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TEST PROGRAM EVALUATION OF HERCULES 3501-6 RESIN.(U)
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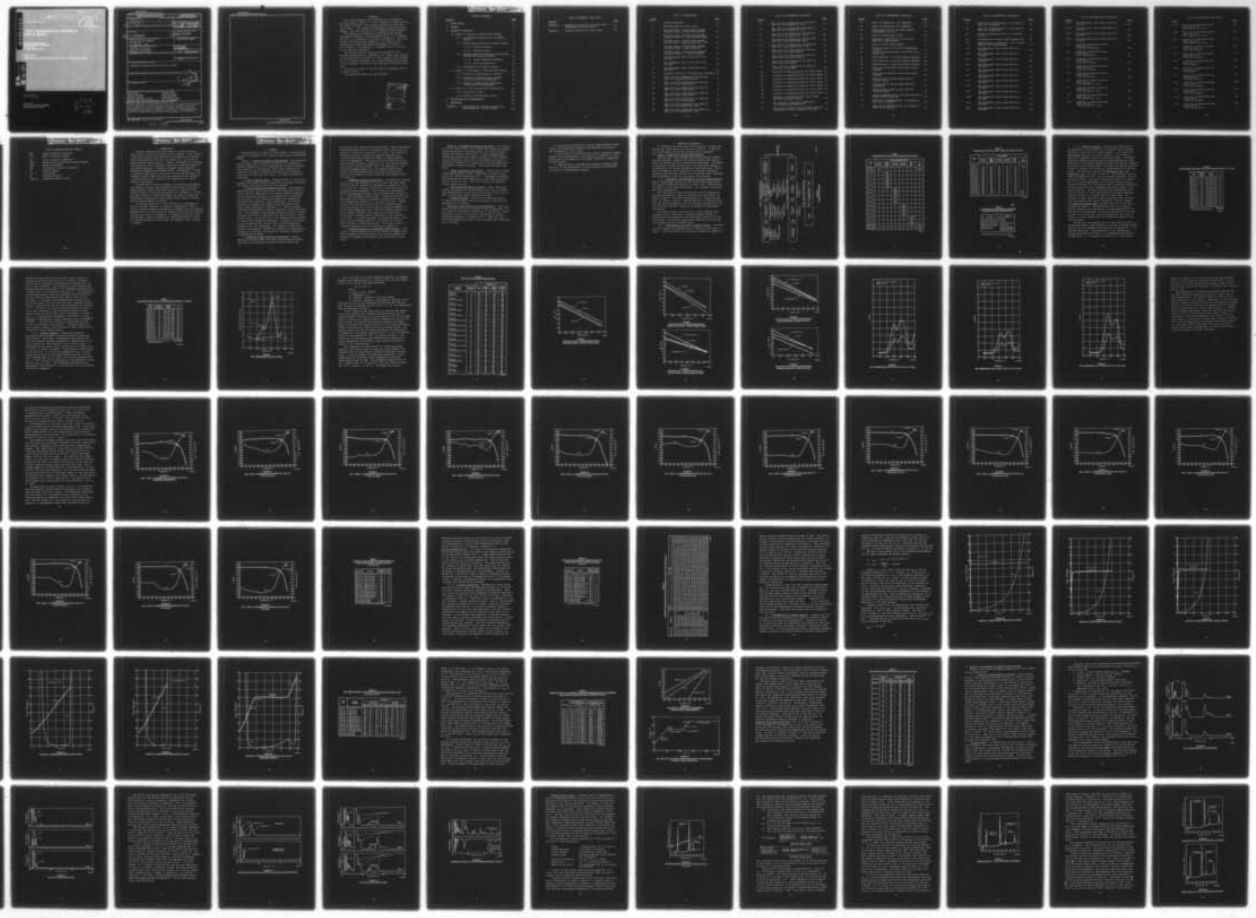

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FOR FURTHER PART II

CONTRACT NO. N00019-77-C-0165

"TEST PROGRAM EVALUATION OF 3501-6 RESIN"

McDonnell Aircraft Company
McDonnell Douglas Corporation
P.O. Box 516
St. Louis, Missouri 63166

MAY 1978
Final Report for Period 28 February 1977 - 28 February 1978

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18. SUPPLEMENTARY NOTES

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Epoxy Resin	Thermal Analysis
Quality Assurance	Viscosity Profile
Chemical Analysis	Atomic Absorption
Dynamic Mechanical Analysis	Infrared Spectroscopy
Reverse Phase Liquid Chromatography	Gas Chromatography

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Sixteen chemically altered batches of 3501-6 resin were analyzed by physiochemical techniques and by dynamic mechanical analysis to determine the effects of known variations in chemical composition on dynamic mechanical properties, processability and moisture sensitivity of this system. An advanced analytical technique, reverse phase liquid-liquid chromatography was also developed.

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FOREWORD

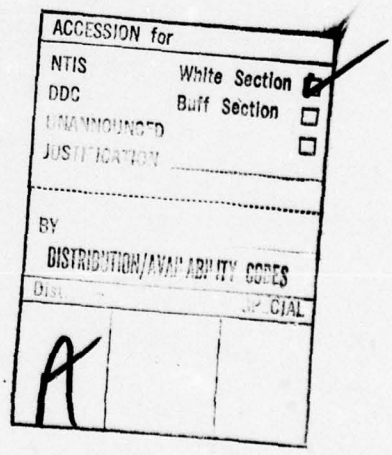
This report describes work performed by the McDonnell Aircraft Company (MCAIR), St. Louis, Missouri, on NASC Contract No. N00019-77-C-0155, "Test Program Evaluation of Hercules 3501-6 Resin". The program was sponsored by Naval Air System Command. Mr. John Gurtowski was the NAVAIR Project Engineer.

