a method for predicting the mechanical properties of TP-H1011 propellant at extended time by determining the chemical reactions, reaction mechanisms, and reaction rates affecting these properties under accelerated aging conditions. Although not a direct objective but a natural result of this program is the extension of the developed procedure to other crosslinked propellant and polymer systems. Accelerated aging by means of elevated temperature environments will then be a meaningful approach to extended time predictions.

C. SCOPE

Both the chemical reaction and mechanical property characteristics of TP-H1011 propellant are being evaluated in this study. An understanding of the chemistry is required to interpret the mechanical properties characteristics observed. Determinations of mechanical behavior as a function of aging time and temperature produces an aging rate curve for each temperature used. Extension of any of these curves required some guidelines. The chemical reactions occurring and the rates of these reactions at each aging condition provide these guidelines and make the aging predictions more reliable. A comparison of the predictions made, using the developed technique, has been accomplished with actual long term aging results from another aging program on TP-H1101 propellant.

II. SUMMARY

An aging program has been undertaken on TP-H1011 propellant to develop a method for predicting the mechanical properties of this material at extended time by determining the chemical reactions, reaction mechanisms, and reaction rates affecting these properties under accelerated aging conditions. A simple and unique method for separating the binder from the propellant solids has been developed and described. This procedure has made chemical analyses more accurate and reproducible and the results have provided a giant step in the understanding of the chemistry of aging specifically for this propellant and generally for other related propellants.

A new approach to mechanical properties interpretation has been used that makes predictions of long time ambient aging behavior possible from the short time accelerated aging data. Parameters of physical significance for viscoelastic interpretation as well as aging have been introduced. These parameters have been used to linearize the aging rate temperature dependence to make an aging time-temperature shift possible similar to that accomplished by the WLF equation for the load time-temperature shift.

It has been suggested in the report that a possibility for second order effects exists that can alter the shape of the aging rate curves. This would appear first at the higher aging temperatures and care must be exercised to avoid incomplete data evaluation. The simple aging rate expression used in this report, $\frac{dp}{dt} = \frac{k}{t}$, can be expanded to higher order terms to account for nonlinear effects that may arise. Although this has not been required for this study and is not included in this report, the procedure is available thereby making the technique a powerful tool for accelerated aging data analysis.

With an understanding of the chemistry of aging and the effect it has on the mechanical properties of propellant, it is possible to utilize available accelerated aging data to make long time predictions for the mechanical behavior of the propellant. A prediction of uniaxial tensile properties using 6 month accelerated aging data for TP-H1011 propellant has been made out to 10 years and compared with actual 10 year aging results from OOAMA for the same propellant.

III. TECHNICAL APPROACH

Samples of Minuteman, Stage I, propellant, TP-H1011, were cast and cured in one-half gallon cartons for the aging study. These cartons of propellant were placed in a large curing oven with the temperature controlled to 135° ± 2° F for the curing time of 96 hours after casting. At the end of cure, the samples were divided and placed in storage at the four temperatures of 75°, 110°, 135°, and 150° F for aging. One carton was sampled periodically during the cure period for chemical reaction studies. The cured samples are being used for both chemical reaction studies and mechanical properties evaluations to determine the effect of the thermal environments during the aging period on these parameters.

The carboxyl and epoxide content has been determined during cure at 135° F and aging at the four temperatures to obtain curing reaction rate data. Reaction rates are usually determined only during the early part of a reaction where the change in reactive species follows some kinetic law. In this case, the cure reaction behaves according to first order kinetics, however, it is of more interest to ascertain the chemical kinetic behavior at longer times where the reaction is approaching completion. These data will define the contribution of the cure reaction to the aging of the propellant.

In addition to the carboxyl-epoxide reaction, it was anticipated that reactions could occur at the sites of unsaturation in the polymer chain. This is especially true in the presence of oxidizing material such as ammonium perchlorate. This reaction is very like. of the free radical initiated type making the possibility of electron paramagnetic resonance (EPR) measurements a feasible approach for determining reaction rates. Measurements of nuclear magnetic resonance (NMR) using ^{13}C NMR spectroscopy is a feasible technique for analysis of double bond concentration in the propellant binder.

The mechanical property evaluations have been made at the same age-time intervals as the chemical analyses making a direct correlation of the data possible. Uniaxial tensile tests are being performed at 75° and 125° F and at 75° F with superimposed hydrostatic pressure at 500 psi. Stress relaxation modulus determinations

are made at 75° F and 2% strain. Constant load and strain endurance tests as well as fracture energy evaluations are used to determine the failure characteristics.

It has been observed that TP-H1011 propellant mechanical properties vary as a function of the cure temperature. It is not possible to produce the same mechanical behavior by curing the propellant at different temperatures regardless of the curing time used. The small changes in mechanical properties observed in propellants aged for short times at different temperatures requires that the initial propellant be as near homogeneous as possible. For this reason, it is essential that the aging samples be cured with identical conditions so the zero age-time properties are the same for all the samples aged at various temperatures.

With an understanding of the chemistry of aging and a measure of its effect on mechanical behavior, a means for making reasonable long time projections from the data obtained on propellant aged at elevated temperatures is suggested. For the first time, accelerated aging data can be used with confidence to determine the TP-H1011 propellant structural capability at some prescribed future time.

IV. RESULTS

A. CHEMICAL ANALYSIS

It is very difficult to perform chemical analyses for determination of reactions occurring in the binder when the binder is such a small percentage of the material as is present in solid propellants. Many techniques have been used to circumvent the problem, however, none have been completely satisfactory. For this program, a procedure for extracting the solids from the binder that appears to cause no change in the binder due to the extraction has been used. This procedure appears to be satisfactory in all respects, giving in the process the sol-gel ratio, the ammonium perchlorate and aluminum percentages, and a solids free binder for chemical analysis of functional groups. The following steps are involved in the procedure:

1. Extraction with cold (room temperature) benzene followed with four benzene washes. The original extract and washes are filtered and combined and contain the soluble portion of the binder.

2. Evaporation of the benzene to dryness (at room temperature) and determination of the carboxyl and the epoxide equivalents found in the sol.

3. Extraction of the insolubles from step 1 with 1:1 HCL in methanol followed by four methanol washes and one benzene wash. This removes the ammonium perchlorate and aluminum from the insoluble portion of the binder (gel).

4. Dry the insolubles (gel) from step 3 and determine the carboxyl and epoxide equivalents.

This technique has been used to evaluate the cure reaction during the cure period (4 days) at 135° F and the aging period (to 39 weeks) at 75, 110, 135, and 150° F.

The sol-gel results are presented in Table I for the four aging temperatures and graphically in Figure 1 for the cure and aging at 135° F. It is obvious that the cure and aging periods follow different kinetics since the data (as presented in Figure 1) do not behave linearly during cure but do provide a linear presentation during the aging period. Other presentations can be made to produce a linear behavior during cure, but now the aging period is not linear. Since no single presentation to produce a linear behavior in both regions can be made, and since the aging period is of prime interest, it was felt that the treatment shown in Figure 1 was best for this study.

The results of the carboxyl-epoxide analyses are tabulated and shown in Table II. These results are presented graphically in Figure 2 for cure and aging at 135° F. It is readily apparent that little, or no, reaction is occurring during the aging period beyond one week from casting. The increase in gel content during the aging period indicates that some crosslinking reaction is occurring. This is particularly apparent when all of the gel data are presented for propellant aged at several temperatures. This can be seen in Figure 3 where only those data obtained from one week after cast to the maximum aging are presented for samples aged at 75, 110, 135, and 150° F. Of particular interest is the linear nature of the curves and the small scatter of data around the curve.

These percent gel curves are sufficiently well defined that one is prompted to use them for evaluation of the aging rate from the chemical change of the propellant binder with time. It was found that the slopes of the curves in Figure 3 obeyed a temperature dependence law similar to the Arrhenius equation, $k = Ae^{B/T}$, where k is the slope of the curves, A is the reaction frequency factor, T is the absolute temperature for the reaction, and B is a function of the activation energy. Expressing this equation in the logarithmic form $\log k = \log A + B/T$, it can be seen that a plot of log k vs 1/T should produce a straight line of slope B for any

TABLE I

WEIGHT PERCENT SOL AND GEL FROM AGED TP-H1011 PROPELLANT BENEZENE EXTRACTION
Mix 6780450

Storage Conditions					
Temp (° F)	Time (Wks)	Soluble %	Gel %	Total %	Recovery* %
75	1	8.21	5.71	13.92	99.4
	2	8.20	6.22	14.42	103.0
	3	8.33	5.52	13.82	98.9
	4	8.29	5.75	14.04	100.3
	6	8.27	5.69	13.96	99.7
	8	8.13	5.72	13.85	98.9
	10	8.11	5.81	13.92	99.4
	12	8.18	5.72	13.90	99.3
	24	8.05	5.81	13.86	99.0
	39	8.10	5.89	13.99	99.9
110	1	8.17	5.86	14.03	100.2
	2	8.21	5.62	13.83	98.8
	3	8.16	5.69	13.85	98.9
	4	8.06	5.81	13.87	99.1
	6	8.09	5.84	13.93	99.5
	8	7.99	5.94	13.93	99.5
	10	8.02	5.97	13.99	99.9
	12	8.26	5.93	14.19	101.4
	24	7.91	6.04	13.95	99.6
	39	7.73	6.23	13.96	99.7

*Based on 14% binder in the propellant.

Table I (Cont)

WEIGHT PERCENT SOL AND GEL FROM AGED TP-H1011 PROPELLANT
BENZENE EXTRACTION
MIX 6780450

Storage Conditions					
Temp (°F)	Time (Wks)	Soluble %	Gel %	Total %	Recovery* %
135	1	8.12	5.85	13.97	98.8
	2	8.15	5.84	13.99	99.9
	3	8.04	5.94	13.98	99.9
	4	7.93	5.94	13.87	99.1
	6	7.91	6.04	13.95	99.6
	8	7.83	6.09	13.92	99.4
	10	7.80	6.24	14.04	100.3
	12	7.76	6.19	13.95	99.6
	24	7.63	6.30	13.93	99.5
	39	7.20	6.60	13.80	98.6
150	1	8.11	5.90	14.01	100.1
	2	7.98	5.85	13.83	98.8
	3	7.88	6.04	13.92	99.4
	4	7.71	6.13	13.84	98.9
	6	7.72	6.34	14.06	100.4
	8	7.52	6.43	13.95	99.6
	10	7.43	6.52	13.95	99.6
	12	7.30	6.60	13.90	99.3
	24	7.03	7.01	14.04	100.3
	39	6.68	7.36	14.04	100.3

*Based on 14% binder in the propellant.

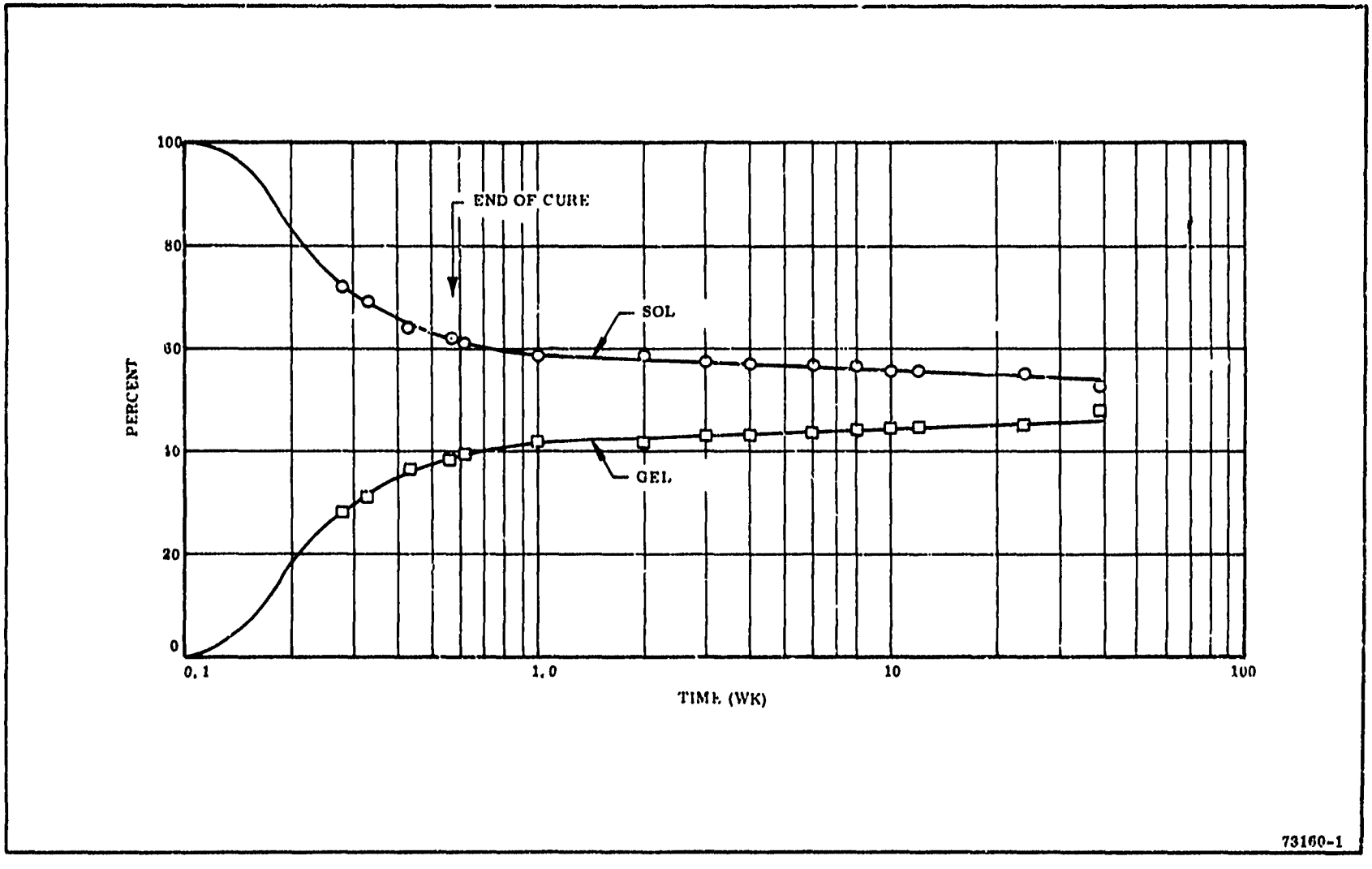


Figure 1. Percent Sol and Gel in TP-H1011 Propellant Binder Cured and Aged at 135°F Benzene Solvent

TABLE II

CHANGE IN CARBOXYL AND EPOXIDE CONCENTRATION
DURING AGING OF TP-H1011
MIX 6780450

Temp (°F)	Time (Wk)	Sol	Gel	Total	Sol	Gel	Total
75	1	0.0187	0.0194	0.0190	0.0080	0.0051	0.0068
	2	0.0196	0.0036	0.0140	0.0098	0.0081	0.0091
	3	0.0174	0.0055	0.0127	0.0082	0.0088	0.0084
	4	0.0183	0.0071	0.0137	0.0092	0.0082	0.0088
	6	0.0182	0.0078	0.0140	0.0071	0.0062	0.0067
	8	0.0186	0.0094	0.0148	0.0084	0.0068	0.0077
	10	0.0185	0.0100	0.0150	0.0077	0.0065	0.0072
	12	0.0189	0.4055	0.0134	0.0067	0.0065	0.0066
	24	0.0193	0.0066	0.0144	0.0076	0.0040	0.0055
	39	0.0219	0.0053	0.0149			
110	1	0.0190	0.0237	0.0231			
	2	0.0162	0.0094	0.0146	0.0092	0.0082	0.0088
	3	0.0164	0.0062	0.0122	0.0083	0.0078	0.0081
	4	0.0164	0.0065	0.0123	0.0098	0.0080	0.0090
	6	0.0177	0.0095	0.0143	0.0077	0.0074	0.0076
	8	0.0173	0.0086	0.0136	0.0075	0.0080	0.0078
	10	0.0187	0.0100	0.0150	0.0067	0.0047	0.0058
	12	0.0173	0.0064	0.0127	0.0164	0.0089	0.0133
	24	0.0175	0.0061	0.0128	0.0077	0.0058	0.0060
	39	0.0190	0.0050	0.0128	0.0097	0.0097	0.0097
135	1	0.0152	0.0263	0.0198	0.0093	0.0058	0.0078
	2	0.0174	0.0082	0.0136	0.0084	0.0082	0.0083
	3	0.0158	0.0074	0.0122	0.0093	0.0085	0.0090
	4	0.0158	0.0075	0.0122	0.0094	0.0082	0.0080
	6	0.0158	0.0086	0.0127	0.0092	0.0086	0.0090
	8	0.0153	0.0070	0.0117	0.0138	0.0059	0.0103
	10	0.0163	0.0054	0.0115	0.0088	0.0079	0.0084
	12	0.0156	0.0090	0.0127	0.0051	0.0101	0.0079
	24	0.0165	0.0065	0.0121	0.0068	0.0050	0.0058
	39	0.0156	0.0072	0.0115	0.0110	0.0083	0.0097
150	1	0.0166	0.0244	0.0199	0.0074	0.0051	0.0064
	2	0.0173	0.0055	0.0136	0.0084	0.0080	0.0082
	3	0.0142	0.0060	0.0106	0.0091	0.0081	0.0087
	4	0.0142	0.0065	0.0108	0.0101	0.0069	0.0087
	6	0.0158	0.0090	0.0127	0.0075	0.0087	0.0080
	8	0.0153	0.0071	0.0115	0.0090	0.0073	0.0085
	10	0.0157	0.0035	0.0100	0.0066	0.0078	0.0072
	12	0.0168	0.0093	0.0132	0.0063	0.0074	0.0068
	24	0.0154	0.0091	0.0108	0.0057	0.0050	0.0071
	39	0.0156	0.0082	0.0117	0.0414	0.0096	0.0120

Initial polymer and curing agent: 0.0494 0.0678

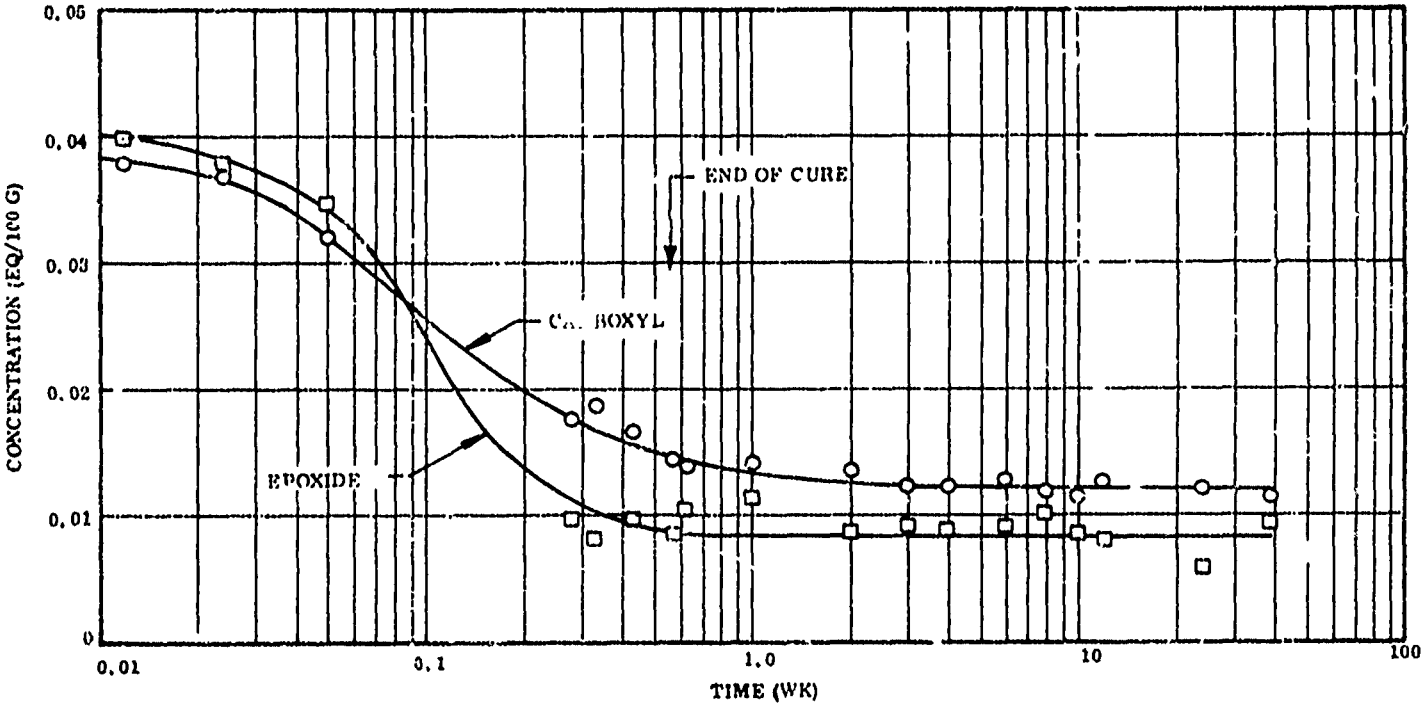


Figure 2. Functional Group Analysis During Cure and Aging at 135°F for TP-H1011 Propellant (6780450)

