CHEMICAL STRUCTURAL AGING STUDIES ON AN HTPB PROPELLANT

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Brigham City, Utah

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FOREWORD

This technical report was submitted by Thiokol Corporation, Wasatch Division, Brigham City, Utah, under Contract F04611-71-C-0049 with the Air Force Rocket Propulsion Laboratory, Edwards, CA 93523. The work reported herein was done under the direction of Dr. Lionel H. Layton.

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An accelerated aging study has been performed with an HTPB propellant having formulation number TP-H1139. An aging model has been suggested to describe the aging effects on the chemical reaction kinetics in the binder and the resulting mechanical properties. The aging model has been used to make long time equivalent aging properties predictions from short time thermally accelerated aging results.

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To accomplish the development of an aging model, measurements were made to determine the reaction chemistry in the binder and the corresponding mechanical properties. It was necessary to separate the binder from the solids in the cured propellant and to perform chemical analyses on the sol and gel fractions of the binder. The cure reaction was found to be completed before the time alloted for cure by total utilization of the curing agent. The excess hydroxyl from the prepolymer remained without further reaction throughout the aging period. The "bonding agent" did not appear to react chemically during the cure or aging period although it did improve mechanical properties in the propellant.

Correlation of the aging reaction (as observed by the change in percent gel in the binder) with the mechanical properties indicates a 1 to 1 relationship through the aging period of this study. Regardless of the aging temperature or aging time, the mechanical properties can be determined from the amount of gel in the binder once the correlation is established. The maximum aging time was 36 weeks from which a maximum projection to 32 years at 75°F can be made without exceeding the mechanical properties values measured at elevated temperature. No long time aging data are available to compare with the prediction.

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1.0 INTRODUCTION

1.1 BACKGROUND

The study of the effect of aging on the mechanical properties of solid propellant has been the subject of many investigations. Accelerated aging studies have been performed at elevated temperature to obtain advance information concerning the aging behavior to be anticipated at some lower temperature aging condition. In all of these studies, the room temperature projections based on the accelerated aging data were much too conservative. Generally no acceptable method for making long time mechanical properties predictions from data obtained after accelerated aging conditions for a short time has been available, until the chemical structural aging studies were initiated.

Three years ago, chemical aging studies were initiated to determine the chemistry of aging with its resulting effect on the mechanical properties of the propellant. Since the chemical reactions occurring during the cure and aging of solid propellant are varied and complex, it becomes necessary to study these reactions individually to understand the curing and aging mechanisms. It is the study of these reactions in TP-H1011 and ANB-3066 propellants[1, 2] that has provided some of the understanding required for interpretation of the observed changes in mechanical properties. A technique for separating the binder and solid materials (oxidizer, fuel, etc.) in a cured and aged propellant sample to prepare a binder sample for chemical analysis has been a big factor in the evaluation of aging behavior of these two propellants.

Use of a model equation is the logical procedure for extrapolating mechanical properties from measured short aging time values to predicted long aging time values. The model equation must fit not only the measured data but also have a reasonable chance for continuing to follow in the direction that the properties will take in the future. A knowledge of the underlying chemical or physical changes occurring during the aging period is essential to development of the proper aging model. While the aging model developed for TP-H1011 propellant differs from

that for ANB-3066 propellant, the procedure used was the same. For these two propellants, long time aging data were available from another laboratory, and the predicted results using the aging model were in excellent agreement with those data.

1.2 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. Chemical reactions other than the cure reaction can, and very likely do, occur as a result of increasing the temperature to accelerate the aging process, and these reactions can have an adverse effect on the propellant mechanical behavior.

The objectives of this study are:

1. To develop the method of chemical analysis necessary to define the chemistry of aging of the HTPB propellant TP-H1139.
2. To correlate the results of the chemical reaction analyses with the changes in mechanical properties with age.
3. To evaluate the chemical aging concepts with a propellant having a chemically different binder from the ANB-3066 and TP-H1011 propellants previously studied.
4. To predict the mechanical properties for TP-H1139 propellant at extended time based on short aging time test results obtained under accelerated aging conditions.

1.3 SCOPE

Both the chemical reaction and mechanical property characteristics of TP-H1139 were evaluated as a function of age in this study. An analytical procedure was developed for separating and analyzing the propellant materials both during the

cure and aging periods. The chemistry of cure and aging produces an appreciation for and description of the mechanism of aging. Determinations of mechanical properties as a function of aging time and temperature produce an aging rate curve for each aging temperature that is correlatable with the chemical changes. Extension of any of these curves beyond the measured results requires some guidelines. Determination of what chemical reactions are occurring and the rates of these reactions at each aging condition provides these guidelines and makes the aging prediction more reliable. A comparison of the predictions, using the developed technique, is made with the limited data available for this propellant at longer aging times for verification of the prediction model.

2.0 SUMMARY

An aging study has been undertaken with a solid propellant formulated with a hydroxy terminated polybutadiene (HTPB) binder to develop an aging model from which long time predictions of propellant properties can be made. The procedure developed for TP-H1011 propellant was used with minor changes necessitated by the different binder. The cure reaction is between the hydroxyls of the polymer and the isocyanate of the curing agent. At the end of cure, the isocyanate is all reacted leaving approximately the amount of hydroxyl that was in excess in the initial formulation.

Propellants made with HTPB binder require an additive for improved mechanical properties. The aziridine used in this propellant is presumed to be an agent for improving the bond between the ammonium perchlorate and the binder. Chemical analysis of the imine group (considered to be the reactive group for the "bonding agent") indicates that no reaction has occurred. The "bonding agent" performs by some other mechanism.

The measure of percent gel (insoluble or crosslinked binder) during the aging period shows that the amount of gel continues to increase and that the rate of increase is greater at elevated temperature. The change in percent gel is linear as a function of logarithmic aging time. This same behavior was found for ANB-3066 propellant. The equation for defining the TP-H1011 propellant required a second term to adequately describe what appeared to be a second order effect. Both the HTPB propellant (TP-H1139) and ANB-3066 had AO2246 as the antioxidant in the polymer; the TP-H1011 had PBNA as the antioxidant. This may possibly account for the different behavior observed.

The mechanical properties measured on TP-H1139 propellant also changed linearly as a function of logarithmic aging time. This suggests a linear correlation between percent gel and the mechanical properties. Plots of all the measured mechanical properties as a function of the change in percent gel with age indeed verify this correlation.

The aging study was for a period of 36 weeks at 75°, 110°, 135° and 150°F aging conditions. The results suggest that the aging model used for ANB-3066 propellant also applies for this HTPB propellant. Using this equation, it is possible to extrapolate the 75°F aging curve to 32 years without exceeding the elevated temperature properties measured after 36 weeks aging. There are no long time aging data available for this propellant for verification of the extrapolated result.

3.0 TECHNICAL APPROACH

Samples of HTPB propellant, designated TP-H1139, were cast and cured in 1/2 gal cartons for the aging study. Propellant from the same mix (Mix No. 8867001) was also cast in an instrumented Minuteman Stage III motor for another study. The cartons of propellant were placed in a large curing oven, with the temperature controlled at 135° ± 2°F for a total curing time of 240 hours. One carton each was also cured at 140°, 145°, 150° and 155°F for 240 hours to evaluate the cure temperature effect. Samples were taken at periodic intervals during cure from the 135°, 145° and 155°F curing ovens for chemical analyses. At the end of cure, mechanical properties were measured on propellant from each of the five curing conditions. The remaining cartons from the 135°F oven were divided at the end of cure and placed in storage at the four aging temperatures of 75°, 110°, 135° and 150°F. The cured samples were used for both chemical reaction studies and mechanical properties evaluations to determine the effect of thermal environments during the aging period on these parameters.

Analysis of isocyanate and hydroxyl (reactive species for cure) were performed during cure and aging to determine the cure reaction completion time. Since there are deliberately more equivalents of hydroxyl than isocyanate in the formulation, hydroxyl remains when all the isocyanate is gone. Analysis for hydroxyl during the aging period was performed to determine if the hydroxyl reacted with any other chemical species and, as such, contributes to the crosslinking of the polymer. These data define the contribution of the cure reaction to the aging changes in the propellant.

In addition to the isocyanate, HTPB propellants contain a "bonding agent" and, in the case of TP-H1139, this is an aziridine. Analysis for this material is performed to determine its contribution to the cure or aging chemistry.

Since the hydroxy terminated polymer has a backbone comprised of butadiene units, it is very similar to the PBAN and CTPB polymers. It was found by electron paramagnetic resonance spectroscopy, for propellant made with these polymers,

that free radical activity was evident suggesting a free radical initiated reaction. Nuclear magnetic resonance spectroscopy indicated that a loss of cis-trans and vinyl unsaturation occurred during the early aging period suggesting that the reaction occurred at sites of unsaturation. The results from the NMR study were a qualitative indication of a reaction occurring at sites of unsaturation in the polymer. Quantitative measurement of the reaction required for reaction rate determinations is lacking. Additionally, the NMR analysis became less sensitive with aging time of the propellant until the measure of unsaturation became totally masked by other moieties.

A measure of the gel formation indicated that the aging reaction contributed to crosslinking in the polymer and, further, that the reaction rate was related to the rate of gel formation. It was felt that the same condition existed with HTPB propellants; therefore, the sol-gel analysis was performed during cure and aging of the TP-H1139 propellant. The rate of gel formation as determined from this analysis contributes to the development of an aging model equation for the propellant.

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 were performed at 10°, 75° and 125°F test temperatures, both at ambient and superimposed hydrostatic pressure. Relaxation modulus determinations were also made at 10°, 75° and 125°F at a 2% strain level. The results of these tests contribute to the development of an aging model equation for the propellant. 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 with propellant aged at elevated temperature is presented. Thermally accelerated aging therefore becomes a useful tool for determining the propellant structural capability at some arbitrary future time.

4.0 RESULTS

4.1 CHEMICAL ANALYSES

The propellant used in this study has an HTPB binder, is cured with an isocyanate, and contains 88% solids. The formulation for this propellant is presented in the final report Development of HTPB Propellants for Ballistic Missiles under the designation of TP-H1139. Because the binder comprises only 12% of the propellant, it is very difficult to perform chemical analyses for determination of reactions occurring in the binder in the presence of the solid materials. For this program, a procedure for extracting the solids from the binder has been used, producing a solids free material for chemical analysis of functional groups. In the process, the soluble and gel portions of the binder are separated, making the sol-gel determination a simple matter of weighing the fractions. The separation procedure is shown in Figure 1 which indicates the analyses performed on each fraction. The steps in the separation and analysis include:

1. Prepare the sample by cutting into shavings no more than 10 mils thick and (with 4 to 6 gram portions) extract the solubles with room temperature benzene followed by four benzene washes. The original extract and washes are centrifuged and combined and contain the soluble portion of the binder.
2. Evaporate the benzene from the sol and determine percent sol. Determine the hydroxyl and isocyanate in the sol by infrared spectroscopy and the aziridine by HBr titration. Determine the molecular weight of the soluble binder by gel permeation chromatography and the unsaturation by iodimetric titration.
3. Extract the insolubles from Step 1 with 1:1 hydrochloric acid in methanol using four methanol washes and dry in

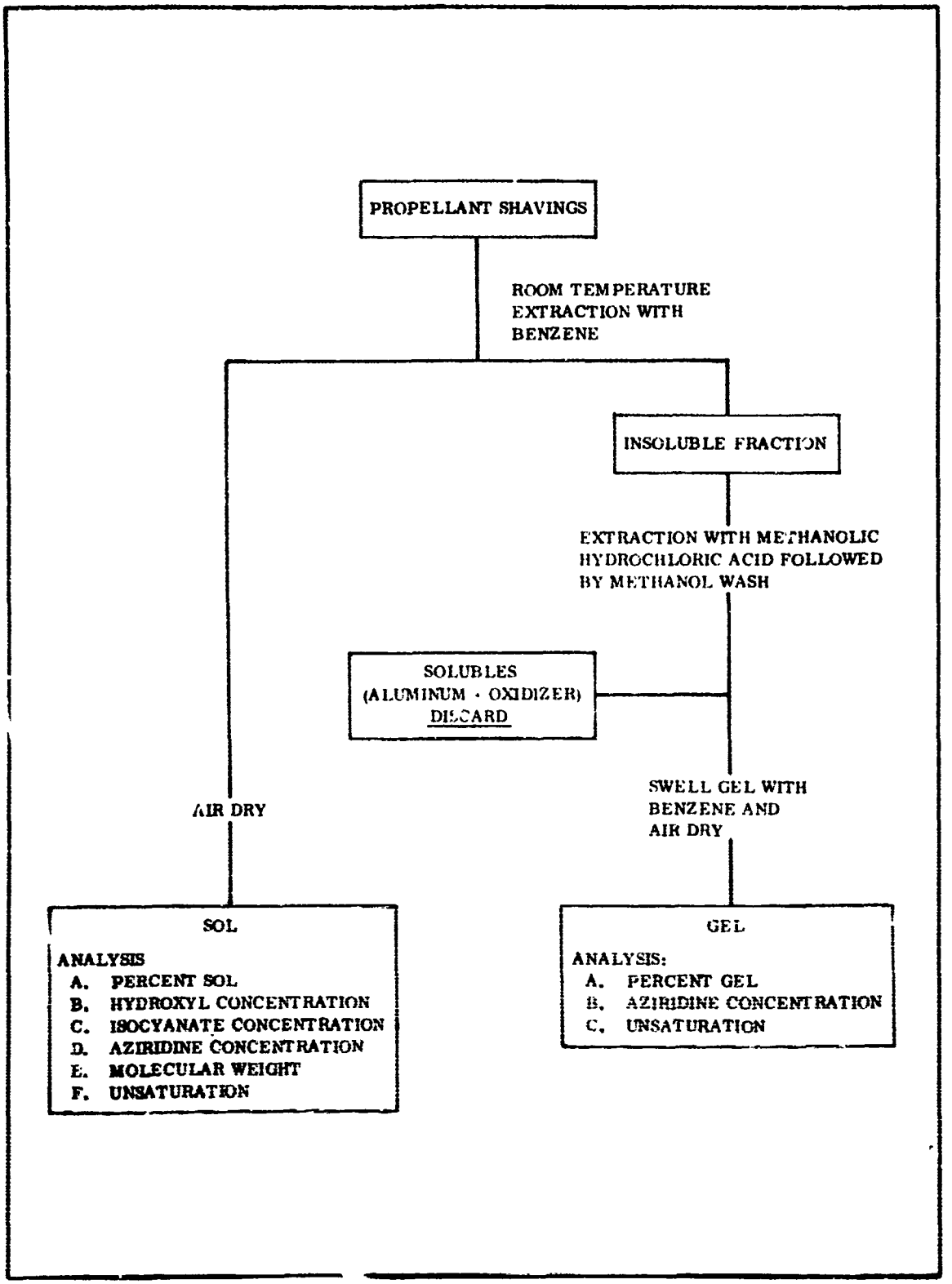

Figure 1. Analytical Approach for Sol-Gel and Functional Group Determinations in Propellant

a Soxhlet extractor. This removes the ammonium perchlorate and aluminum from the insoluble portion of the binder (gel).

4. Dry the insolubles and determine the percent gel and then unsaturate by iodimetric titration.
5. Calibration curves for the infrared analysis were prepared by making standard solutions with the polymer and curing agent raw materials for preparing standard IR scans.

4.1.1 Cure Study

The cure reaction for HTPB propellants is between the hydroxyl of the polymer and the isocyanate of the curing agent. To determine the extent of cure reaction, it is necessary to determine the amount of these chemical species remaining at any time. In this study, the analyses were made by means of infrared (IR) spectroscopy using the binder extracted from the propellant at various cure times. Propellant samples were cured at five temperatures (135°, 140°, 145°, 150° and 155°F) for 240 hours (10 days). Analyses were performed at intervals during cure on samples cured at 135°, 145° and 155°F and at the end of cure on samples cured at all five temperatures.

In addition to the cure reaction, an analysis of the "bonding agent" used in HTPB propellants to obtain maximum mechanical property was made. In TP-H1139 the bonding agent is an aziridine. Analysis for the aziridine and any oxazoline from a rearrangement is performed by an HBr titration of the binder extracted from the propellant at the same time intervals and after the same exposure conditions as the cure reaction study. Any reaction with the imine ring during the cure period would be detected by this analysis and would show a decreased amount of aziridine.

Molecular weight of the extracted binder was determined by gel permeation chromatography. The change in molecular weight in the sol portion of the binder is most drastic in the weight average molecular weight because of the large size the molecules attain before crosslinking occurs to remove them from the sol.

During the extraction of the binder from the propellant, the analysis for soluble (sol) binder and insoluble (gel) binder is obtained by drying and weighing the two fractions. These results have proven to be very valuable in interpreting other chemical data. The high precision of the sol and gel determinations has made it possible to observe the effect of the aging reaction on the propellant binder characteristics. The molecular weight determinations of the sol fraction indicate an average value of 150,000 or less. Uncrosslinked polymers in this molecular weight range are easily dissolved in solvents. Crosslinks formed in polymers of this molecular weight rapidly cause an insoluble gel. This suggests a direct relationship between gel and crosslink formation in the polymer. Also, the amount of uncrosslinked (soluble) material remains near 50% even after aging for long periods of time. This contributes to the tendency for new crosslinks to form more gel by reacting with the more mobile uncrosslinked material rather than the crosslinked gel.

The measure of crosslink density would be a more direct evaluation of crosslinking; however, our crosslink density data were not sufficiently precise to detect the difference in aging rates for the various aging temperatures. As a result, the change in crosslinking in the binder with aging time is inferred from the change in sol-gel ratio.

The results of these chemical analyses during cure are presented in Table I and for immediately after cure in Table II. There is an obvious difference in the amount of gel obtained after 10 days cure (the only point coincident in time in Tables I and II). For instance, the gel for the 135°F cure at 10 days is 35.3% in one case and 40.4% in the other. The samples for the cure study (Table I) were 1/2 pint containers so that at each test increment a container could be removed from the curing oven without disturbing the remaining samples. The samples for the end of cure evaluation were 1/2 gallon containers since both chemical analyses and mechanical properties were to be evaluated. It appears that a difference in the amount of crosslinking occurs in the different containers although the same oven was used. While this bias does not compromise any of the conclusions made in this study, it should be recognized as a potential problem in cure studies.

Table I

Chemical Analysis of TP-H1139 Propellant During Cure

Cure Temp (°F)	Cure Time (hr)	Sol (%)	Gel (%)	Isocyanate* (meq/100 gm)	Aziridine* (meq/100 gm)	Molecular Weight*
135	4	100	---	15.0	8.0	16,300
	6	100	---	13.4	8.7	15,800
	8	100	---	13.2	8.3	15,200
	12	100	---	10.7	8.4	23,400
	20	100	---	8.4	9.0	67,900
	36	100	---	4.7	10.3	93,200
	68	95.8	4.2	1.8	7.2	149,100
	132	71.4	28.6	0.7	8.9	106,600
	244	64.7	35.3	---	8.3	106,400
145	4	100	---	15.0	8.0	16,300
	6	100	---	12.5	8.9	15,400
	8	100	---	11.1	8.5	23,700
	12	100	---	8.5	8.8	23,800
	20	100	---	5.7	9.0	79,300
	36	92.1	7.9	2.3	7.4	151,400
	68	75.4	24.6	0.8	9.5	128,500
	132	65.1	34.9	0.4	8.3	93,100
	244	61.2	38.8	---	8.8	88,000
155	4	100	---	15.0	8.0	16,300
	6	100	---	11.8	8.0	16,800
	8	100	---	11.5	9.3	27,400
	12	100	---	8.4	8.5	51,200
	20	100	---	4.7	8.9	79,500
	36	92.9	7.1	2.4	7.2	145,300
	68	72.8	27.2	0.7	9.7	108,700
	132	62.2	37.8	---	8.2	90,900
	244	57.4	42.6	---	7.7	74,900

Initial isocyanate concentration: 52.1 meq/100 gm of binder.

*Analysis of sol.

Table II

Effect of Cure Temperature on the Cure Chemistry in the Binder of TP-H1139 Propellant (10 Day Cure)

Cure Temp (°F)	Sol (%)	Gel (%)	Sol Analysis			Molecular Weight	Iodine No.		
			Isocyanate (meq/100 gm)	Hydroxyl (meq/100 gm)	Aziridine (meq/100 gm)		Sol	Gel	Total
135	59.6	40.4	---	17.3	9.3	66,500	394	361	380
140	57.9	42.1	---	22.0	9.0	73,900	403	334	374
145	57.5	42.5	---	22.2	10.0	81,200	423	365	398
150	57.4	42.6	---	21.3	9.3	67,600	418	339	384
155	56.7	43.3	---	21.9	8.8	66,900	389	299	350

The changes in isocyanate concentration, molecular weight, and percent gel with cure temperature are presented graphically in Figures 2, 3, and 4, respectively. Since the isocyanate completely reacts, it is not possible to see any difference in the end result other than a shorter time for reaction completion. It is obvious that reaction completion occurs in less than 244 hours for 135°F cure and less than 132 hours for 155°F cure. The molecular weight suggests that the extent of cross-linking is greater at 155°F than at 135°F cure. One must recall, however, that more aging reaction has occurred during the cure period at the higher temperature. The amount of gel in the binder is greater at the end of cure for the higher cure temperature probably for the same reason that molecular weight in the sol is lower.

4.1.2 Aging Study

Samples for chemical analyses during the aging period were taken from the same 1/2 gallon cartons that were used for mechanical property test specimens. All cartons for this study were cured at 135°F for 10 days. Since aging reactions also occur during the cure period, the end of cure (10 days) is shown as 1.4 week aging, with all subsequent periods being based on the same time zero.

All evidence for curing agent (isocyanate) disappeared before the end of the 10 day cure period, and at no time did the IR analysis indicate any in the aged samples. The hydroxyl concentration remains at an average value of 22.7 meq/100 gm of binder for all aging temperatures, indicating no reaction with the remaining hydroxyls (see Table III). It is of interest that the initial hydroxyl and isocyanate concentrations were 70.5 and 52.1 meq/100 gm, respectively. If there were a 1 to 1 reaction, the amount of hydroxyl that would remain is 18.4 meq/100 gm. Since the average analyzed concentration is 22.7 meq/100gm, it means that approximately 4.3 meq/100 gm of isocyanate reacted with some other material. If the other material were water, it would require 7.7 mg water/100 gm binder or 0.0077% water in the binder. No analysis was performed for moisture in the binder; however, this is not an unreasonable amount.

The analysis for aziridine indicates no change either during the cure or the aging period. The amount of "bonding agent" added to the propellant formulation