The program was conducted by the Material and Process Development Department, and was managed by Mr. R. J. Juergens, with Dr. J. F. Carpenter as Principal Investigator. Major contributors to the program include Mr. T. A. Sewell of the Material and Process Development Department and Messers T. T. Bartels, J. B. Maynard, W. A. Mathew, and C. E. wilson of the Materials Laboratory.

Data reported herein was primarily generated in the Engineering Laboratories. Hercules, Inc., Magna, Utah supplied all the altered resin batches of 3501-6 tested in this program. Dr. R. E. Hoffman, Hercules, Inc., has provided valuable input to this program in the form of test data and technical discussions.

This report covers the contract period 28 February 1977 to 28 February 1978.

This technical report has been reviewed.



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LIST OF ABBREVIATIONS AND SYMBOLS

DMA	Dynamic Mechanical Analysis
BF_3	Boron trifloride catalyst
Tg	Glass transition temperature
RPLLC	Reverse Phase Liquid-Liquid Chromatography
WPE	Weight Per Epoxide
DSC	Differential Scanning Calorimetry
E*	Complex modulus
Tan δ	Loss tangent
IS	Internal Standard
Peak (A)	Advancement Peak of 3501-6

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1. INTRODUCTION

Advanced composites are being used in primary structural applications in high performance military aircraft. Until recently the user relied almost entirely on performance tests such as short-term mechanical testing, flow times, etc., as a means of batch-to-batch quality control. However, processability, strength and durability of any structural resin must ultimately depend on the system chemistry. Formulative changes cannot always be detected by mechanical performance tests. Consequently, a number of composite fabricators, principally airframe manufacturers and composite prepreg suppliers, have been developing and implementing additional quality assurance test capabilities to insure chemical consistency.

A background of chemical composition information and methods for component analysis was previously established for AS/3501-6 graphite/epoxy prepreg under NASC Contract No. N00019-76-0138 "Quality Control of Structural Nonmetallics" (Reference 1). Multiple batch testing of production batches was used as a basis for establishing statistically valid compositional limits to control batch-to-batch chemical uniformity.

The primary objective of this program was to determine the effects of known variations in chemical composition of 3501-6 resin on dynamic mechanical properties, processability and moisture sensitivity of the cured resin and assess current quality assurance criteria and revise, if necessary. A secondary objective of the program was to develop advanced test methods applicable to chemical characterization of 3501-6 resin and composite resin systems in general.

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2. SUMMARY

The program was divided into three phases. The objectives as well as a summary of the results for each phase are described below:

Phase I - Testing of Special Resin Batches - The objective of this phase was to determine the effects of variations in chemical composition on the processability and dynamic mechanical properties of the Hercules 3501-6 resin system and to determine the effect of chemical variations on the moisture sensitivity of the cured neat resin. This phase involved the following:

o Procure Special Resins - Sixteen batches of 3501-6 were prepared with varied chemical composition by Hercules Corporation, Magna, Utah and procured for this program.

o Conduct Chemical and Thermal Analysis - Physiochemical analytical tests were carried out on the as-received resins to verify that the composition of the special batches conformed to the variations required for the program and to establish the viability of the chemical and thermal test methods for detecting broad changes in resin formulation. The thermal analysis and chemical test methods used were derived from those already developed in Reference (1). Thermal analysis consisted of differential scanning calorimetry (DSC) determinations. DSC thermograms were obtained showing the rate of energy released (exotherm) vs temperature for three different linear heating rates. Critical points on the thermograms were related to chemical and processing parameters. Changes in the amounts of curing agent and BF_3 catalyst gave the most pronounced changes in the DSC thermograms. The results of these tests indicate the necessary sensitivity to defect and differentiate intentional variations in processing or chemical formulation introduced by the vendor.

o Determine Dynamic Mechanical Properties - Dynamic Mechanical Analysis (DMA) for cured resin specimens prepared from each of the special "off-specification" batches was

determined using a Rheovibron Viscoelastomer. Dynamic mechanical measurements were made at a frequency of 100 Hz from room temperature to 270°F at a scan rate of 1° C/MIN. The effects of chemical variations on dynamic mechanical properties are illustrated by plots showing the change in complex modulus (E*) with temperature. The effect of resin variations on the dynamic glass transition temperature (T_g) were also determined from plots of the loss tangent (TAN δ) vs temperature. The difference between dynamic T_g's and complex modulus among batches with varied chemistry were smaller than expected. Changes in the amount of curing agent had the greatest effect on dynamic T_g.

o Determine Processing Parameters - The effects of chemical variations on the rheology of the neat resin melt were determined and the data related to processability parameters, such as flow and gel. Viscosity profiles as a function of time and temperature were determined. The viscosity of experimental resins was monitored through a range from minimum viscosity to gel at three different heating rates. Determinations were also made under four different isothermal conditions and over the time/temperature conditions of a typical cure cycle. Batches of resin with less curing agent than the standard formula exhibited greater flow, while batches with greater amounts of curing agent showed less flow. The most dramatic changes in flow, however, resulted from changes in the percent BF_3. An increase in catalyst greatly shortened the gel time and total flow. In a practical sense, the latter condition could result in gel occurring ahead of the application of autoclave pressure in processing prepreg. This could result in composite laminates with low interlaminar properties.

o Establish Chemical and Mechanical Relationships - Variations in resin formulation and their effect on dynamic mechanical properties were established and the relationships are presented in tabular and graphical form in the text of this report.