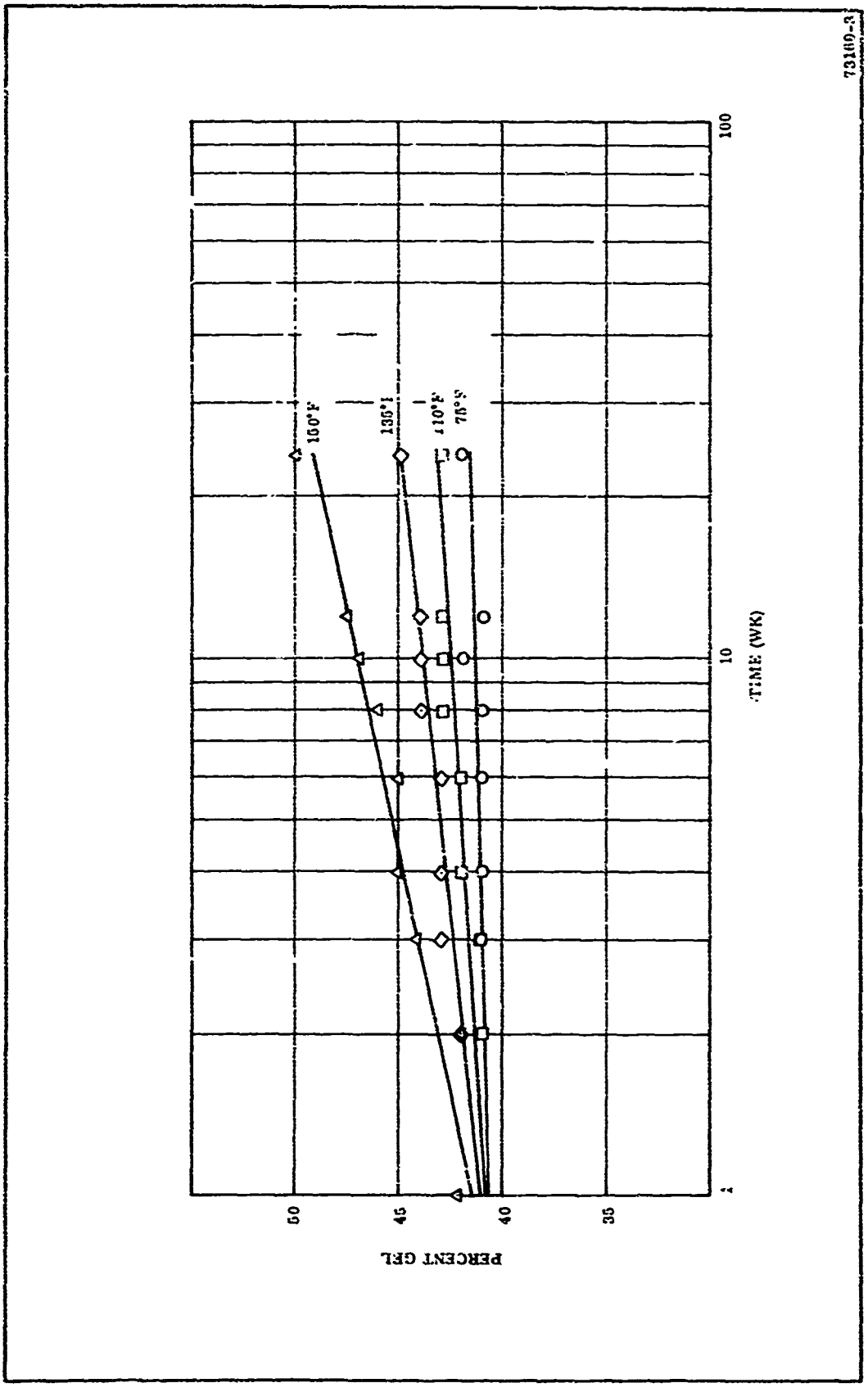


Figure 3. Percent Gel as a Function of Aging Time for TP-H1011 Propellant

reactions obeying this temperature dependence law. The slopes of the curves shown in Figure 3 have been used to make the curve shown in Figure 4. It can be seen that these data are well behaved and that a linear expression is perhaps the best presentation for them. This being the case, the gel formation rate can be determined for at least any temperature between 75 and 150° F from measurements made on propellant aged at one temperature. Of even more significance, these data give strong evidence that some chemical reaction is occurring during the aging period and that reaction is resulting in a net increase in crosslinking of the binder.

The curing reaction of carboxylic acid from the prepolymer and epoxide from the curing agent appears to be completed soon after one week. This is evident at all aging temperatures. The residual carboxyl and epoxide groups appear to be unreactive since the same level of concentration is achieved at all aging conditions. Continuation of the cure reaction cannot account for the continuation of crosslink formation during aging. Since there are many sites of unsaturation along the polymer chain, it seems likely that oxidative crosslinking might occur. The first consideration for analysis of the change in double bond concentration was infrared spectroscopy. It was found, however, that either the changes were too small to be detected or the complexity of the system masked the effect. Recent advances in carbon-13 nuclear magnetic resonance (NMR) spectroscopy make this tool attractive for analysis of polymer unsaturation.

Since ^{13}C NMR spectroscopy is relatively new, standards for the assignment of absorption peaks have not been extensively determined. Assignment of many of the absorptions in the binder was aided by first determining the NMR spectrum of pure curing agent and model compounds with structural characteristics similar to the polymer backbone. The spectrum of the epoxy curing agent (ECA) is shown in Figure 5 and some of the pertinent chemical shifts are presented in Table III. The chemical shift values are reported in parts-per-million (ppm, δ) referenced to methylene chloride, the solvent used for these studies. Chemical shifts up field from the reference are arbitrarily assigned a positive value and those downfield are considered as being negative.

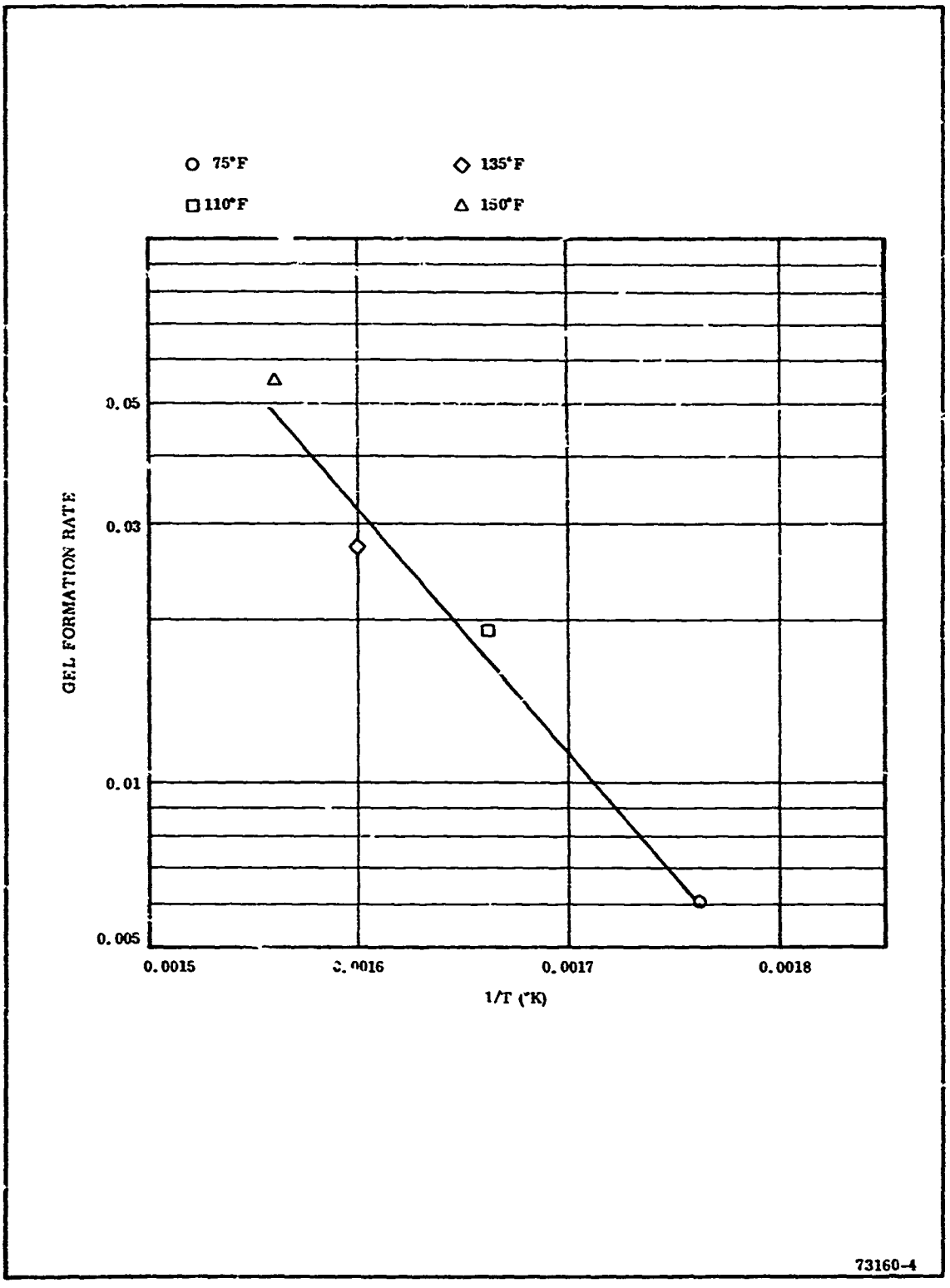


Figure 4. Temperature Dependence of the Gel Formation Rate in TP-H1011 Propellant

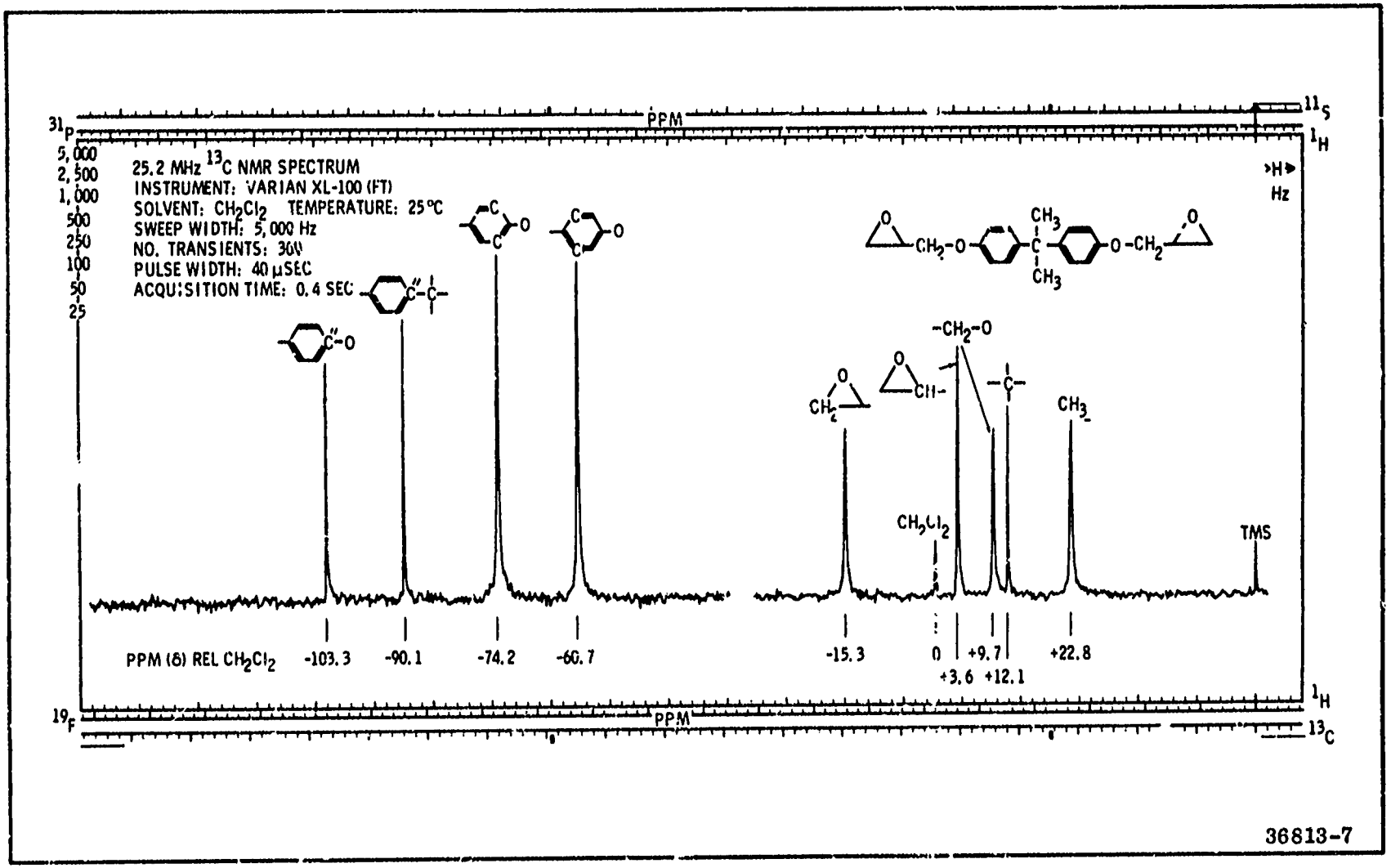
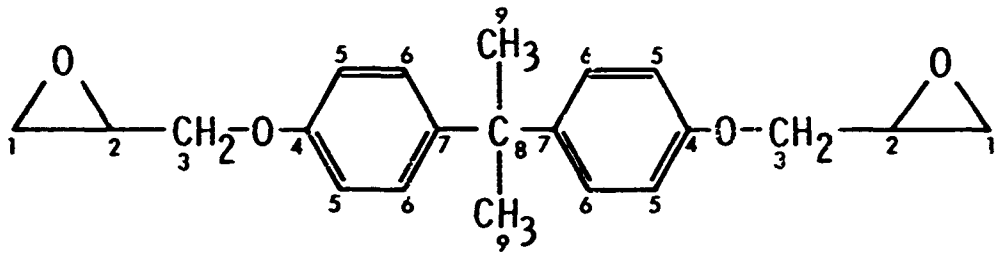


Figure 5. ^{13}C NMR Spectrum of TP-H1011 Curing Agent, the Diglycidyl Ether of Bisphenol A

TABLE III

ASSIGNMENTS FOR ^{13}C NMR SPECTRUM OF THE DIGLYCIDYL ETHER OF BISPHENOL A

(TP-H1011 CURING AGENT)



Carbon	Chemical Shift (ppm, δ)*
1	-15.3
2	+3.6
3	+9.7
4	-103.3
5	-74.2
6	-60.7
7	-90.1
8	+12.1
9	+22.8

*Relative to internal CH_2Cl_2 reference solvent.

Many chemical compounds have been used as references for ^{13}C NMR work; however, no standard reference is in use. There is no strict convention for the negative or positive assignment of chemical shifts as there is in proton NMR work. The following conversion factors are useful in converting the chemical shift values reported here to some more common references used in ^{13}C NMR studies

$$\delta CH_2Cl_2 = \delta CS_2 - 140 \text{ ppm}$$
$$\delta CS_2 = \delta C_6H_6 + 64.8 \text{ ppm}$$
$$\delta TMS = \delta CHCl + 53.4 \text{ ppm}$$

The spectrum and the assignment of the major portion of the absorptions with the HB-ECA-20% AP material (simulated propellant) are shown in Figure 6 and Table IV. Since the change in spectra from zero time to 4 hours cure was insignificant, only the spectrum for the material cured for 4 hours at 135° F is shown. The only assignments which have been made are those associated with the polybutadiene portion of the backbone. The low field (-60 to -90 ppm) signals are due to the unsaturated carbons (cis, trans, and vinyl) while those at high field (+10 to +40 ppm) are due to saturated carbons in the polymer chain.

The spectrum after 72 hours of cure at 135° F for the same material is shown in Figure 7. Three things are readily apparent in the spectrum: (1) the quality of the spectrum has degraded somewhat, i.e., poorer resolution (2) the vinyl absorptions at -90 and -60 ppm have decreased in relative intensity; and (3) the peaks attributed to the epoxide have disappeared. The poorer resolution is not unexpected in view of the increase in crosslink density with subsequent loss of polymer solubility and mobility. The decrease in the vinyl absorption intensity has been attributed to a reaction taking place at the vinyl group that is detectable in the NMR spectrum during cure and is likely the reaction taking place during the aging period. The disappearance of epoxide is, of course, expected since the ECA has reacted, thereby significantly restricting the mobility of the carbons attached to the epoxide.

The significance of these NMR studies is that a reaction has been detected that can account for the continued crosslinking and increased gel formation after

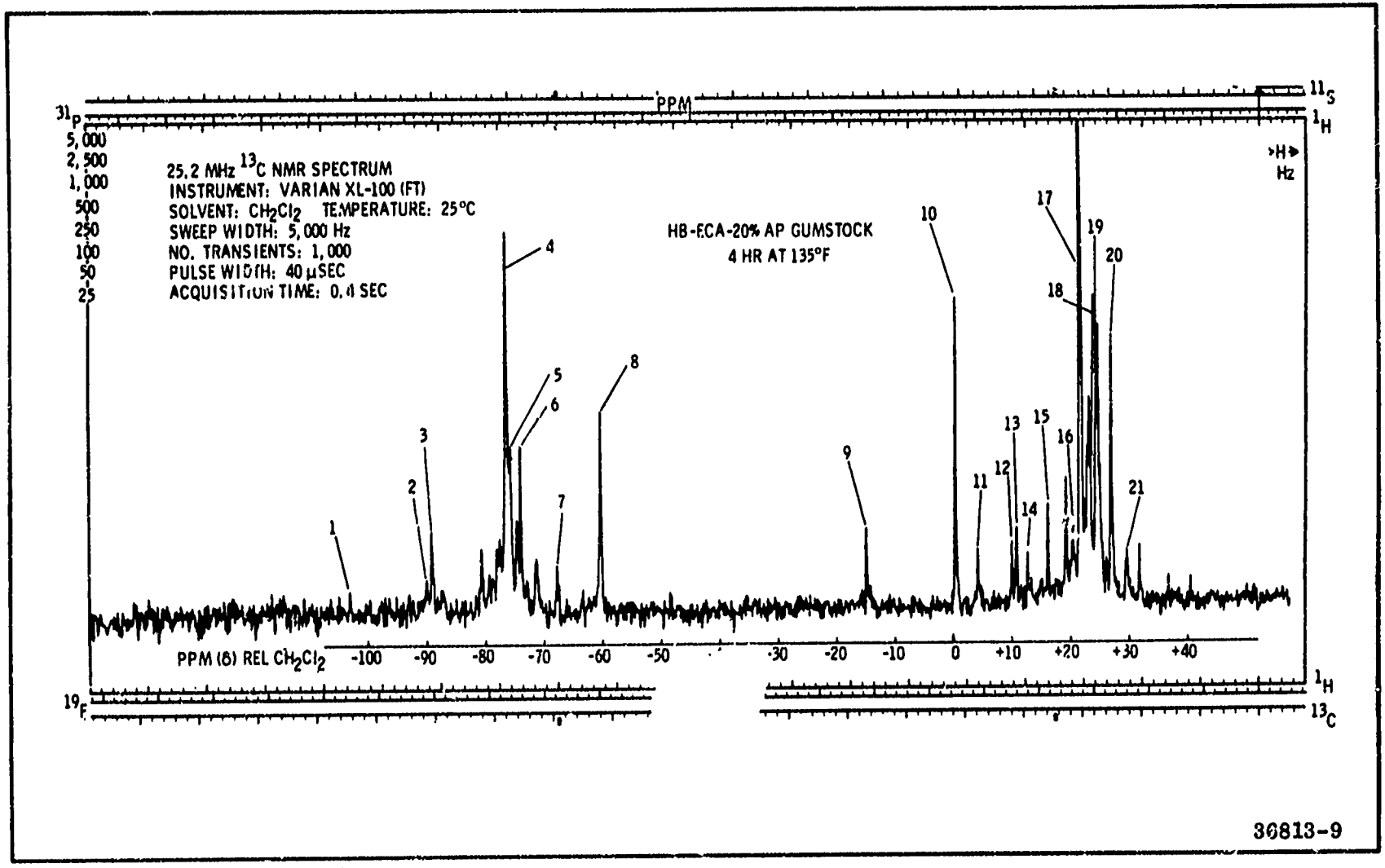
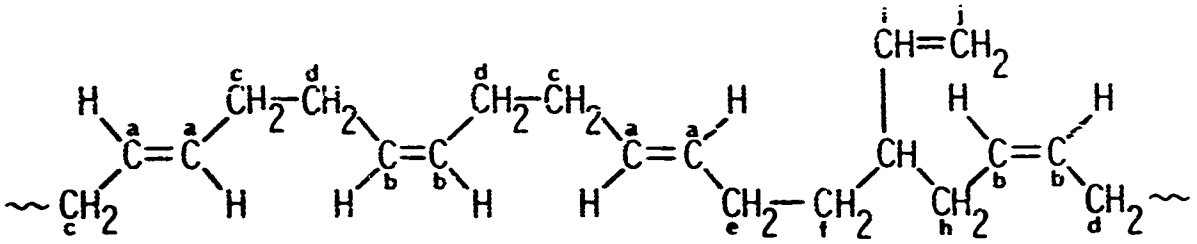


Figure 6. ^{13}C NMR Spectrum of HB-ECA-20% AP GumstockCured 4 Hours at 135° F

TABLE IV

ASSIGNMENTS FOR ^{13}C NMR SPECTRUM OF HB-ECA-20% AP GUMSTOCK CURED 4 HOURS AT 135° F



Line No.*	Carbon	Chemical Shift (ppm, δ)***
1	ECA 4**	-103.3
2	ECA 7	-90.1
3	i	-88.8
4	a	-76.2
5	b	-75.4
6	ECA 5	-74.2
7	Nitrile (-C≡N)	-67.5
8	j and ECA 6	-60.7
9	ECA 1	-15.3
10	CH_2Cl_2	-0.0
11	ECA 2	+3.6
12	ECA 3	+9.7
13	g	+10.7
14	ECA 8	+12.1
15	h trans	+15.3
16	f	+20.2
17	c and h cis	+21.1
18	ECA 9	+22.8
19	e trans	+24.0
20	d	+26.5
21	e cis	+29.3

*Figure 2.
**Table I.
***Relative to CH_2Cl_2 solvent.