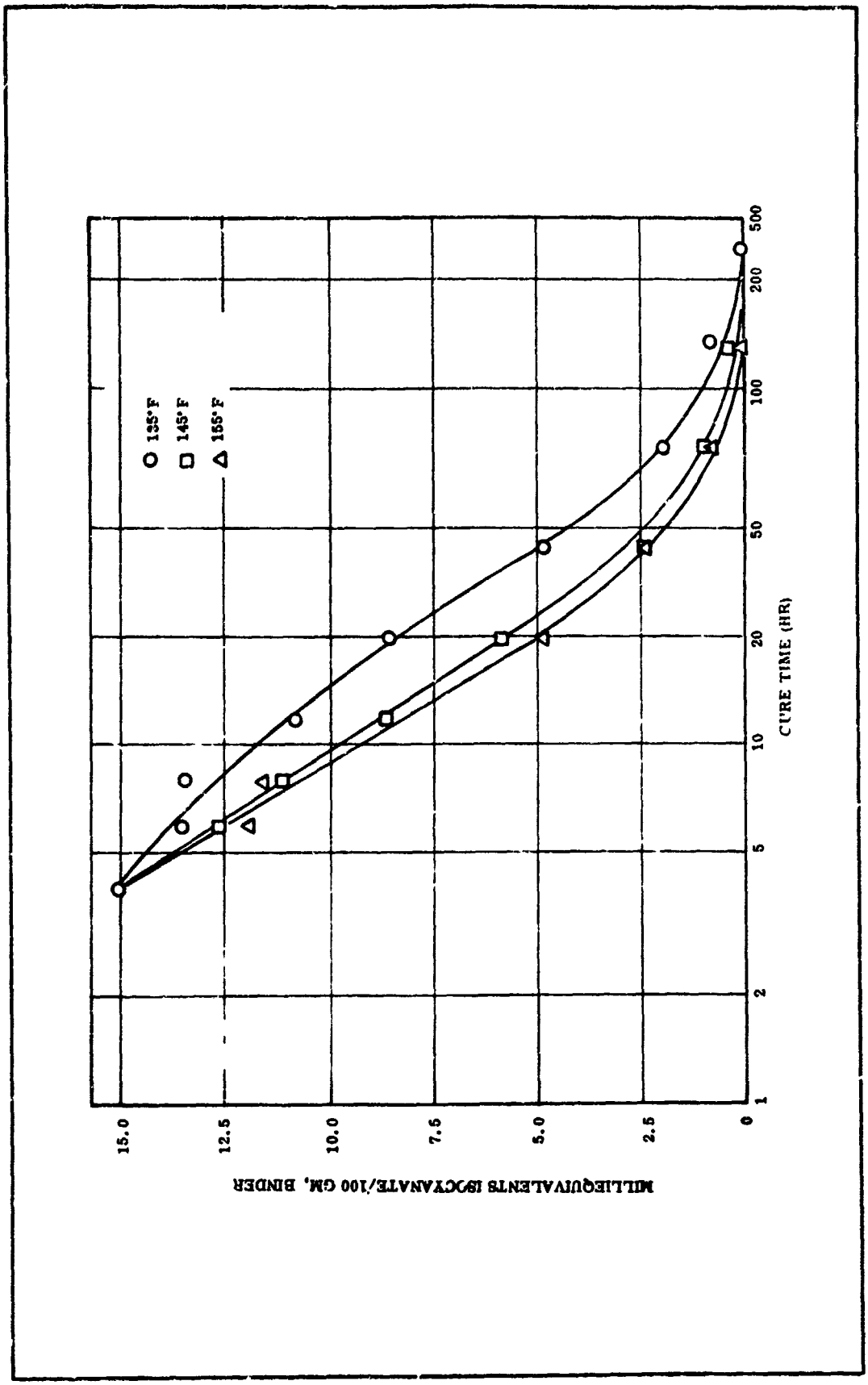

Figure 2. Effect of Cure Temperature on the Isocyanate Reaction

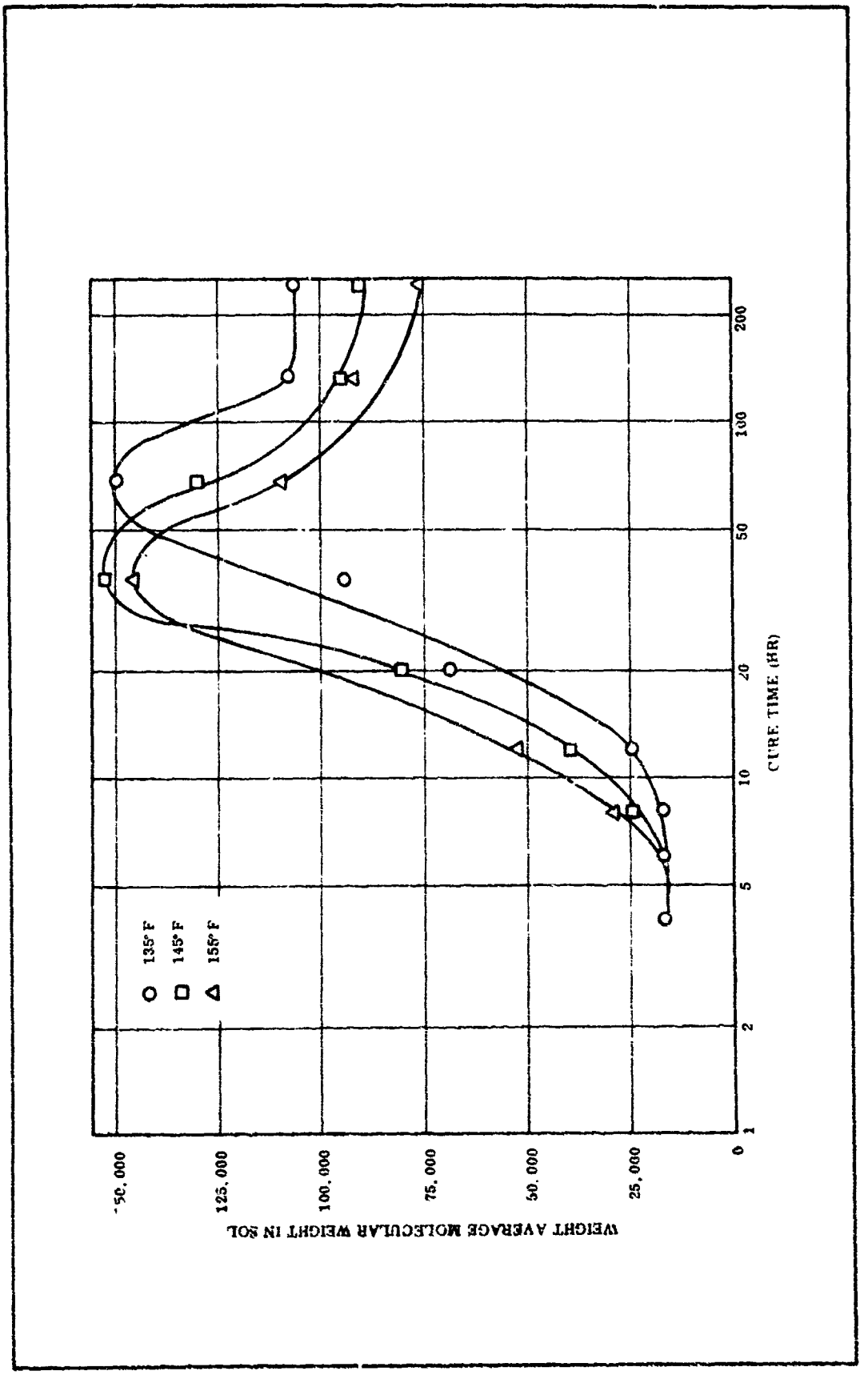

Figure 3. Effect of Cure Temperature on the Molecular Weight of the Binder Sol

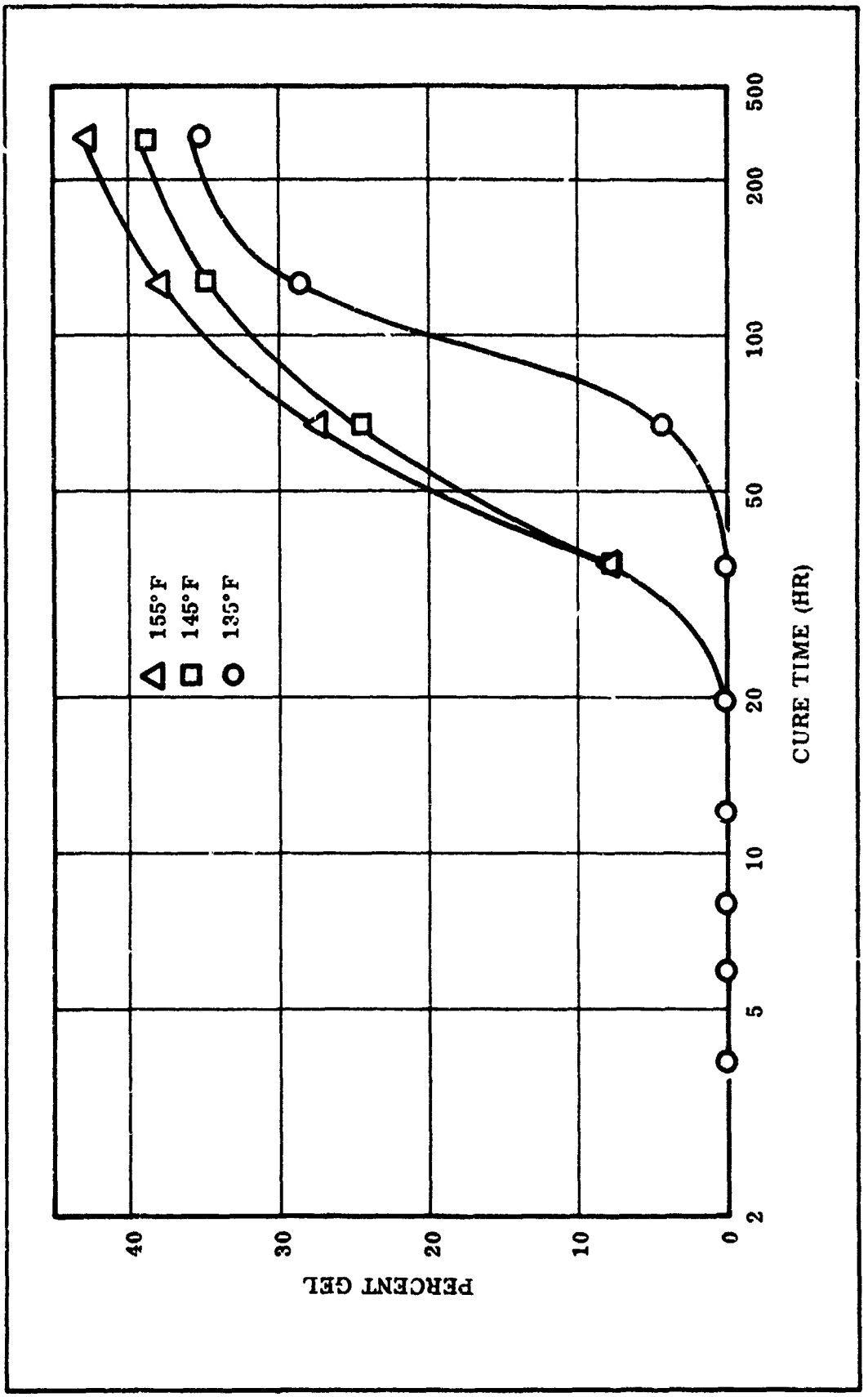

Figure 4. Effect of Cure Temperature on the Gel Formation

Table III

Chemical Analysis During Aging of TP-H1139 Propellant Binder

Aging Temp (°F)	Aging Time (wk)	Sol (%)	Gel (%)	Sol Analysis			Iodine No.		
				Isocyanate (meq/100 gm)	Hydroxyl (meq/100 gm)	Aziridine (meq/100 gm)	Sol	Gel	Total
75	1.4	59.6	40.4	---	22.4	9.3	394	361	380
	2	57.8	42.2	---	21.5	8.2	407	338	378
	3	58.5	41.5	---	22.3	8.2	393	369	383
	4	58.1	41.9	---	24.9	9.1	384	358	373
	6	57.8	42.2	---	21.4	10.4	387	329	362
	8	57.0	43.0	---	21.9	8.5	391	346	372
	10	56.6	43.4	---	22.1	9.5	388	352	372
	16	56.4	43.6	---	22.7	9.6	405	355	383
	26	54.9	45.1	---	22.8	8.9	386	325	358
	36	54.2	45.8	---	22.9	8.6	391	315	356
110	1.4	59.6	40.4	---	22.4	9.3	394	361	380
	2	58.2	41.8	---	21.5	9.0	387	320	359
	3	57.3	42.7	---	21.5	7.9	393	349	374
	4	56.9	43.1	---	23.3	9.6	391	357	376
	6	56.6	43.4	---	22.7	11.5	378	311	349
	8	54.8	45.2	---	22.6	7.9	386	343	367
	10	54.0	46.0	---	22.7	7.3	394	352	375
	16	53.2	46.8	---	24.4	7.8	390	262	330
	26	51.1	48.9	---	23.2	8.5	381	247	315
	36	50.2	49.8	---	24.0	8.1	386	243	315
135	1.4	59.6	40.4	---	22.4	9.3	394	361	380
	2	57.6	42.4	---	21.0	8.8	391	357	376
	3	56.7	43.3	---	20.1	10.3	400	362	383
	4	56.5	43.5	---	22.8	9.5	399	353	379
	6	55.4	44.6	---	22.1	8.5	386	353	371
	8	53.6	46.4	---	23.7	8.8	394	31[illegible]	356
	10	53.8	46.2	---	23.6	8.6	390	349	371
	16	51.5	48.5	---	24.8	8.1	396	295	347
	26	50.7	49.3	---	22.8	6.8	380	229	305
	36	48.1	51.9	---	24.7	8.3	387	258	320
150	1.4	59.6	40.4	---	22.4	9.3	394	361	380
	2	57.2	42.8	---	24.3	8.4	377	334	358
	3	56.6	43.4	---	21.5	10.1	399	369	385
	4	55.6	44.4	---	22.1	9.4	381	366	374
	6	55.3	44.7	---	23.0	8.7	392	332	365
	8	52.8	47.2	---	23.7	8.8	397	313	359
	10	51.7	48.3	---	24.0	8.0	390	284	340

Initial hydroxyl concentration: 70.5 meq/100 gm binder.

should produce a concentration of aziridine of 8.6 meq/100 gm of binder. This is very similar to the average value found of 8.8 meq/100 gm of binder, suggesting that if any chemical bond occurred between the aziridine and the oxidizer, it did not occur with the imine ring.

Titration of the sol and gel fractions of the binder with iodine produced a very interesting result. It appears there is no change in unsaturation in the sol fraction, while a very consistent decrease in iodine number in the gel fraction occurred both with age-time and with age-temperature. The change in iodine number is sufficiently consistent to suggest that the amount of unsaturation is diminishing. This is probably due to the fact that reactions occur with the sol, which causes the reacted molecule to become part of the crosslinked network. As a result no change in net unsaturation is apparent in the remaining sol. Since the large majority of gel is formed by the cure reaction where the unsaturation is unaffected, and any new gel formed by the aging reaction has a reduced unsaturation, the result is a decrease of unsaturation in the gel.

The percent gel continues to increase from the end of cure value of 40.4% to 45.8% up to 36 weeks at 75°F. Higher aging temperatures cause a greater change in the amount of gel. Some chemical reaction is continuing during the aging period, and with the isocyanate curing agent gone it cannot be the initial cure reaction. Nevertheless, the aging reaction is very consistent and follows the linear change with logarithmic time found with ANB-3066 propellant.[2] The results are presented graphically in Figure 5 where the ordinate is displaced for each aging temperature presentation to separate the points. The four lines all initiate at the same point at 1.4 weeks (end of cure at 135°F) since all propellant for analysis was cured at the same time and place. These results indicate that the aging reaction rate is consistent with time and that elevated temperature accelerates the reaction in a manner that is satisfactorily defined by the aging model:

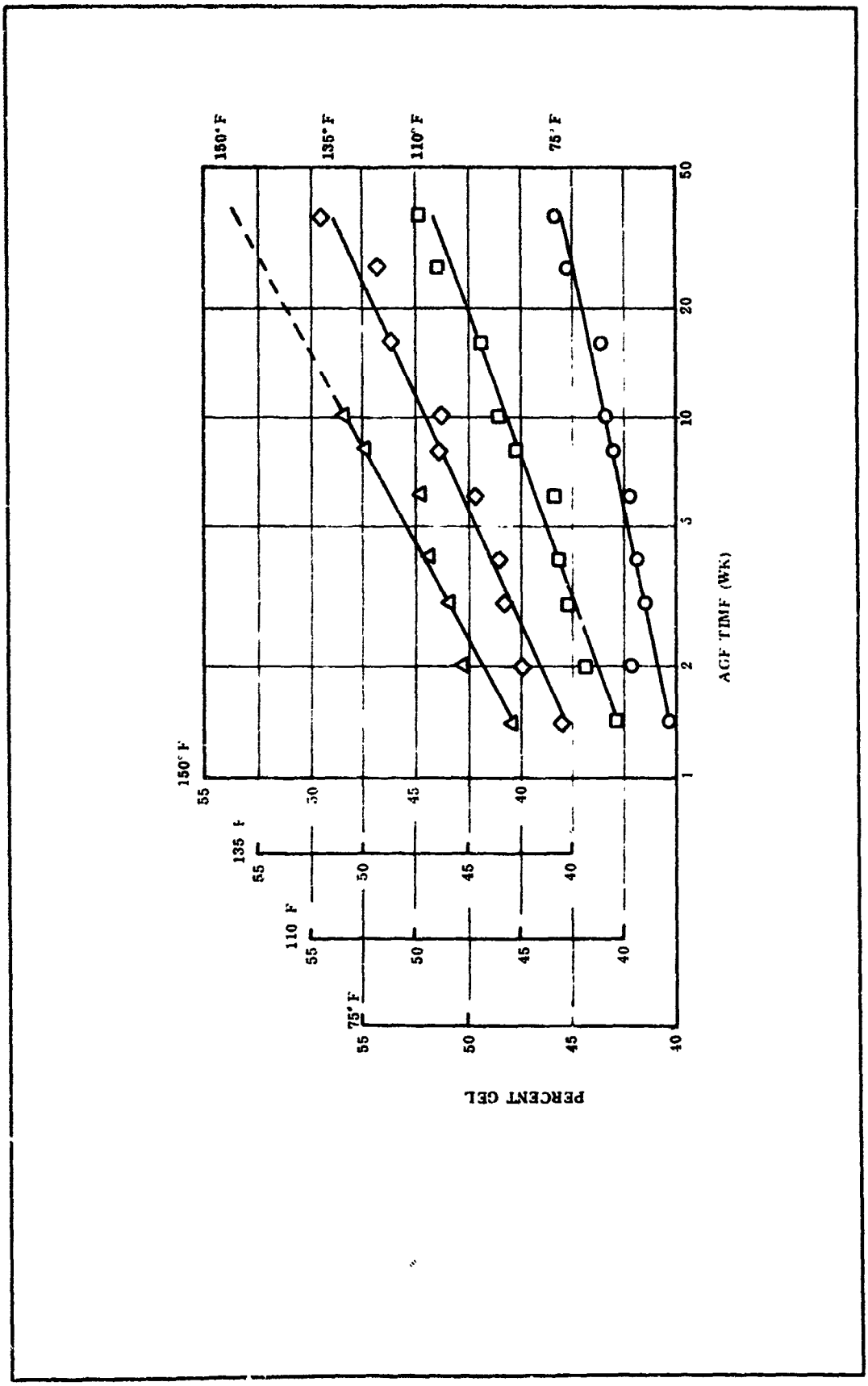

Figure 5. Aging Effect on Percent Gel in the Binder, TP-H1139 Propellant

$$g(T,t) = k_g(T) \log t + g_o$$

where $g(T,t)$ = percent gel at age temp, T, and time, t

g_o = percent gel at 1 week

$k_g(T)$ = rate of change of percent gel at temperature, T

4.2 MECHANICAL PROPERTIES

The aging sample was a 1/2 gallon unlined carton with the top and bottom taped closed. The tape was used more for mechanical support for the uncured propellant than for a barrier to atmospheric conditions during aging; however, the tape was left on the samples during aging. The ovens used for maintaining temperature during aging were sufficiently large that spaces were left between cartons for circulation around each carton. Aging temperatures of 75°, 110°, 135° and 150°F were used and samples were removed at periodic intervals from which both chemical analyses and mechanical properties tests were performed. The mechanical properties tests were:

1. Uniaxial tensile tests at 2 in/min, at 10°, 75° and 125°F, and at ambient pressure and 500 psi superimposed pressure.
2. Relaxation modulus tests at 2% strain and 10°, 75° and 125°F.

No tests were performed to determine if a variation in properties exists across the aged cartons; however, since a variation has been observed with other propellants, precautions were taken to reduce data scatter from any possible variability. Specimens for a particular test were always taken from the same location in the carton. It was anticipated that a comparison with some of the available aging data would be made; therefore, the samples for 75°F uniaxial tests were taken from the center of the carton to be as near as possible to the carton location from which specimens for other aging studies were taken. A "standard" propellant was always tested before any program specimens were tested to check the equipment operation.

4.2.1 Uniaxial Tensile Tests

These tests were performed using a JANNAF Class B tensile specimen. The sample was placed in an Instron tensile tester with a temperature conditioning chamber to maintain the temperature to $\pm$ 2°F of the test temperature. An auxiliary load cell was used in place of the Instron weighing system. An optical device was used to track the displacement of a 1 in. section in the center of the specimen. Signals from the load cell and the optical displacement device were fed to a recorder and to an on-line computer. The computer provided a printout of the reduced data, and the curve was used for backup, providing a permanent record for review at a later time if necessary.

The uniaxial tests under superimposed hydrostatic pressure were performed inside a pressure vessel having controlled temperature capability. After the sample was placed in the jaws of the tester and the vessel closed, the pressure was increased by adding dry nitrogen. The load was applied by means of a pneumatic ram with rate control through a hydraulic system. The load, displacement, and recording were performed in the same manner as the ambient pressure tests.

The results of the uniaxial tensile tests are presented in Tables IV thru IX. The properties shown are: modulus calculated with a 2.6 in. effective gage length ($E^{2.6}$), maximum stress (σ_m), true strain at maximum stress (ϵ_m^t), and true strain at sample failure (ϵ_f^t). Each point is the average of three tests; however, no other manipulation of the data has been performed.

The data for the stress and strain parameters have been plotted as a function of log aging time and are presented in Figures 6 thru 17. It is apparent that, as far as the data go, the linear relationship to logarithmic time seems to apply. The aging model $p = k \log t + a$ appears to be a satisfactory representation of the data and could be used to make predictions of aging behavior. This is in excellent agreement with the model suggested for the change in gel with age-time.

Table IV

Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Tested at 2 in/min, 10°F, and Ambient Pressure

Aging Temp (°F)	Aging Time (wk)	$E^{2.6}$ (psi)	σ_m (psi)	ϵt_m (%)	ϵt_f (%)
75	1.4	1340	195	52	77
	2	1180	210	45	65
	3	1660	213	49	67
	4	1600	208	55	81
	6	1950	231	53	75
	8	2020	233	47	67
	10	1700	220	51	70
	16	1650	226	48	68
	26	1590	236	43	64
	36	1330	225	50	61
	39	2890	239	48	68
110	1.4	1340	195	52	77
	2	1580	210	46	75
	3	1760	225	48	69
	4	1700	215	52	73
	6	1720	236	49	67
	8	2130	242	47	63
	10	1910	232	50	75
	16	1800	235	47	63
	26	1760	245	43	62
	36	1440	250	52	67
	39	2830	251	48	68
135	1.4	1340	195	52	77
	2	1500	217	48	67
	3	1690	227	50	67
	4	1790	231	50	67
	6	1770	252	50	63
	8	2080	245	44	61
	10	1760	234	52	72
	16	2100	237	53	70
	26	1750	265	45	67
	36	1420	260	51	59
	39	3010	265	48	68
150	1.4	1340	195	52	77
	2	1260	216	48	72
	3	1620	228	52	73
	4	1860	239	52	73
	6	1790	250	47	62
	8	2170	255	46	66
	10	2030	248	51	65

Table V

Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Tested at 2 in/min, 75°F, and Ambient Pressure

Aging Temp (°F)	Aging Time (wk)	$E^{2.6}$ (psi)	σ_m (psi)	ϵ_m^t (%)	ϵ_f^t (%)
75	1.4	391	104	52	62
	2	352	116	56	65
	3	358	119	50	58
	4	475	121	50	62
	6	458	118	55	71
	8	523	118	52	65
	10	594	118	55	66
	16	601	121	49	64
	26	600	125	50	64
	36	608	129	51	56
110	1.4	391	104	52	62
	2	373	113	54	62
	3	503	121	49	61
	4	503	122	44	53
	6	519	125	51	65
	8	557	123	49	63
	10	587	125	55	72
	16	619	123	47	58
	26	637	136	48	60
	36	617	133	54	60
135	1.4	391	104	52	62
	2	530	123	54	67
	3	501	122	49	63
	4	522	122	48	53
	6	534	127	51	64
	8	612	131	48	60
	10	576	136	54	70
	16	657	139	46	56
	26	608	141	49	59
	36	677	144	49	55
150	1.4	391	104	52	62
	2	500	121	56	67
	3	440	125	48	54
	4	517	130	45	53
	6	571	125	52	64
	8	615	133	50	59
	10	670	135	52	64

Table VI

Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Tested at 2 in/min, 125°F, and Ambient Pressure

Aging Temp (°F)	Aging Time (wk)	$E^{2.6}$ (psi)	σ_m (psi)	ϵ_m^t (%)	ϵ_f^t (%)
75	1.4	204	89	59	66
	2	278	98	43	45
	3	271	98	50	53
	4	360	97	51	59
	6	350	98	55	64
	8	340	100	48	56
	10	371	101	48	52
	16	382	99	51	5[illegible]
	26	370	100	53	[illegible]
	36	388	101	45	[illegible]
110	1.4	204	89	59	66
	2	270	97	46	48
	3	294	98	50	53
	4	403	100	50	59
	6	375	98	54	64
	8	385	99	49	57
	10	419	107	48	52
	16	439	106	48	53
	26	413	106	49	54
	36	446	113	42	45
135	1.4	204	89	59	66
	2	385	101	41	43
	3	359	100	50	53
	4	404	104	54	62
	6	406	104	54	63
	8	411	102	48	52
	10	445	116	50	55
	16	462	111	48	5[illegible]
	26	445	112	47	51
	36	433	115	46	49
150	1.4	204	89	59	66
	2	376	102	43	45
	3	298	104	50	54
	4	432	109	46	49
	6	424	107	52	57
	8	432	109	52	57
	10	420	115	49	54

Table VII

Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Tested at 2 in/min, 10°F, and 500 psi Superimposed Pressure

Aging Temp (°F)	Aging Time (wk)	$E^{2.6}$ (psi)	σ_m (psi)	ϵ_m^t (%)	ϵ_f^t (%)
75	1.4	2720	386	65	81
	2	2550	396	59	78
	3	2350	386	52	58
	4	2750	391	58	69
	6	2660	403	60	76
	8	2450	420	57	72
	10	2380	418	61	75
	16	2470	403	58	66
	26	2560	446	55	69
	36	2200	450	58	63
110	1.4	2750	386	65	31
	2	2740	391	63	77
	3	2920	404	58	68
	4	3260	410	57	69
	6	2290	429	61	73
	8	2300	425	59	74
	10	2670	419	54	66
	16	2140	420	61	73
	26	2660	464	56	66
	36	2250	444	57	69
135	1.4	2750	386	65	81
	2	2760	405	62	77
	3	2600	428	59	68
	4	3200	426	55	60
	6	2640	445	54	66
	8	2600	431	55	73
	10	2990	462	56	69
	16	2190	450	61	74
	26	2720	456	52	65
	36	2890	490	57	65
150	1.4	2750	386	65	81
	2	2350	375	61	79
	3	2160	425	57	66
	4	3160	425	59	68
	6	2700	438	52	56
	8	2540	444	56	70
	10	2320	457	54	66

Table VIII

Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Tested at 2 in/min, 75°F, and 500 psi Superimposed Pressure

Aging Temp (°F)	Aging Time (wk)	$E^{2.6}$ (psi)	σ_m (psi)	ϵ_m^t (%)	ϵ_f^t (%)
75	1.4	441	204	73	80
	2	553	218	70	76
	3	573	207	72	78
	4	491	210	69	73
	6	586	219	71	79
	8	603	255	68	74
	10	445	212	66	72
	16	665	231	71	79
	26	612	221	67	75
	36	544	224	68	72
110	1.4	441	204	73	80
	2	473	206	66	70
	3	647	222	72	77
	4	481	213	73	85
	6	563	224	69	76
	8	633	247	65	75
	10	535	224	67	76
	16	658	238	70	77
	26	728	249	65	70
	36	594	235	65	75
135	1.4	441	204	73	80
	2	502	217	69	75
	3	631	228	70	77
	4	520	220	74	82
	6	567	234	66	70
	8	688	260	65	73
	10	559	241	63	72
	16	610	242	71	79
	26	658	248	63	69
	36	659	247	63	68
150	1.4	441	204	73	80
	2	552	223	68	75
	3	650	229	73	84
	4	558	228	68	73
	6	658	240	66	68
	8	606	266	64	70
	10	605	254	64	72

Table IX

Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Tested at 2 in/min, 125°F, and 500 psi Superimposed Pressure

Aging Temp (°F)	Aging Time (wk)	$E^{2.6}$ (psi)	σ_m (psi)	ϵ^t_m (%)	ϵ^t_f (%)
75	1.4	261	152	74	82
	2	286	159	75	82
	3	355	162	75	84
	4	273	156	74	81
	6	295	167	71	77
	8	306	166	76	85
	10	315	171	72	81
	16	334	159	73	80
	26	288	167	72	79
	36	317	174	73	75
110	1.4	261	152	74	82
	2	290	160	72	78
	3	334	165	73	81
	4	304	166	69	74
	6	333	174	75	83
	8	306	169	71	79
	10	309	177	70	79
	16	396	183	71	78
	26	355	184	70	78
	36	329	188	70	73
135	1.4	261	152	74	82
	2	309	163	76	82
	3	304	170	71	78
	4	333	167	70	73
	6	391	180	69	75
	8	296	175	69	75
	10	359	189	64	70
	16	412	192	68	76
	26	339	193	67	73
	36	349	205	66	71
150	1.4	261	152	74	82
	2	299	166	71	77
	3	288	176	71	77
	4	334	176	66	71
	6	381	187	67	75
	8	369	186	69	72
	10	343	191	68	75