Phase II - Advanced Test Method Development - The objective of the second phase of the program was to develop improved methods applicable to characterization and chemical quality control of composite matrix resin. Liquid chromatography methods were selected for emphasis because of rapid advances in the technology of this type of instrumentation and its particular suitability for examination of resin systems used for graphite composite prepregs. This phase included three tasks.

o Select and Refine Test Methods - Reverse phase liquid-liquid chromatography (RPLLC) methods were selected for advanced test method development work. Instrumental parameters were optimized for RPLLC application to the chemical quality control of 3501-6 resin. Both the isocratic and gradient elution modes were used.

o Test Production Batches of Resin - Three production batches of prepreg resin were tested in replicate to investigate reproducibility of the RPLLC method test results and to note any detectable batch-to-batch variations.

o Document Methods - Detailed test method parameters for RPLLC were documented and are presented in the text and appendices of this report.

Phase III - Data Analysis and Interpretation - The final phase included an overall evaluation of the program data, for the purpose of determining the adequacy of the quality control acceptance criteria for AS/3501-6 graphite/epoxy prepreg, previously established in Reference (1). There were three major considerations involved in the evaluation and interpretation of the data.

- Accuracy and precision of existing physiochemical quality control test methods for detecting and measuring variations in the formulation of 3501-6 resin.
- Suitability of existing quality control acceptance limits, based on the determination of the effects of variations in resin formulation on processability and dynamic mechanical properties of 3501-6 resin.
- Applicability of advanced test methods, developed under Phase II, to the improvement of quality assurance requirements for AS/3501-6 graphite/epoxy prepreg.

3. TECHNICAL DISCUSSION

To accomplish the objectives of this program, the work was divided into three phases as outlined in Figure 1. A description of each phase and the work accomplished is presented.

3.1 Phase I - Testing of Special Resin Batches

Special 3501-6 resin batches with varied chemical composition were procured. Chemical and thermal analyses were used to check the composition and to characterize each batch. The effect of variations in resin formulation on the properties affecting processability for prepreg applications were determined. The effect of changes in resin chemistry on the dynamic mechanical properties and moisture sensitivity of cured neat resin specimens were determined for each of the special resin batches.

3.1.1 Procurement and Description of Special Resin Batches - Special experimental batches of 3501-6 resin were prepared for the program by Hercules Corporation, Magna, Utah. Approximately one gallon of each batch was prepared. All shipment and storage was under refrigeration.

The variations in starting materials for the experimental batches were made on a parts per hundred resin (phr) basis, as shown in Table 1. The varied formulations on a weight percent basis are given in Table 2. Batches CRT-75-15 and CRT-75-16 are the same starting composition as the standard formulation of the control batch, CRT-76-1, except for the degree of advancement (B-staging).

The larger percent variations for a given component were selected with the intention of showing a definite effect on processability of the resin or the mechanical properties of the cured resin. The smaller changes were selected to be near what was estimated to be a threshold effect.

3.1.2 Physiochemical Analysis of Special Resins - The altered resin batches were analyzed by physiochemical tests shown in Table 3. The test methods are described in detail in Appendix A.