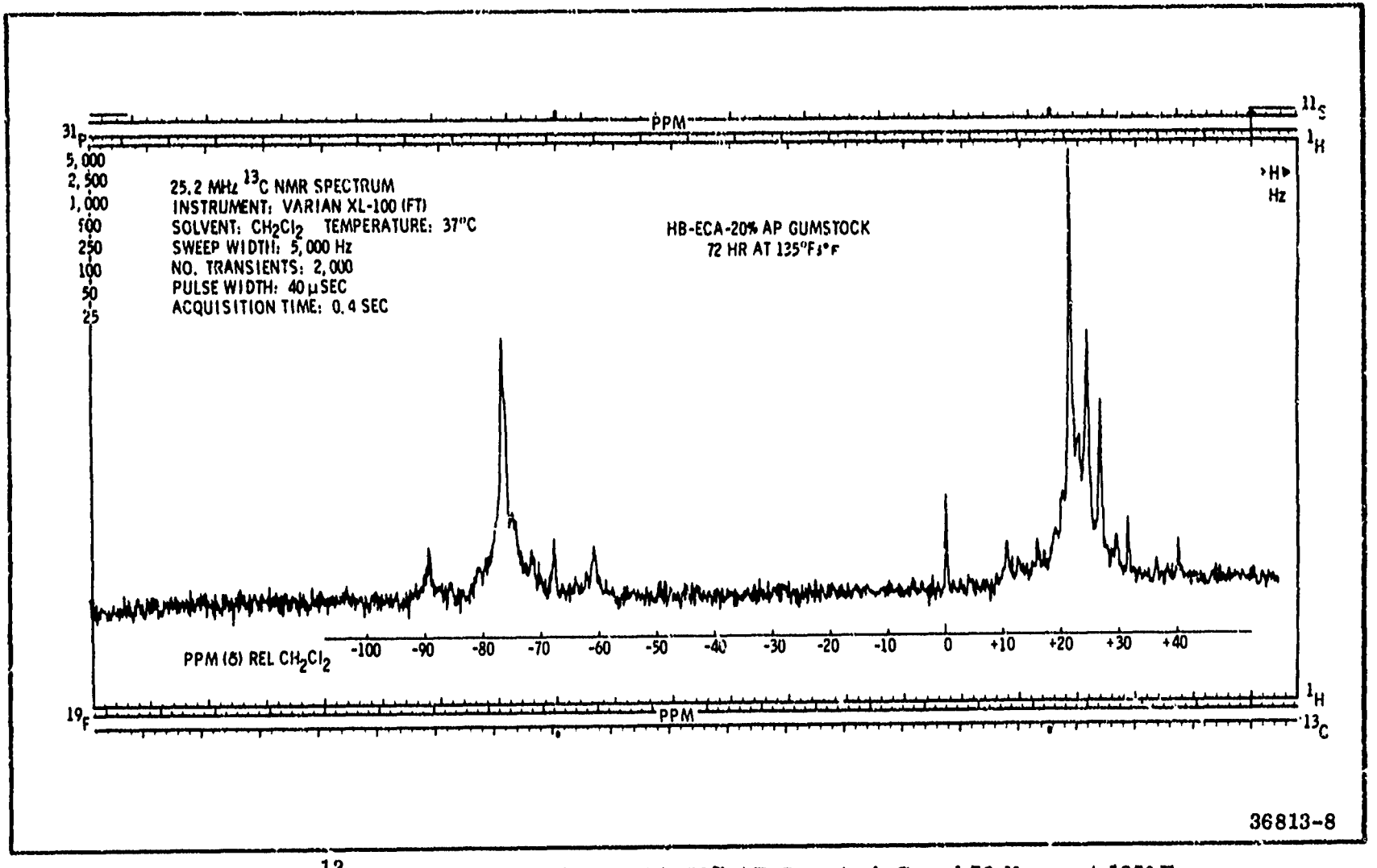


Figure 7. ^{13}C NMR Spectrum of HB-ECA-20% AP Gumstock Cured 72 Hours at 135° F

the carboxyl-epoxide reaction appears to have ceased. This reaction is considered to be the cause for the change in mechanical properties with age.

B. MECHANICAL PROPERTIES

Mechanical properties have been measured at the same aging time intervals as the chemical analyses were performed on samples aged at 75, 110, 135, and 150° F. The tests performed at each time interval are (1) uniaxial tensile tests at ambient pressure and at 75 and 125° F, as well as at 500 psi superimposed hydrostatic pressure at 75° F, (2) stress relaxation at 2% strain and 75° F, (3) fracture energy, (4) constant load and constant strain tests, and (5) thermal coefficient of linear expansion. The data are tabulated and presented in the appendix.

It has been recognized that a small variation in properties exists across a carton sample. This variation is rather consistent, therefore, it was assumed that the aging rate was the same for the entire sample although a consistent bias existed. With this assumption it was possible to reduce data scatter by always taking specimens for a particular test from the same general location in the cartons throughout the program. Since aging rate is the subject of this study and not test comparison with other studies, this seems like an easy means for making maximum usage of the propellant. Since it was anticipated that a comparison would be made with the OOAMA Minuteman Stage I surveillance data, the specimens for the 75° F uniaxial test were taken from the center of the carton to be as nearly consistent with the standard surveillance procedure as possible.

It has been seen in the past that TP-H1011 propellant becomes very stable with age-time at 75° F after it has aged for several years. Samples of this propellant that had aged at 75° F for eight years were available and used as a "standard." At each test increment, a specimen of this "standard" was tested and compared with the previous results before tests on the aging program propellant were made. If the test data did not agree with the previous results, a check was made of the procedure and corrections made, if necessary. When it was concluded that no testing problems existed, samples for the program were tested. With test

variability reduced to a minimum only the carton to carton variability remained over which there was no control.

A total of three specimens was tested at each point. The data presented in this report are the average values for the three tests.

C. DATA CORRELATION AND ANALYSIS

The chemical analyses that were performed indicate that the chemistry of cure of TP-H1011 propellant is very well behaved. The kinetics of the cure reaction obey a first order law until near reaction completion where significant deviations occur. Of more importance is the result showing the curing reaction to be sufficiently complete within one week that continued reaction during the aging period is less than can be detected for any of the aging temperatures investigated.

The change in gel concentration in the propellant binder (Figure 3) during aging indicates that some chemical crosslink reaction is continuing. It is necessary for utilization of elevated temperature data for long time predictions at a lower temperature to have an expression for the reaction rate temperature dependence. This is normally achieved for most chemical reactions using the Arrhenius equation. It was pointed out earlier that this expression does not hold for a system having simultaneous reactions with differing activation energies. Since the curing reaction has reached completion and only one reaction has been identified, it seems reasonable to use this relationship for reaction rate and temperature. It has been shown in Figure 4 that the rates of gel formation determined at each of the four temperatures do have a linear temperature dependence. Since the chemical reactions appear to behave very normally for both cure and aging, it is possible to perform an analysis of the mechanical properties data with confidence that an unknown change in chemistry is not likely to occur.

It was shown that the change in gel concentration was a linear function of log aging time. Viscoelastic behavior of the propellant also exhibits wide regions of linear change with log load time. If the chemical reaction rates during aging are

controlled by the mobility of the polymer chains, then it might be expected that the mechanical properties also change as a function of log aging time.

The test results presented tabularly in the appendix have been plotted as a function of logarithmic age-time over the total time of the aging program to date. The data for maximum stress, strain at maximum stress, and modulus for uniaxial tensile tests at 75° F are presented in Figures 8-10. It can be seen that all the curves for the four aging temperatures come to the same point at 0.57 weeks time. This is the end of cure for the propellant, and since all samples were cast and cured at the same time, the properties must of necessity be the same at this point. This is not a measured property but was used as an aid in developing the best fit to the experimental data. The same set of curves are presented in the appendix with all the data points to show the amount of scatter and the fit obtained.

Since it appears that the change in mechanical properties with aging time is a linear function of log age-time for all aging temperatures used, it was tempting to determine the dependence of the rate of change on temperature. Again, the Arrhenius expression was used and a plot of $\log \frac{\Delta p}{\Delta \log t}$ vs 1/T was made where p was the maximum stress parameter. The result shown in Figure 11 agrees with all previous attempts to use elevated temperature aged propellant to predict room temperature results--it can't be done with the simple Arrhenius equation because of the nonlinear temperature dependence. A curve of the same shape was obtained with the strain at maximum stress and modulus parameters.

It has been found that a linear relationship can be achieved (Figure 12) for the three sets of data by subtracting a constant value from the temperature producing a term $T-T_o$, similar to that in the WLF equation for time-temperature superposition. The value of T_o required to produce the linear relationship is not the glass transition temperature as is the case in the WLF equation but is a temperature greater than the highest aging temperature condition. For these data it is 346° K (163° F) and probably is the highest aging temperature that can be used with this propellant and hope to maintain a linear behavior by this means. Undoubtedly, other chemical reactions become significant contributors to the aging process as the temperature is increased. The real importance of T_o, however, is that it

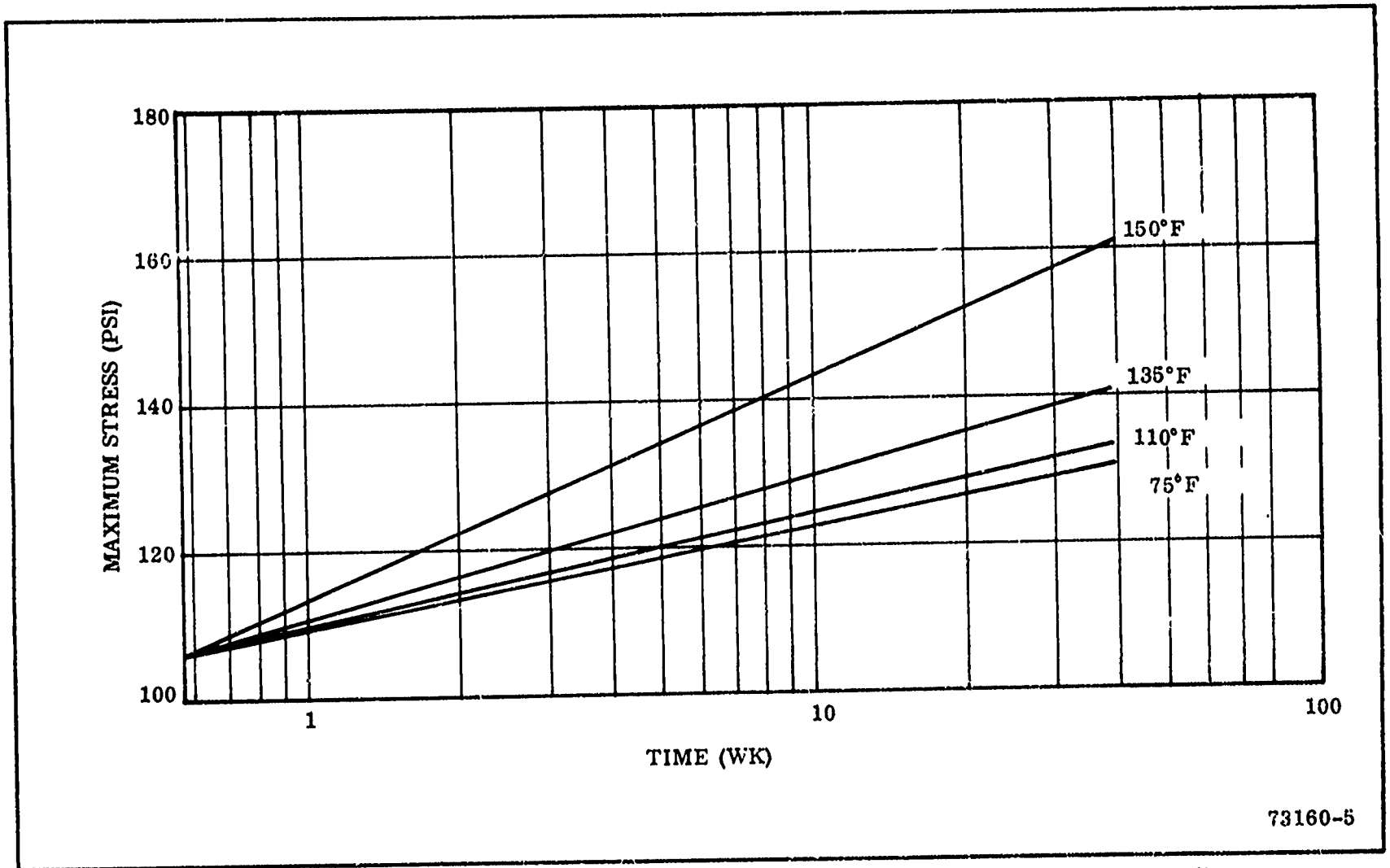


Figure 8. Effect of Aging Time and Temperature on Maximum Stress for TP-H1011 Propellant Tested at 75°F

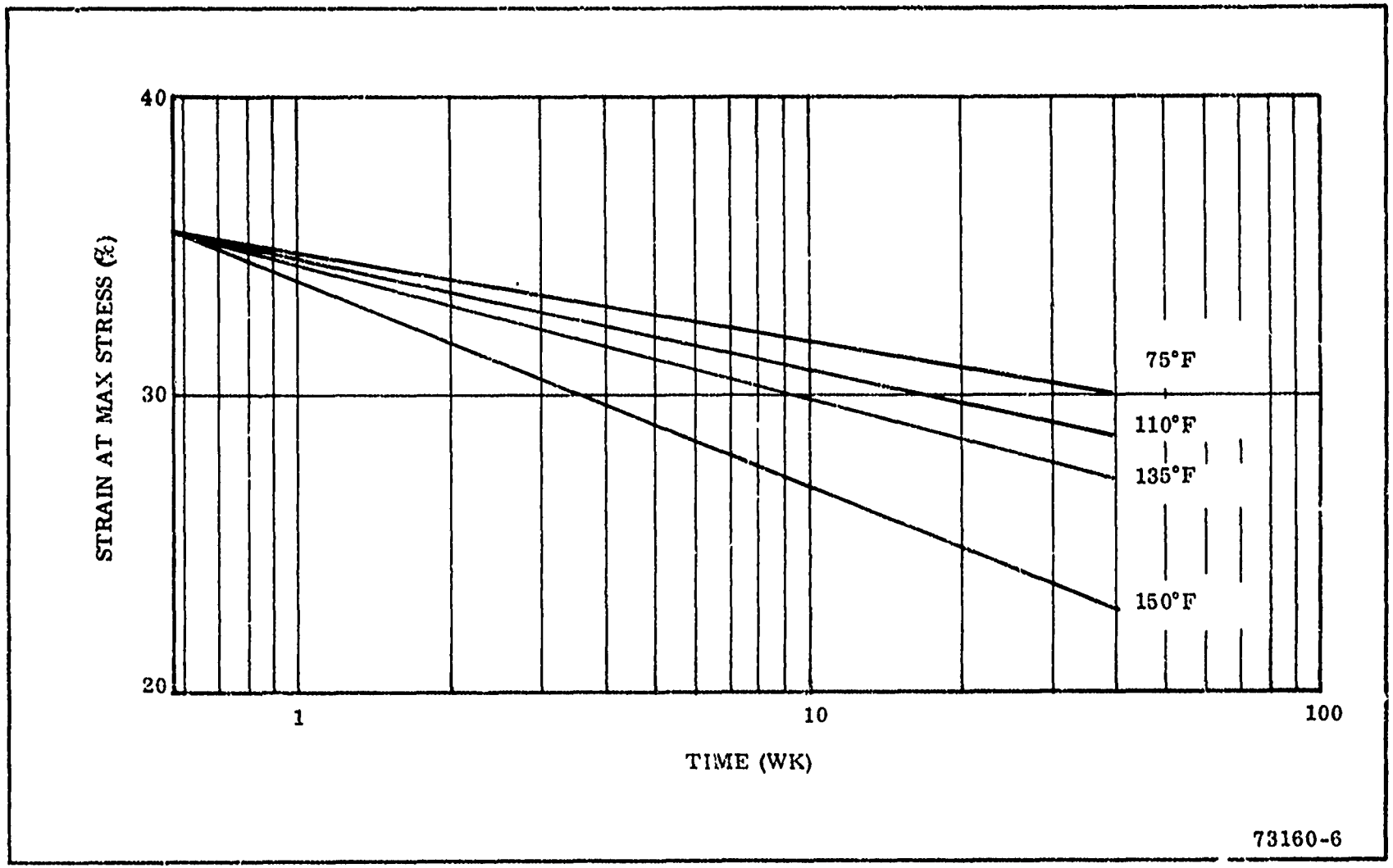


Figure 9. Effect of Aging Time and Temperature on Strain at Maximum Stress for TP-H1011 Propellant Tested at 75°F