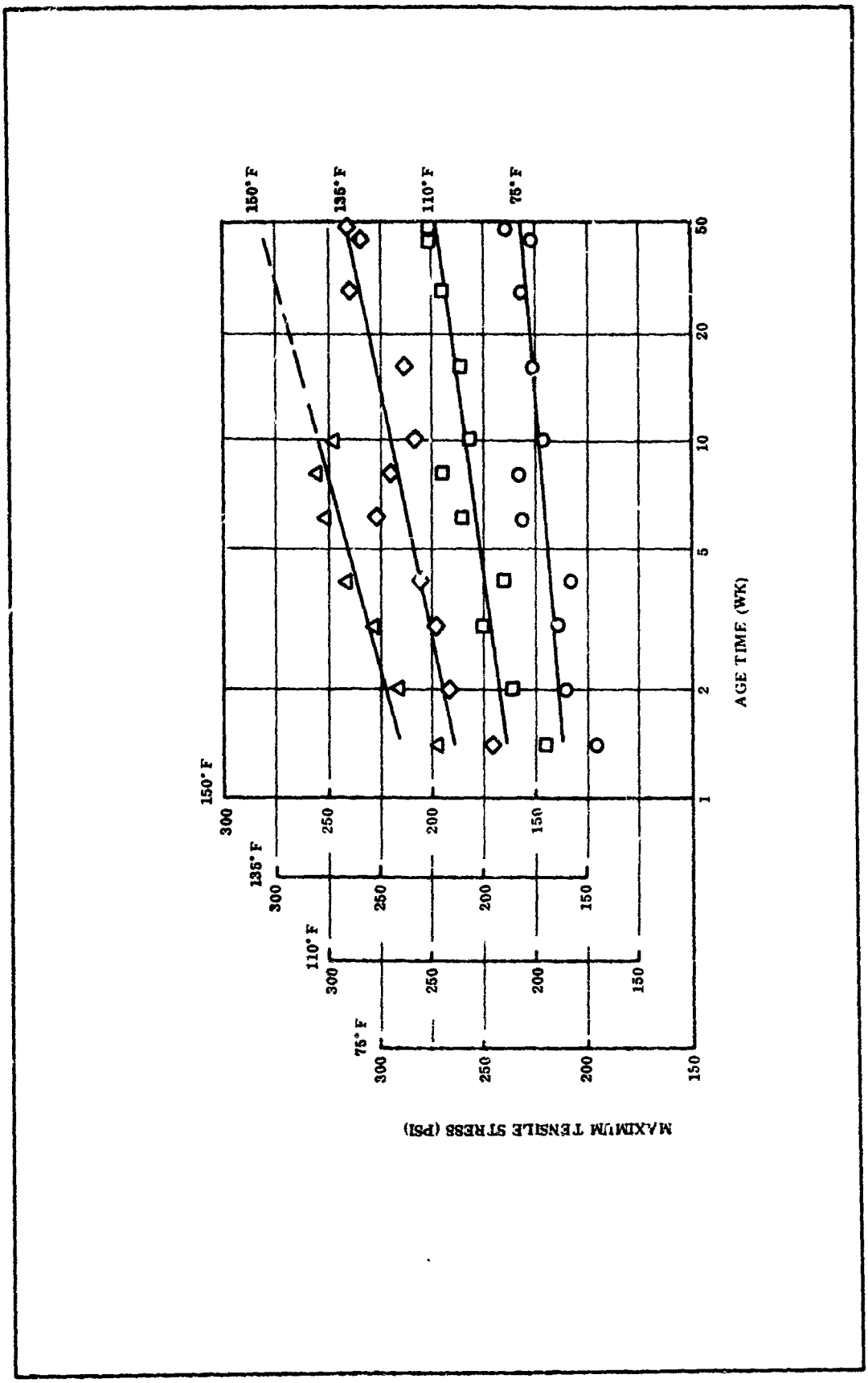

Figure 6. Aging Effect on Maximum Tensile Stress, 10°F Test Temperature

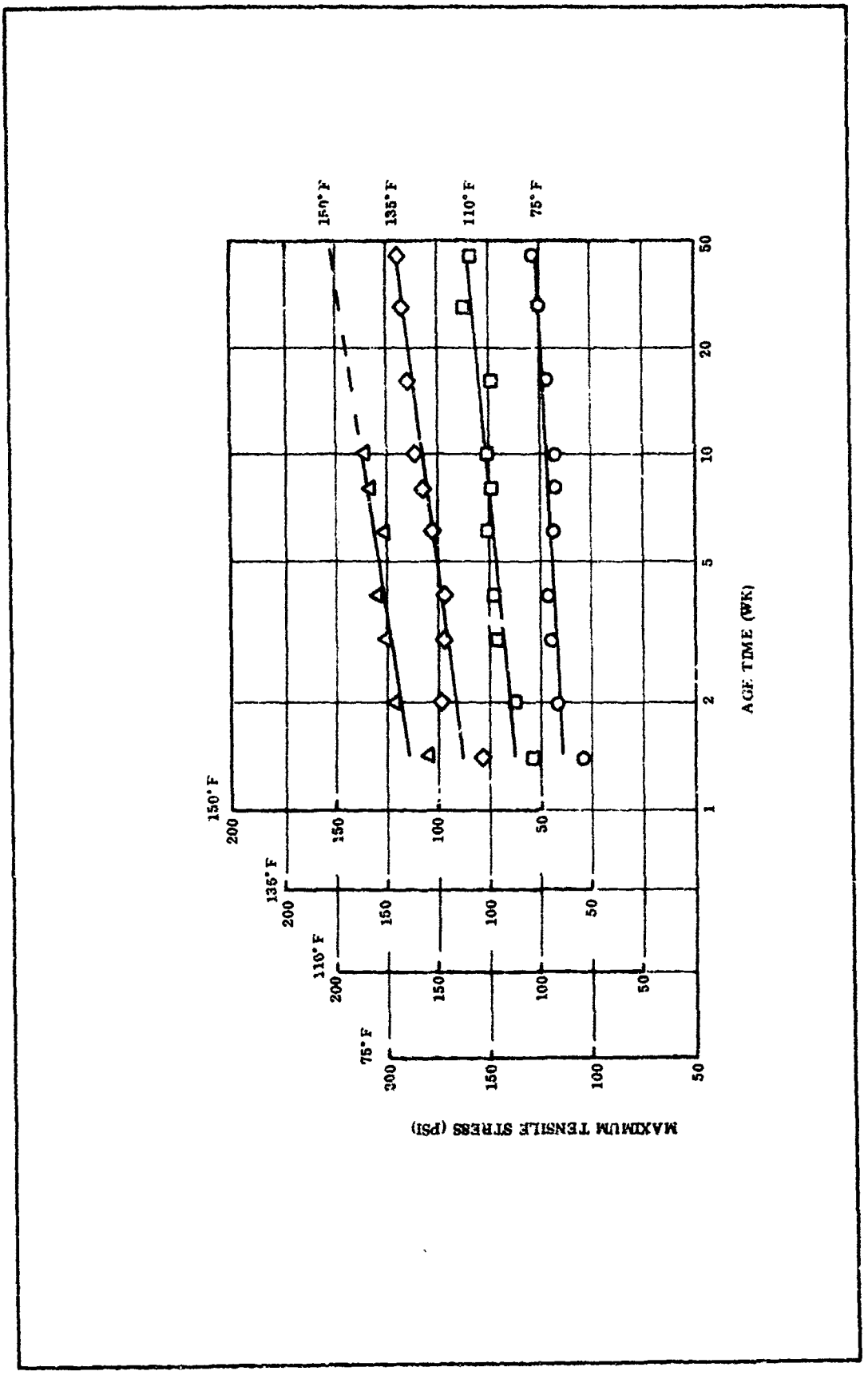

Figure 7. Aging Effect on Maximum Tensile Stress, 75°F Test Temperature

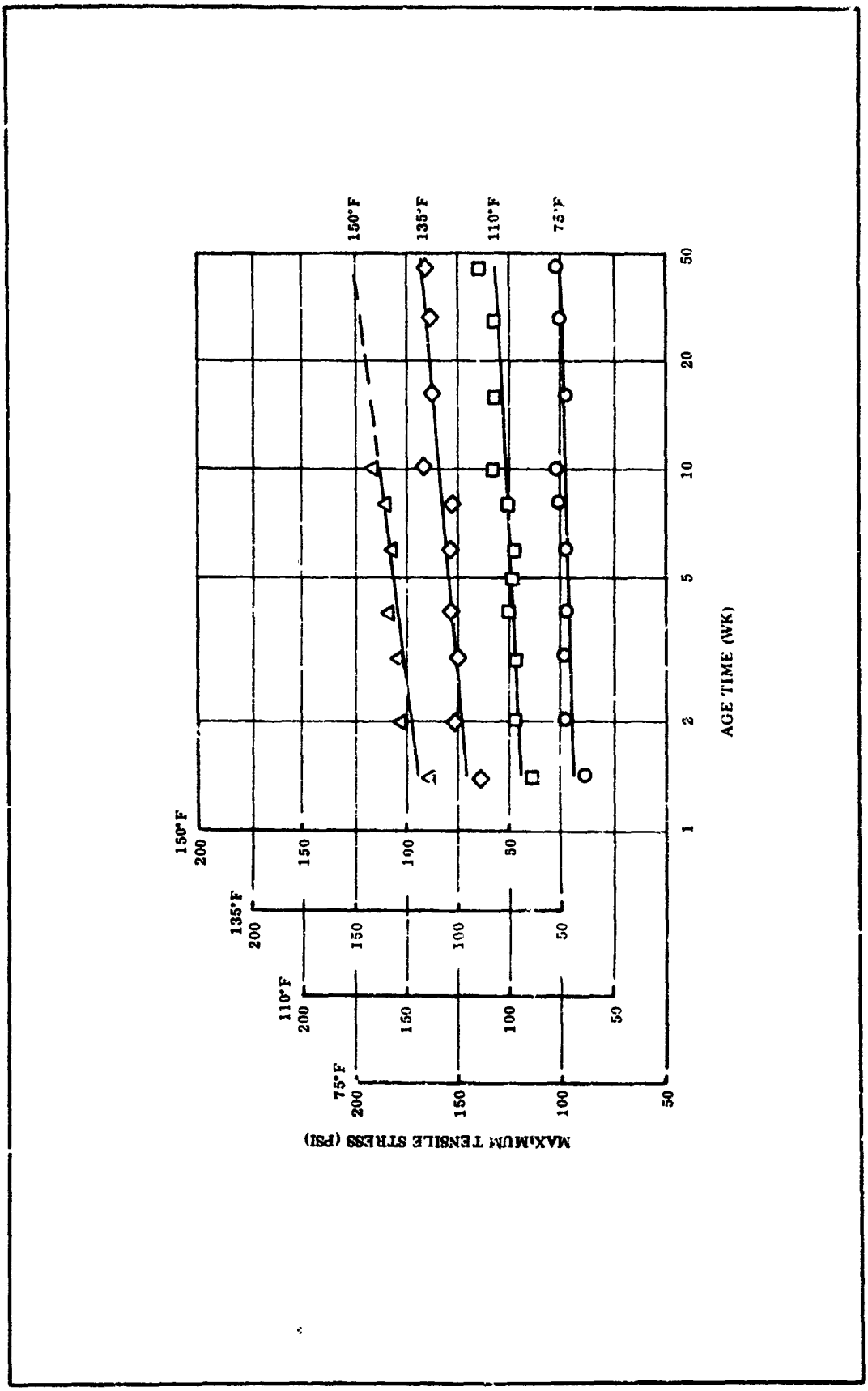

Figure 8. Aging Effect on Maximum Tensile Stress, 125°F Test Temperature

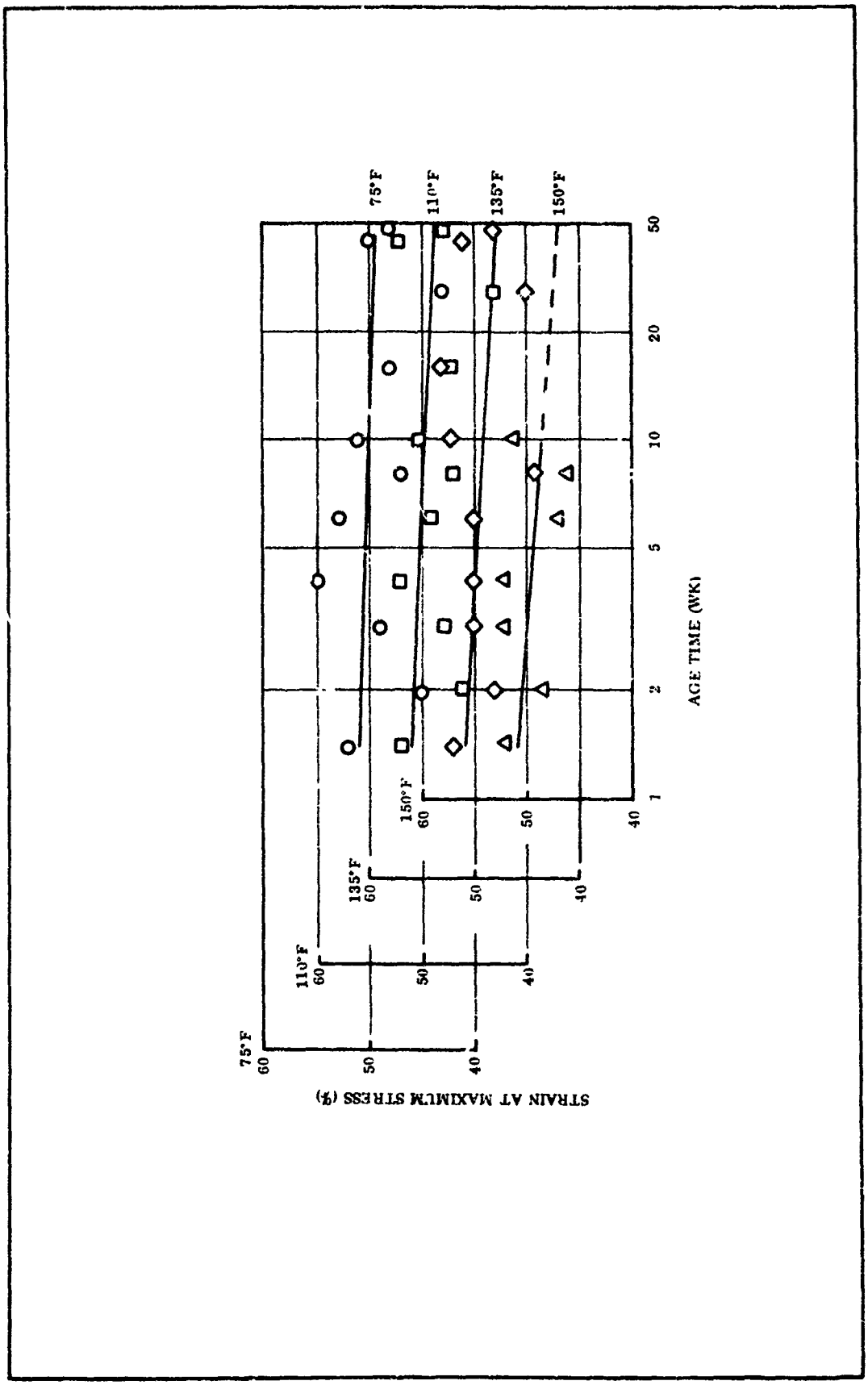

Figure 9. Aging Effect on Strain at Maximum Stress, 10°F Test Temperature

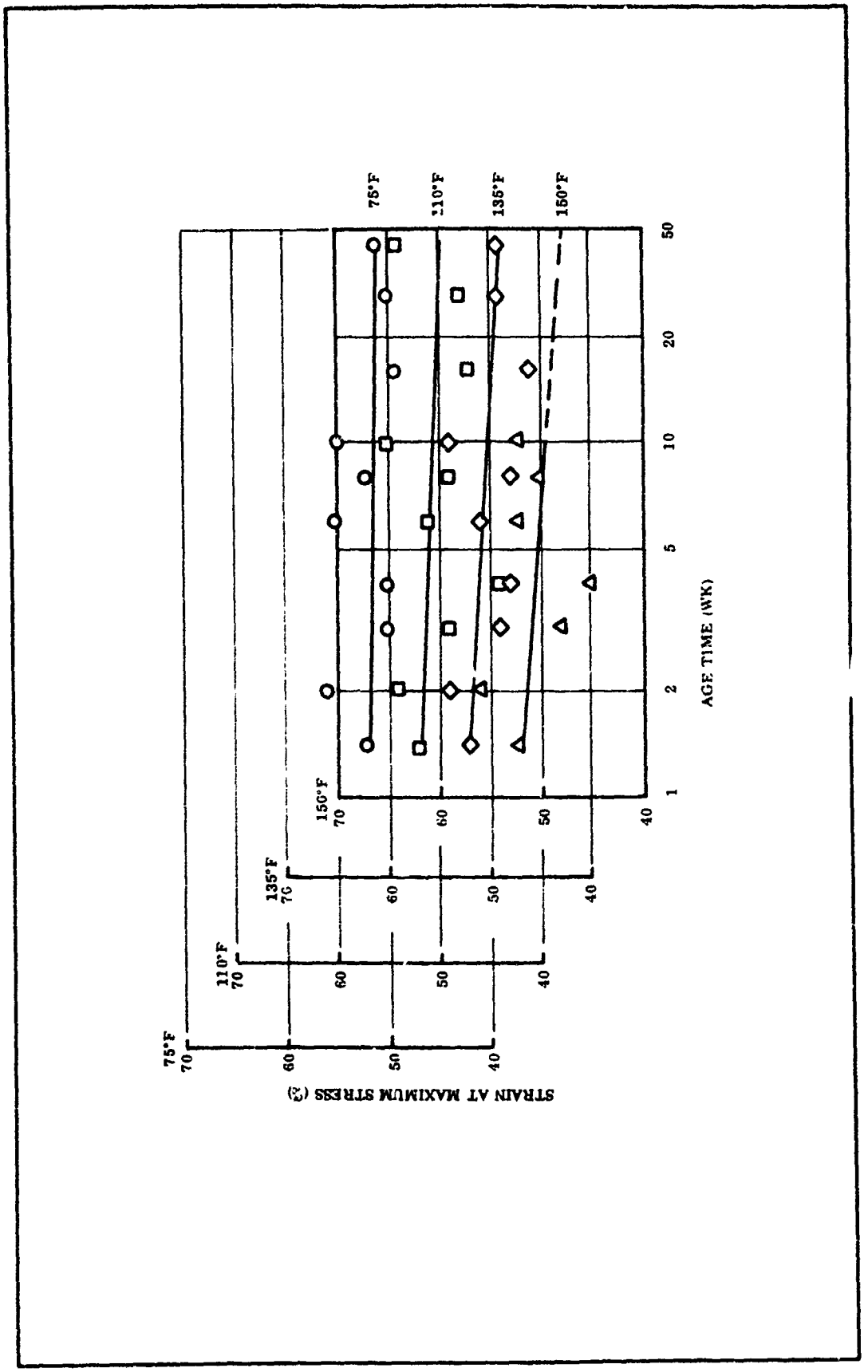

Figure 10. Aging Effect on Strain at Maximum Stress, 75°F Test Temperature

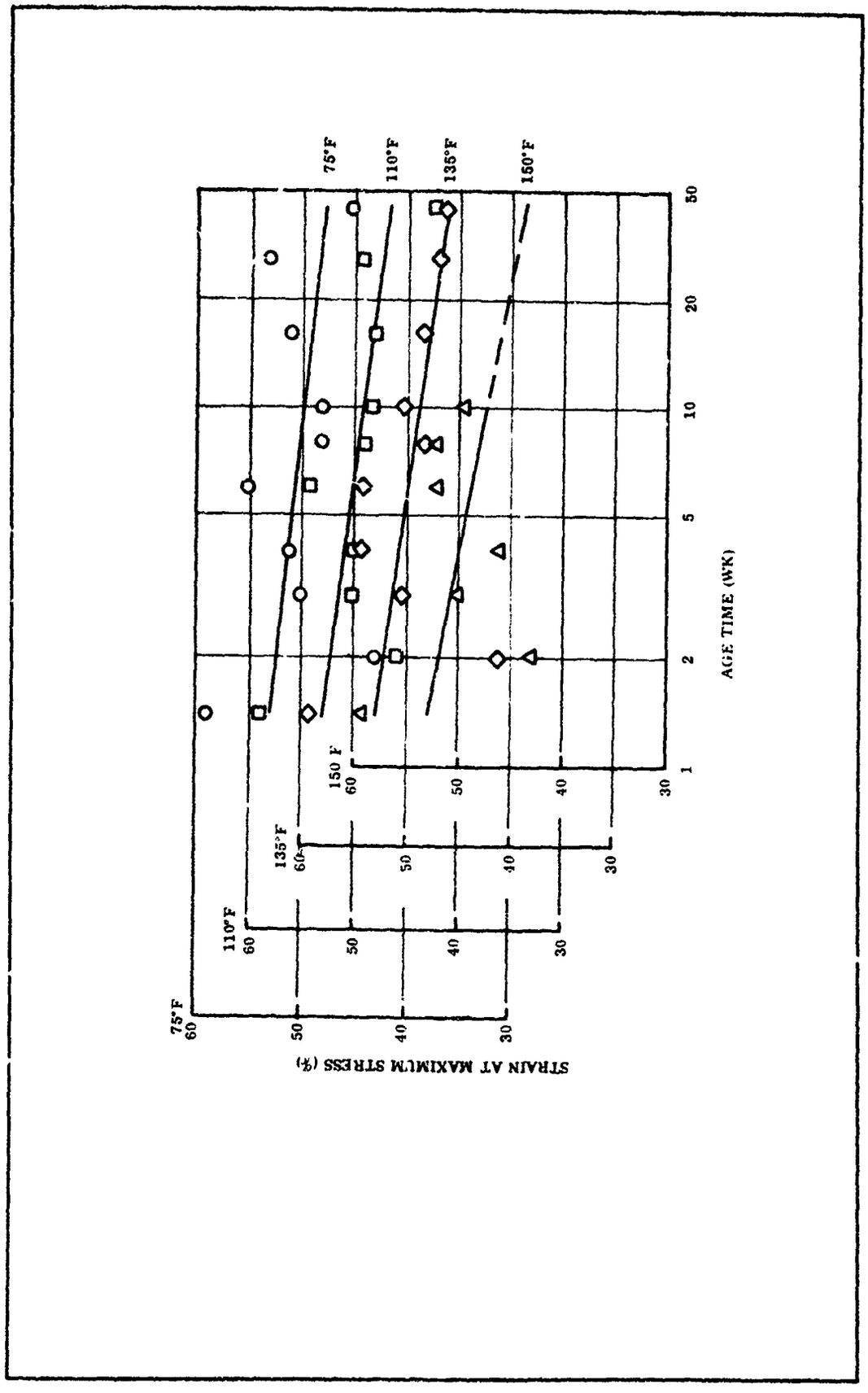

Figure 11. Aging Effect on Strain at Maximum Stress, 125°F Test Temperature

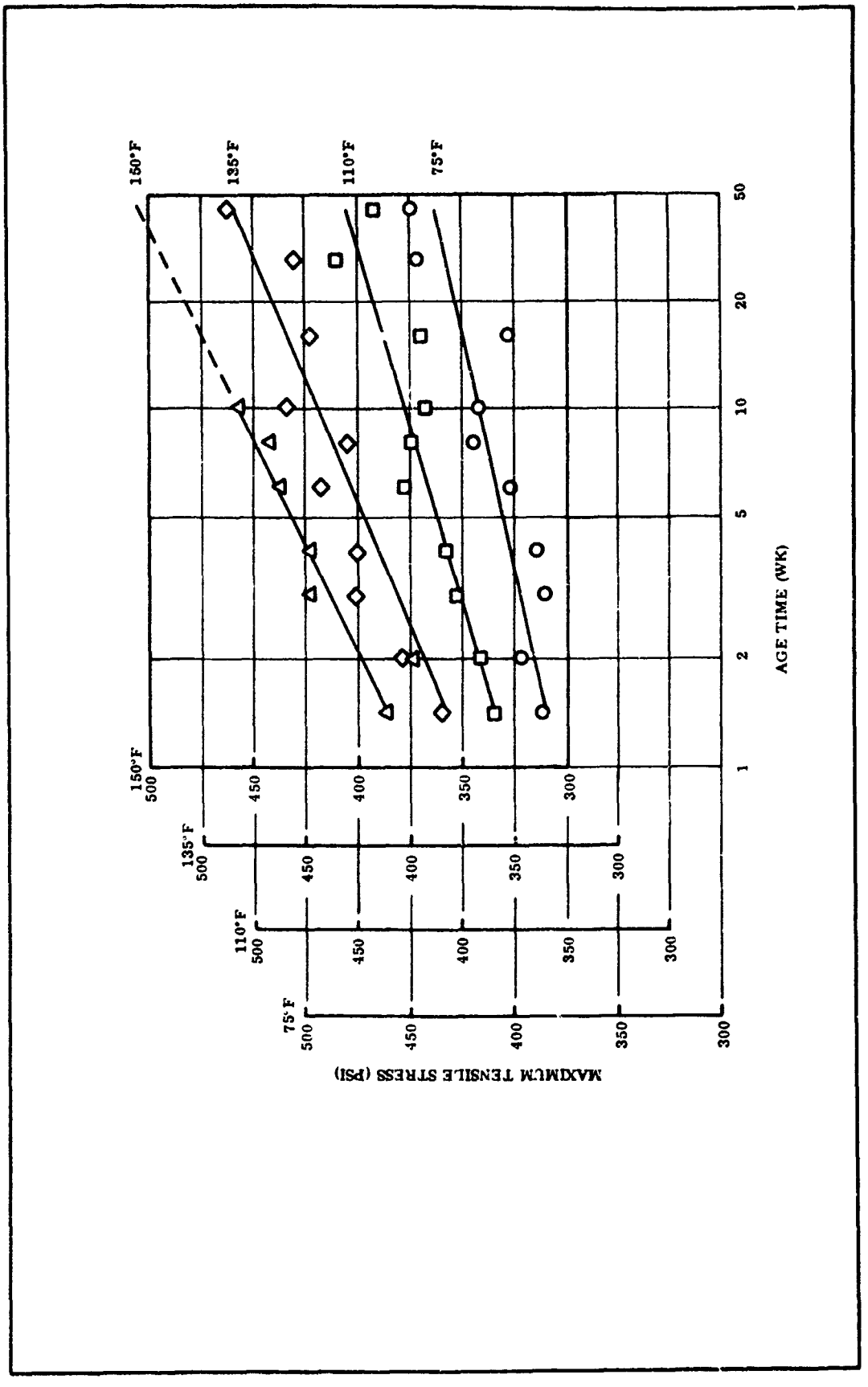

Figure 12. Aging Effect on Maximum Tensile Stress, 10°F Test Temperature, 500 psi Pressure