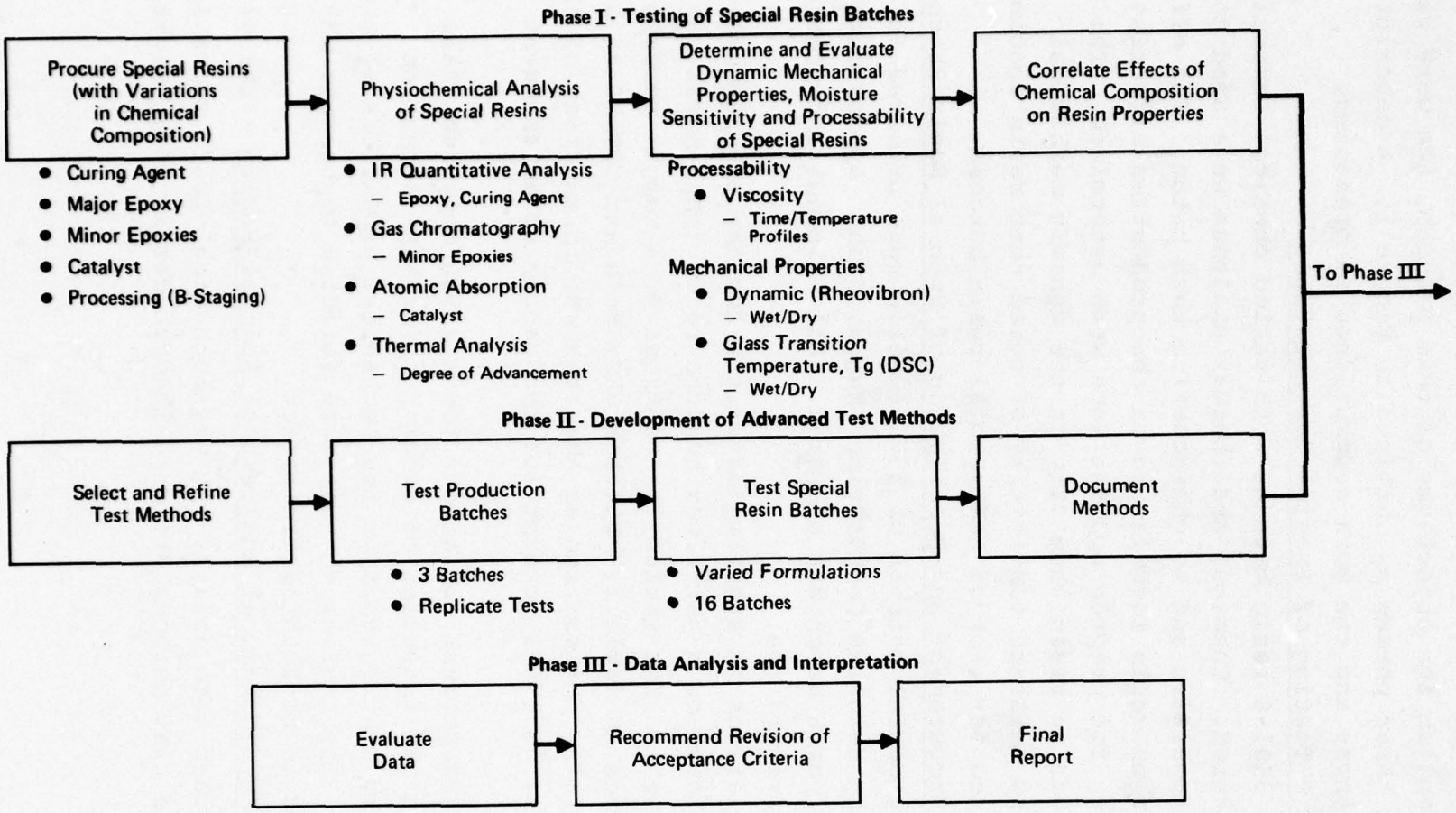

FIGURE 1
TECHNICAL APPROACH

TABLE 1
COMPOSITION OF SPECIAL 3501-6 RESIN BATCHES (PHR)

Batch No.	Parts/Hundred Resin (PHR)					
	Epoxide No. 1(H)	Curing Agent (DDS)	Epoxide No. 2(H)	Epoxide No. 3(H)	BF_3 Catalyst	"B" Stage
CRT-76-1 (Control)	100	44	16	15	2	Standard
CRT-77-2	↓	48.4 (+10%)	↓	↓	↓	↓
CRT-77-3	↓	39.6 (−10%)	↓	↓	↓	↓
CRT-79-4	↓	52.8 (+20%)	↓	↓	↓	↓
CRT-79-5	↓	35.2 (−20%)	↓	↓	↓	↓
CRT-76-6	↓	44	19.2 (+20%)	↓	↓	↓
CRT-78-7	↓	↓	12.8 (−20%)	↓	↓	↓
CRT-76-8	↓	↓	22.4 (+40%)	↓	↓	↓
CRT-78-9	↓	↓	9.6 (−40%)	↓	↓	↓
CRT-76-10	↓	↓	16	22.5 (+50%)	↓	↓
CRT-79-11	↓	↓	↓	7.5 (−50%)	↓	↓
CRT-76-12	↓	↓	↓	30 (+100%)	↓	↓
CRT-75-13	↓	↓	↓	15	1.0 (−50%)	↓
CRT-75-14	↓	↓	↓	↓	4.0 (+100%)	↓
CRT-75-15	↓	↓	↓	↓	2.0	Under
CRT-75-16	↓	↓	↓	↓	↓	Over

GP78-0353-2

TABLE 2
COMPOSITION OF SPECIAL 3501-6 RESIN BATCHES (%-WT/WT)

Batch No.	Percent (Wt/Wt)					
	Epoxide No. 1(H)	Curing Agent (DDS)	Epoxide No. 2(H)	Epoxide No. 3(H)	BF_3 Catalyst	"B" Stage
CRT-76-1 (Control)	56.5	24.9	9.0	8.5	1.13	Standard
CRT-77-2	55.1	26.7	8.8	8.3	1.10	
CRT-77-3	57.9	22.9	9.3	8.7	1.16	
CRT-79-4	53.8	28.4	8.6	8.1	1.08	
CRT-79-5	59.4	20.9	9.5	8.9	1.19	
CRT-76-6	55.5	24.4	10.6	8.3	1.10	
CRT-78-7	57.5	25.3	7.4	8.6	1.15	
CRT-76-8	54.5	24.0	12.2	8.2	1.09	
CRT-78-9	58.6	25.8	5.6	8.8	1.17	
CRT-76-10	54.2	23.8	8.7	12.2	1.08	
CRT-79-11	59.0	26.0	9.4	4.4	1.18	
CRT-76-12	52.1	22.9	8.3	15.6	1.04	
CRT-75-13	56.8	25.0	9.1	8.5	0.57	
CRT-75-14	55.9	24.6	8.9	8.4	2.23	
CRT-75-15	56.5	24.9	9.0	8.5	1.13	Under
CRT-75-16	56.5	24.9	9.0	8.5	1.13	Over

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TABLE 3
PHYSIOCHEMICAL ANALYSES AND METHODS FOR 3501-6 SPECIAL RESIN BATCHES

Test	Method
Curing Agent (DDS), % wt/wt	Infrared
Epoxide No. 2(H), % wt/wt	Infrared
Epoxide No. 3(H), % wt/wt	Gas Chromatography
Weight per Epoxide (WPE)	Titrametric
BF_3 Catalyst, % wt/wt	Atomic Absorption
Thermal Analysis	Differential Scanning Calorimetry (DSC)

(1) Detailed description of test method is given in Appendix

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3.1.2.1 Chemcial Analysis - The chemical components for the experimental resin batches were determined by the methods indicated in the first five items of Table 3. The results for curing agent analysis are given in Table 4. The analytical data are in agreement with the formulation values. The average difference between duplicate tests are approximately the same magnitude as the average difference between the Hercules formulated values and the average MCAIR analytical test results, which indicates an accuracy and precision of approximately the same magnitude. The analytical results for Epoxide No. 2(H) and Epoxide No. 3(H) are given in Table 5. The analytical test results for Epoxide No. 2(H) are in acceptable agreement with the formulated values. The value obtained by analysis for Epoxide No. 3(H) by gas chromatography is the "free" epoxide and the difference between the total amount added in Hercules formulation and the analytical value represents the amount reacted during resin processing. The data indicates that approximately one third of Epoxide No. 3(H) has reacted during vendor processing, probably forming a 1:1 adduct with the curing agent. The exception is batch CRT-75-14 (excess catalyst) which indicates that approximately one half of Epoxide No. 3(H) has reacted. The Weight per Epoxide (WPE) was determined and is the data is presented in Table 6. The WPE measures the total unreacted epoxide present in the formulation, including Epoxide No. 1(H) and the two minor epoxides. The major contribution to the magnetude of this value will come from Epoxide No. 1(H) which is present in a much higher percent by weight than either of the minor epoxides.