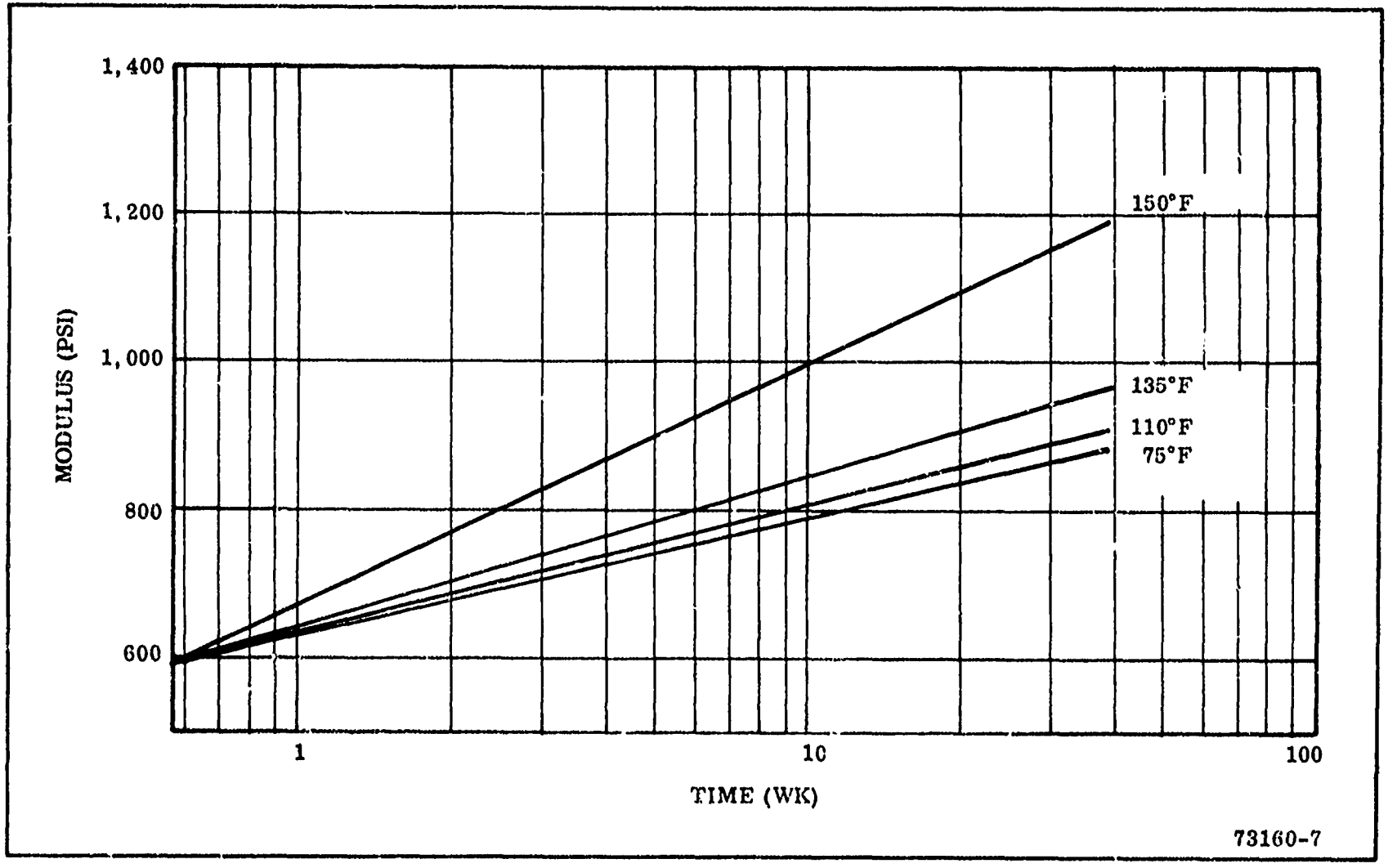


Figure 10. Effect of Aging Time and Temperature on Modulus for TP-H1011 Propellant Tested at 75°F

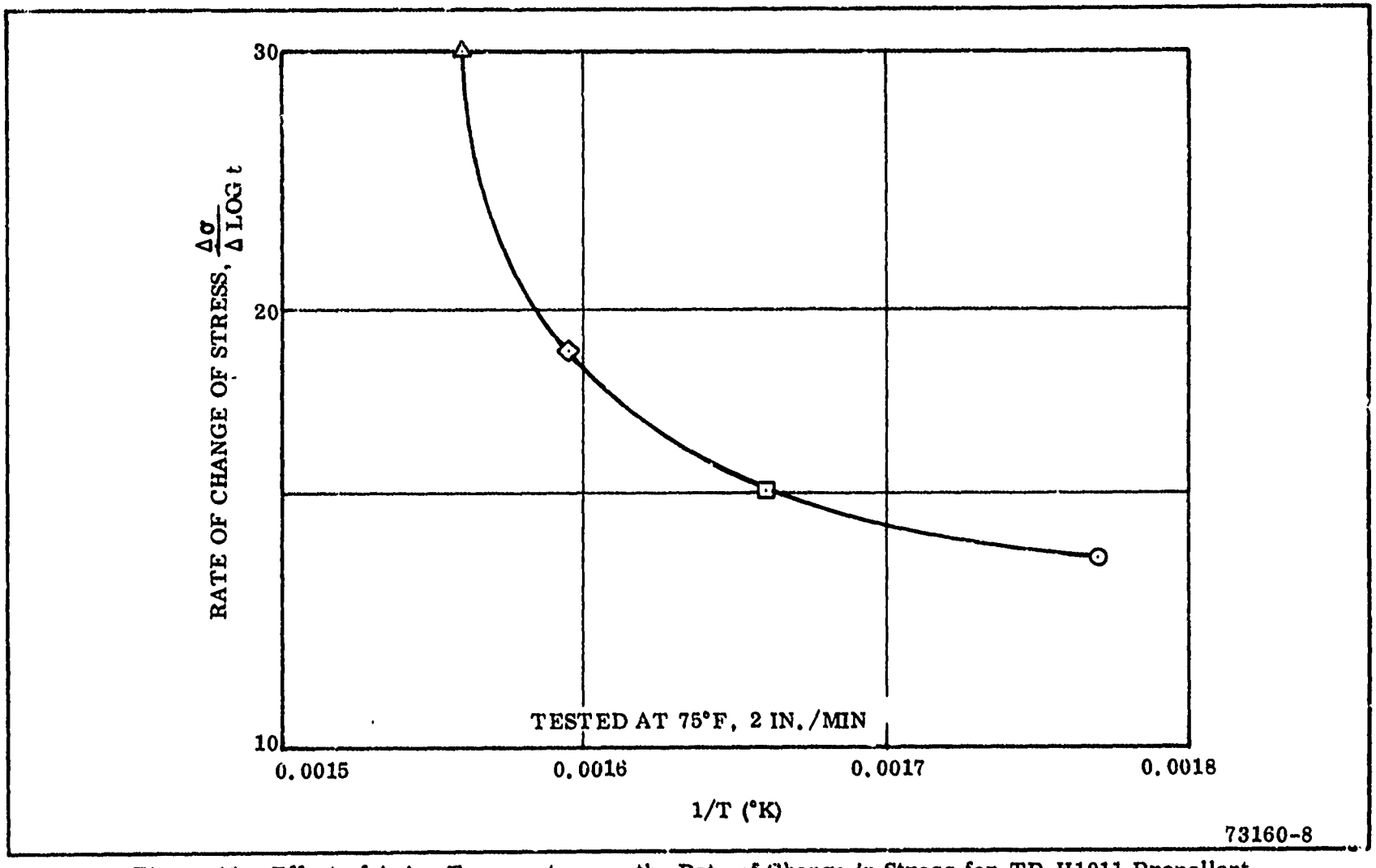


Figure 11. Effect of Aging Temperature on the Rate of Change in Stress for TP-H1011 Propellant

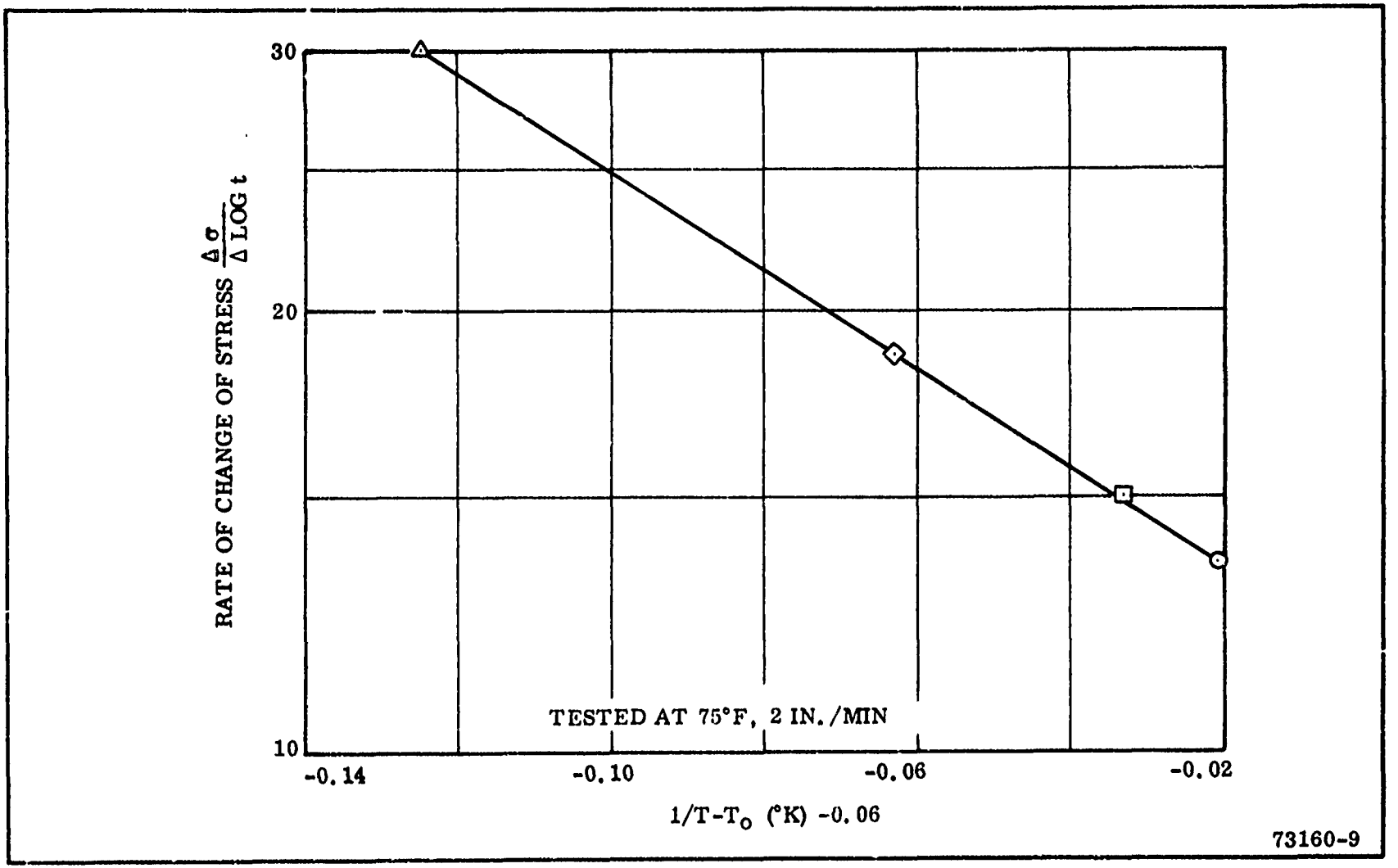


Figure 12. Effect of Aging Temperature on the Rate of Change of Stress for TP-H1011 Propellant

makes possible a mathematical treatment of the accelerated aging data to predict long time equivalent room temperature aging mechanical properties from data obtained after aging a short time at elevated temperature.

Other types of mechanical property tests were performed and a similar treatment of these data revealed the astonishing result that the same value of T_o (346°K) was required to produce a linear temperature dependence. These data are presented in Figures 13-15 for uniaxial tensile tests at 75° F under superimposed hydrostatic pressure of 500 psi, and in Figure 16 for stress relaxation tests. Again, the same curves are presented in the appendix with the data points to show how well the curves fit the points and the data scatter around the curve. It is essential to note that all curves are brought to the same point at 0.57 weeks to represent the condition when all the propellant had been exposed to the same environmental conditions.

The results of tests performed at 125° F were entirely different from those tested at 75° F. Again, it was possible to obtain a linear representation of the data as a function of log age-time (Figures 17-19). It was not possible to obtain a linear temperature dependence with the same value of T_o, however, when this parameter was increased to 361°K from the 346°K previously used, the equation for the relationship of aging rate to aging temperature still held. This interesting result indicates that T_o has some physical significance for both aging and testing rate behavior. The mechanical properties data are presented in the appendix with the data points included for clearly defining the age-rate curves.

It has been shown that during the first six months of this aging study the chemical reactions occurring behave in a consistent manner at all temperatures. The reaction rate at one temperature can be used to obtain the rate at any other temperature within the range studied. The rate of change of mechanical properties with age can, in a like fashion, be determined for any aging temperature within the range studied. It seems reasonable that an extrapolation of the curves obtained at the lower aging temperatures can be made with assurance that the behavior will follow the same path so long as the extrapolation does not extend beyond the point

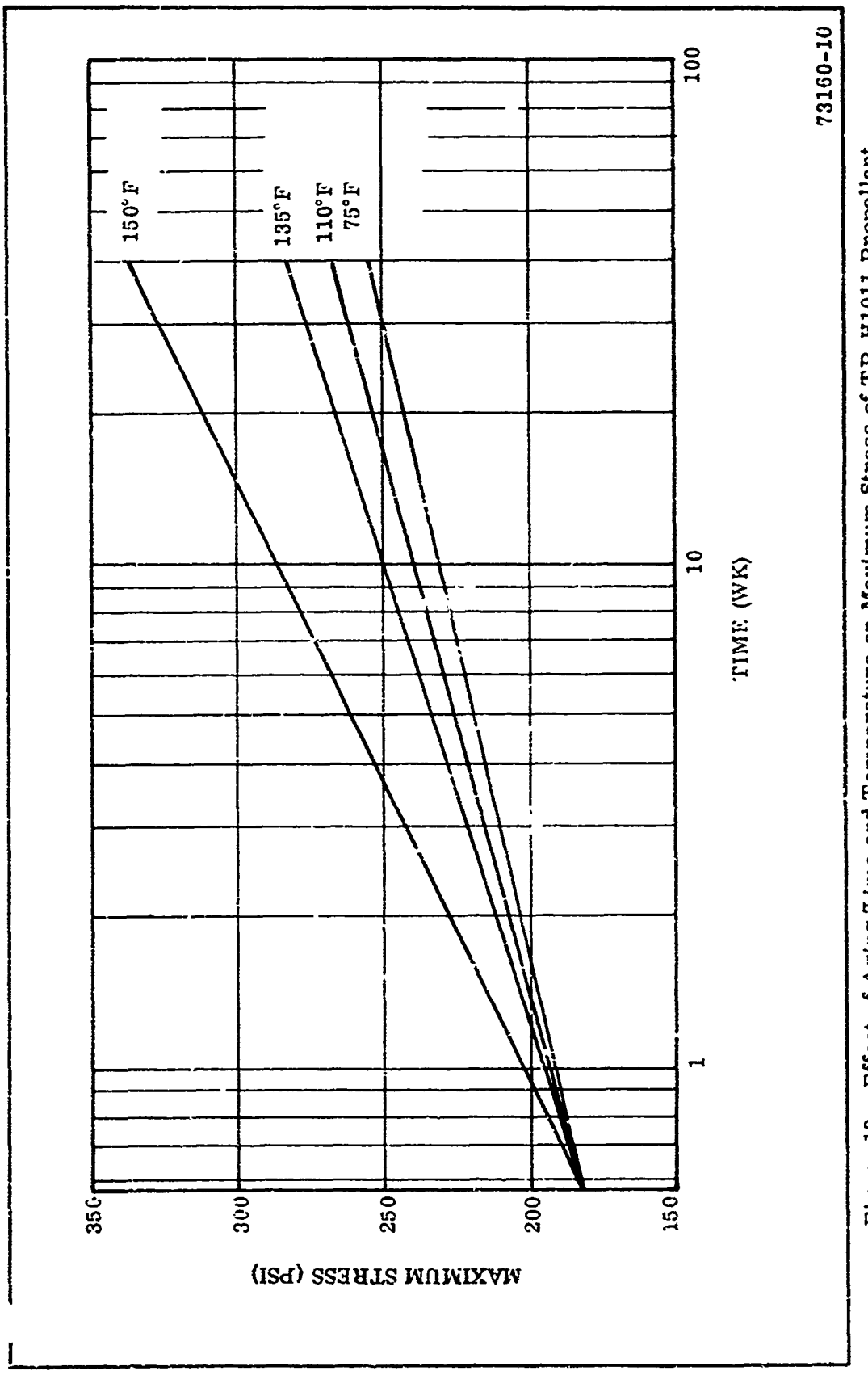


Figure 13. Effect of Aging Time and Temperature on Maximum Stress of TP-H1011 Propellant Tested at 75°F and 500 Psi

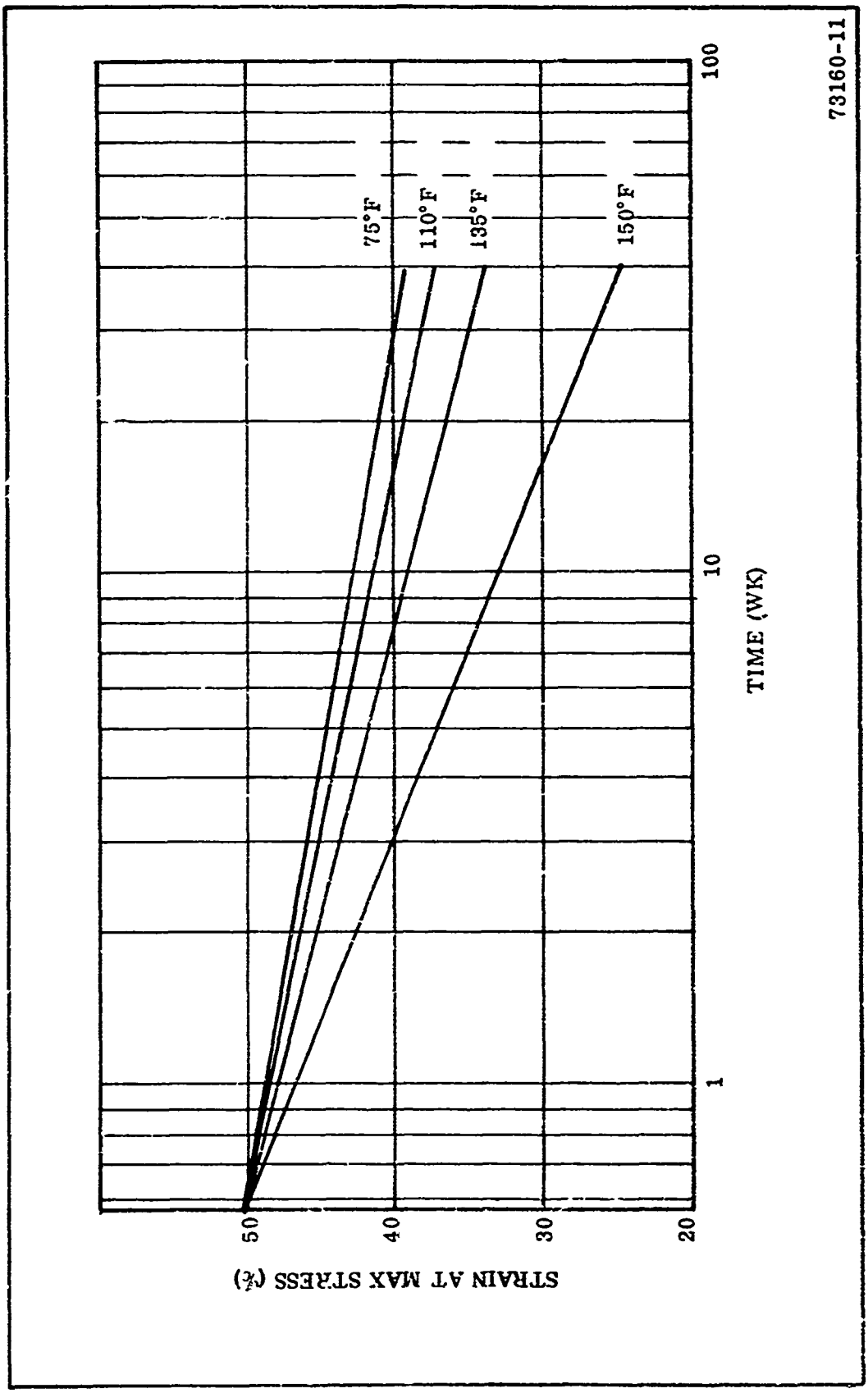


Figure 14. Effect of Aging Time and Temperature on Strain at Maximum Stress for TP-H1011 Propellant Tested at 75°F and 500 Psi