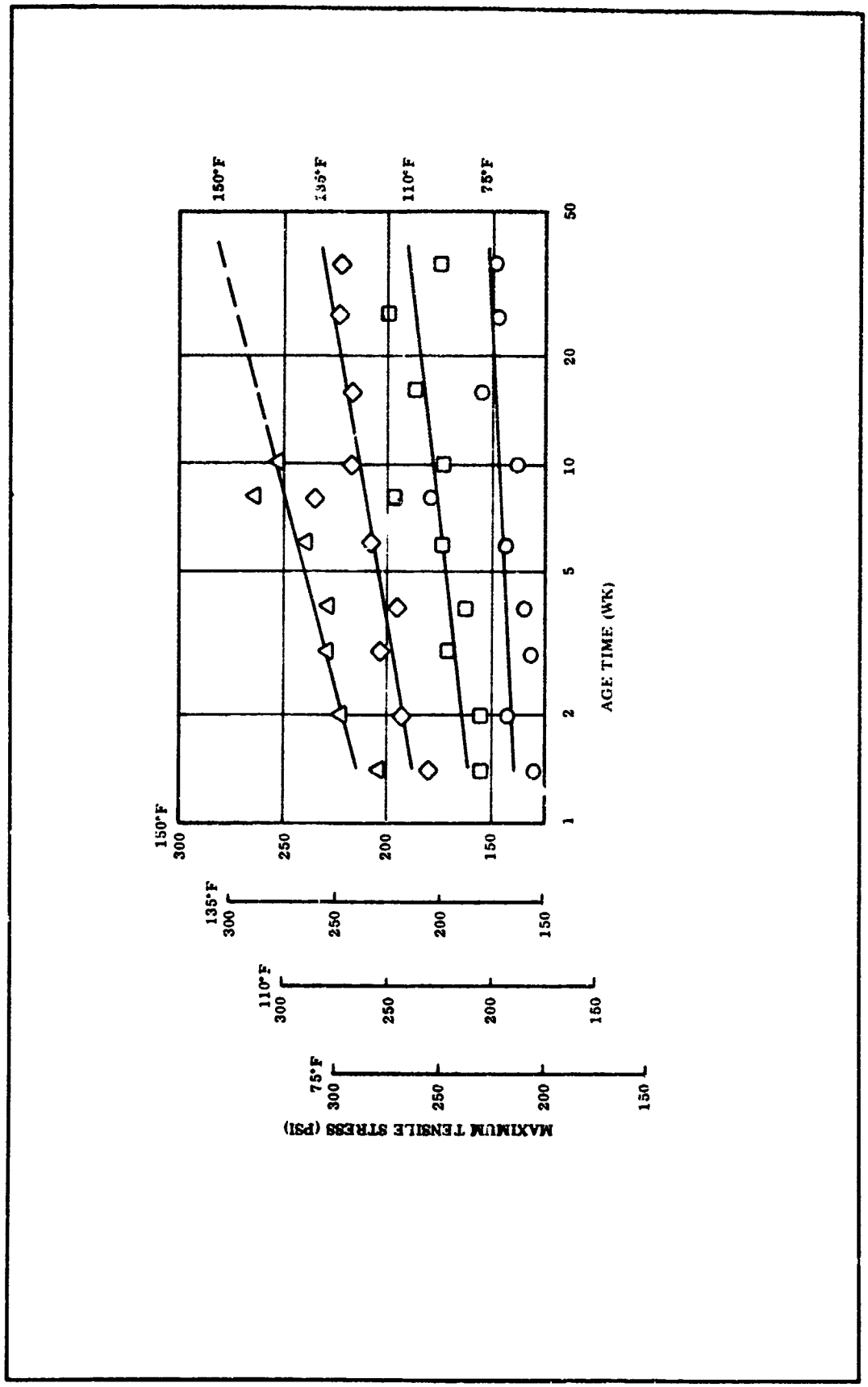

Figure 13. Aging Effect on Maximum Tensile Stress, 75°F Test Temperature, 500 psi Pressure

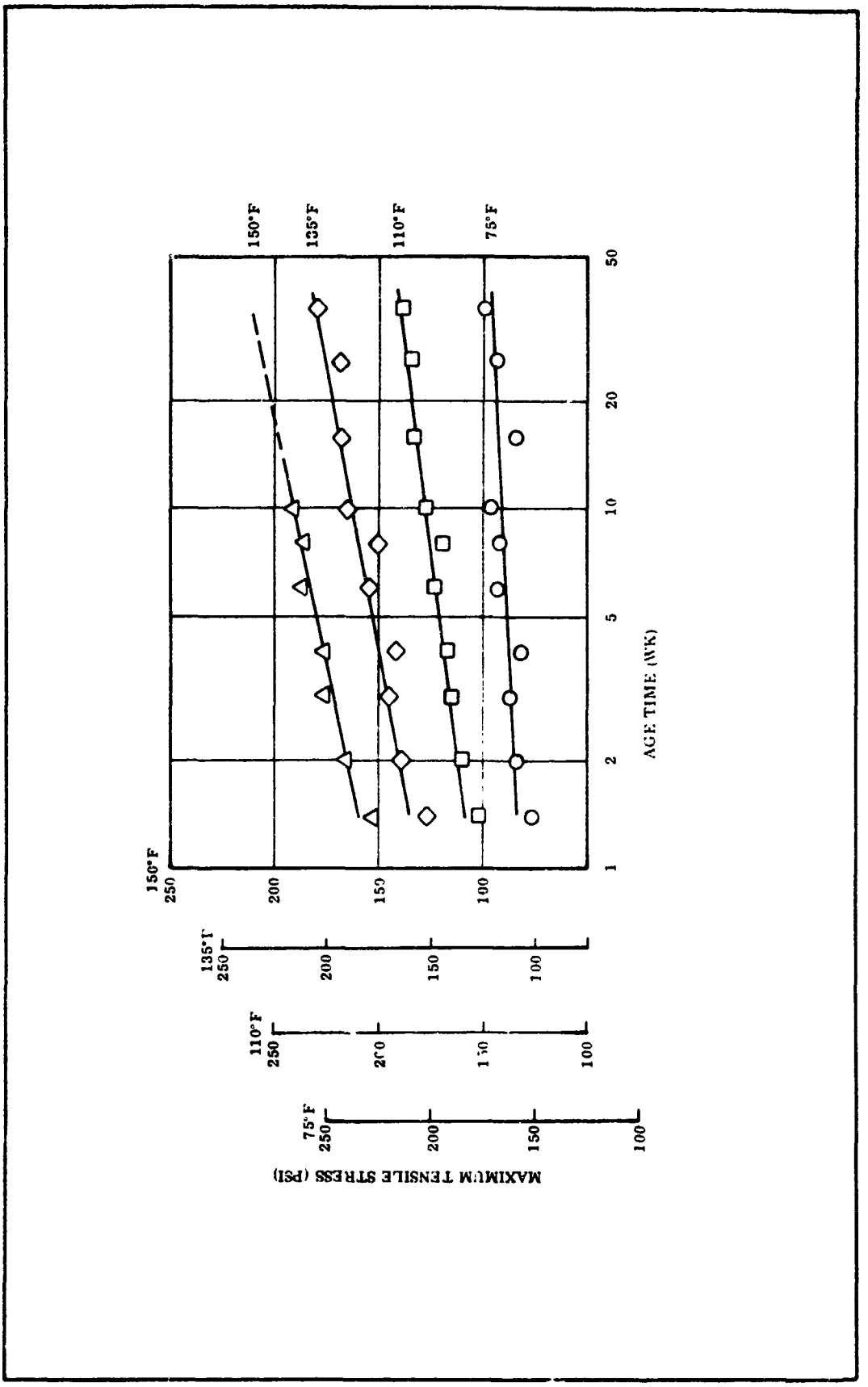

Figure 14. Aging Effect on Maximum Tensile Stress, 125°F Test Temperature, 500 psi Pressure

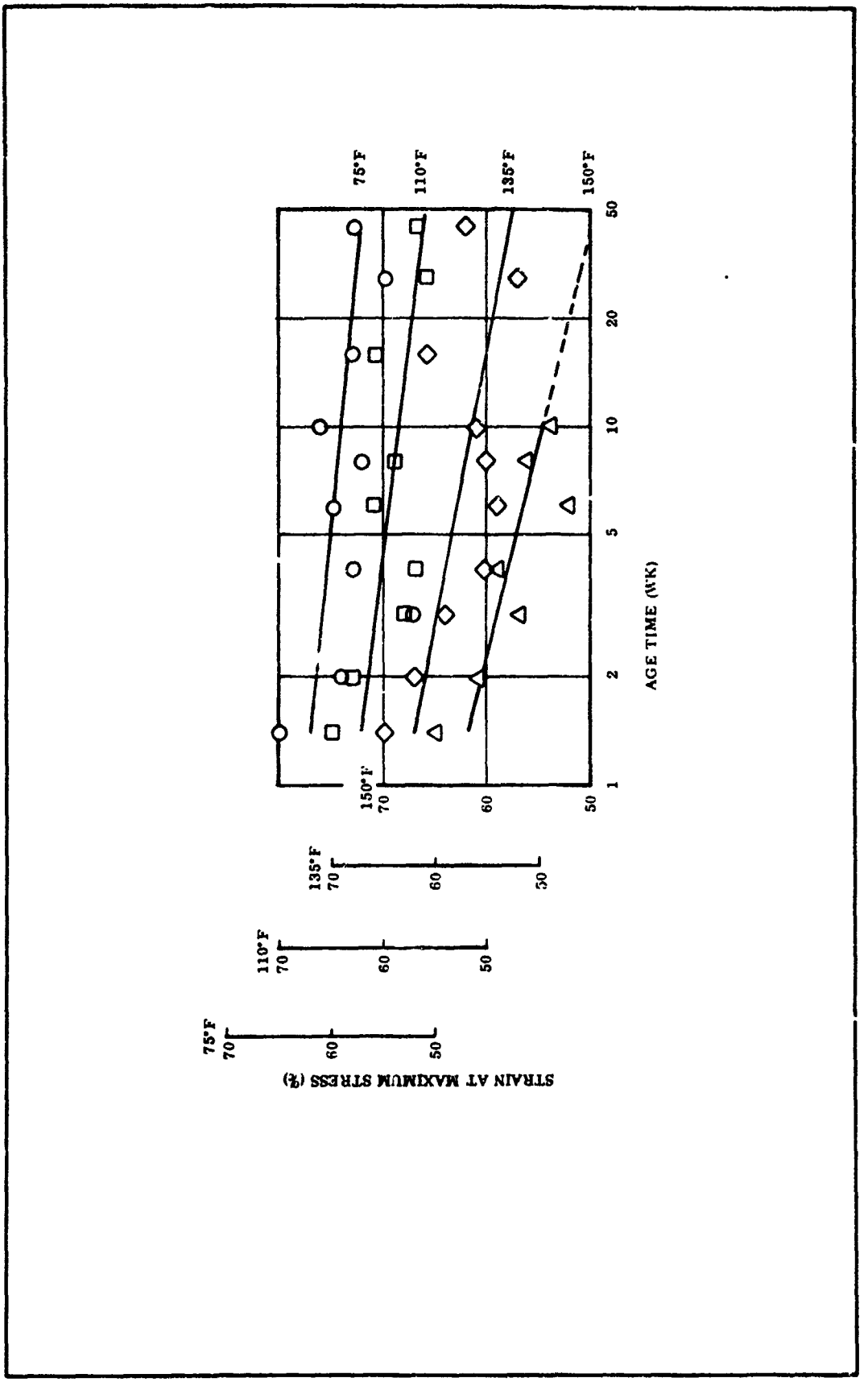

Figure 15. Aging Effect on Strain at Maximum Stress, 10°F Test Temperature, 500 psi Pressure

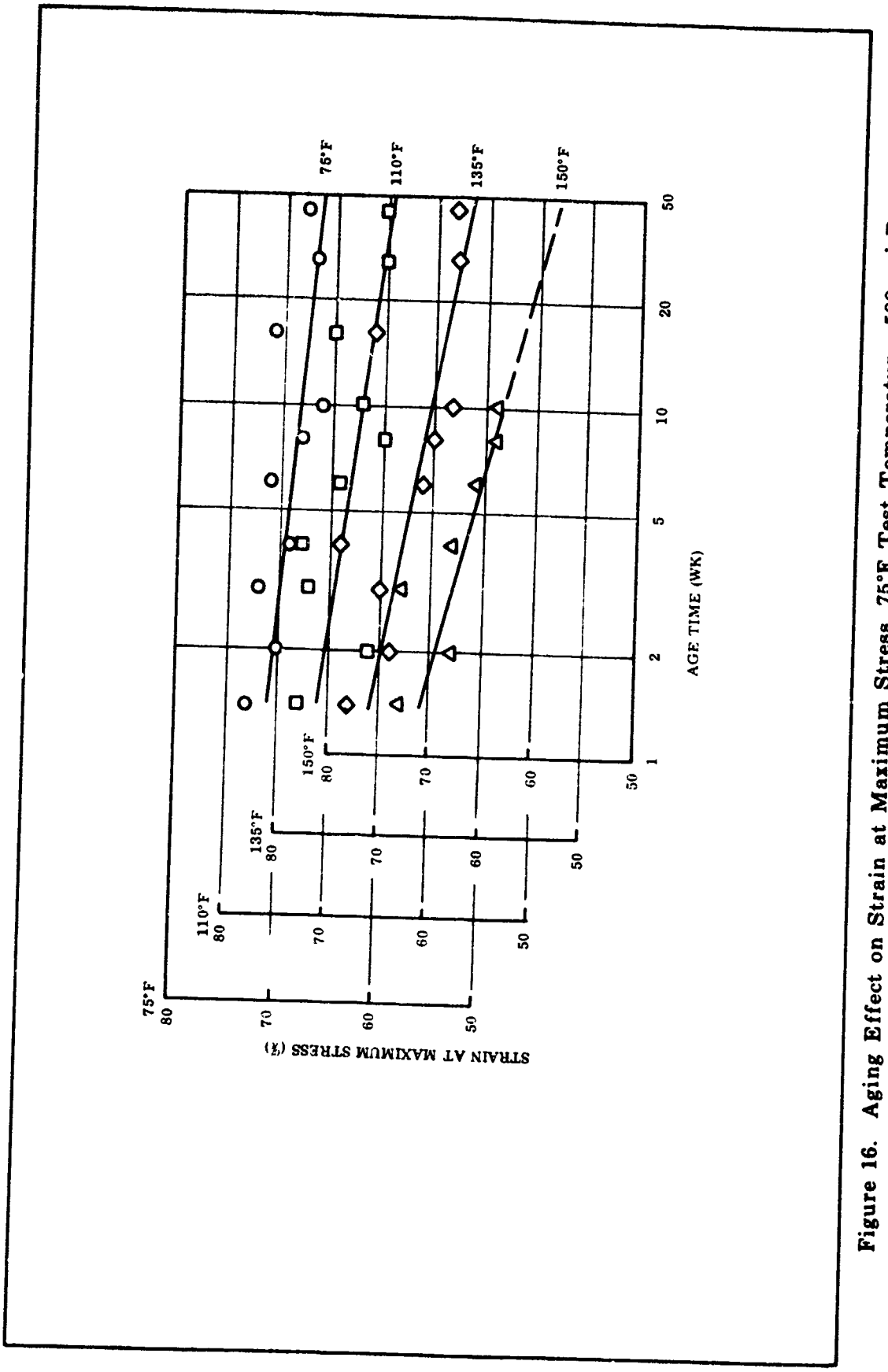

Figure 16. Aging Effect on Strain at Maximum Stress, 75°F Test Temperature, 500 psi Pressure

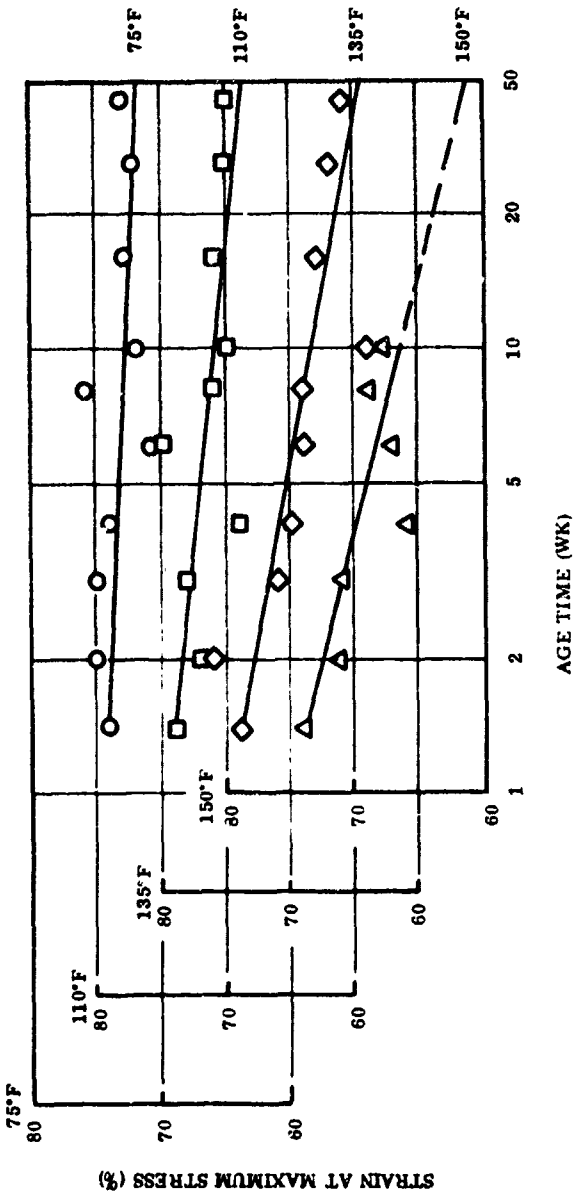

Figure 17. Aging Effect on Strain at Maximum Stress, 125°F Test Temperature, 500 psi Pressure

4.2.2 Relaxation Modulus

These tests were performed using the JANNAF Class A uniaxial tensile specimen. The specimen is clamped in the test fixture of a pneumatically loaded test machine that loads to a preset strain level at a rate approximately 400 in/min. A strain level of 2% was used for these tests. The load response was recorded continuously for 1,000 seconds. The actual strain on each specimen was measured in a 1.5 in. length of the gage section by means of a cathetometer. The effect of aging on the relaxation modulus is shown for the 1,000 sec load time only. These data are presented in Table X and represent the average of three tests. No curve smoothing has been done to obtain these values.

These data have been plotted as a function of logarithmic aging time and are presented in Figures 18 to 20. It is again apparent that the property changes with logarithmic age-time in a linear fashion. This is in agreement with the other measured properties with this propellant and adds support to the linear aging model.

4.2.3 Cure Temperature Study

Carton samples of propellant were cured at 135°, 140°, 145°, 150° and 155°F for 10 days to determine the effect of cure on the propellant properties. At the end of cure, uniaxial tensile tests were performed using the same test conditions as the aging program. Aging tests were only performed with the 135°F cured propellant. The results of the uniaxial tests are presented in Table XI and are shown in Figures 21 thru 24.

It is readily apparent that increased cure temperature has no other effect on the mechanical properties than that expected by the additional aging that occurs. It appears from the chemical analyses for isocyanate that the curing agent is totally reacted before 5.5 days at 155°F cure temperature and requires 10 days at 135°F cure temperature. This means the sample at 155°F has 4.5 days of aging at 155°F beyond the end of cure by the time the 10 day cure period was terminated, while the sample at 135°F has no aging. Comparing the stress value for the 155°F cure with the 2 week point (6 days aging) on the 150°F aging curve for the 75°F test condition, the

Table X

Relaxation Modulus of TP-H1139 Propellant, Mix 8867001, Tested at 2% Strain Level at Ambient Pressure

Aging Temp (°F)	Aging Time (wk)	Test Temperature (°F) Relaxation Modulus at 1000 sec (psi) 10°F	75°F	125°F
75	1.4	235	115	96
	2	180	142	88
	3	268	133	108
	4	300	150	119
	6	278	168	116
	8	272	179	114
	10	470	176	135
	16	297	193	140
	26	319	208	140
	36	323	208	123
110	1.4	235	115	96
	2	225	131	95
	3	264	129	115
	4	288	163	122
	6	264	186	141
	8	310	176	145
	10	435	186	161
	16	343	178	136
	26	340	223	170
	36	393	265	174
135	1.4	235	115	96
	2	305	135	120
	3	314	156	123
	4	308	187	148
	6	369	190	156
	8	358	192	151
	10	502	212	163
	16	425	241	182
	26	526	233	192
	36	467	277	207
150	1.4	235	115	96
	2	330	163	108
	3	312	140	130
	4	400	187	153
	6	398	200	152
	8	425	189	157
	10	474	228	180