The WPE test was required for the resin quality control as established earlier under Reference 1, because a suitable method, specific for the independent determination of Epoxide No. 1, had not been developed. The suitability of the advanced test methods developed under Phase II for independent determination of Epoxide No. 1 is discussed in Section 3.3 of this report.

TABLE 4
CURING AGENT ANALYSIS FOR ALTERED RESIN BATCHES (% - WT/WT)

Batch No.	Hercules Formulation	MCAIR Analysis	Δ(1)
CRT-76-1	24.9	24.1 (24.2, 23.9)	0.8
CRT-77-2	26.7	25.8 (25.5, 26.1)	0.9
CRT-77-3	22.9	22.3 (22.5, 22.1)	0.6
CRT-79-4	28.4	29.0 (28.7, 29.2)	0.6
CRT-79-5	20.9	21.2 (21.1, 21.3)	0.3
CRT-76-6	24.4	24.4 (24.8, 23.9)	0.0
CRT-78-7	25.3	25.5 (25.3, 25.6)	0.2
CRT-76-8	24.0	24.3 (24.6, 24.0)	0.3
CRT-78-9	25.8	24.9 (25.2, 24.6)	0.9
CRT-76-10	23.8	23.1 (23.0, 23.2)	0.7
CRT-79-11	26.0	25.6 (25.5, 25.7)	0.4
CRT-76-12	22.9	22.2 (22.5' 21.8)	0.7
CRT-75-13	25.0	24.6 (24.3, 24.8)	0.4
CRT-75-14	24.6	24.5 (24.5, 24.5)	0.1
CRT-75-15	24.9	24.4 (24.4, 24.4)	0.5
CRT-72-16	24.9	23.9 (23.8, 23.9)	1.0
			0.5 Avg

(1) Absolute difference between Hercules formulation and MCAIR test data (ave.)

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TABLE 5
ANALYSIS FOR MINOR EPOXIDES IN ALTERED RESIN BATCHES (% - WT/WT)

Batch No.	Epoxide No. 2(H)			Epoxide No. 3(H)		
	Hercules Formulation	MCAIR Analysis	Δ	Hercules Formulation	MCAIR Analysis (1)	Δ(2)
CRT-76-1	9.0	9.5 (10.1, 8.9)	0.5	8.5	5.6 (5.5, 5.7)	2.9
CRT-77-2	8.8	8.6 (8.6, 8.5)	0.2	8.3	5.4 (5.4, 5.4)	2.9
CRT-77-3	9.3	8.8 (8.9, 8.6)	0.5	8.7	6.2 (6.3, 6.0)	2.5
CRT-79-4	8.6	7.6 (7.8, 7.4)	1.0	8.1	5.4 (5.2, 5.5)	2.7
CRT-79-5	9.5	8.5 (8.2, 8.7)	1.0	8.9	5.9 (6.1, 5.6)	3.0
CRT-76-6	10.6	9.8 (9.8, 9.7)	0.8	8.3	5.1 (5.3, 4.9)	3.2
CRT-78-7	7.4	6.9 (6.7, 7.0)	0.5	8.6	5.5 (5.5, 5.5)	3.1
CRT-76-8	12.2	11.0 (11.2, 10.7)	1.2	8.2	6.0 (5.8, 6.1)	2.2
CRT-78-9	5.6	6.1 (6.4, 5.8)	0.5	8.8	5.7 (5.8, 5.6)	3.1
CRT-76-10	8.7	8.9 (9.0, 8.7)	0.2	12.2	8.3 (8.5, 8.6)	3.9
CRT-79-11	9.4	9.3 (9.2, 9.3)	0.1	4.4	3.3 (3.4, 3.2)	1.1
CRT-76-12	8.3	8.7 (8.5, 8.9)	0.4	15.6	11.5 (11.1, 11.8)	4.1
CRT-75-13	9.1	8.9 (8.8, 9.0)	0.2	8.5	5.9 (5.9, 5.9)	2.6
CRT-75-14	8.9	9.0 (8.9, 9.0)	0.1	8.4	4.3 (4.2, 4.3)	4.1
CRT-75-15	9.0	9.0 (8.8, 9.1)	0.0	8.5	5.6 (5.6, 5.6)	2.9
CRT-75-16	9.0	8.8 (8.8, 8.8)	0.2	8.5	5.0 (5.2, 4.7)	3.5
			0.5 Avg			

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(1) Analysis method gives uncombined (FREE) Epoxide No. 3(H)
(2) Difference represents amount combined with curing agent

TABLE 6
ANALYSIS FOR WEIGHT PER EPOXIDE (WPE)
FOR ALTERED RESIN BATCHES

Batch No.	WPE	Δ (Replicates)
CRT-76-1	188 (188, 188)	0
CRT-77-2	181 (177, 185)	8
CRT-77-3	185 (189, 180)	9
CRT-79-4	181 (177, 185)	8
CRT-79-5	180 (177, 182)	5
CRT-76-6	196 (201, 191)	10
CRT-78-7	188 (185, 190)	5
CRT-76-8	183 (180, 185)	5
CRT-78-9	200 (198, 201)	3
CRT-76-10	185 (186, 184)	2
CRT-79-11	186 (185, 187)	2
CRT-76-12	193 (195, 191)	4
CRT-75-13	185 (184, 185)	1
CRT-75-14	185 (188, 181)	7
CRT-75-15	193 (189, 196)	7
CRT-72-16	190 (189, 190)	1
		± 5 Avg