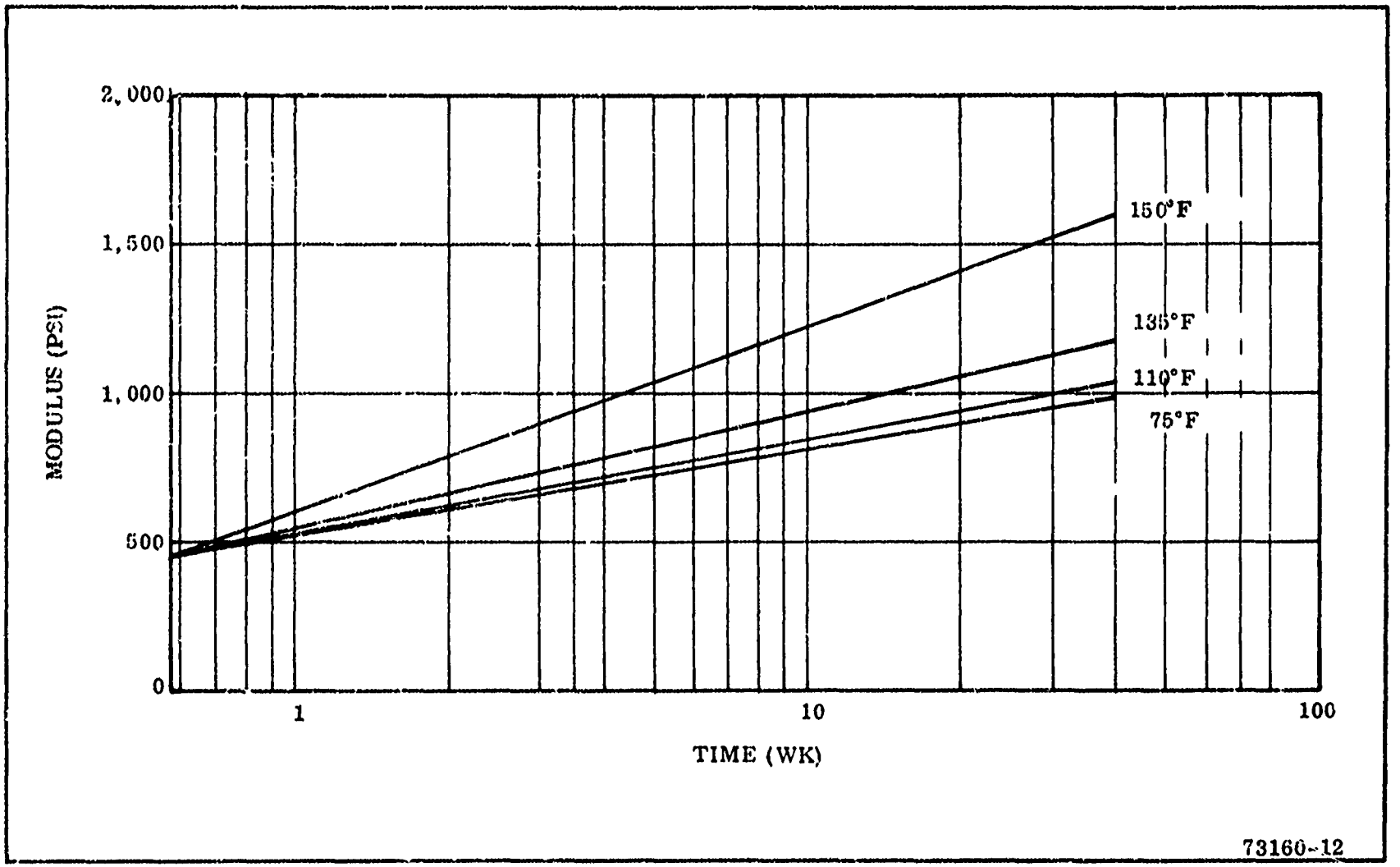


Figure 15. Effect of Aging Time and Temperature on Modulus of TP-H1011 Propellant Tested at 75°F and 500 Psi

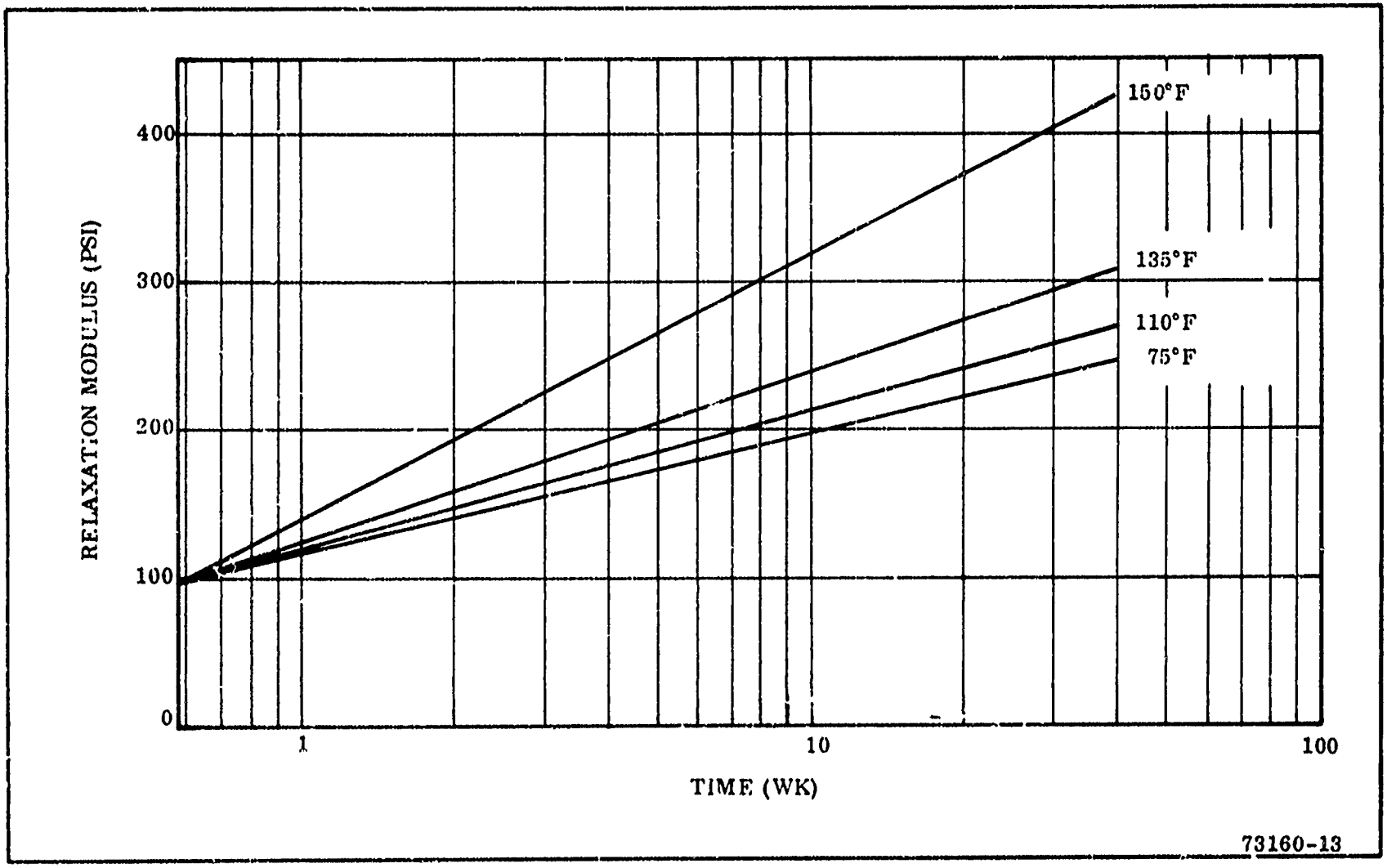


Figure 16. Effect of Aging Time and Temperature on Relaxation Modulus at 10,000 Seconds for TP-H1011 Propellant 2% Strain at 75°F

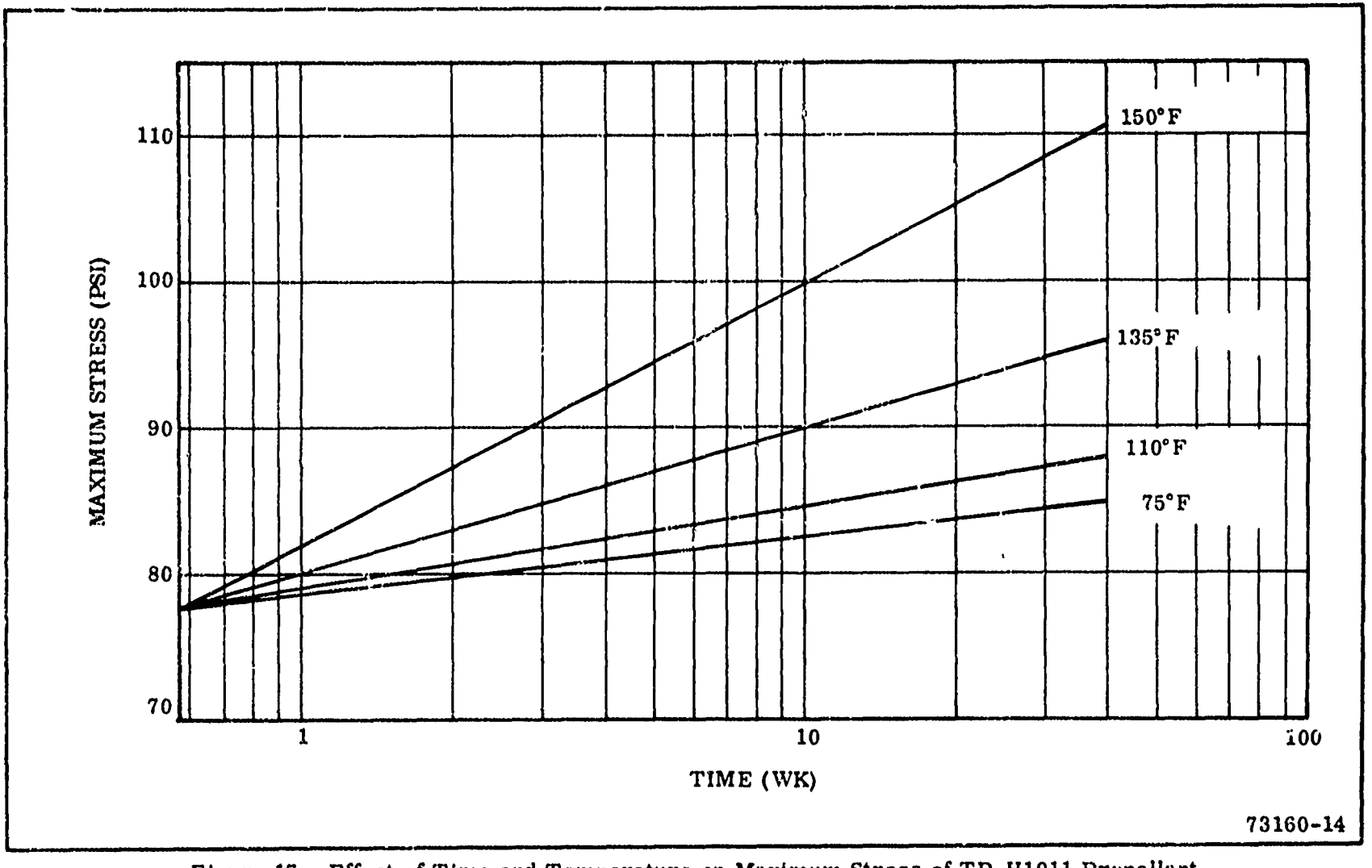


Figure 17. Effect of Time and Temperature on Maximum Stress of TP-H1011 Propellant Tested at 125°F

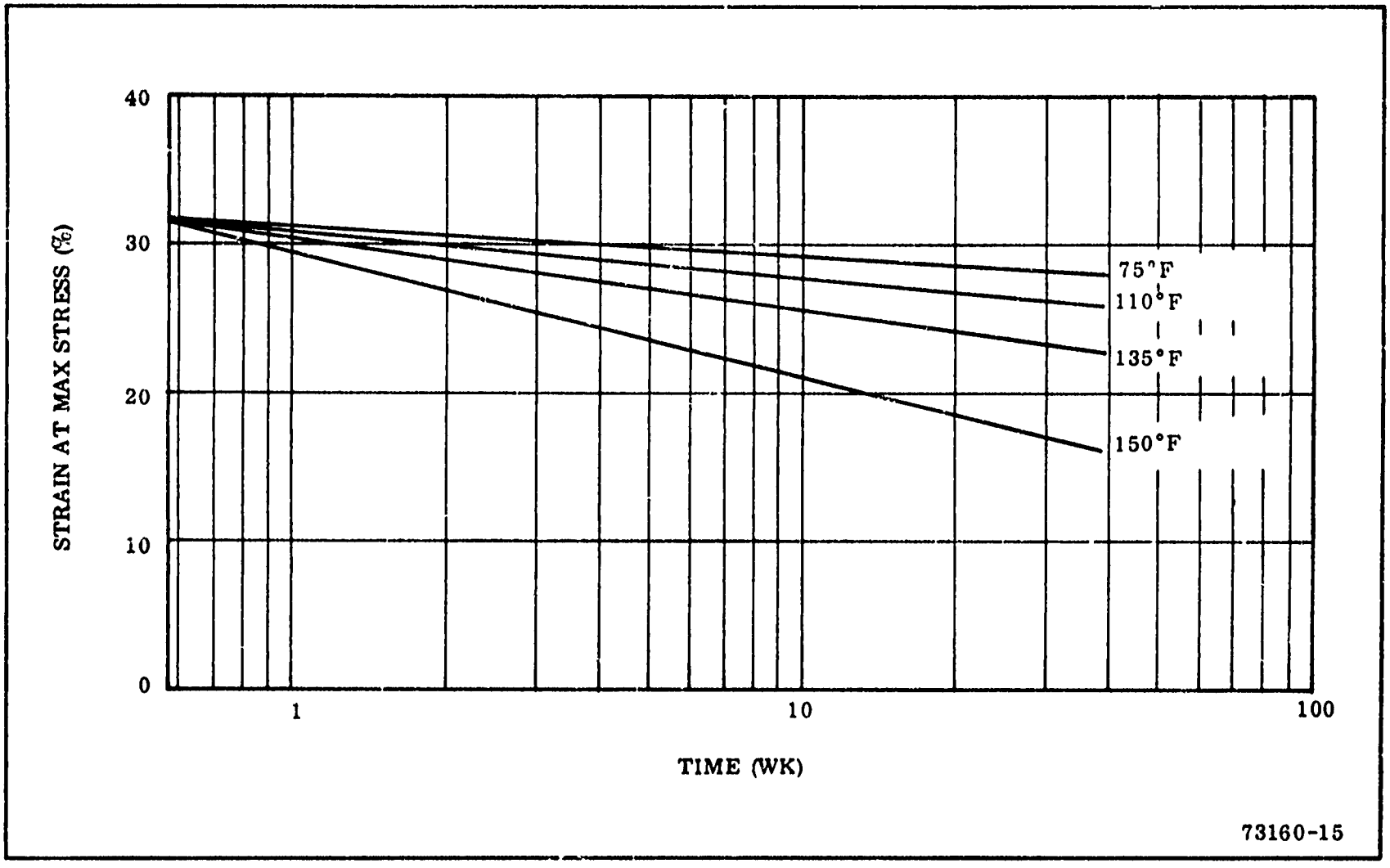


Figure 18. Effect of Aging Time and Temperature on Strain at Maximum Stress for TP-H1011 Propellant Tested at 125°F

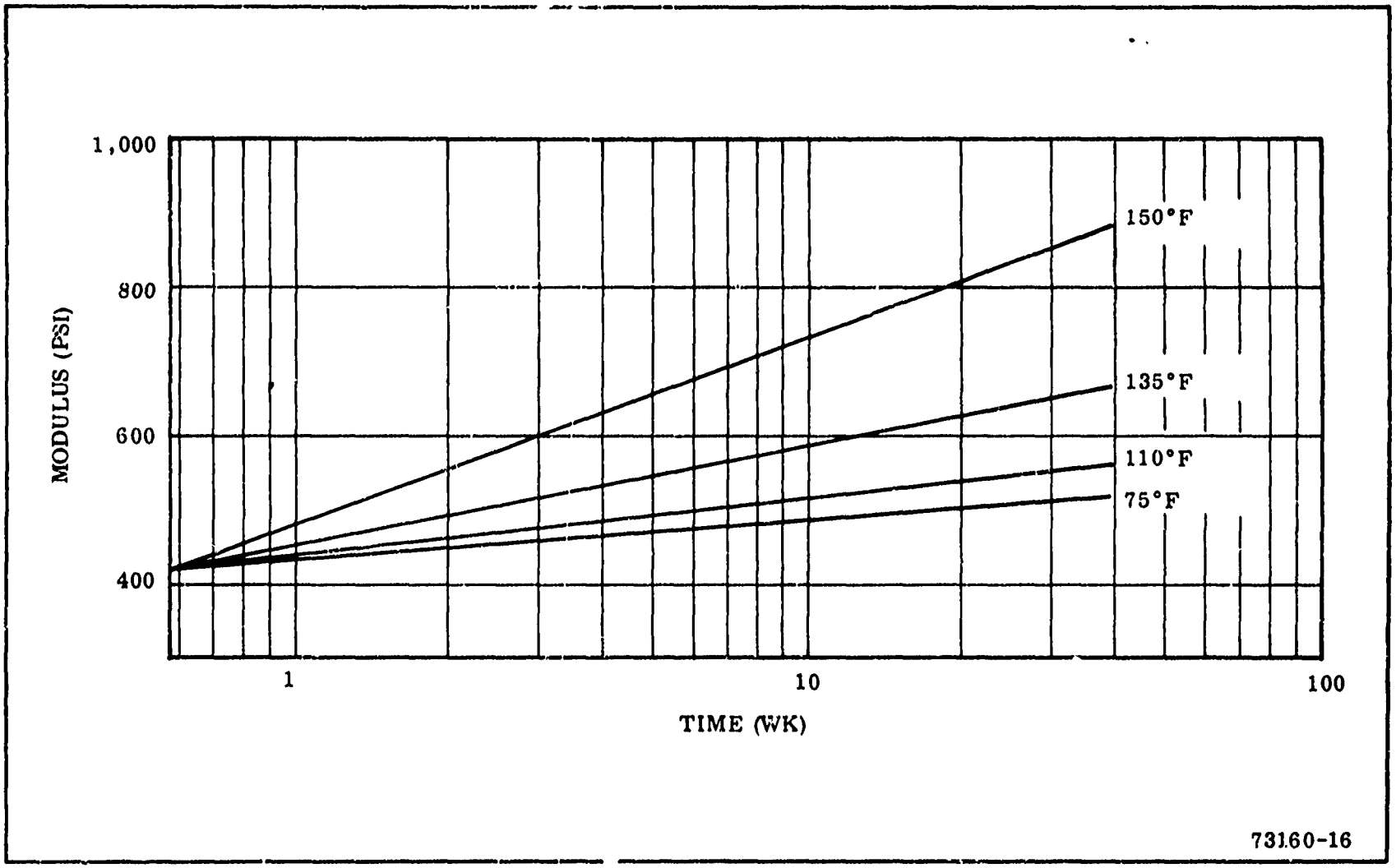


Figure 19. Effect of Aging Time and Temperature on Modulus of TP-H1011 Propellant

where the property change is greater than that observed at the high aging temperature. It is possible for secondary effects to become significant contributors to the mechanical and chemical change with age at any time and cause a deviation from the linear curve. This will show up first at the high aging temperature, therefore, one should not attempt to extrapolate the lower aging temperature curves beyond the point where the property change exceeds that measured at the high temperature. The parameters for the aging rate equation, $p = k \log t + c$, obtained from the data plots are presented in Table V. These parameters can be used to mathematically extrapolate any of the curves. This has been done for the uniaxial test performed at 75° F and a comparison with data obtained from OOAMA for ten years aging time at 75° F made. The comparison is shown in Figures 20-22 for the stress, strain and modulus properties with excellent agreement. These data are tabulated and presented in Table VI.

TABLE V

PARAMETERS FOR AGING RATE EQUATION FOR TP-H1011 PROPELLANT

Property	Test Conditions	Property Rate of Change* At Aging Temperatures, °F				Property at Logt = 0 At Aging Temperatures, °F				T_o^{**}
		75	110	135	160	75	110	135	160	°K
JANNAF Tensile Modulus	2 in./min at 75° F and 500 psi	288.0	320.0	400.0	640.0	520.0	525.0	540.0	605.0	346
Maximum Tensile Stress	2 in./min at 75° F and 500 psi	39.0	43.2	54.0	80.5	185.0	187.0	190.0	198.0	346
Strain at Max Tensile Stress	2 in./min at 75° F and 500 psi	-6.3	-7.0	-8.75	-14.0	48.6	48.4	48.0	46.6	346
JANNAF Tensile Modulus	2 in./min at 75° F	150.0	166.0	206.0	330.0	635.0	646.0	655.0	685.0	346
Maximum Tensile Stress	2 in./min at 75° F	13.5	15.0	18.7	30.0	110.0	111.0	112.0	114.0	346
Strain at Max Tensile Stress	2 in./min at 75° F	-3.0	-3.3	-4.1	-6.6	35.0	34.8	34.6	34.0	346
Relaxation Modulus	2% Strain at 75° F	81.0	90.0	112.0	180.0	117.0	120.0	126.0	144.0	346
Cohesive Fracture Energy	2 in./min at 75° F	0.243	0.270	0.340	0.540	0.76	0.77	0.79	0.84	346
JANNAF Tensile Modulus	2 in./min at 125° F	55.0	77.0	135.0	245.0	440.0	445.0	460.0	485.0	361
Maximum Tensile Stress	2 in./min at 125° F	4.0	5.6	9.9	18.0	78.5	79.0	79.8	82.0	361
Strain at Max Tensile Stress	2 in./min at 125° F	-1.9	-2.7	-4.7	-8.0	32.2	31.8	31.4	30.4	361

*The property change per logarithmic decade of time where time is in weeks.