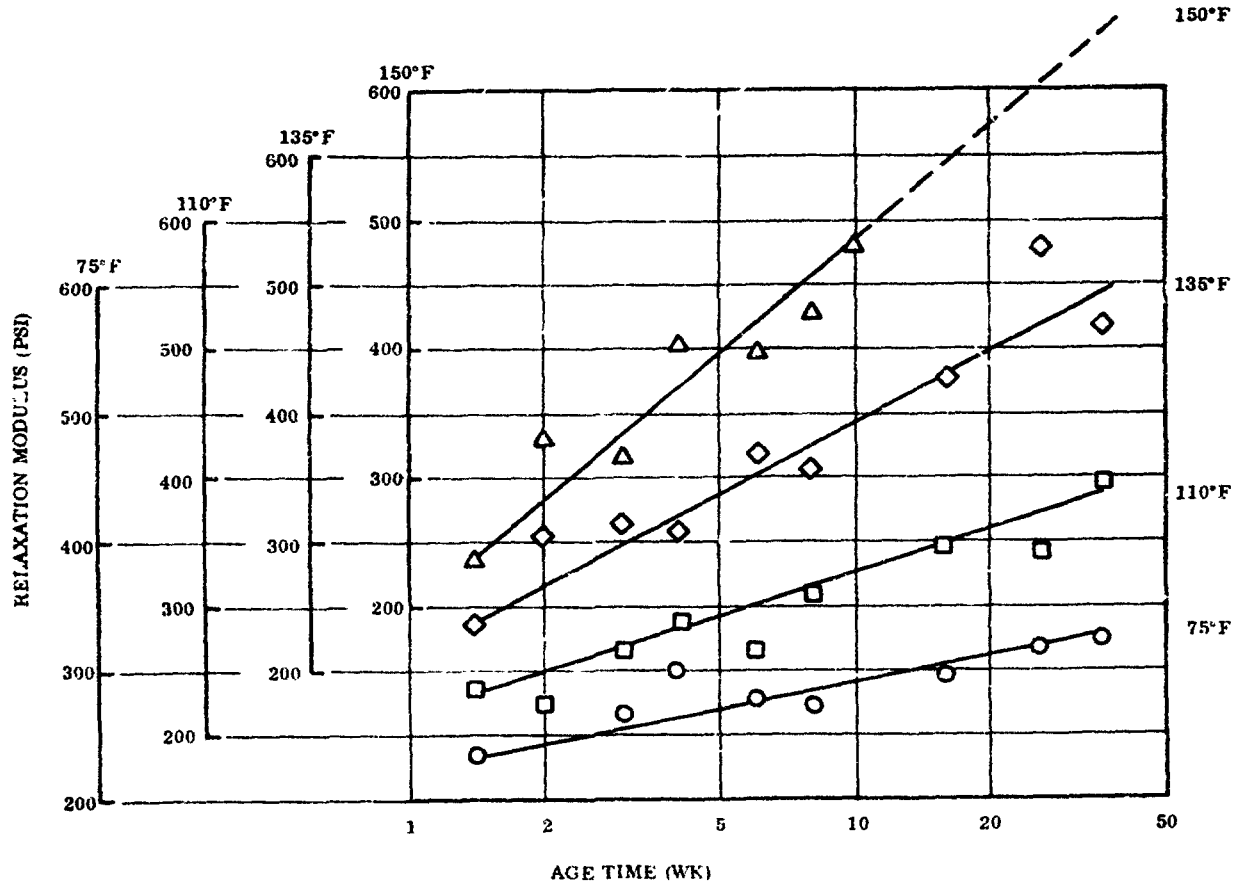

Figure 18. Aging Effect on Relaxation Modulus, 10°F Test Temperature

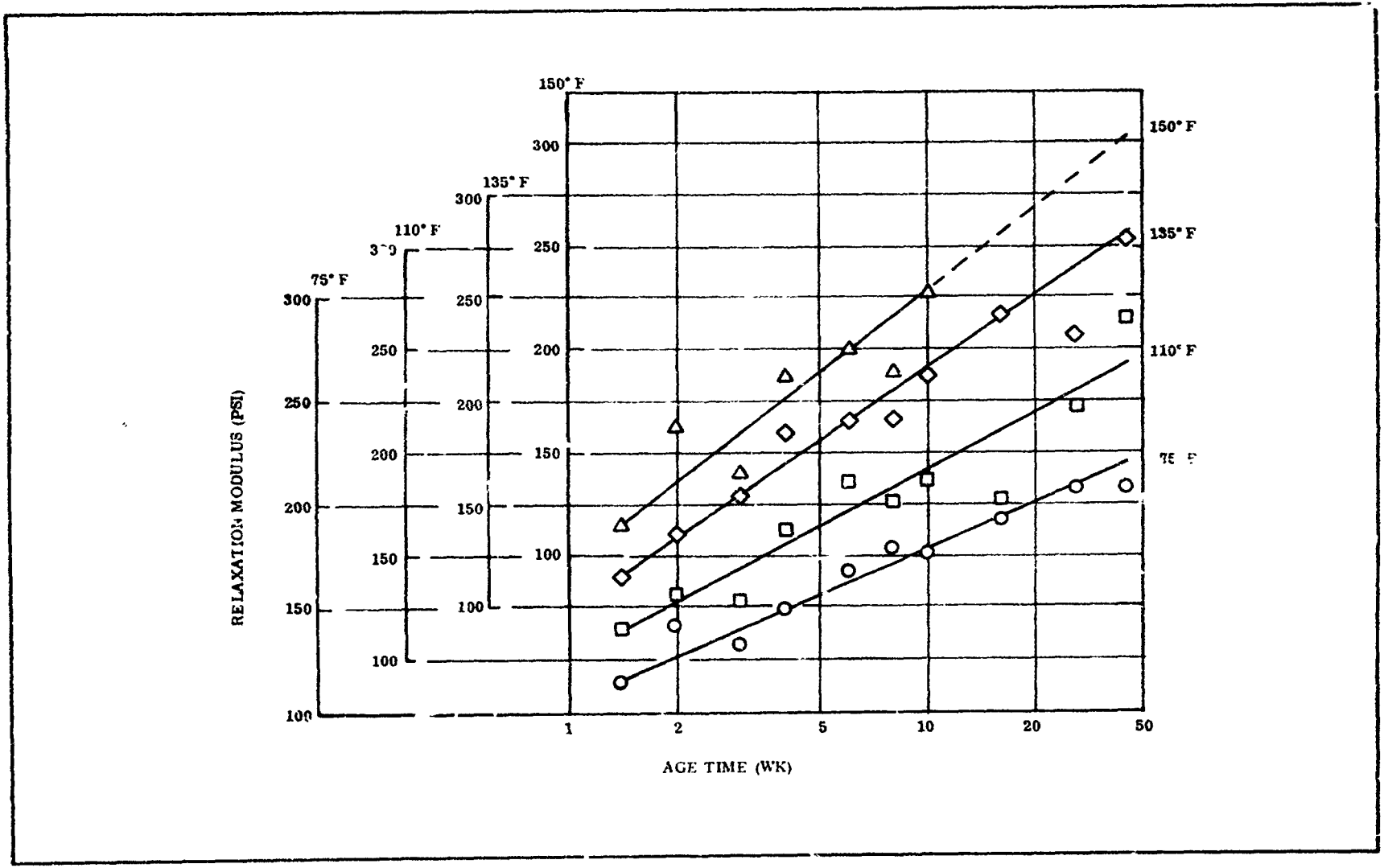

Figure 19. Aging Effect on Relaxation Modulus, 75°F Test Temperature

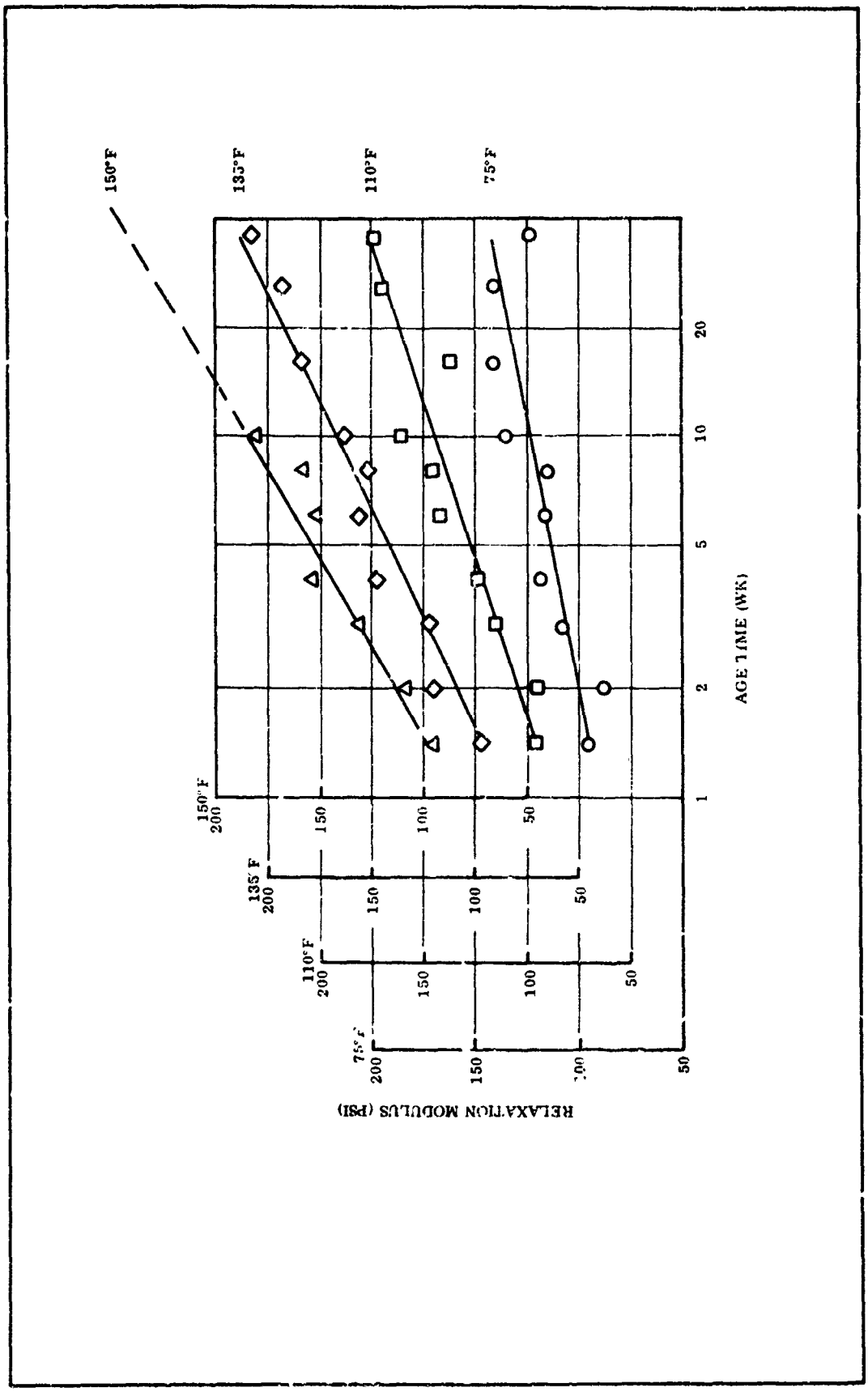

Figure 20. Aging Effect on Relaxation Modulus, 125°F Test Temperature

TABLE XI

Effect of Cure Temperature on the Uniaxial Tensile Properties of TP-H1139 Propellant, Mix 8867001, Cured 10 Days, Tested at 2 in/min

Test Pressure	Test Temp (°F)	Cure Temp (°F)	$E^{2.6}$ (psi)	σ_m (psi)	ϵ_m^t (%)	ϵ_f^t (%)
Ambient	10	135	1340	195	52	77
		140	1540	198	50	72
		145	1700	207	50	71
		150	1510	211	52	74
		155	1520	217	50	68
	75	135	391	104	52	62
		140	489	109	49	62
		145	416	112	47	54
		150	448	113	51	61
		155	421	119	52	57
	125	135	204	89	59	66
		140	213	96	51	54
		145	270	101	51	53
		150	278	98	50	52
		155	292	103	44	46
500 psi	10	135	2750	475	65	81
		140	3510	486	58	71
		145	3070	517	67	81
		150	3190	513	59	70
		155	3070	518	59	68
	75	135	441	204	73	80
		140	503	212	69	77
		145	642	215	69	75
		150	611	215	68	73
		155	537	222	65	69
	125	135	261	152	74	82
		140	302	168	67	74
		145	270	163	70	78
		150	301	163	68	71
		155	290	174	67	69

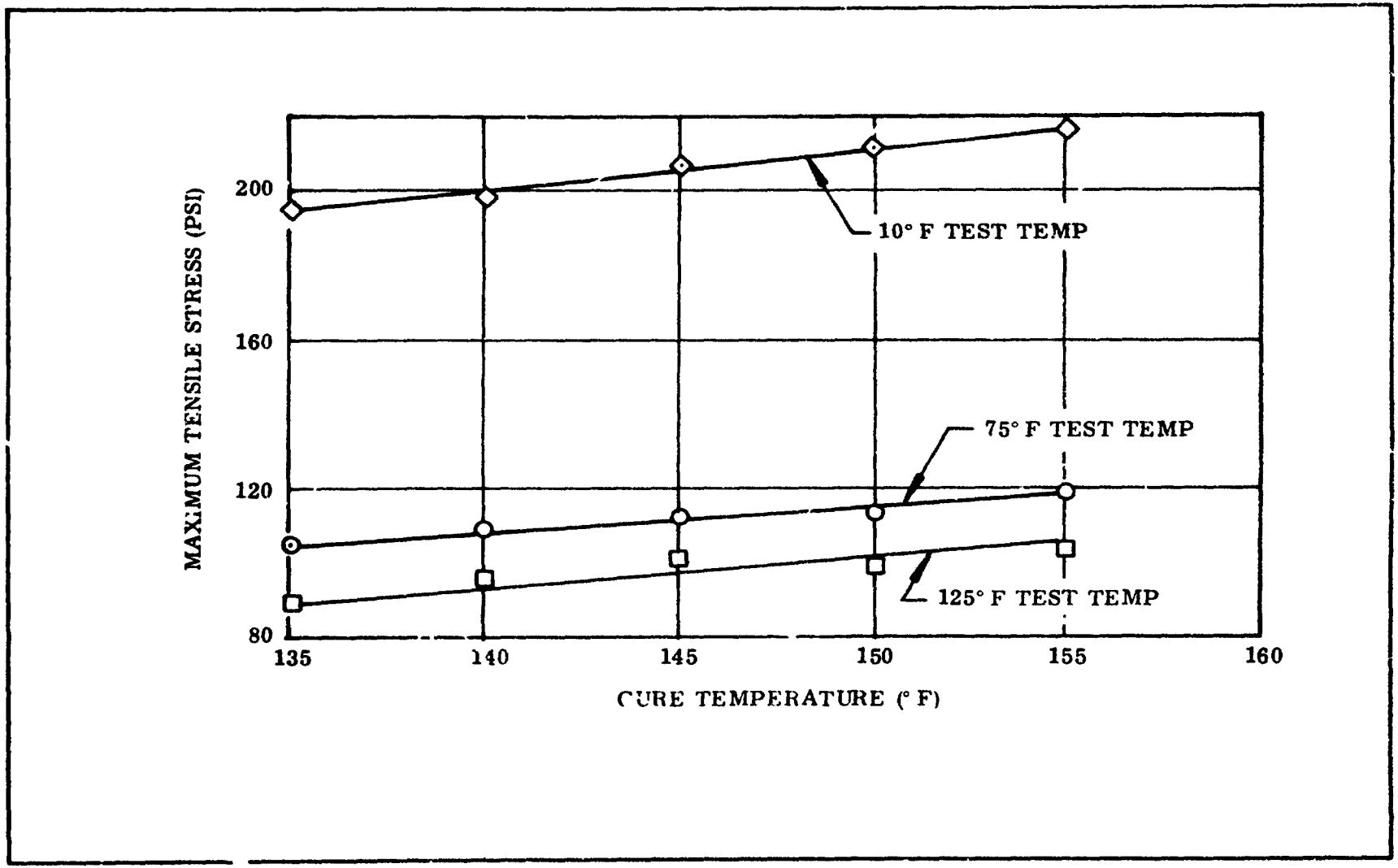

Figure 21. Effect of Cure Temperature on Uniaxial Tensile Stress, 10 Day Cure

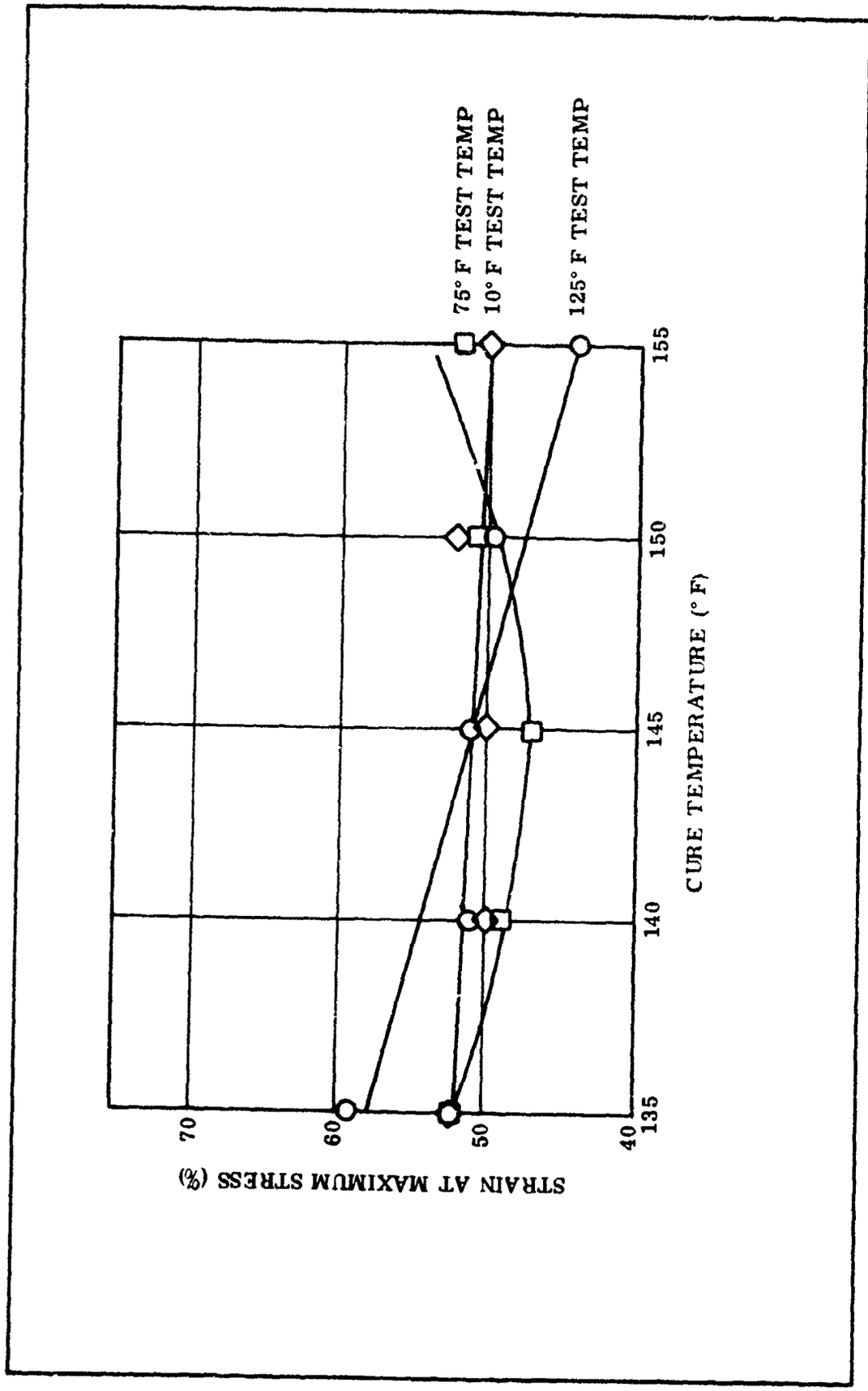

Figure 22. Effect of Cure Temperature on Strain at Maximum Stress, 10 Day Cure

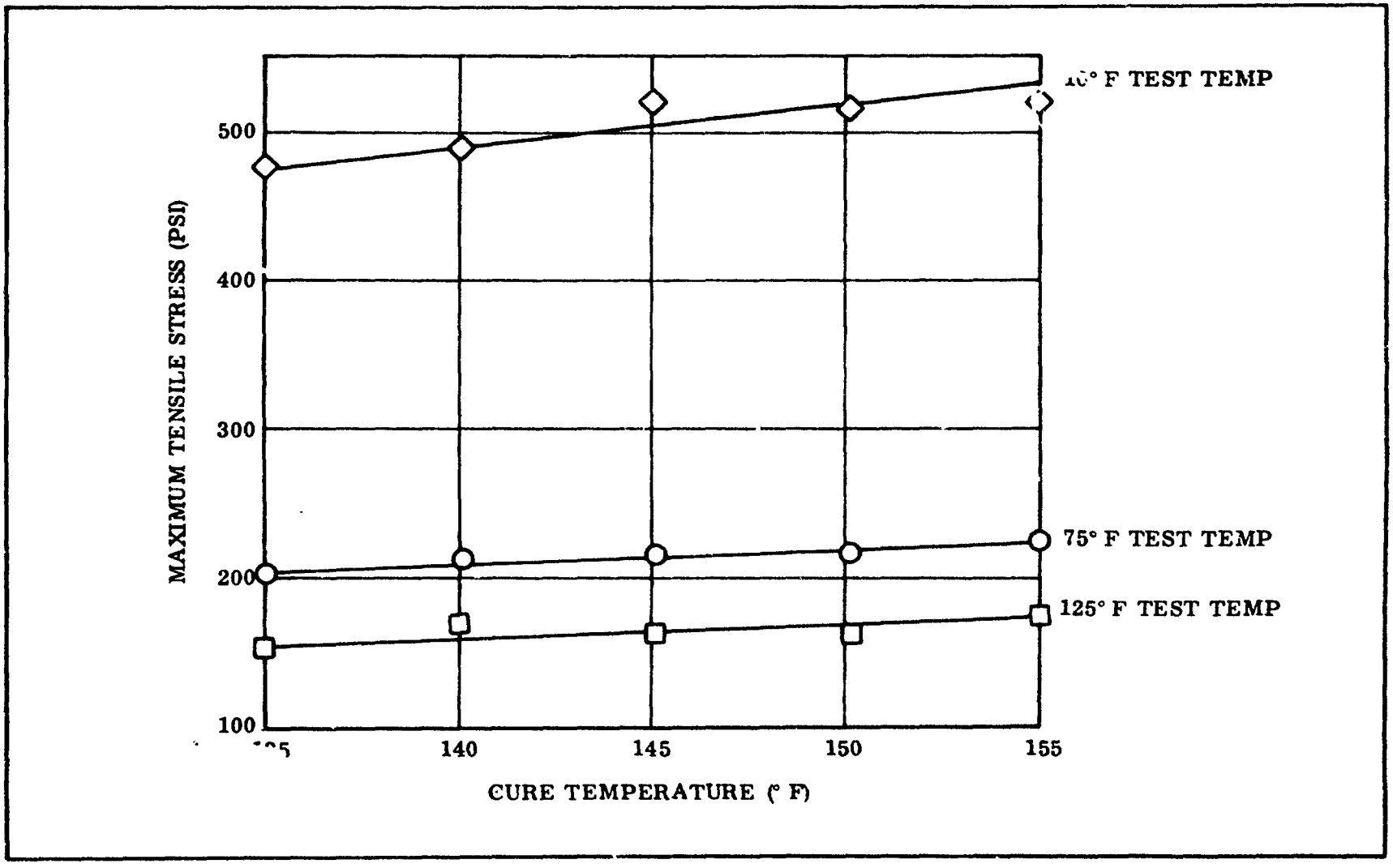

Figure 23. Effect of Cure Temperature on Uniaxial Tensile Stress, 10 Day Cure, 500 psi Pressure

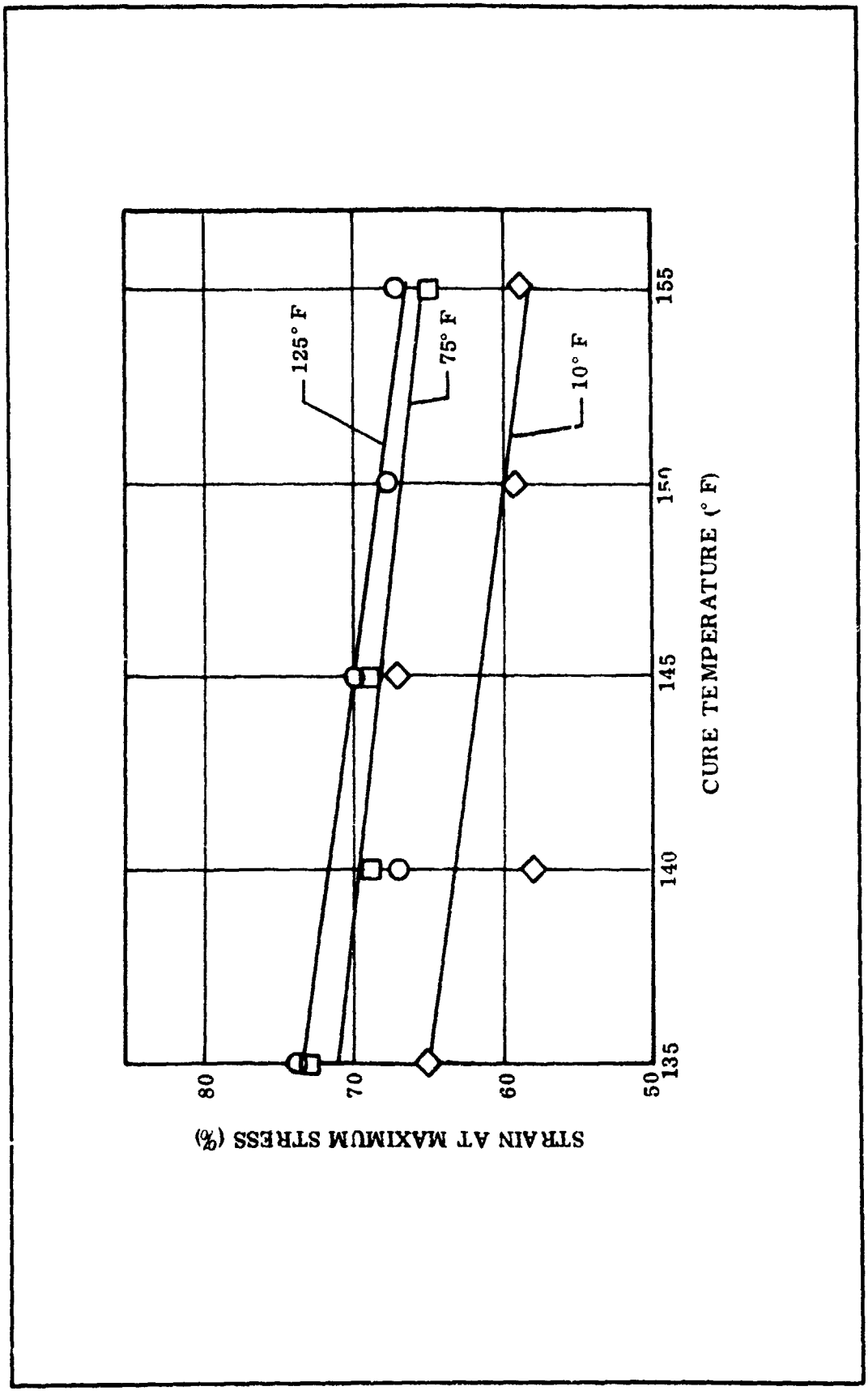

Figure 24. Effect of Cure Temperature on Strain at Maximum Stress, 10 Day Cure, 500 psi Pressure

values of 117 to 121 psi are obtained. It may therefore be concluded that between the temperatures of 135° and 155°F the mechanism of cure remains the same with only the reaction rate being affected.

5.0 DISCUSSION

Throughout Section 4.0, it is obvious that the aging data at 150° F do not extend beyond 10 weeks, while all other aging temperatures show data to 36 weeks. This unfortunate circumstance is due to an intermittent oven malfunction that started sometime after the 10th week and was not satisfactorily corrected until near the 36th week. The data are suspect and therefore not presented. As far as the 150° F aging data go, they seem to be following the same linear change that the rest of the results show. It does reduce the maximum time that one can extend the curves for lower aging temperatures. No curve should be extended to a property level greater than the maximum level experienced by the highest aging condition. In the case of the maximum stress parameter tested at 75° F, the time to reach the level of 10 weeks at 150° F is 5.35 years for the 75° F age temperature. Thirty-six weeks at 135° F is equivalent to 32.0 years at 75° F. This appears to be adequate even without the remaining 150° F data. These times are possible only because of the small change experienced with this propellant as a function of age.

The chemical analyses performed for evaluation of the cure reaction during the cure period of TP-H1139 propellant show that the isocyanate (curing agent) disappears in a very well behaved manner, and before the end of cure (10 days) the isocyanate level drops below our ability to detect it. The analysis for hydroxyl was not sufficiently precise in the early portion of the cure to be presented. As the gel began to form, the hydroxyl analysis seemed to settle down and during the aging period a constant value was maintained. While this leaves some doubt as to the validity of the hydroxyl analysis, it is interesting to compare the initial level with the final. The isocyanate level before any reaction occurred was 52.1 meq/100 gm of binder and the hydroxyl level was 70.5 meq/100 gm. The final level of hydroxyl was 22.7 meq/100 gm of binder, suggesting a near one to one reaction and lending support to the validity of the measurement. It is not difficult to expect some isocyanate to react with possible residual moisture in the propellant. If all the isocyanate that did not react with hydroxyl reacted with water, the water level in the binder would be 77 ppm or 9 ppm in the propellant.

A real surprise was to find that the level of "bonding agent" remained a constant as measured by the presence of imine. The average measured level was the same amount of imine added to the formulation to perform the function of bonding agent. This suggests that the mechanism of the "bonding agent" for improving mechanical properties may not be the improving of the binder-solid interfacial bond. This is also backed up by a large improvement experienced in tensile strength as a result of superimposed pressure. The tensile strength of a material having a high binder-solid interfacial bond strength would not be greatly changed by exposure to elevated pressure.

The evidence presented by the iodimetric titration suggests that double bonds in the polymer chain are disappearing with age; however, this is only occurring in the gel portion of the binder. Because of this characteristic, it is not clear whether the double bonds are reacting to form crosslinks or whether the titration of the gel becomes more incomplete as the percent gel increases. It is conclusive, however, that the gel is increasing with age and that the cure reaction is not contributing.

The change in gel follows a linear path as a function of logarithmic age-time. The mechanical properties exhibit the same aging trend, making the simple first order equation a satisfactory aging model. This behavior was exhibited by ANB-3066 propellant (CTPB binder) but not by TP-H1011 propellant (PBAN binder). The conclusion drawn for the TP-H1011 propellant[1] was that some residual antioxidant remained in the propellant at the end of cure that became ineffective at some later time in the aging period. The result was an increased aging rate resulting in a nonlinear change in properties. The TP-H1011 propellant contains PBNA as an antioxidant in the polymer. Both the ANB-3066 and TP-H1139 propellants contain AO2246 as the antioxidant in the binder. One is immediately tempted to think that the AO2246 is remaining longer and is the better antioxidant. While that is a distinct possibility, it could be gone before the aging period commences, thereby causing no interference. Measurements specifically for the antioxidant would be required to answer the question.

Since the change in gel and the change in the mechanical properties for TP-H1139 propellant are both linear functions of logarithmic age-time, there should be a linear correlation between these two properties. Solving the aging model equation for the aging time function for both the gel and the mechanical properties, an expression is obtained showing this correlation.

$$g = k_g(T) \log t + g_o$$

$$\frac{g-g_o}{k_g(T)} = \log t = \frac{p-p_o}{k_p(T)}$$

and

$$p = \frac{k_p(T)}{k_g(T)} \Delta g + p_o$$

A plot of mechanical properties (p) as a function of the change in percent gel (Δg) with age should produce a line of slope $k_p(T)/k_g(T)$.

The stress and strain values for the uniaxial tests performed at the two pressures and three test temperatures and the relaxation modulus values for the three test temperatures have all been plotted as a function of the change in percent gel (Δg) from the end of cure to 36 weeks aging. The results shown in Figures 25 thru 39 show an amazingly good correlation regardless of the aging temperature used. This suggests that the crosslinking reaction that is related to the gel formation in the binder, and the change in mechanical properties with age-time, is accelerated by increased temperature without a change in mechanism.

It was found with TP-H1011 and ANB-3066 propellants that the 10° F test condition did not produce mechanical properties that changed linearly as the 75° and 125° F test conditions did. For the TP-H1139 propellant, the 10° F test results follow the same aging model as the higher test conditions, indicating a wider temperature range of consistent results. It is still anticipated that at some test temperatures, outside the range tested, the same kind of deviation from linearity will result. The analysis for defining the aging effect on the entire time-temperature spectrum has not been determined.