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The WPE test was required for the resin quality control as established earlier under Reference 1, because a suitable method for the independent determination of Epoxide No. 1 (H) had not been developed. The suitability of the advanced test methods developed under Phase II for independent determination of Epoxide No. 1 are discussed in Section 3.3. The accuracy of the WPE determination cannot be determined since the WPE for the resin starting materials by this type of test are not available. For example, the uncombined major epoxide alone could vary as much as 16 units on the resin formulation basis, against a typical value for the total uncombined resin mixture of 179. The WPE for a typical as-received production batch of resin after processing is 208 indicating reaction of some epoxide groups has taken place during the supplier's processing, i.e., B-staging and prepregging. The analysis for BF_3 Catalyst, as determined by atomic absorption (AA) is presented in Table 7. The very close duplicate results show the precision of the method to be excellent. The MCAIR analytical tests results, however, were consistently higher than Hercules indicated as being formula weights.

3.1.2.2 Thermal Analysis - Differential scanning calorimetry (DSC) was used to thermally analyze the altered resin batches. Data plots or thermograms were obtained for the rate of energy released (exotherm) vs. temperature for the curing reaction at three different linear heating rates. A thermogram for the control batch carried out at a heating rate of 5°C/min, is shown in Figure 2. Identifiable critical points on the curve are: (a) the on-set temperature (T_1), at 100°C, indicating the start of the polymerization reaction, (b) the minor exotherm peak (T_2) at 149°C, (c) the major exotherm peak (T_3), at 213°C and (d) the temperature at the completion of the reaction (T_4), at 253°C. DSC thermograms obtained for the experimental resin batches at a heating rate (ϕ) of 10°C/minute are given in Appendix B.

TABLE 7
BF_3 CATALYST ANALYSIS OF ALTERED RESIN BATCHES (% - WT/WT)

Batch No.	Hercules Formulation	MCAIR Analysis	Δ[1]
CRT-76-1	1.13	1.24 (1.24, 1.24)	+0.11
CRT-77-2	1.10	1.22 (1.23, 1.21)	+0.12
CRT-77-3	1.16	1.29 (1.27, 1.30)	+0.13
CRT-79-4	1.08	1.18 (1.17, 1.18)	+0.10
CRT-79-5	1.19	1.38 (1.40, 1.36)	+0.19
CRT-76-6	1.10	1.23 (1.23, 1.23)	+0.13
CRT-78-7	1.15	1.31 (1.30, 1.32)	+0.16
CRT-76-8	1.09	1.22 (1.22, 1.22)	+0.13
CRT-78-9	1.17	1.32 (1.32, 1.32)	+0.15
CRT-76-10	1.08	1.20 (1.23, 1.17)	+0.12
CRT-79-11	1.18	1.29 (1.27, 1.32)	+0.11
CRT-76-12	1.04	1.17 (1.16, 1.17)	+0.13
CRT-75-13	0.57	0.64 (0.65, 0.62)	+0.07
CRT-75-14	2.23	2.44 (2.45, 2.43)	+0.21
CRT-75-15	1.13	1.28 (1.26, 1.30)	+0.15
CRT-72-16	1.13	1.45 (1.47, 1.43)	+0.32
			+0.14 Avg.

(1) Difference between Hercules formulation and MCAIR test data (ave.)

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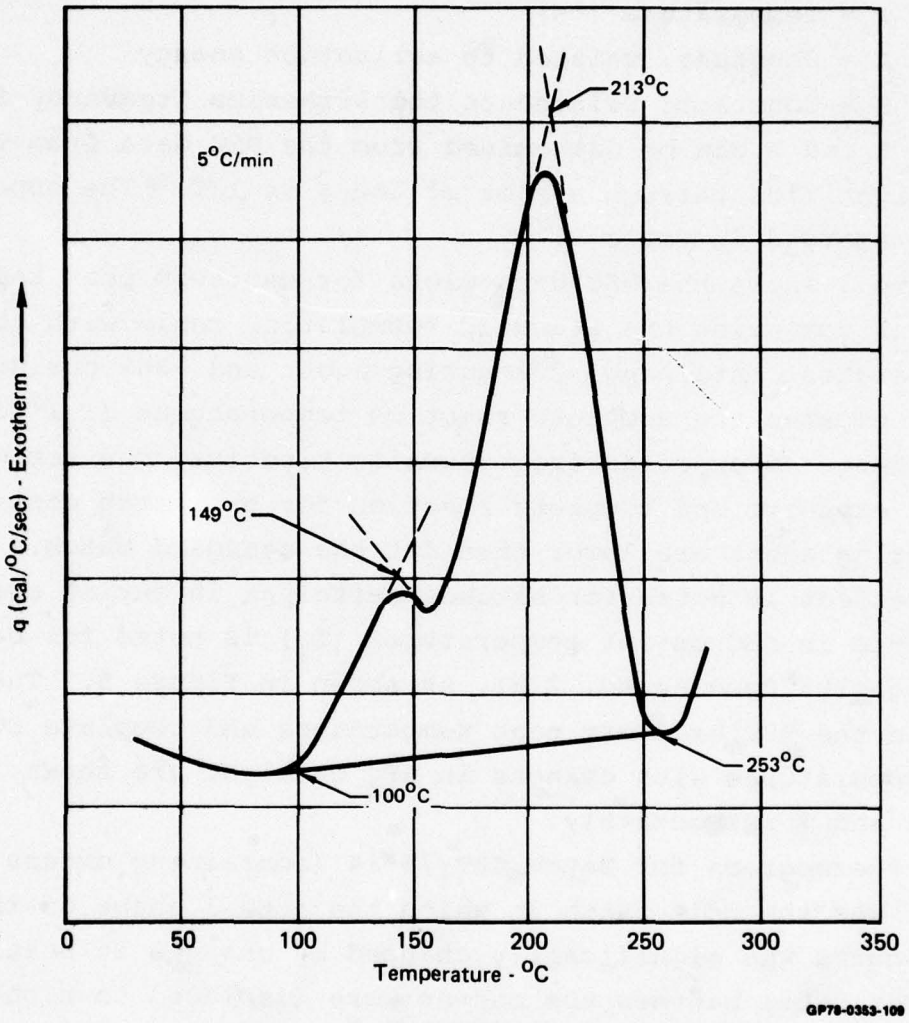