**The temperature required to produce a constant B in the equation: $K = Ae^{B/T-T_o}$

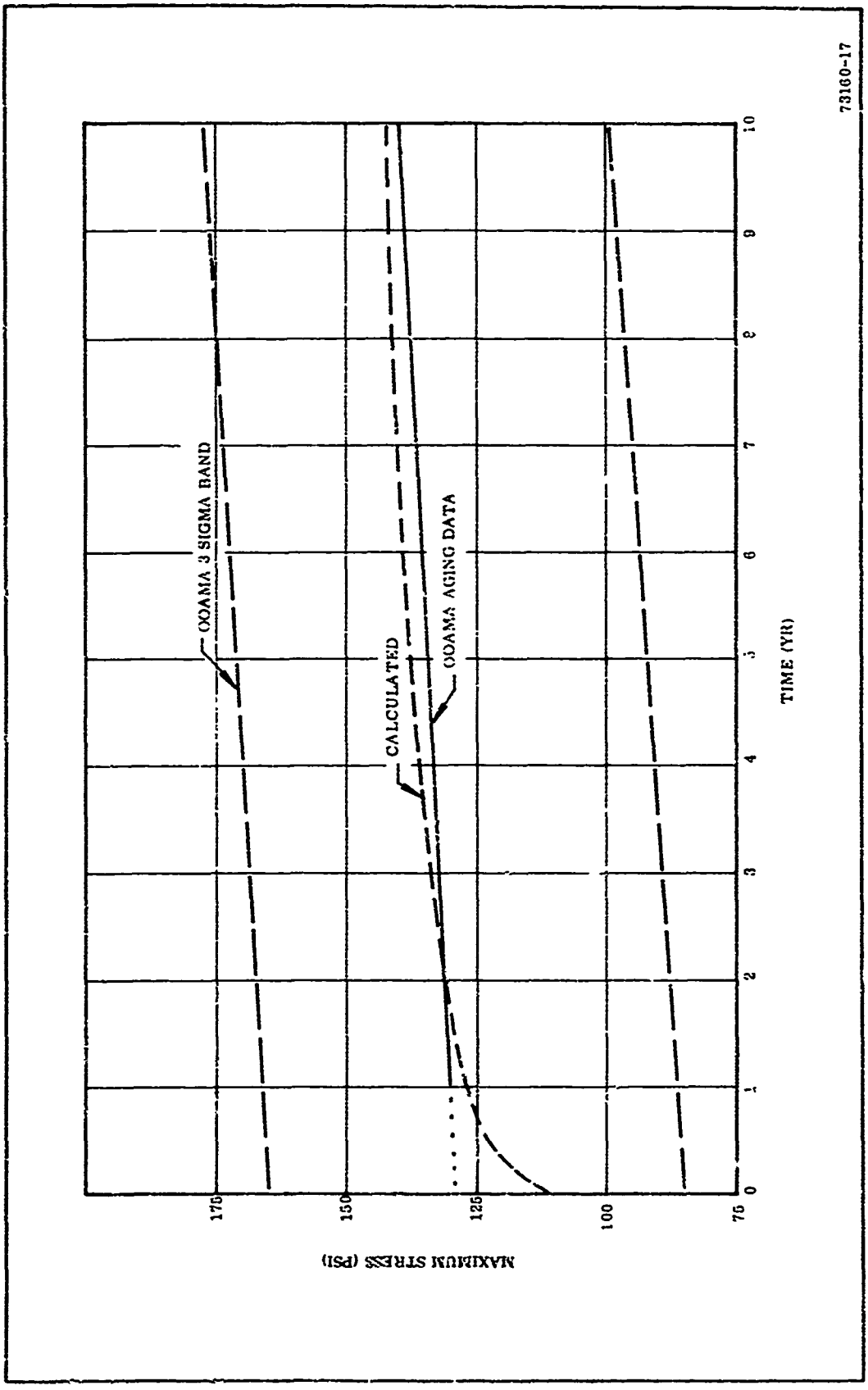


Figure 20. Comparison of Calculated and Measured JANNAF Tensile Stress, TP-H1011 Propellant

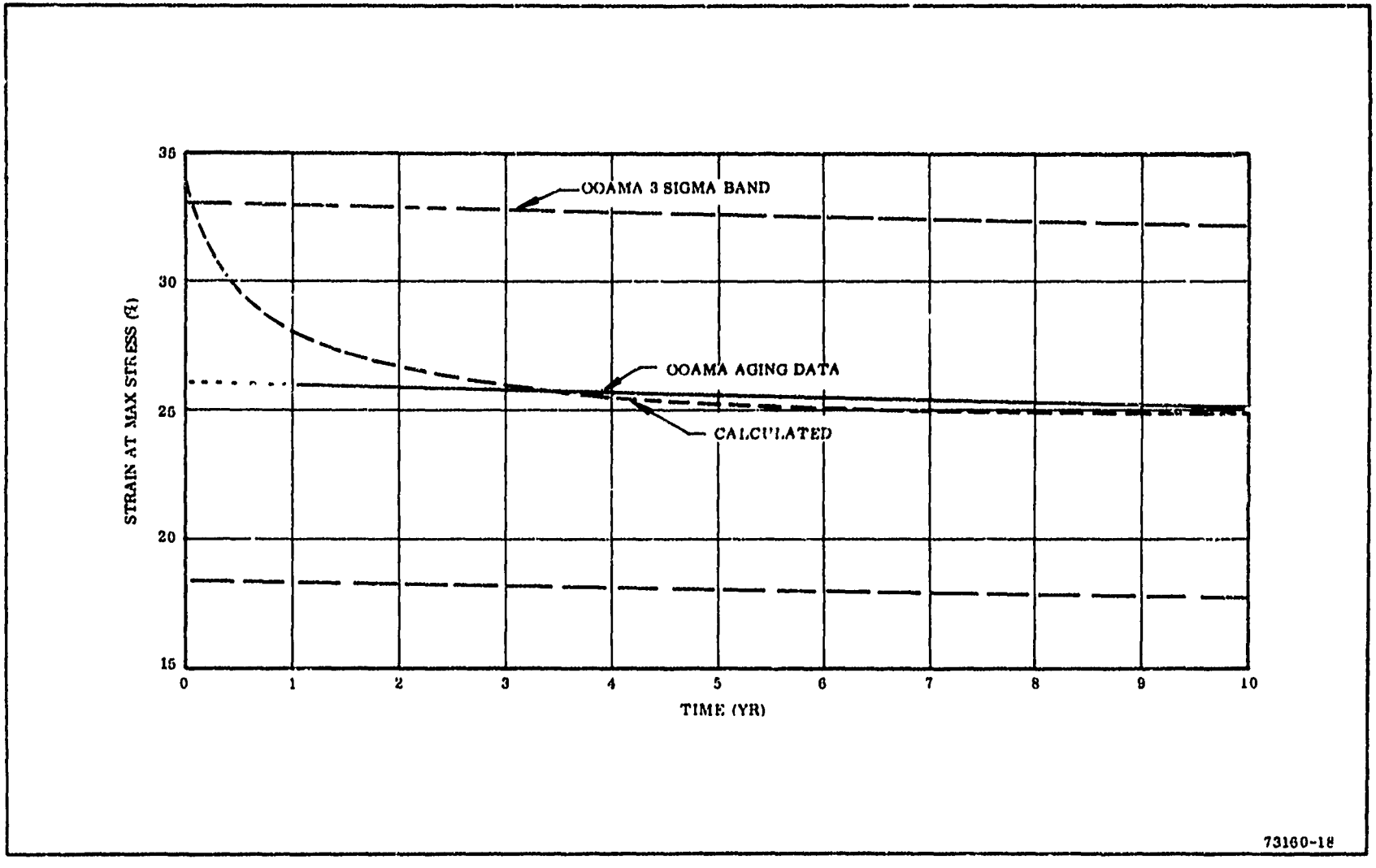


Figure 21. Comparison of Calculated and Measured JANNAF Tensile Strain, TP-H1011 Propellant

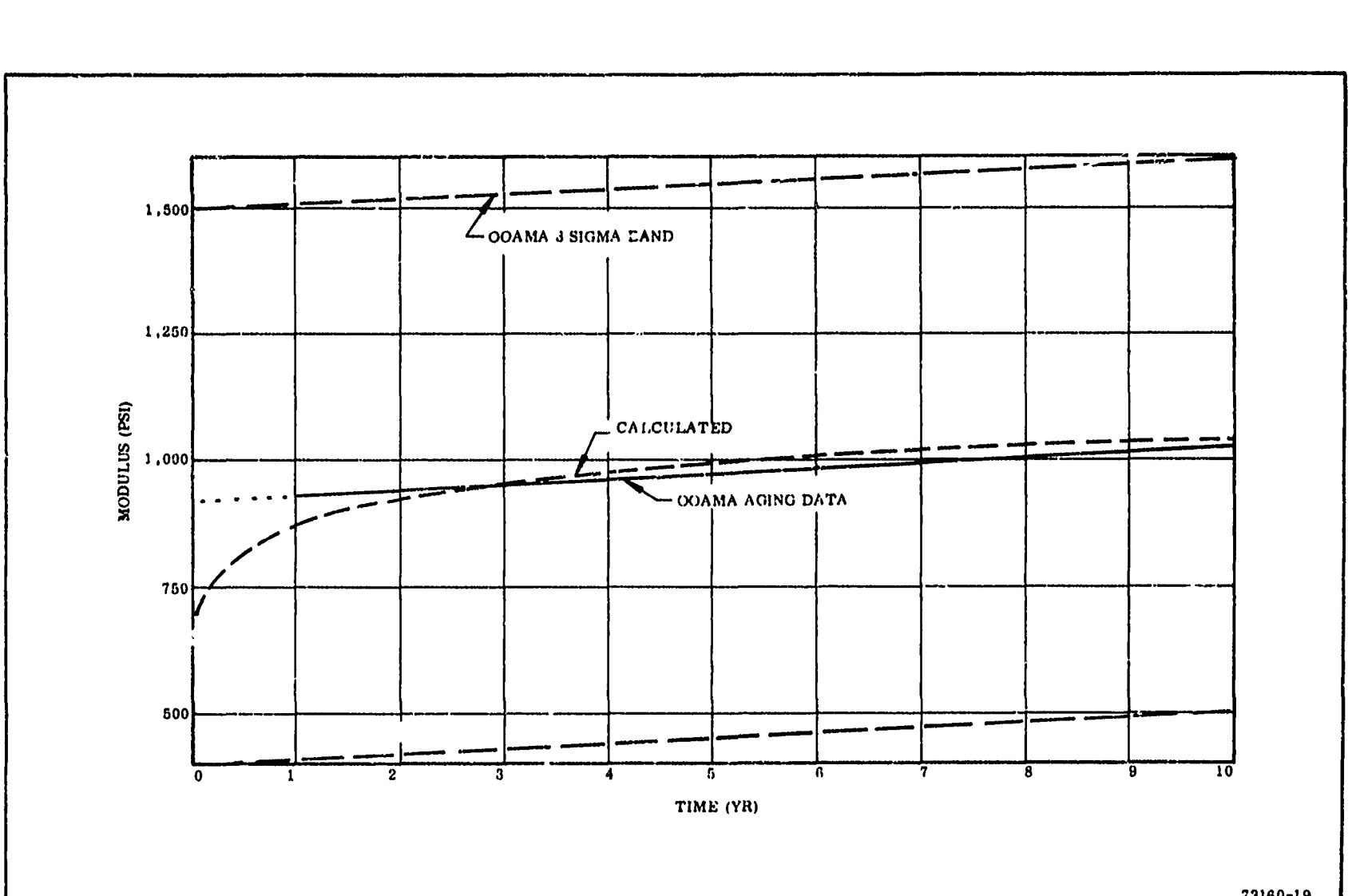


Figure 22. Comparison of Calculated and Measured JANNAF Tensile Modulus, TP-H1011 Propellant

TABLE VI

COMPARISON OF CALCULATED AND MEASURED JANNAF PROPERTY FOR TP-H1011 PROPELLANT

Time (yrs)	Calculated Parameters			OOAMA Aging Data		
	σ_m	ϵ_m	E	σ_m	ϵ_m	E
1	128	28	885	130	26	940
2	132	27	930	131	26	950
3	135	26	956	132	26	960
4	136	26	975	133	26	970
5	138	26	990	134	26	980
6	139	26	1,002	135	26	990
7	139	25	1,012	136	26	1,000
8	140	25	1,020	137	25	1,010
9	141	25	1,028	139	25	1,020
10	142	25	1,035	140	25	1,030

V. RECOMMENDATIONS

Although the results of this study are very interesting and, for the first time, make reasonable aging predictions possible there are still many questions to be answered. For this reason, the study should be continued to find these answers. It is recognized that TP-H1011 propellant is perhaps one of the most simple and best understood of the solid propellants which was an aid in developing hypotheses proposed, however the following ideas need further development:

1. Is the linear presentation as a function of log age-time satisfactory for analysis or should second or even higher orders be included?
2. Does the parameter, T_o, have a physical significance for viscoelastic behavior as well as aging?
3. What effect does strain have on the rate of aging?
4. If aging is performed at several temperatures for various periods of time on the same sample can an aging rate be assigned to each aging period to determine the total aging experienced?
5. Does humidity have an effect on the chemistry of aging or is it a physical phenomenon?

A similar approach should be used with other propellants that are chemically related and unrelated to TP-H1011 to determine the extent of applicability of these theories.

APPENDIX

All the mechanical and physical properties data obtained to date on this program are tabulated and included in this appendix. These tables of data have in no way been treated but represent the raw test results as obtained. It is from these data that the curves (also shown in this appendix) were prepared. These curves have been prepared with a shifted scale for each aging condition so the points don't overlap significantly. The point indicated at the end of cure (0.57 weeks) is common to each set of four curves representing the four aging temperatures. These same curves have been used, without the data points, in the report and are the bases of the analyses performed and discussed.

STRAIN ENDURANCE
TP-H1011 PROPELLANT - MIX 6780450

Storage Time (Weeks)	Storage Temperature (°F)			
	77	110	135	150
	Failure Strain (%)			
1	22	23	26	24
2	20	20	20	21
3	23	22	24	22
4	26	24	23	21
5	23	--	--	--
6	24	20	20	19
7	22	--	--	--
8	22	21	19	22
10	19	19	21	21
12	20	21	20	18
14	23	--	--	--
16	19	--	--	--
24	21	22	24	15
39	23	20	14	13

STRESS ENDURANCE*
TP-H1011 PROPELLANT - MIX 6780450

Storage Time (Weeks)	Storage Temperature (°F)			
	77	110	135	150
	Hours to Failure			
1	1.3	1.0	1.4	0.5
2	1.5	1.8	3.0	3.5
3	1.1	3.9	4.1	5.2
4	2.5	3.9	2.7	9.6
5	2.6	—	—	—
6	3.2	4.9	4.3	11.5
8	1.5	6.2	7.7	11.5
10	2.3	3.3	6.4	17.8
12	3.1	3.3	6.9	7.6
14	6.1	—	—	—
16	0.6	—	—	—
24	7.6	4.0	2.3	89.2
39	1.8	4.4	12.9	24.3

*12.5 lb load was used to obtain these results.

STRESS RELAXATION MODULUS AT 10,000 SECONDS
TP-H1011 PROPELLANT - Mix 6780450

Storage Time (Weeks)	Storage Temperature (°F)			
	77	110	135	150
	Stress Relaxation Modulus (psi)			
1	130	199	168	180
2	131	200	170	209
3	132	200	170	240
4	132	202	170	248
5	155	--	--	--
6	159	215	195	275
8	180	215	200	290
10	190	215	240	330
12	190	230	240	330
14	190	--	--	--
16	190	--	--	--
24	200	225	320	540
39	250	285	435	760

COHESIVE FRACTURE ENERGY
TP-H1011 PROPELLANT - MIX 6780450

Storage Time (Weeks)	Storage Temperature (°F)			
	77	110	135	150
	Cohesive Fracture Energy (in-lb/in.^{2})			
1	0.79	1.30	0.95	0.88
2	1.23	1.17	1.31	1.20
3	0.94	1.16	0.98	1.04
4	0.88	1.22	0.91	1.12
5	1.21	--	--	--
6	0.86	1.17	0.91	1.25
8	0.96	1.46	0.98	1.54
10	0.91	1.01	1.10	1.26
12	1.00	1.30	1.03	1.28
14	1.11	--	--	--
16	1.11	--	--	--
24	0.92	0.95	1.41	1.65
39	1.32	1.19	1.34	1.95

THERMAL COEFFICIENT OF LINEAR EXPANSION
TP-H1011 PROPELLANT - MIX 6789450

RDLNB Reference	Storage Time (Weeks)	Storage Temperature (°F)			
		77	110	135	150
F-516 page:		TCLE x 10^{-5} (in./in./°F)			
6	1	4.7	4.7	4.8	4.7
6	2	4.7	5.0	4.9	5.1
19	3	4.8	5.1	5.0	5.1
19	4	5.2	5.0	5.0	5.1
26	6	4.8	4.7	4.9	5.1
26	8	5.0	5.0	5.1	5.9
32	10	4.9	5.2	4.9	5.9
32	12	5.3	5.4	5.2	5.3
43	24	4.8	4.8	5.1	5.6
43	39	5.0	4.5	5.0	4.5

UNIAXIAL TENSILE DATA FROM AMBIENT AGED PROPELLANT
TESTED AT 77° F AND AMBIENT PRESSURE
TP-H1011 PROPELLANT - MIX 6780450

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	697	33	38	118
2	851	35	41	121
3	810	33	40	124
4	755	31	37	119
5	802	30	36	124
6	775	29	36	124
8	739	33	41	122
10	814	32	37	130
12	855	30	34	132
14	913	25	28	125
16	803	30	34	127
24	974	31	34	130
39	815	30	34	126

UNIAXIAL TENSILE DATA FROM PROPELLANT AGED AT 110°F, TESTED AT 77°F AND AMBIENT PRESSURE

Storage Time (Weeks)	$E^{3.0}$ (psi)	ε_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	661	35	40	113
2	699	38	45	119
3	766	35	40	118
4	743	31	37	122
5	--	--	--	--
6	773	30	36	121
8	777	34	39	119
10	761	33	38	127
12	761	30	34	132
24	827	32	36	132
39	880	25	30	129

UNIAXIAL TENSILE DATA FROM PROPELLANT AGED AT 135° F, TESTED AT 77° F AND AMBIENT PRESSURE

Storage Time (weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	661	34	39	114
2	720	35	39	120
3	766	35	40	118
4	690	31	36	119
5	--	--	--	--
6	780	30	36	126
8	886	30	35	130
10	858	33	35	131
12	828	30	33	131
24	828	30	34	131
39	1,160	20	23	149

UNIAXIAL TENSILE DATA FROM PROPELLANT AGED AT 150° F, TESTED AT 77° F AND AMBIENT PRESSURE

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	673	32	37	113
2	800	33	38	123
3	791	33	40	122
4	797	30	35	124
5	—	--	--	--
6	953	29	32	134
8	923	29	33	141
10	989	31	34	152
12	1,020	27	31	145
24	1,387	24	25	177
39	1,527	16	18	173

UNIAXAL TENSILE DATA FROM AMBIENT AGED PROPELLANT
TESTED AT 125° F AND AMBIENT PRESSURE

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	517	25	27	85
2	501	32	39	81
3	460	30	35	82
4	472	30	35	80
5	498	25	33	85
6	453	29	36	78
8	450	29	35	82
10	482	31	37	82
12	506	27	32	82
14	534	25	32	85
16	508	27	32	85
24	510	26	33	82
39	492	31	38	82

UNIAXIAL TENSILE DATA FROM PROPELLANT AGED AT 110° F,
TESTED AT 125° F AND AMBIENT PRESSURE

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	444	32	38	77
2	478	31	37	84
3	529	27	32	84
4	492	29	34	83
5	--	--	--	--
6	528	27	34	82
8	556	27	33	86
10	483	30	37	82
12	501	28	32	80
24	543	23	28	85
39	655	29	34	88