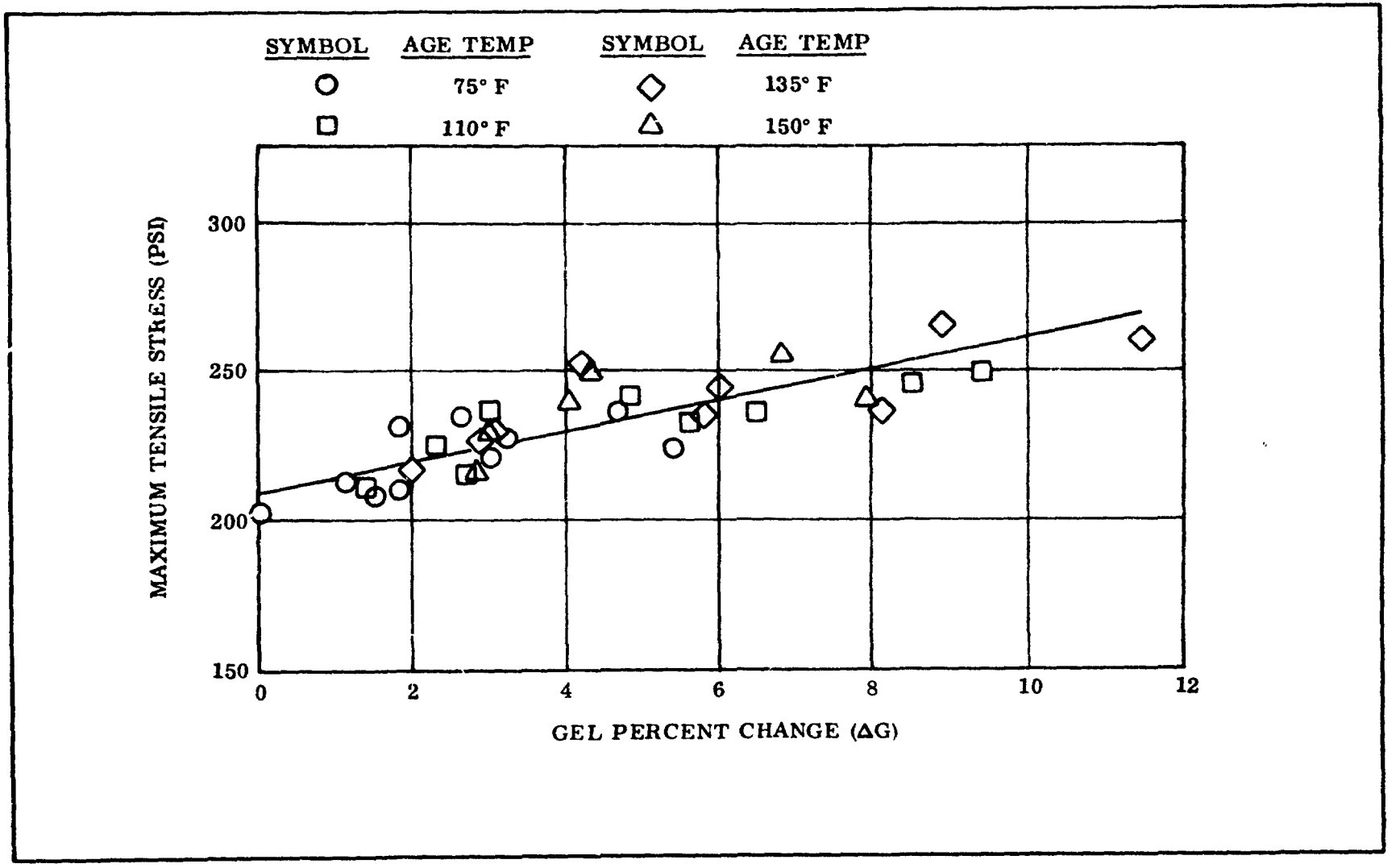

Figure 25. Maximum Tensile Stress as a Function of Age Induced Change in Gel, 10° F Test Temperature

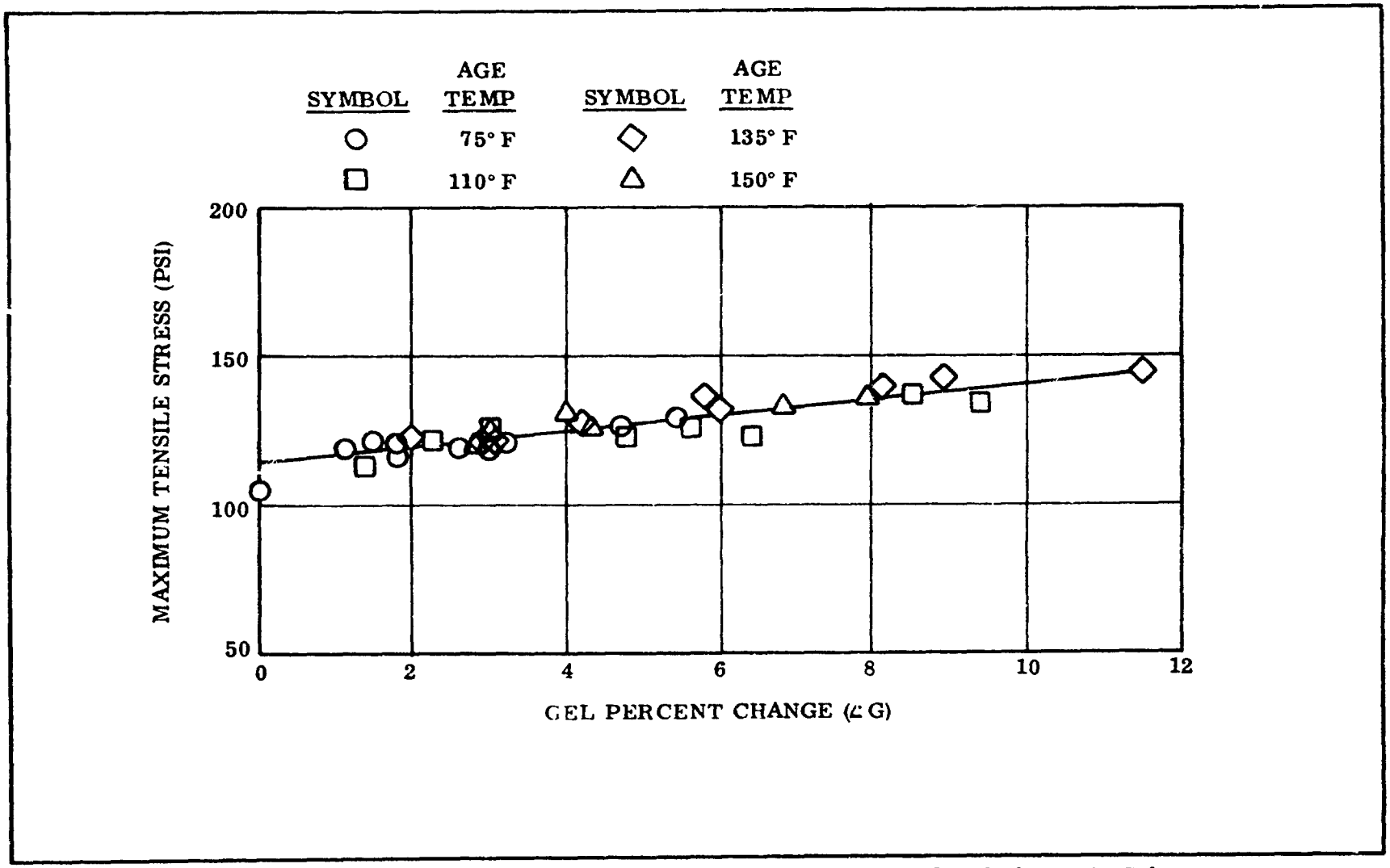

Figure 26. Maximum Tensile Stress as a Function of Age Induced Change in Gel, 75° F Test Temperature

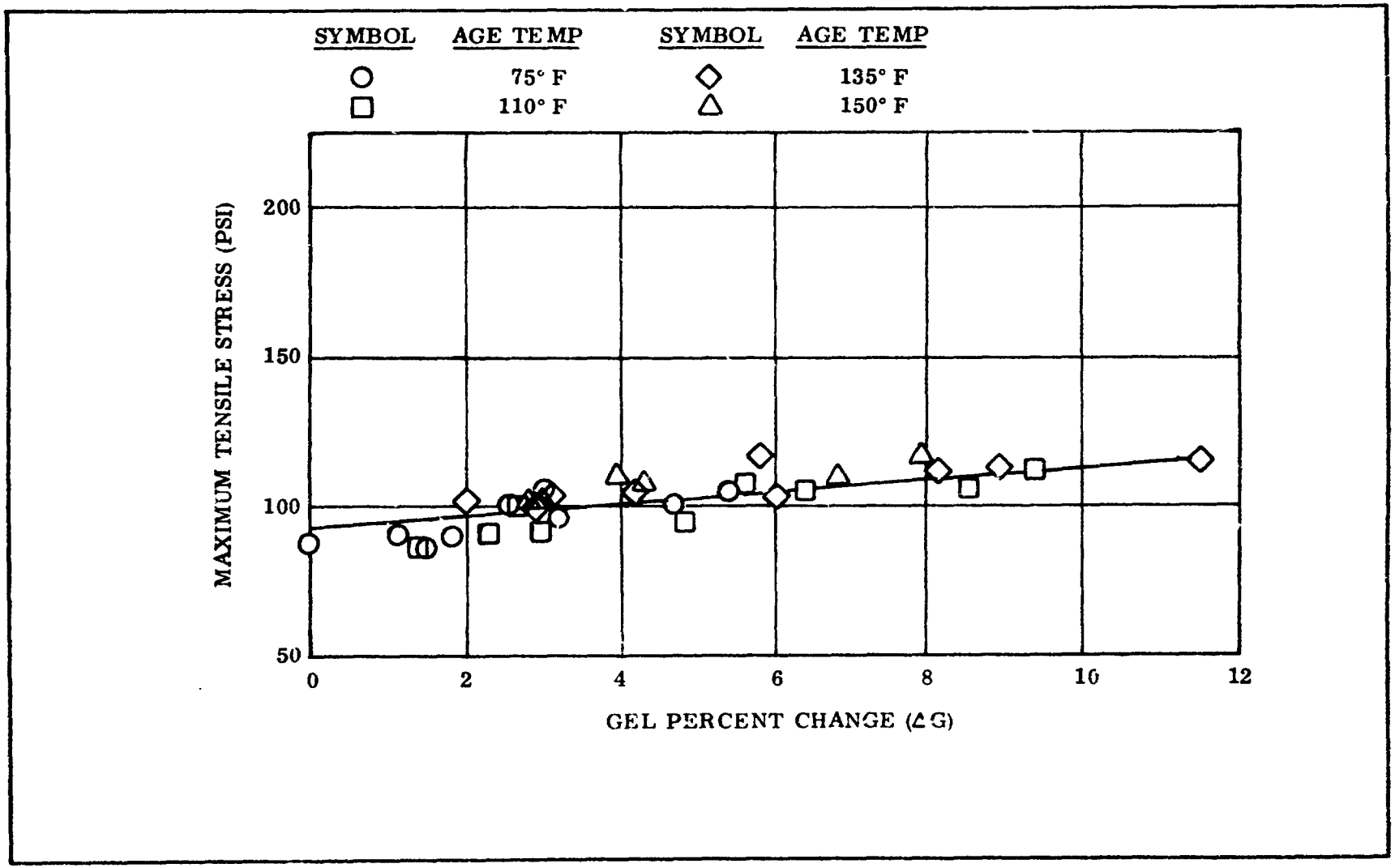

Figure 27. Maximum Tensile Stress as a Function of Age Induced Change in Gel, 125° F Test Temperature

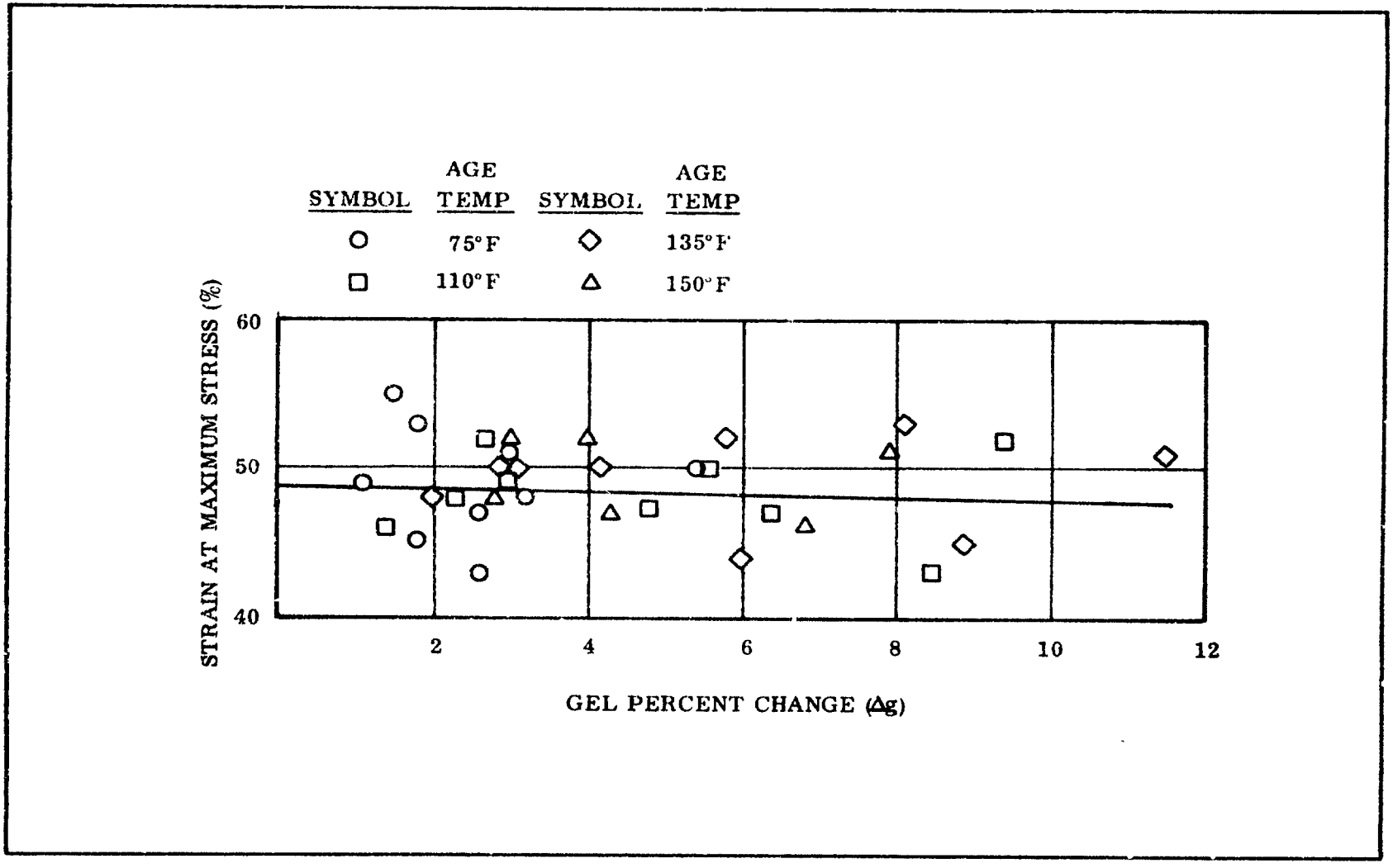

Figure 28. Strain at Maximum Stress as a Function of Age Induced Change in Gel, 10°F Test Temperature

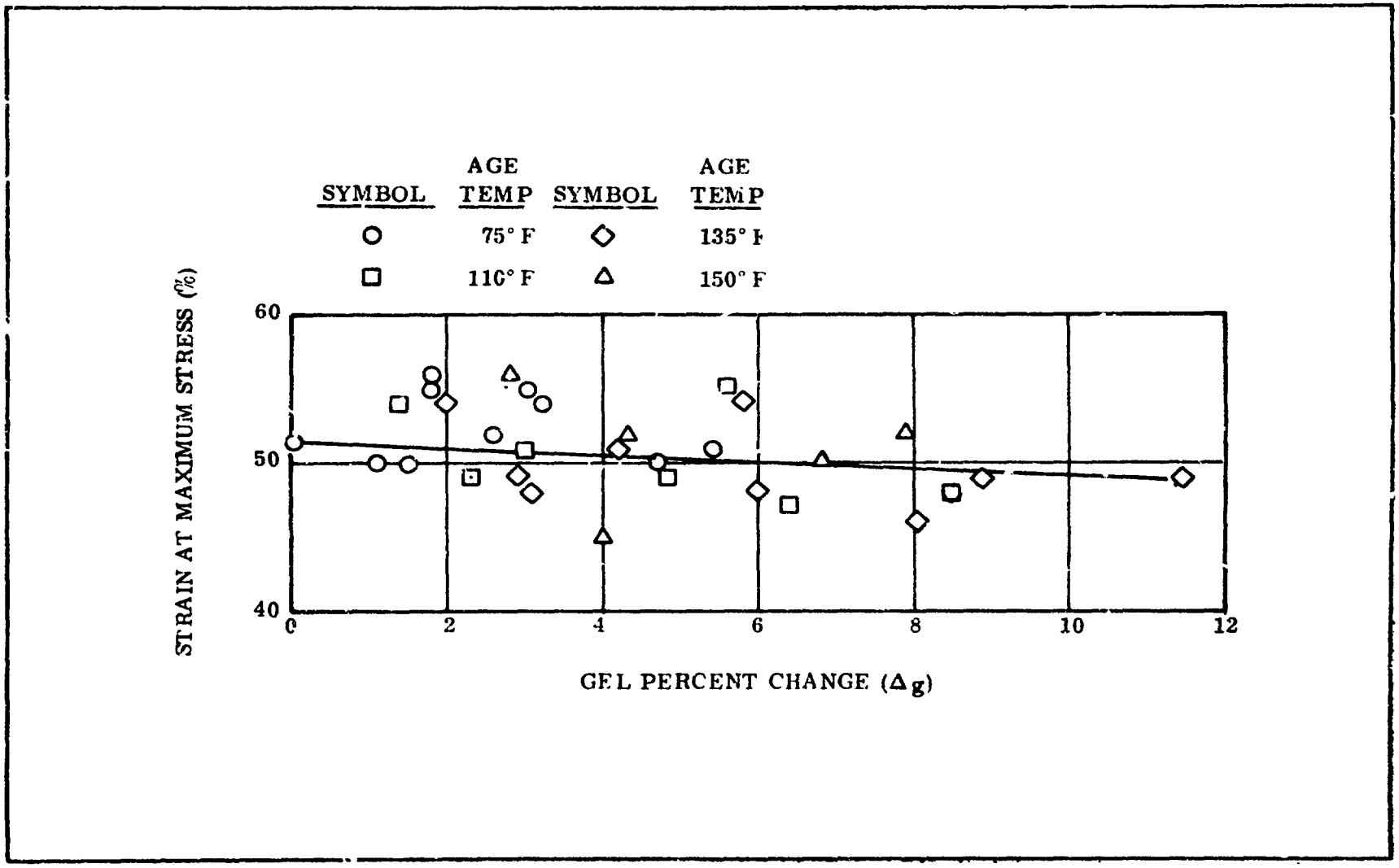

Figure 29. Strain at Maximum Stress as a Function of Age Induced Change in Gel, 75° F Test Temperature

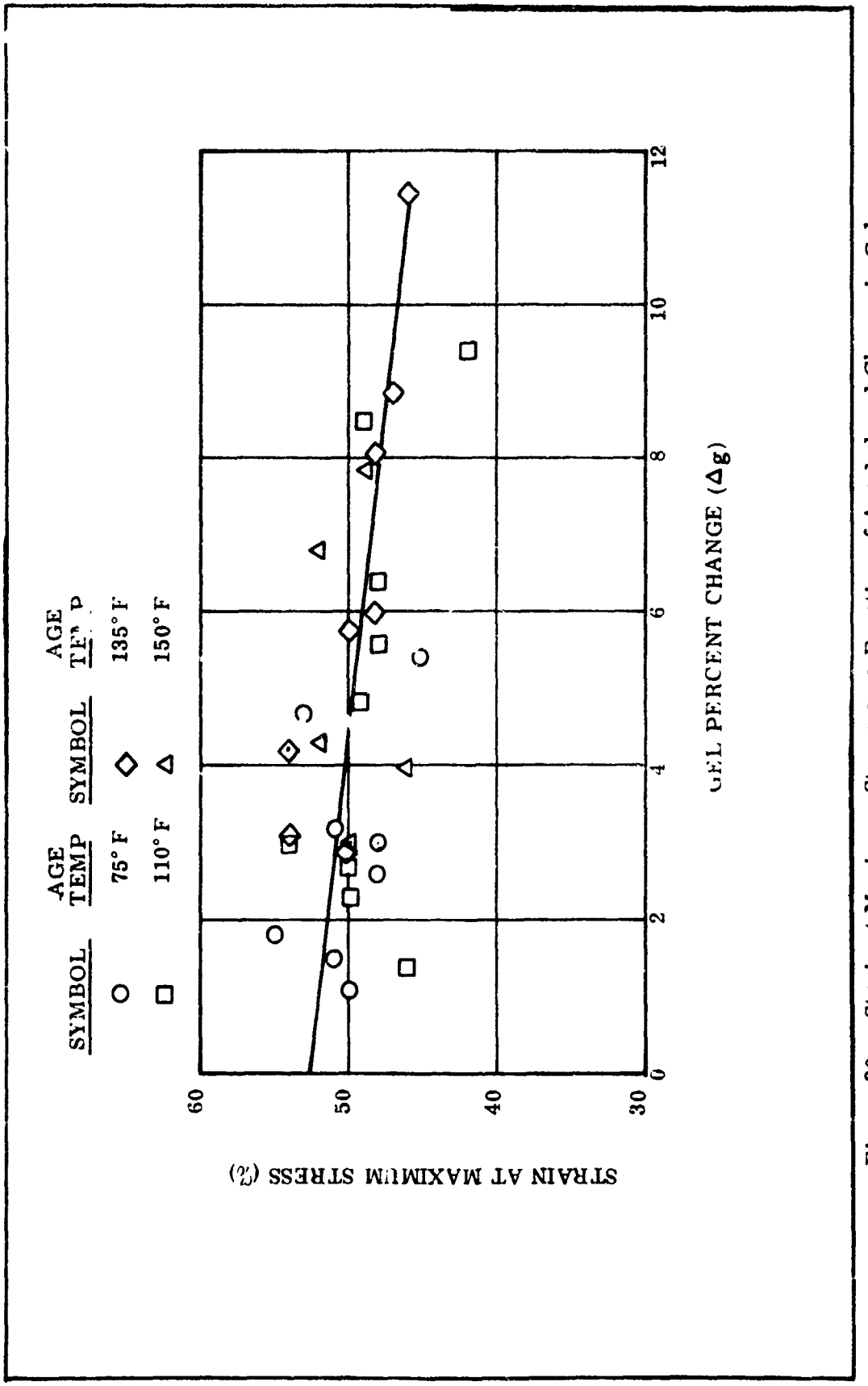

Figure 30. Strain at Maximum Stress as a Function of Age Induced Change in Gel, 125° F Test Temperature

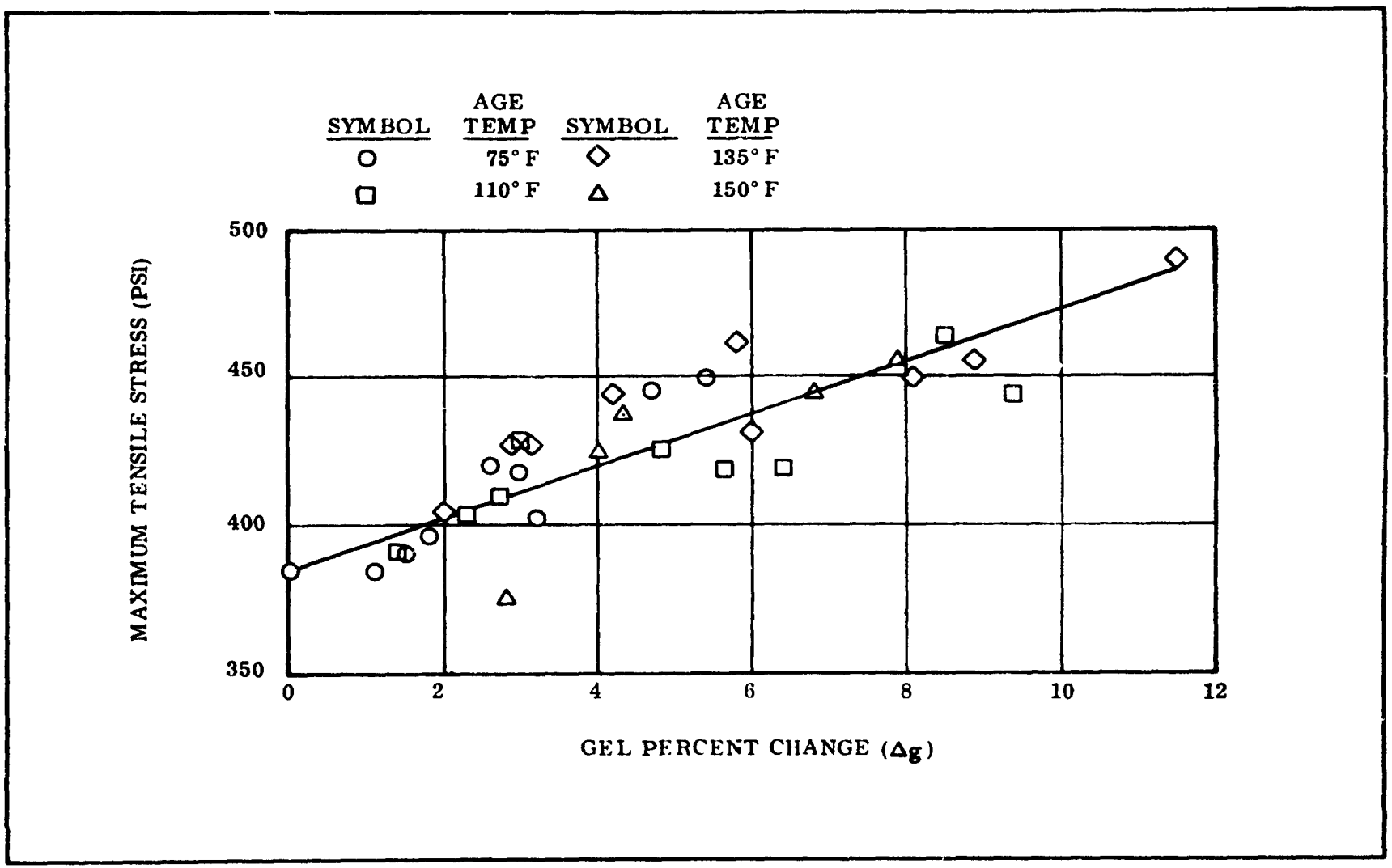

Figure 31. Maximum Tensile Stress as a Function of Age Induced Change in Gel, 10° F Test Temperature, 500 psi Pressure