FIGURE 2
DSC THERMOGRAM FOR 3501-6 RESIN

Any of the sets of critical temperature points, for example, exotherm peak temperatures, for a series of DSC runs are related to heat up rate by the following expression:

$$\log \phi = A/T + B$$

Where:

ϕ = Heat up rate (°C/Min)

T = Temperature (°K)

A = Constant, related to activation energy

B = Constant, related to the Arrhenius frequency factor

Constants A and B can be determined from the DSC data from the best straight line through a plot of log ϕ vs 1/T. The experimental data are recorded in Table 8.

Figure 3 shows the DSC data plots for exotherm peak temperatures (T_3) comparing the standard formulation resin with the altered batches containing +20% curing agent and -20% curing agent. Figure 4 compares the complete reaction temperatures (T_4) for the same batches. As expected from reaction kinetics, the temperatures of exotherm and complete reaction for the batch containing excess curing agent are lower than for the standard batch. The opposite effect is noted for batches deficient in curing agent. A difference in DSC on-set temperatures (T_1) is noted for batches containing $\pm$20% Epoxide No. 2(H), as shown in Figure 5. The changes in the DSC exotherm peak temperature and complete reaction temperatures with changes in BF_3 catalyst are shown in Figures 6 and 7 respectively.

The thermograms for Batch CRT-75-14 (containing excess catalyst) was the only batch in which the actual shape of the exotherm curve was significantly changed by changes in heating rates. For other batches the curves were displaced to higher temperatures as the heating rates increased but the curve shapes stayed much the same. The thermograms obtained for all three heating rates (5, 10 and 20°C 1 min) are shown for batch CRT-75-14, Figures 8, 9, and 10. The excess BF_3 Catalyst

TABLE 8
DSC DATA FOR ALTERED RESIN BATCHES

Batch No. (Variation)	Heating Rate (°C/min)	Temperature - °C			
		On Set, T_1	Minor Exotherm, T_2	Major Exotherm, T_3	Complete Reaction, T_4
CRT-76-1 (Standard)	5	100	149	213	253
	10	115	162	232	267
	20	132	171	252	287
CRT-77-2 (+10% Curing Agent)	5	103	149	207	250
	10	118	162	227	266
	20	123	176	247	278
CRT-77-3 (−10% Curing Agent)	5	94	144	210	250
	10	112	160	232	268
	20	127	176	252	288
CRT-79-4 (+20% Curing Agent)	5	107	147	205	247
	10	117	165	225	263
	20	143	175	244	277
CRT-79-5 (−20% Curing Agent)	5	104	149	217	258
	10	110	160	237	275
	20	132	173	257	288
CRT-76-6 (+20% Epoxide No. 2(H))	5	103	149	213	255
	10	117	160	233	270
	20	137	174	250	284
CRT-78-7 (−20% Epoxide No. 2(H))	5	100	147	210	252
	10	112	160	228	267
	20	121	172	247	281
CRT-76-8 (+40% Epoxide No. 2(H))	5	110	140	215	265
	10	115	165	237	273
	20	135	172	250	283
CRT-78-9 (−40% Epoxide No. 2(H))	5	103	150	211	258
	10	110	162	232	270
	20	120	172	249	282
CRT-76-10 (+50% Epoxide No. 3(H))	5	102	152	219	258
	10	112	164	237	274
	20	122	177	254	290
CRT-79-11 (−50% Epoxide No. 3(H))	5	101	150	214	254
	10	112	165	234	267
	20	122	175	250	285
CRT-76-12 (+100% Epoxide No. 3(H))	5	105	153	221	263
	10	112	165	235	277
	20	149	175	255	296
CRT-75-13 (−50% BF_3 Catalyst)	5	106	138	219	267
	10	120	153	243	285
	20	122	175	265	298
CRT-75-14 (+100% BF_3 Catalyst)	5	107	146	212	253
	10	112	166	230	261
	20	125	177	245	278
CRT-75-15 (Understaged)	5	103	152	215	257
	10	113	165	235	274
	20	127	178	253	287
CRT-75-16 (Overstaged)	5	104	149	212	258
	10	112	165	232	270
	20	128	172	252	289