UNIAXIAL TENSILE DATA FROM PROPELLANT AGED AT 135°F, TESTED AT 125°F AND AMBIENT PRESSURE

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	435	31	37	77
2	481	31	37	85
3	552	27	30	90
4	521	28	33	88
6	535	28	33	87
8	613	25	30	96
10	584	29	37	89
12	606	25	32	89
24	677	22	25	100
39	887	25	28	106

UNIAXIAL TENSILE DATA FROM PROPELLANT AGED AT 150°F, TESTED AT 125°F AND AMBIENT PRESSURE

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	473	28	33	79
2	555	29	34	85
3	571	28	32	92
4	598	27	32	92
5	--	--	--	--
6	678	25	29	94
8	679	23	27	101
10	720	26	29	104
12	74[illegible]	22	27	100
24	890	19	22	115
39	1,200	19	21	128

PRESSURIZED UNIAXIAL TENSILE DATA FROM PROPELLANT STORED AT 77° F, TESTED AT 77° F, ½ IN./MIN AND 500 PSI

Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	708	44	50	223
2	655	44	49	215
3	612	48	54	207
4	698	44	50	225
6	637	43	48	221
8	645	43	50	221
10	858	41	47	236
12	1,035	39	45	271
24	1,024	39	45	245
39	906	43	49	259

PRESSURIZED UNIAXIAL TENSILE DATA FROM PROPELLANT STORED AT 110° F, TESTED AT 77° F, 2 IN./MIN AND 500 PSI

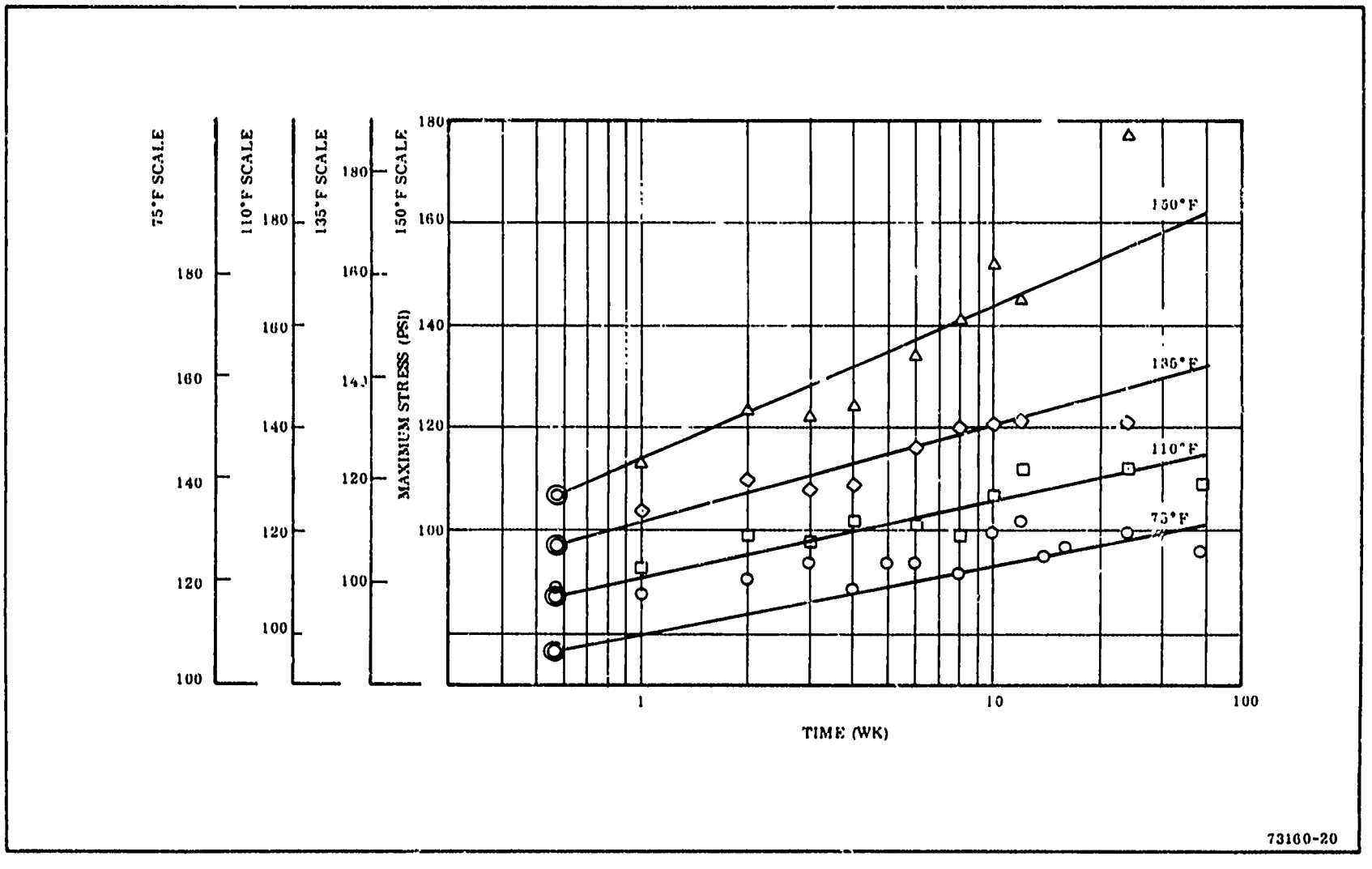
Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	656	47	53	203
2	651	46	51	215
3	612	48	54	207
4	698	44	50	225
6	683	41	46	218
8	724	42	48	206
10	913	42	47	249
12	779	41	46	262
24	1,082	36	41	257
39	1,099	37	40	263

PRESSURIZED UNIAXIAL TENSILE DATA FROM PROPELLANT STORED AT 135° F, TESTED AT 77° F, 2 IN./MIN AND 500 PSI

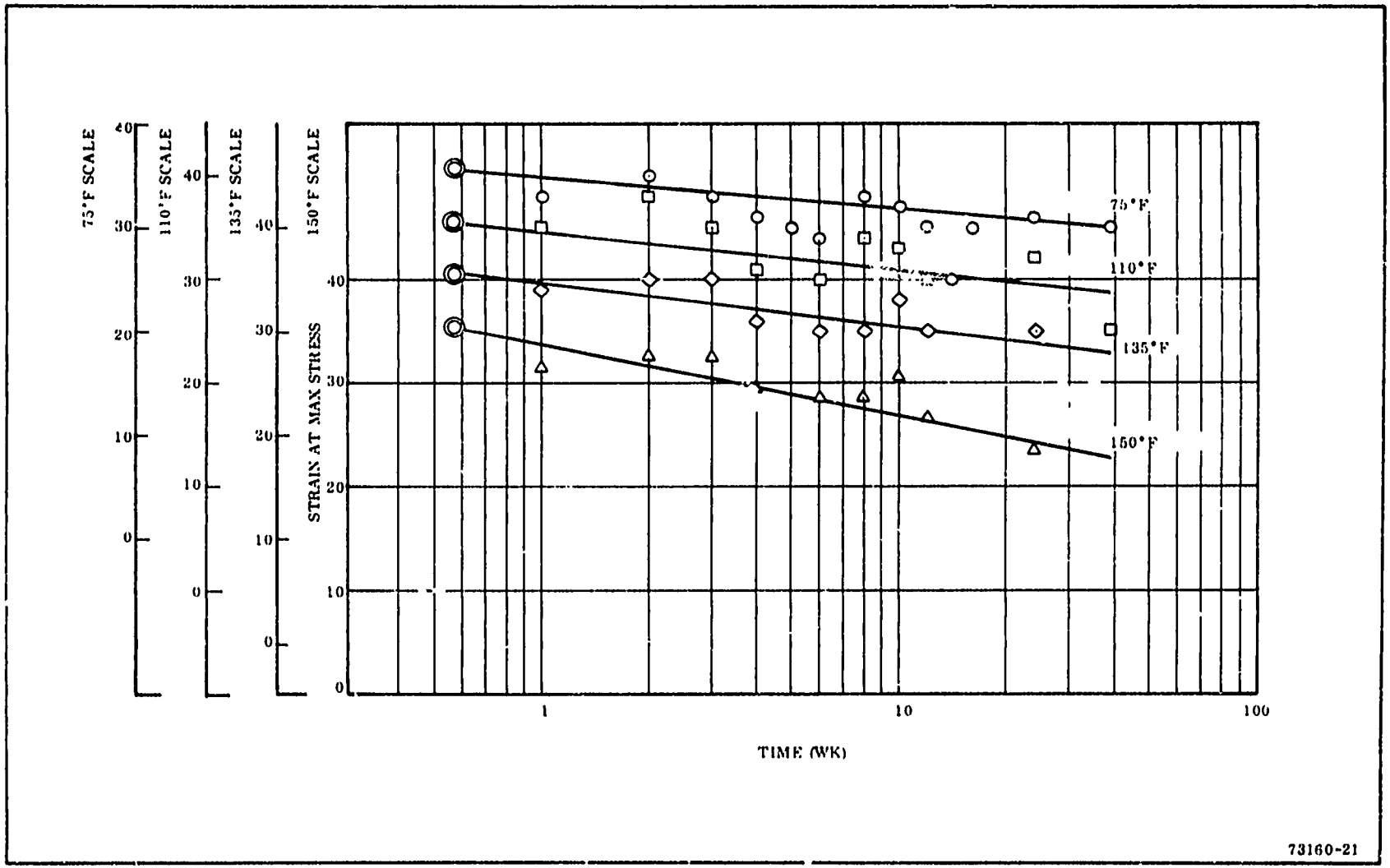
Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	661	45	51	208
2	667	46	53	213
3	703	41	49	224
4	692	43	49	215
6	762	42	47	233
8	841	44	49	237
10	1,119	39	41	264
12	1,160	36	41	280
24	1,014	33	38	263
39	1,301	30	31	304

PRESSURIZED UNIAXIAL TENSILE DATA FROM PROPELLANT STORED AT 150° F, TESTED AT 77° F, 2 IN./MIN AND 500 PSI

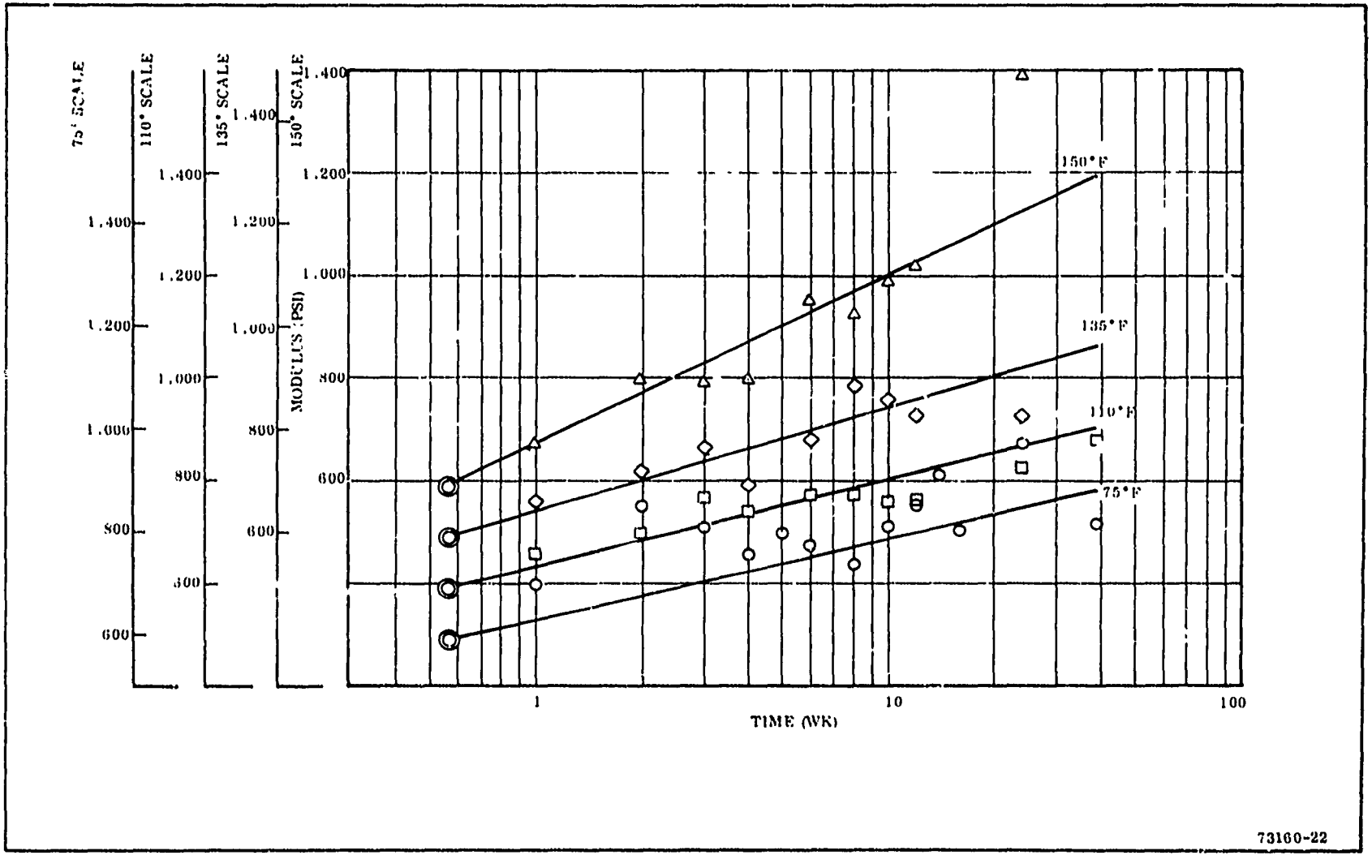
Storage Time (Weeks)	$E^{3.0}$ (psi)	ϵ_m^t (%)	ϵ_R^t (%)	σ_m (psi)
1	686	40	47	205
2	748	41	46	221
3	741	39	43	229
4	787	42	46	236
6	921	45	49	251
8	972	35	43	258
10	1,148	34	39	281
12	1,370	32	36	304
24	1,561	27	29	314
39	1,604	28	29	345



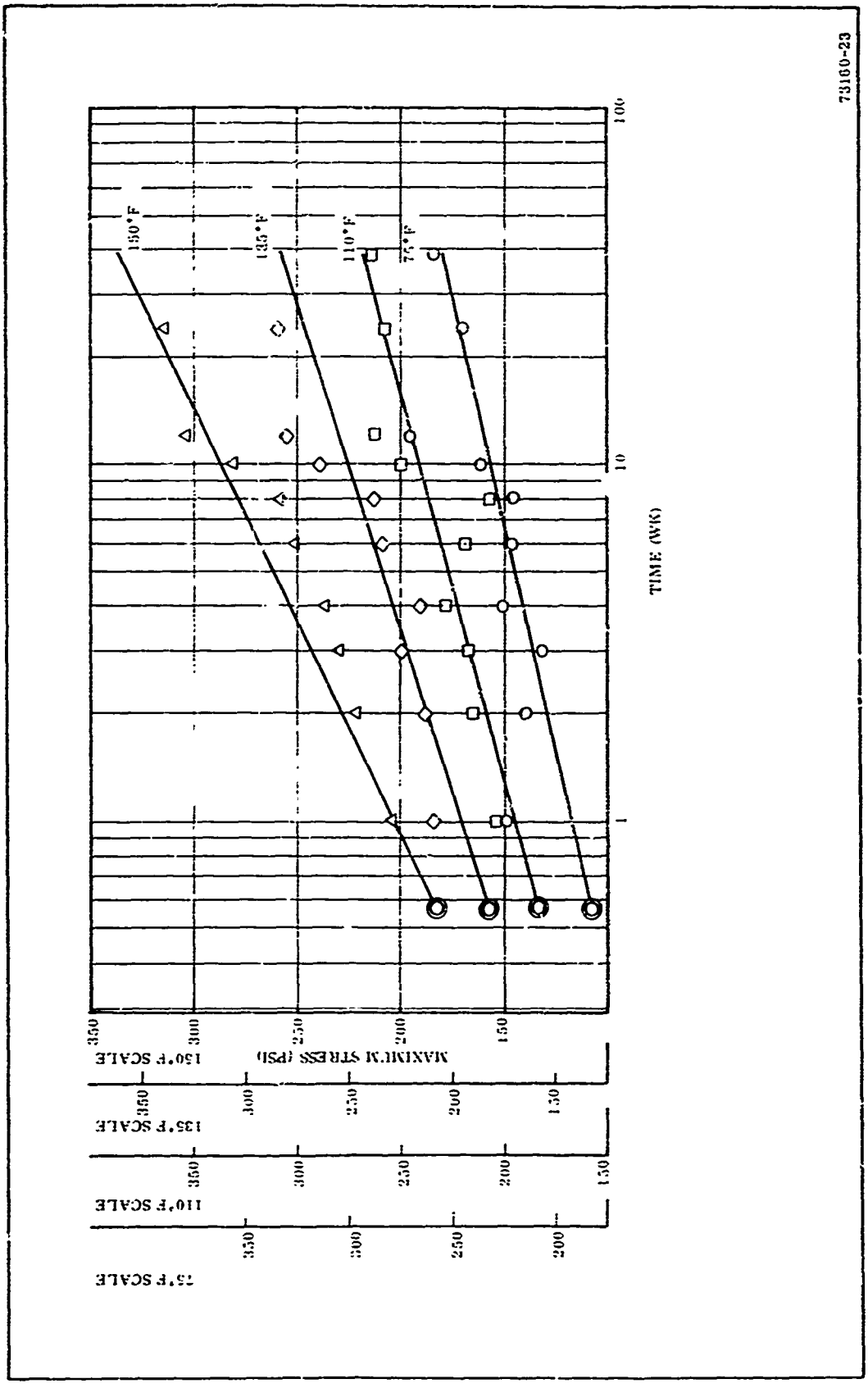
Effect of Aging Time and Temperature on Maximum Stress for TP-H1011 Propellant Tested at 75°F



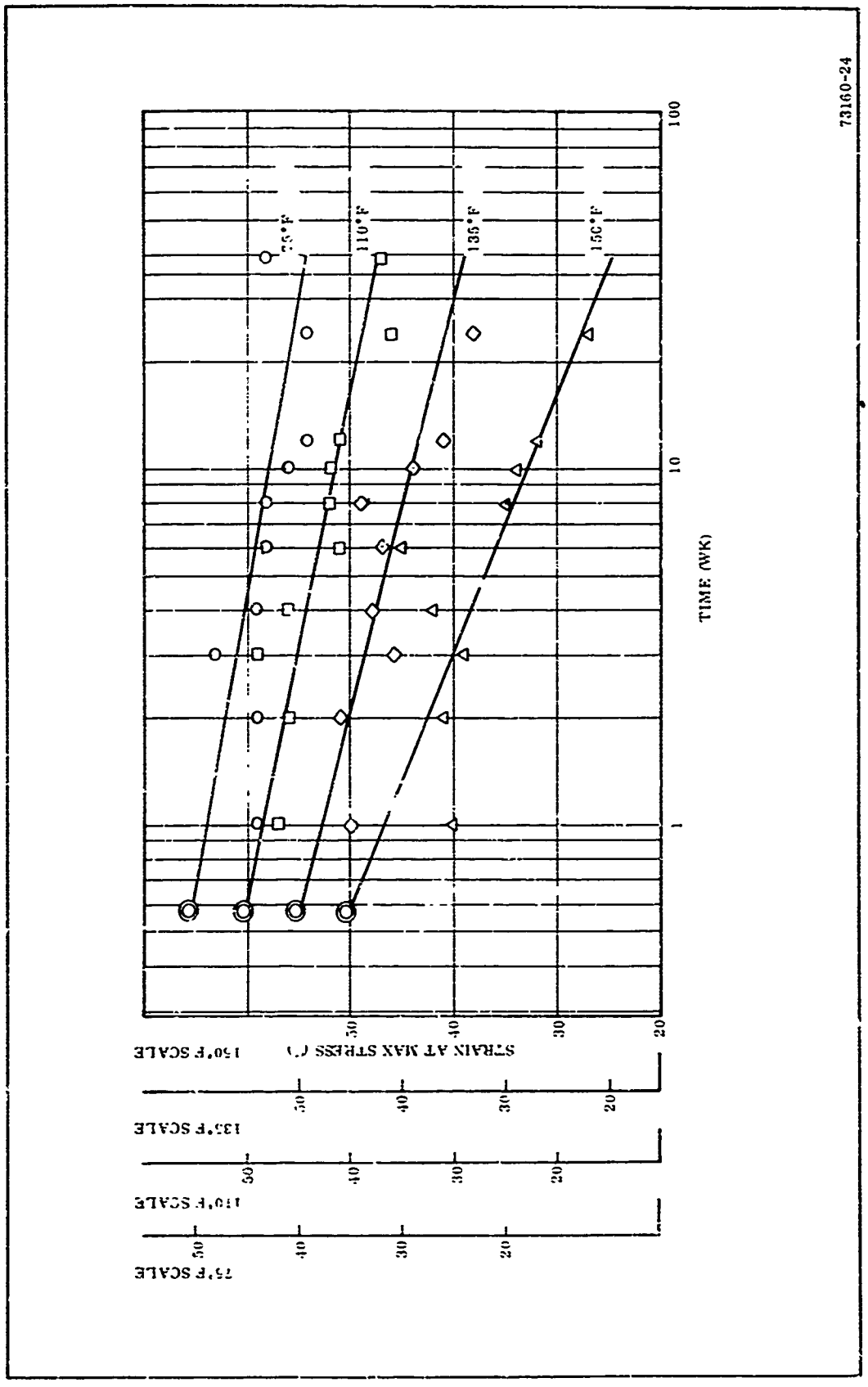
Effect of Aging Time and Temperature on Strain at Maximum Stress for TP-H1011 Propellant Tested at 75°F