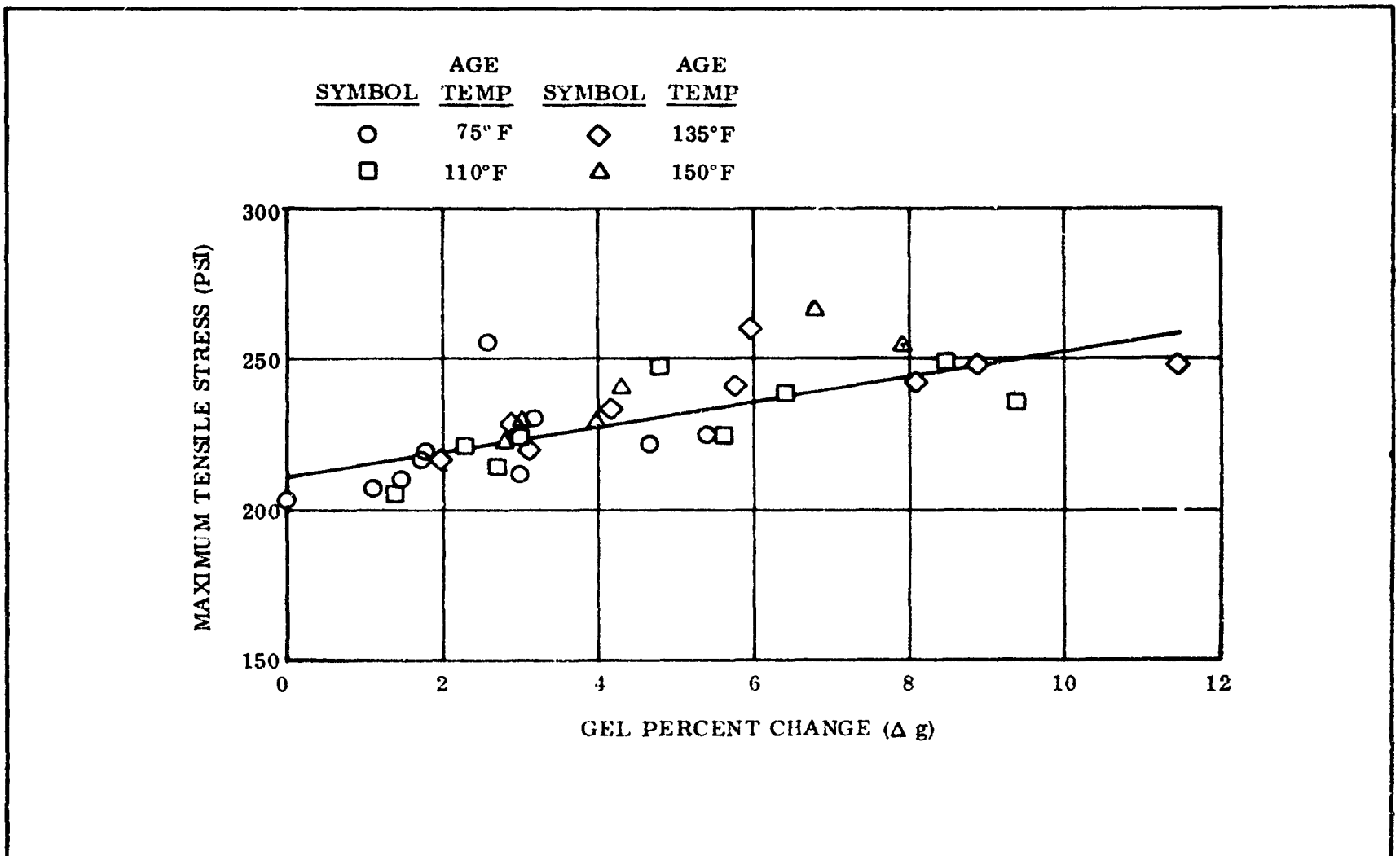

Figure 32. Maximum Tensile Stress as a Function of Age Induced Change in Gel, 75°F Test Temperature, 500 psi Pressure

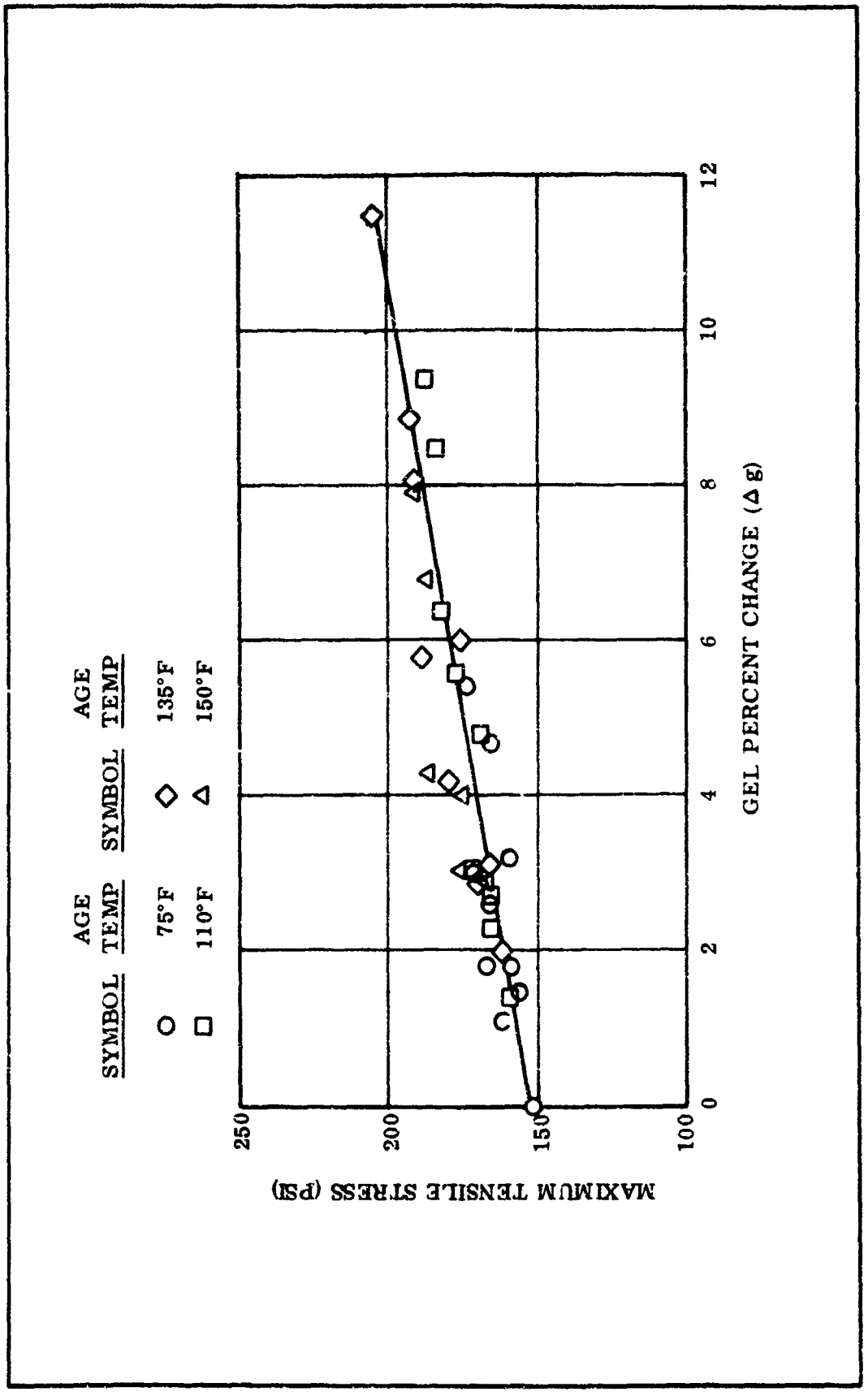

Figure 33. Maximum Tensile Stress as a Function of Age Induced Change in Gel, 125°F Test Temperature, 500 psi Pressure

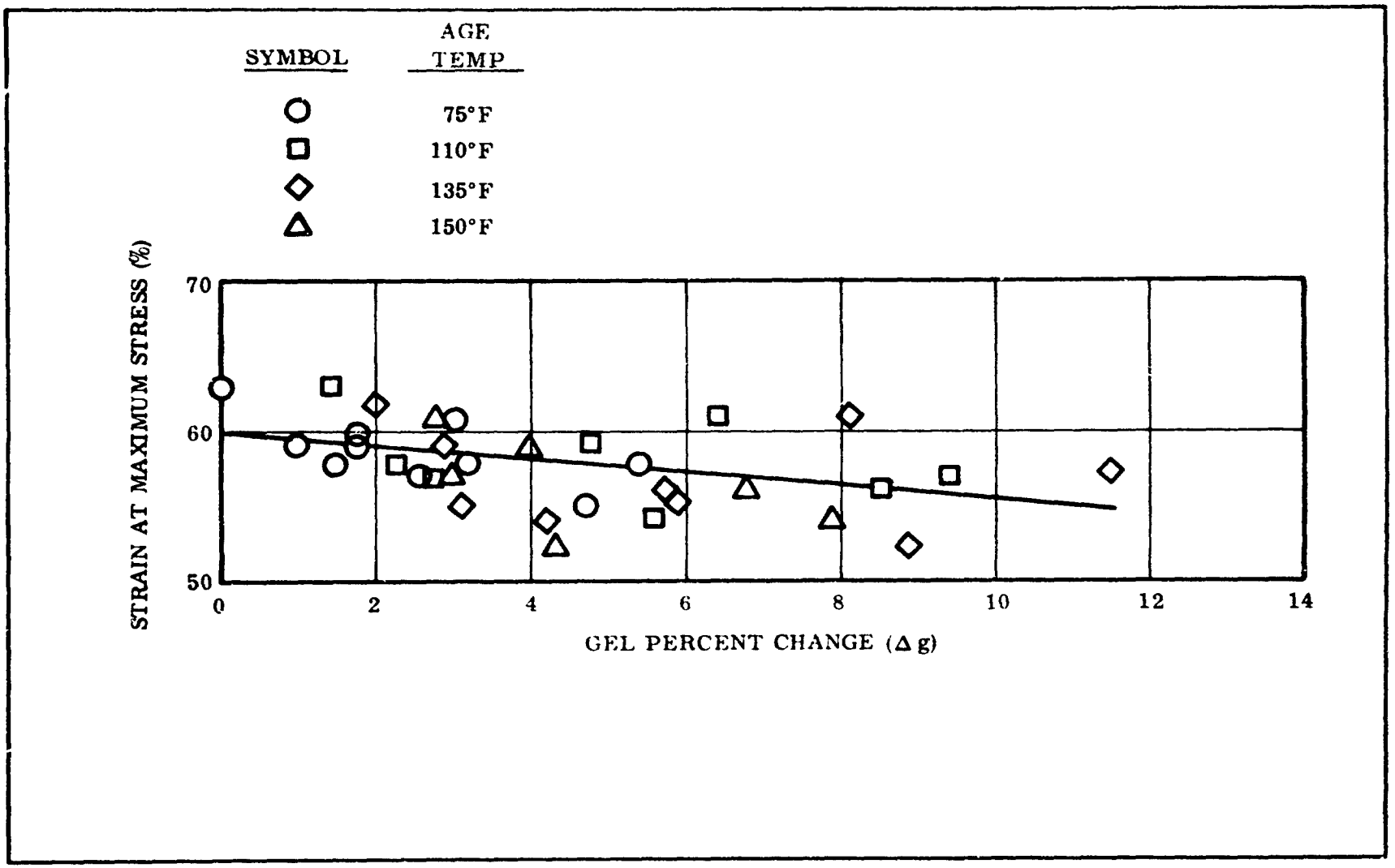

Figure 34. Strain at Maximum Stress as a Function of Age Induced Change in Gel, 10°F Test Temperature, 500 psi Pressure

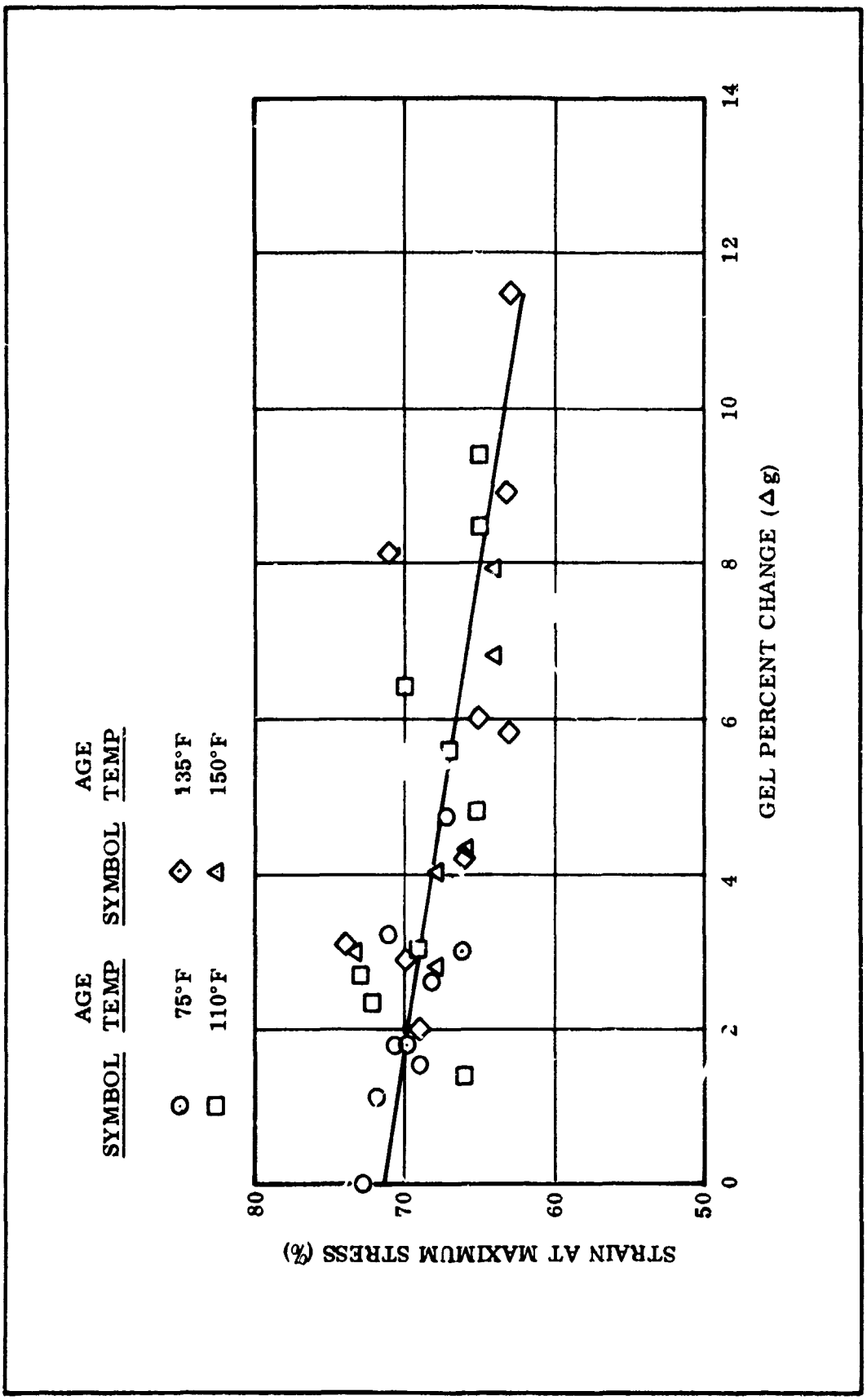

Figure 35. Strain at Maximum Stress as a Function of Age Induced Change in Gel, 75°F Test Temperature, 500 psi Pressure

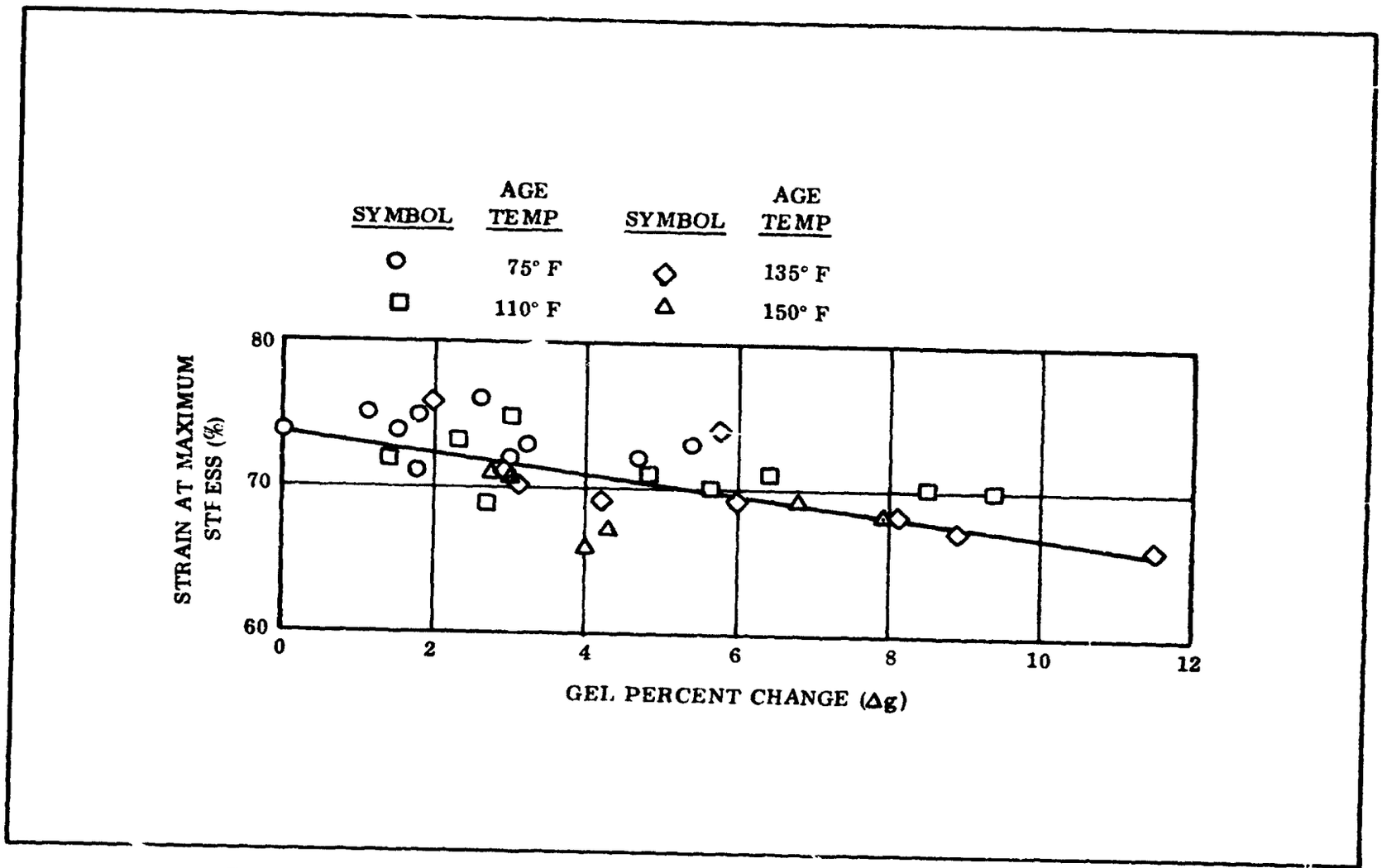

Figure 36. Strain at Maximum Stress as a Function of Age Induced Change in Gel, 125° F Test Temperature, 500 psi Pressure

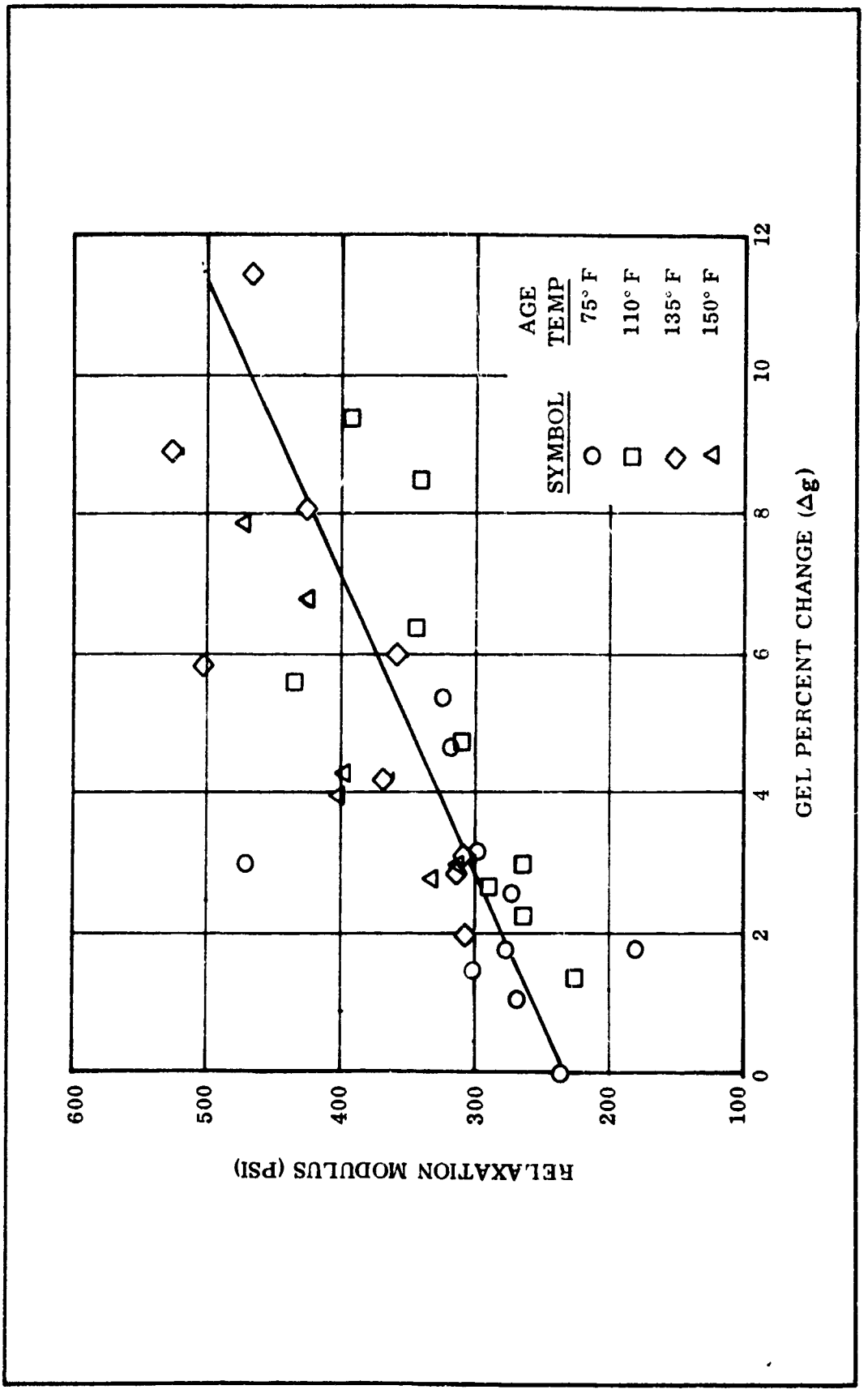

Figure 37. Relaxation Modulus as a Function of Age Induced Change in Gel, 10° F Test Temperature

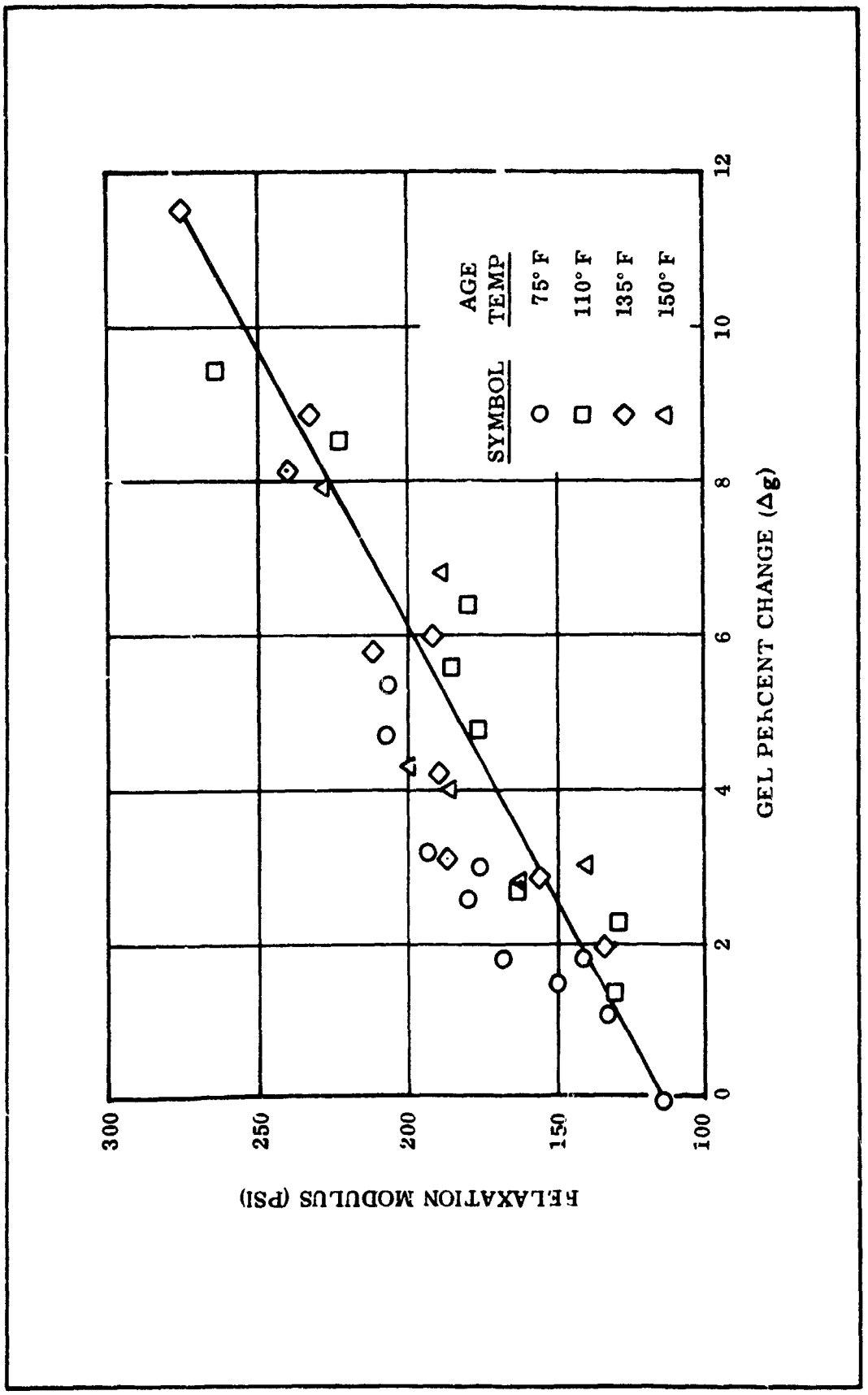

Figure 38. Relaxation Modulus as a Function of Age Induced Change in Gel, 75° F Test Temperature

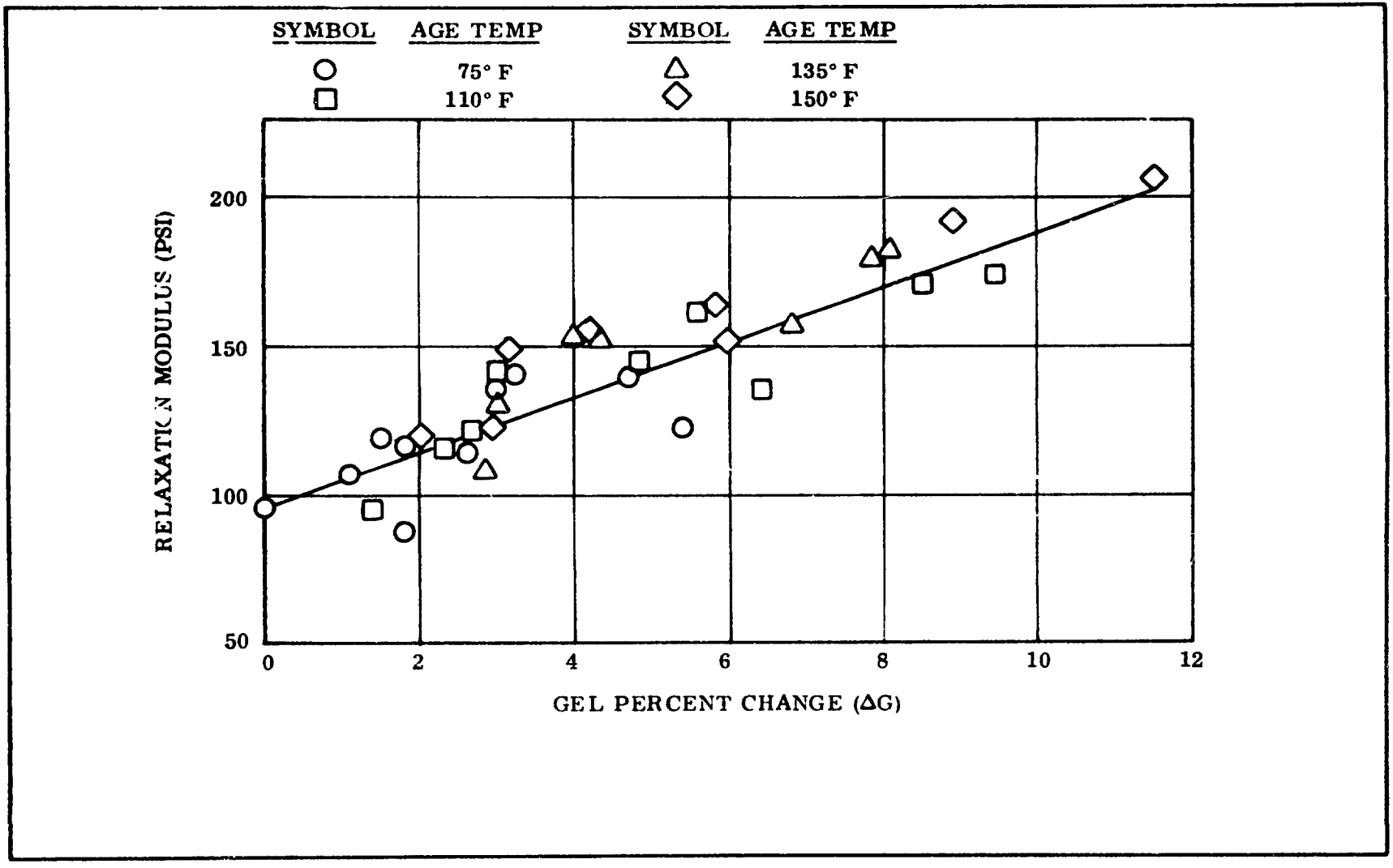

Figure 39. Relaxation Modulus as a Function of Age Induced Change in Gel, 125° F Test Temperature

There are no long time aging results for TP-H1139 propellant with which to make a comparison of predicted and measured data. The longest age-time data available are a maximum of 2 years.[3] About all that can be seen from these data is that the aging trend is in the same direction and the aging rate is approximately the same. Since the two propellant mixes resulted in material having different moduli, it is necessary to shift the data for comparison. The maximum stress data for the 2 year aged propellant were shifted vertically by adding 23 psi to all measured values. The results are presented in Figure 40 where the lines are taken from the Development of HTPB Propellants program[3] and the points are plotted from this chemical aging study. The comparison is favorable if not conclusive.

While there is no long time aging data for TP-H1139 with which to make a comparison of measured and predicted results, it is of interest to compare the aging behavior with another propellant. For this comparison, the results from the ANB-3066 propellant study[2] were selected. The results of change in the maximum stress parameter are shown in Figure 41. The slope of the ANB-3066 line for aging at 150° F is 44, while that for the TP-H1139 is 26 and the comparison at 75° F aging conditions is 15 and 9. It is readily apparent that the HTPB propellant is less subject to aging changes than the ANB-3066.

A further comparison is made for the strain values in Figure 42 which shows not only a smaller change in strain with age for TP-H1139 but also a higher level of strain capability. Both propellants were formulated to have the same level of solids; therefore, the comparison is made with propellants as nearly similar as possible. It can therefore be concluded that TP-H1139 exhibits the better initial mechanical properties and the lesser change with aging of the two propellants.

The aging behavior of propellants may be easily compared when the aging change is some linear function of time. It is a simple matter of comparing the slopes of the property vs f(t) lines. To facilitate this comparison with other propellants, the aging rate values for the TP-H1139 formulation determined from this study are presented in Table XII. It can be seen from these values that the rate of change of properties per logarithmic decade of time is small.

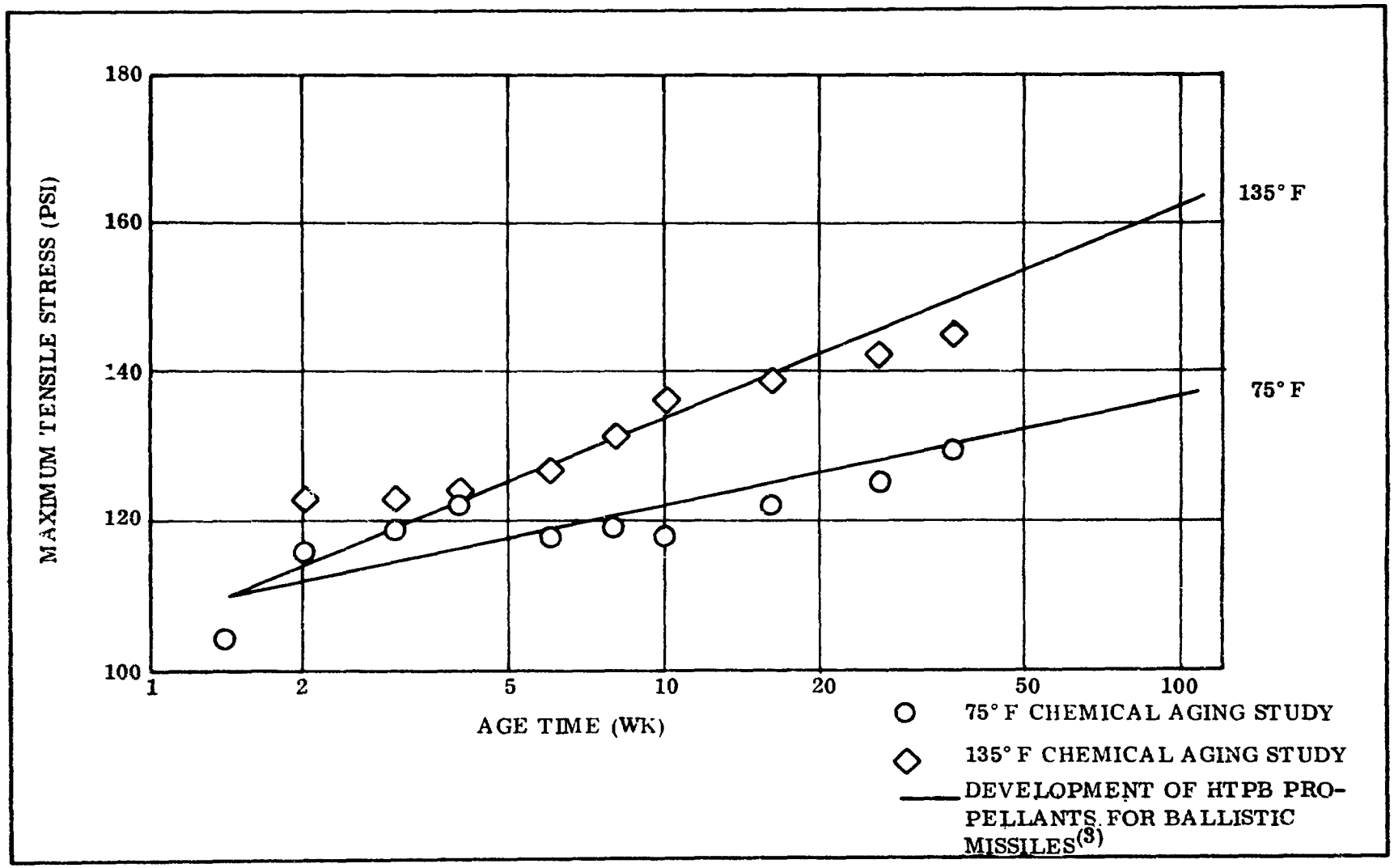

Figure 40. Comparison of Maximum Tensile Stress, TP-H1139 Propellant

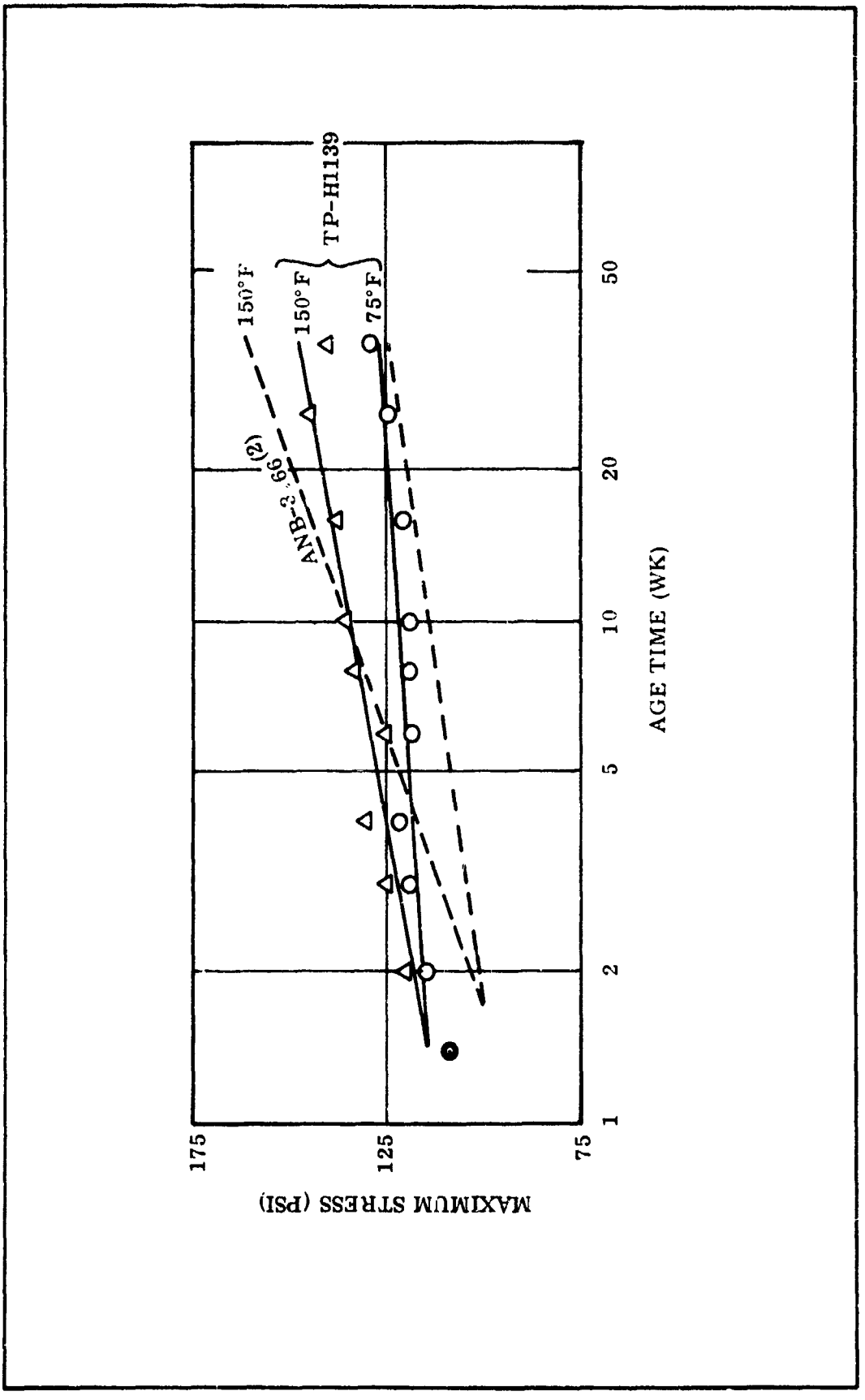

Figure 41. Effect of Aging on Maximum Stress

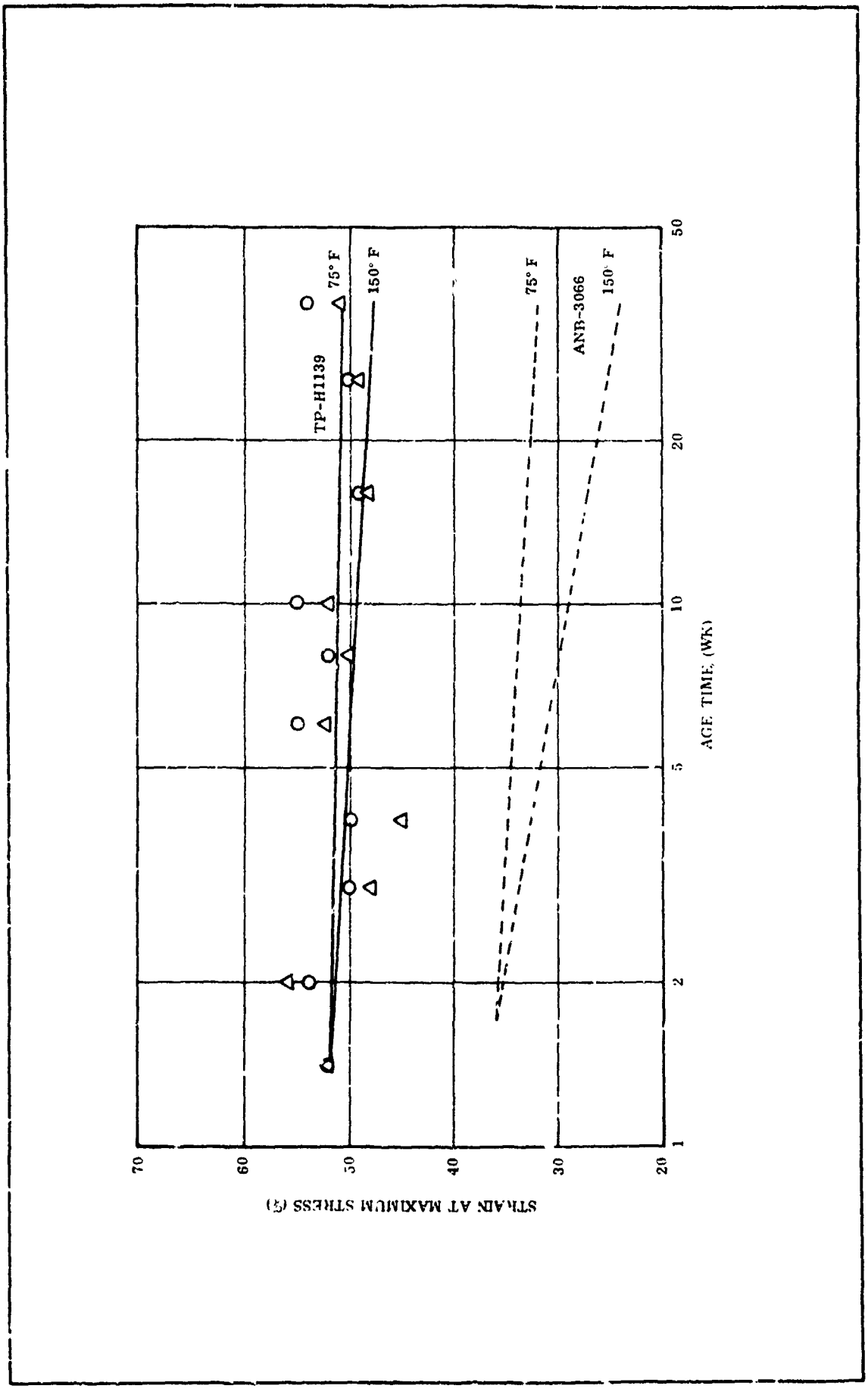

Figure 42. Effect of Aging on Strain

Table XII

Aging Rate Constants for TP-H1139 Propellant

Aging Temperature (°F)	Aging Constants, k (T) 75	110	135	150
Percent Gel	3.6	6.1	7.4	9.4
Maximum Tensile Stress at 10°F	12	23	35	48
Maximum Tensile Stress at 75°F	9	15	21	26
Maximum Tensile Stress at 125°F	4	9	14	20
Strain at Maximum Stress at 10°F	-1.0	-1.5	-2.2	-3.0
Strain at Maximum Stress at 75°F	-.7	-1.5	-2.0	-2.6
Strain at Maximum Stress at 125°F	-3.3	-4.3	-4.8	-6.6
Maximum Tensile Stress at 10°F, 500 psi	33	50	71	86
Maximum Tensile Stress at 75°F, 500 psi	9	19	30	43
Maximum Tensile Stress at 125°F, 500 psi	9	25	31	36
Strain at Maximum Stress at 10°F, 500 psi	-3.5	-5.0	-6.0	-8.5
Strain at Maximum Stress at 75°F, 500 psi	-2.8	-4.2	-6.2	-8.6
Strain at Maximum Stress at 125°F, 500 psi	-1.5	-3.4	-6.2	-8.6
Relaxation Modulus at 10°F	65	108	183	290
Relaxation Modulus at 75°F	72	93	117	133
Relaxation Modulus at 125°F	34	56	81	103

The temperature dependence of the aging rate is most easily determined by means of an Arrhenius type presentation. This is shown in Figure 43 where the rate of change of stress is presented as a reciprocal function of the aging temperature. The slope then becomes a means for determining the activation energy of the aging reaction. In this case, the activation energy is determined to be 5.1 Kcal/mole. This is somewhat low for a normal free-radical oxidative-type reaction where values four or five times higher are normally obtained. While the aging reaction has not been determined, it has been assumed to be a reaction on sites of unsaturation in the polymer chain of the propellant binder. It is entirely conceivable that because of the crosslinked network of the binder the molecules are somewhat restricted and motion over a distance large enough for reactive chemical species to come together becomes a process not too different from diffusion. This would be consistent with the low activation energy value obtained in this work.

Determinations of activation energies for each of the parameters revealed values ranging from 4.4 to 6.5 Kcal/mole. Low activation energies (6.0 to 11.1 Kcal/mole) have been reported by Barrer[4] for the diffusion of a series of gases through neoprene rubber. Corman, et al.,[5,6] have studied the activation energies of diffusion for hydrocarbon oils through a series of rubbers using ^{14}C-labeled compounds. The activation energies found ranged from 3.1 to 9.9 Kcal/mole. Smith, et al.,[7] determined the activation energy for the loss of antioxidant from neoprene rubber to be 5.1 Kcal/mole. Each of these studies, made in polymeric systems, corroborate the magnitude of the activation energy for aging changes in propellant and tend to substantiate the assumption of an oxidative reaction on sites of unsaturation.

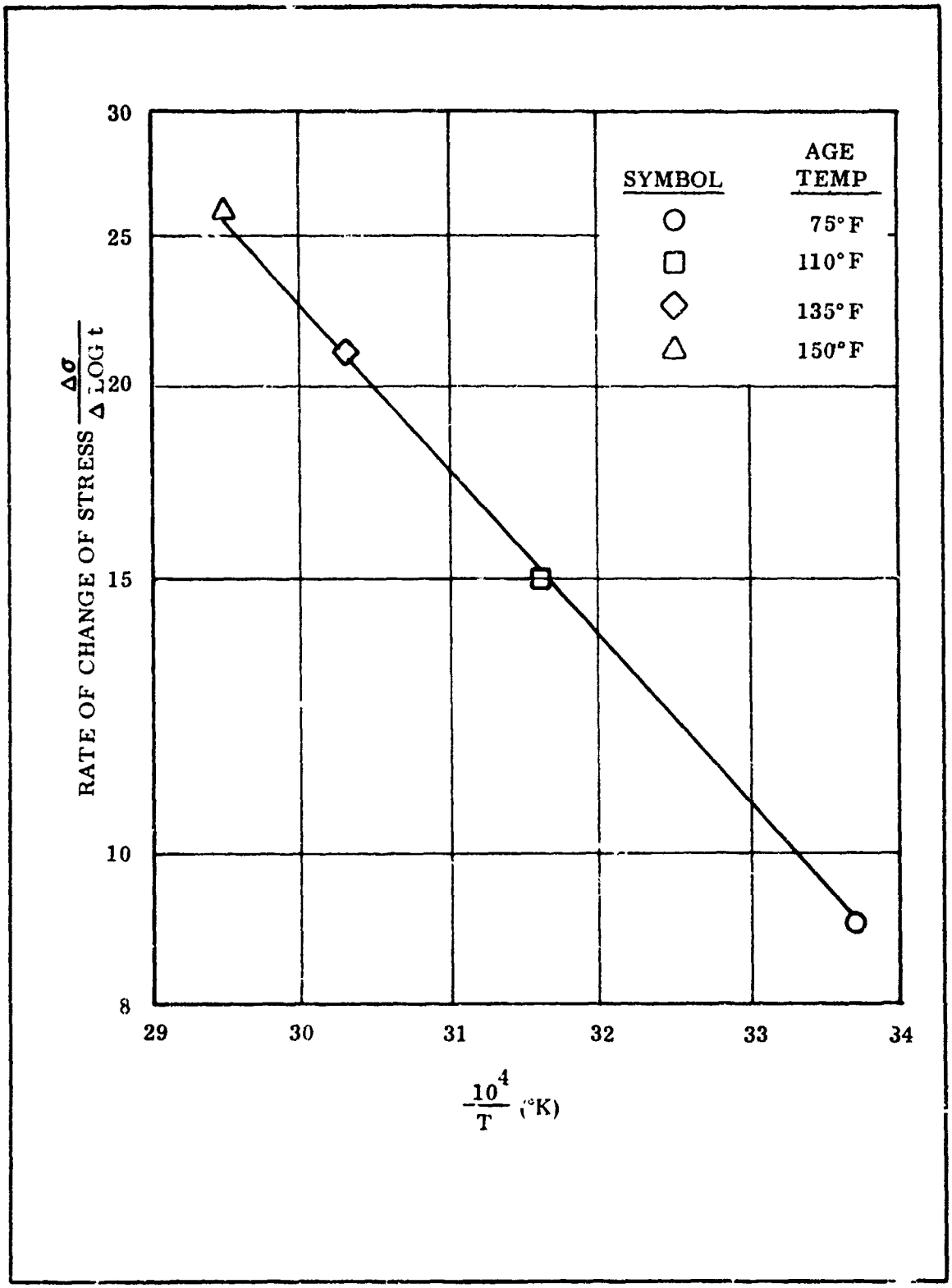

Figure 43. Aging Rate Temperature Dependence

6.0 ACCOMPLISHMENTS AND RECOMMENDATIONS

6.1 ACCOMPLISHMENTS

The results from this study were obtained by utilizing the recommended technique[1] for studying and interpreting accelerated aging data for long time projections of aging behavior. The success of the program verifies the approach (suggesting that where the major change in propellant properties is due to a chemical reaction affecting the crosslinking of the polymeric binder, a chemical evaluation of that reaction is very valuable in assessing the aging behavior). Some of the accomplishments that have contributed to the success of this study are:

1. The method for separating the solids from the binder of cured propellant, developed on earlier programs[1,2] has been modified to work for this propellant. The resulting soluble and insoluble binder fractions were then available for analyses without interference from the aluminum and ammonium perchlorate found in the propellant.
2. The analysis for curing agent has shown that this material is completely reacted by the end of cure period; therefore, the cure reaction of isocyanate with hydroxyls of the polymer does not contribute to the aging reaction.
3. The effect of cure temperature on the resulting properties of this propellant seems to be more one of differing aging effects than a change in the mechanism of the cure reaction. As a result it should be possible to make the same propellant by curing at different temperatures for times that are determined to allow the same degree of reaction. This is not true for all propellants.
4. It has been verified that changes in mechanical properties that occur early in the aging study are important to

the interpretation of aging data and the development of an aging model.

5. The change in percent gel with aging time is directly related to the change in mechanical properties for all temperatures of aging studied.

6.2 RECOMMENDATIONS

1. All HTPB propellants contain a small amount of an additive to improve mechanical properties. This additive has been called a bonding agent because the mechanism by which it improves mechanical properties is thought to be a chemical reaction with the oxidizer that improves the binder-oxidizer bond. Since all the "bonding agent" added to this propellant remains as a measurable material, the expected reaction did not take place. The additive does improve mechanical properties by some undetermined mechanism. Studies are needed to determine the mechanism by which it works, making further improvements possible.
2. The iodimetric titration for unsaturation in the binder has not been sufficiently definitive to make an assessment of reaction rates or even tie down the reaction. A technique to obtain, quantitatively, the aging reaction rate is needed.
3. The effect of humidity has been deliberately ignored. For some propellants and motor systems, this environmental condition can have gross effects on motor grain structural integrity. This is a condition requiring continued study.
4. The entire time-temperature spectrum has not been defined. Effort should be continued to determine a general aging model

that defines the aging effects in all regions of the failure boundary within the time-temperature regime of significance to rocket motor grains.

7.0 REFERENCES

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4. Barrer, R. M., Transactions of the Faraday Society, 35, p 628 (1939).

5. Corman, B. G., et al., Rubber Chem. Technol., 42, p 474 (1969).

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7. Smith, J. D. B., et al., Journal of Applied Polymer Science, 18, p 3,543 (1974).