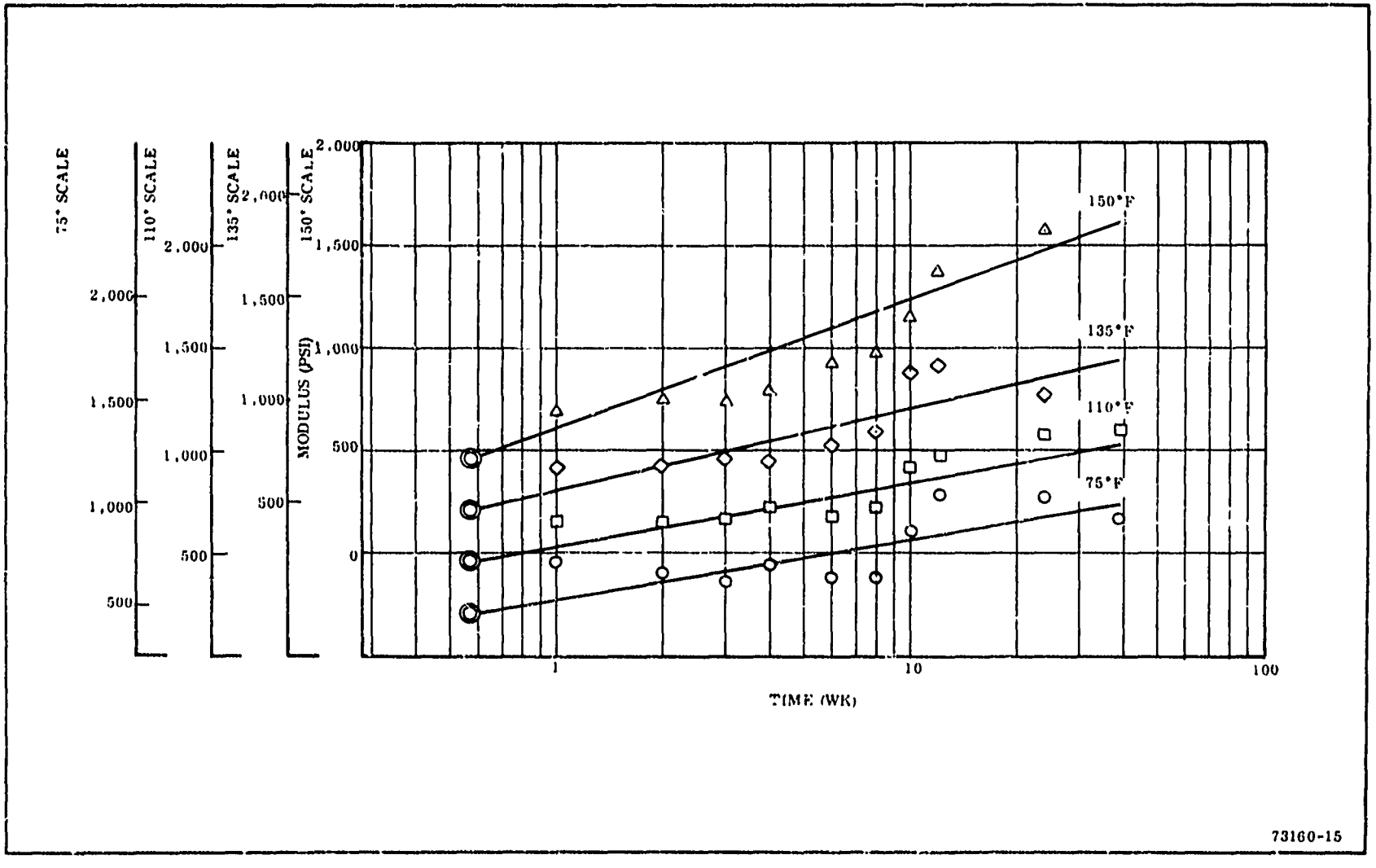
Effect of Time and Temperature on Modulus for TP-H1011 Propellant Tested at 75°F



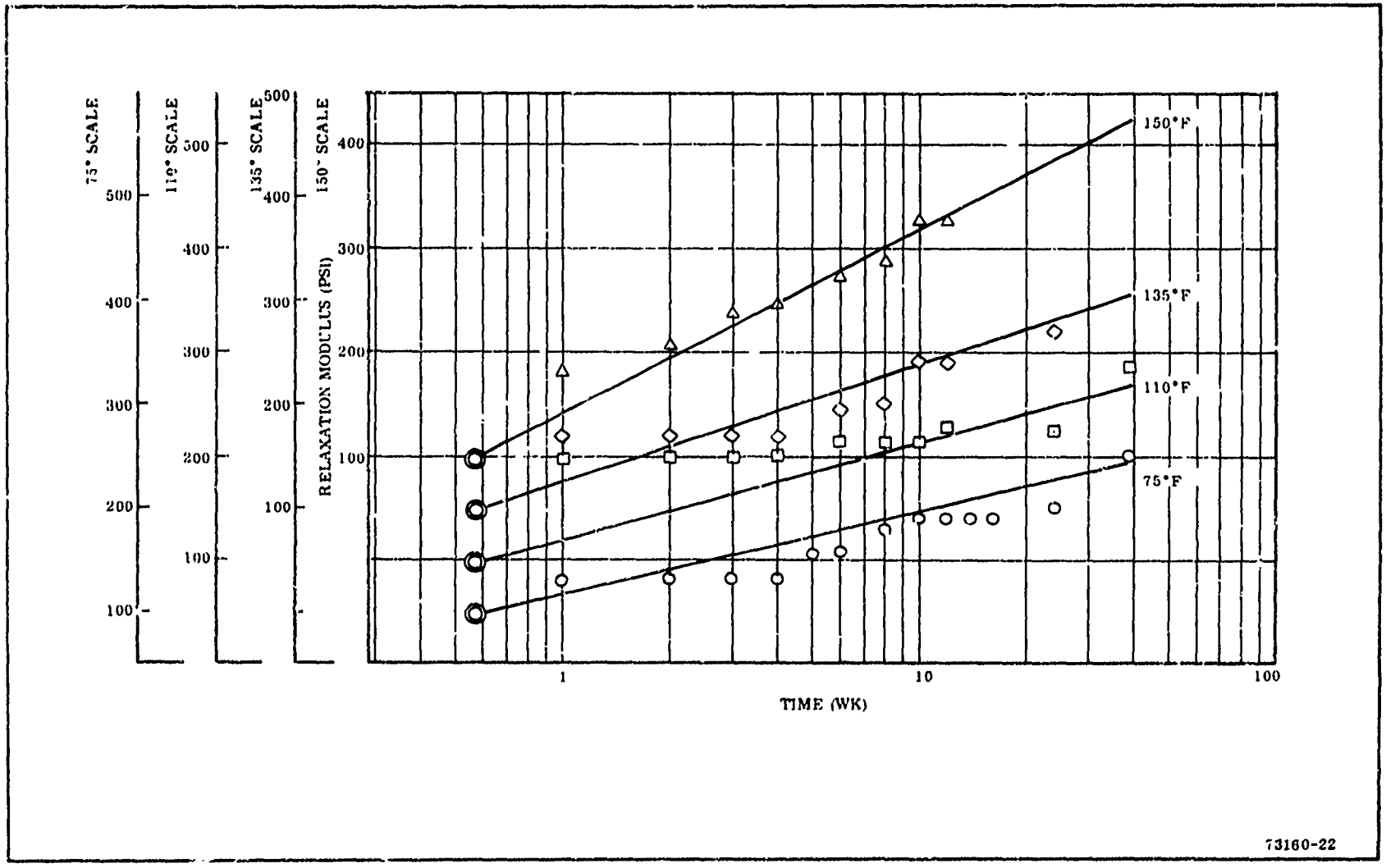
Effect of Aging Time and Temperature on the Maximum Stress of TP-H1011 Propellant Tested at 75°F and 500 psi



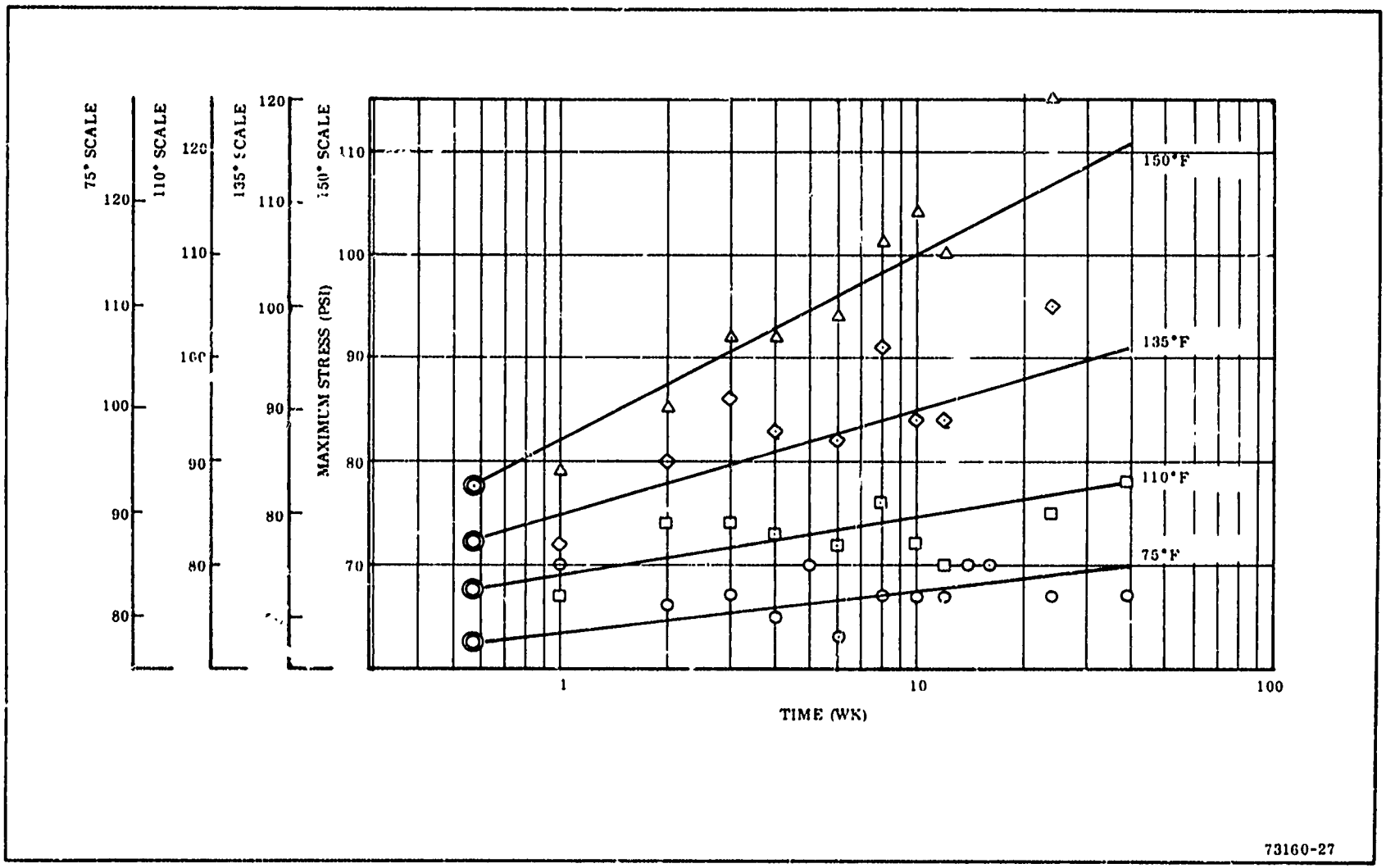
Effect of Aging Time and Temperature on the Strain at Maximum Stress for TP-H1011 Propellant Tested at 75°F and 500 psi



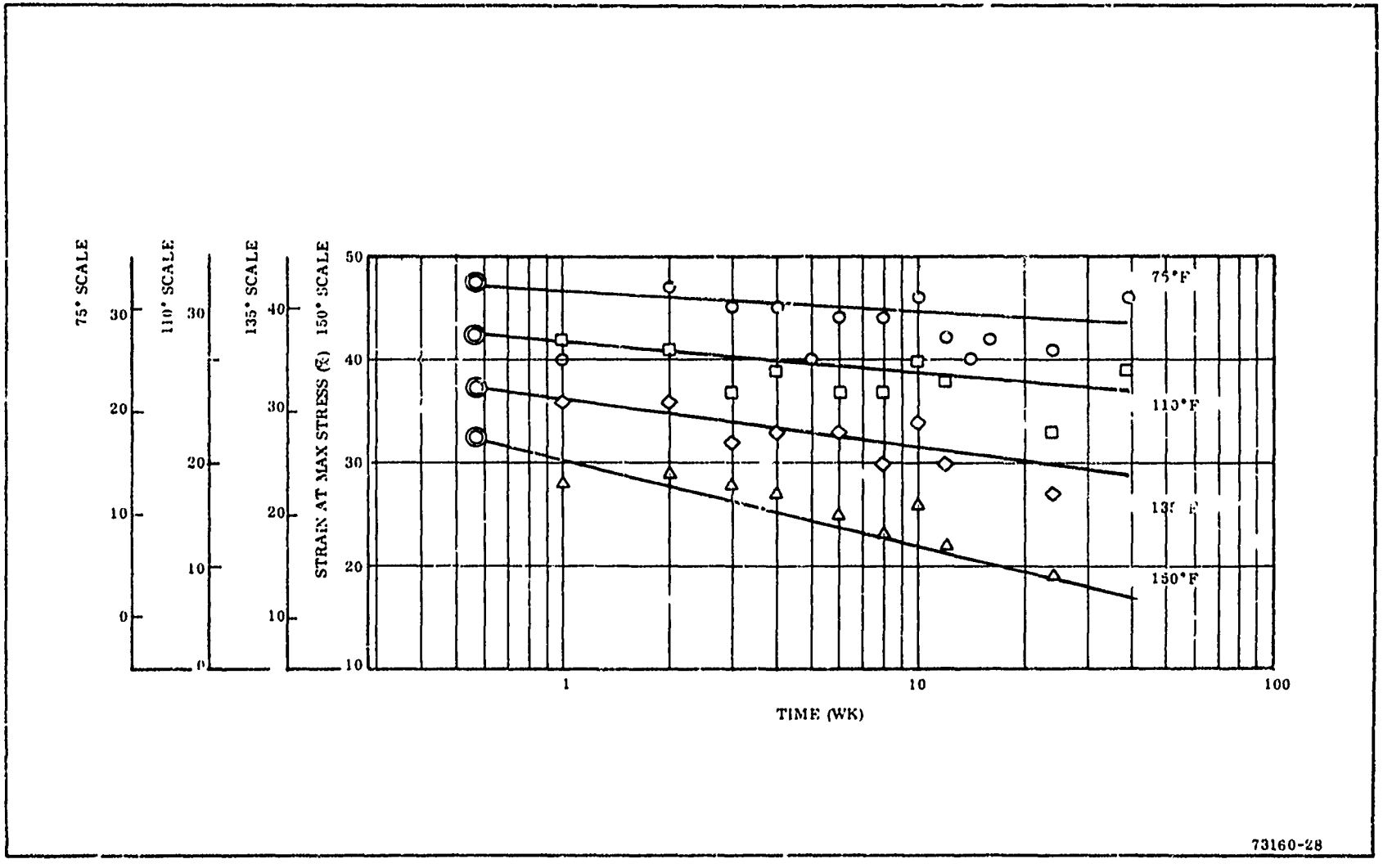
Effect of Aging Time and Temperature on the Modulus of TP-H1011 Propellant Tested at 75°F and 500 psi



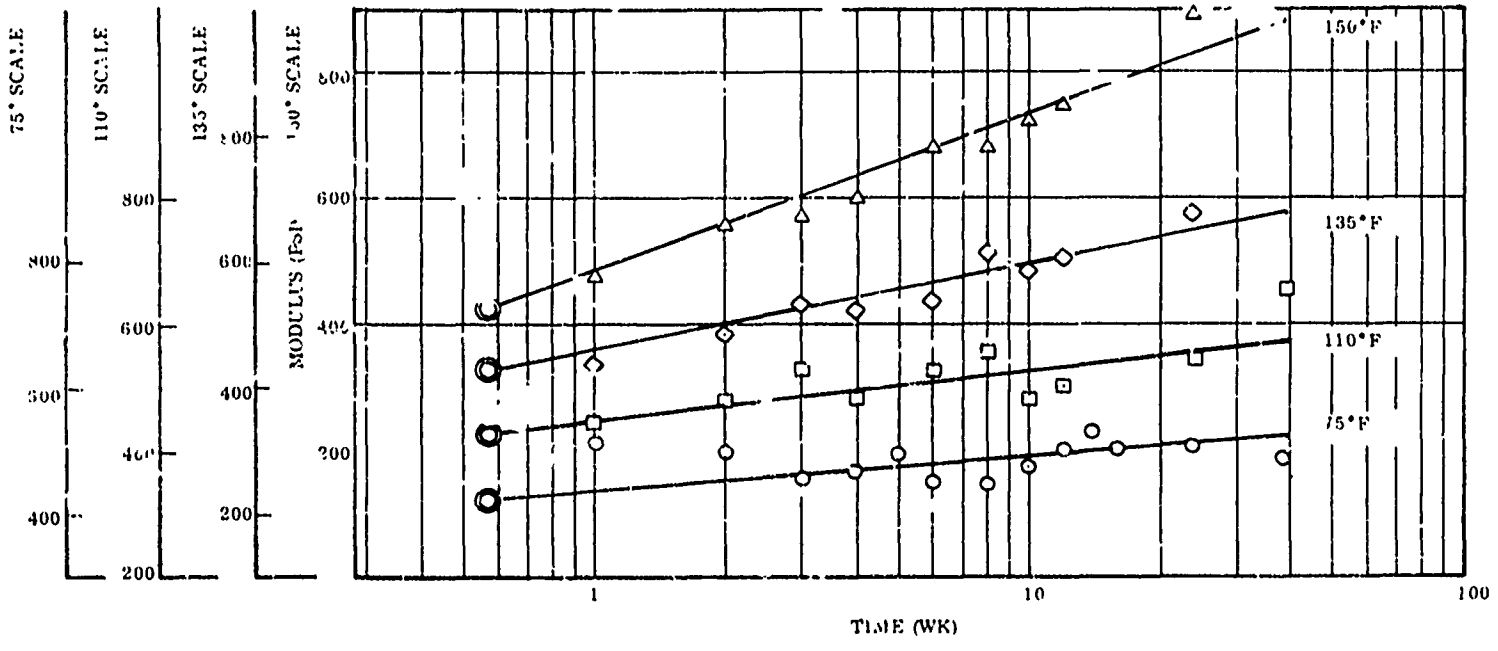
Effect of Aging Time and Temperature on Relaxation Modulus 10,000 Seconds for TP-H1011 Propellant 2% Strain at 75°F



Effect of Aging Time and Temperature on the Maximum Stress of TP-H1011 Propellant Tested at 125°F



Effect of Aging Time and Temperature on the Strain at Maximum Stress for TP-H1011 Propellant Tested at 125°F



Effect of Aging Time and Temperature on Modulus of TP-H1011 Propellant Tested at 125°F