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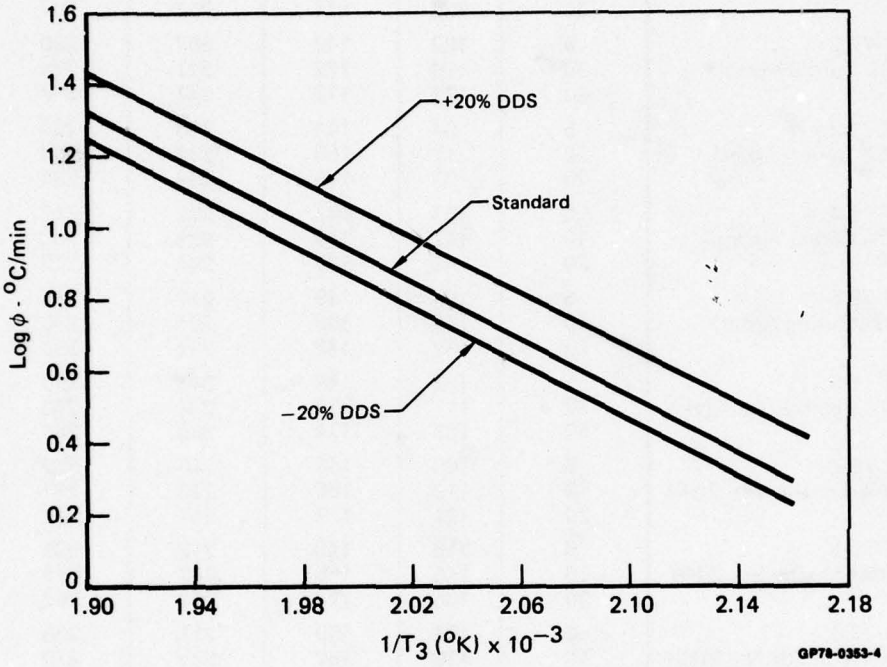

FIGURE 3
DSC DATA PLOTS: ALTERED RESIN BATCHES
(EXOTHERM PEAKS - VARIED CURING AGENT)

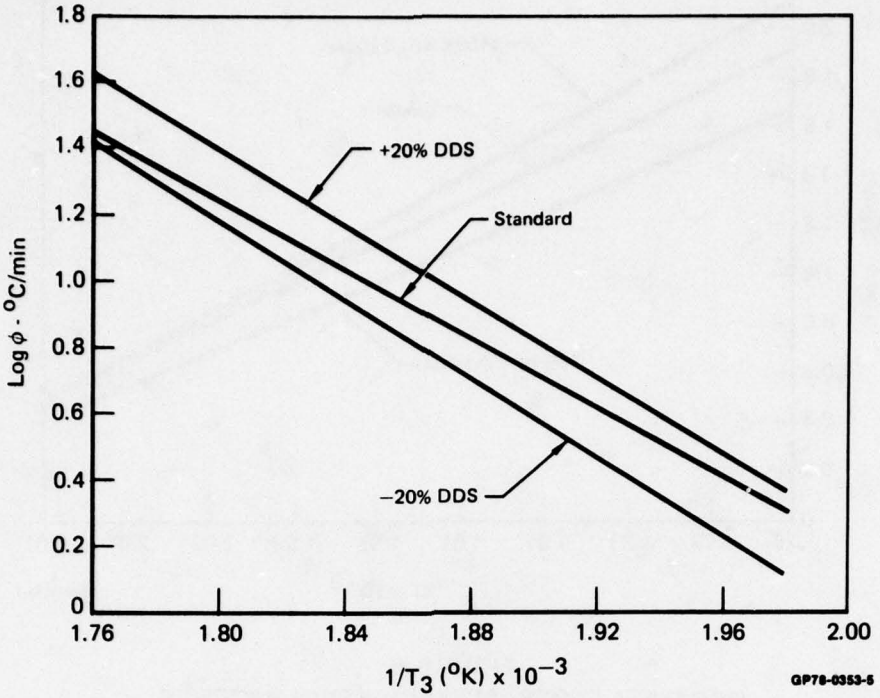

FIGURE 4
DSC DATA PLOTS: ALTERED RESIN BATCHES
(COMPLETE REACTION - VARIED CURING AGENT)

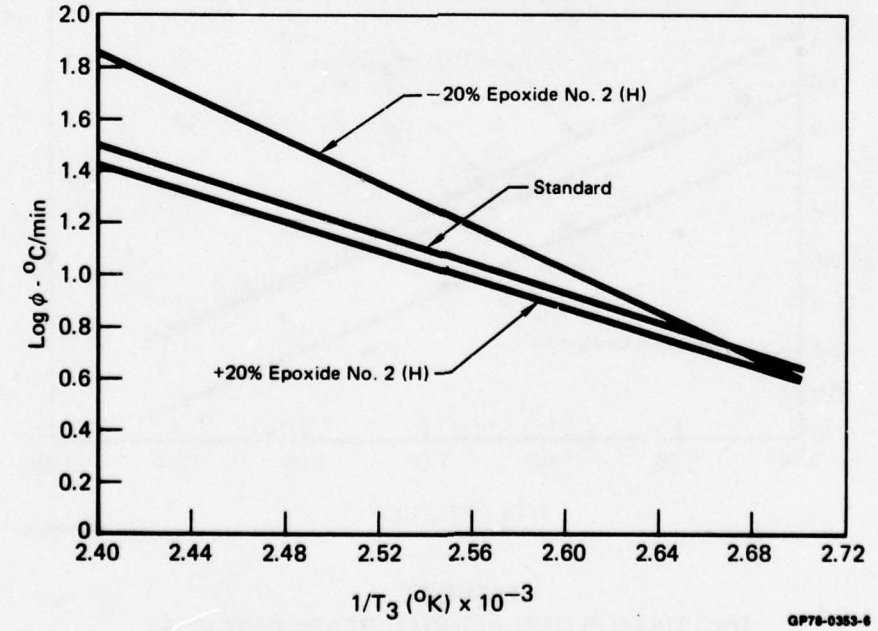

FIGURE 5
DSC DATA PLOTS: ALTERED RESIN BATCHES
(ON-SET PEAKS - VARIED EPOXIDE NO. 2(H))

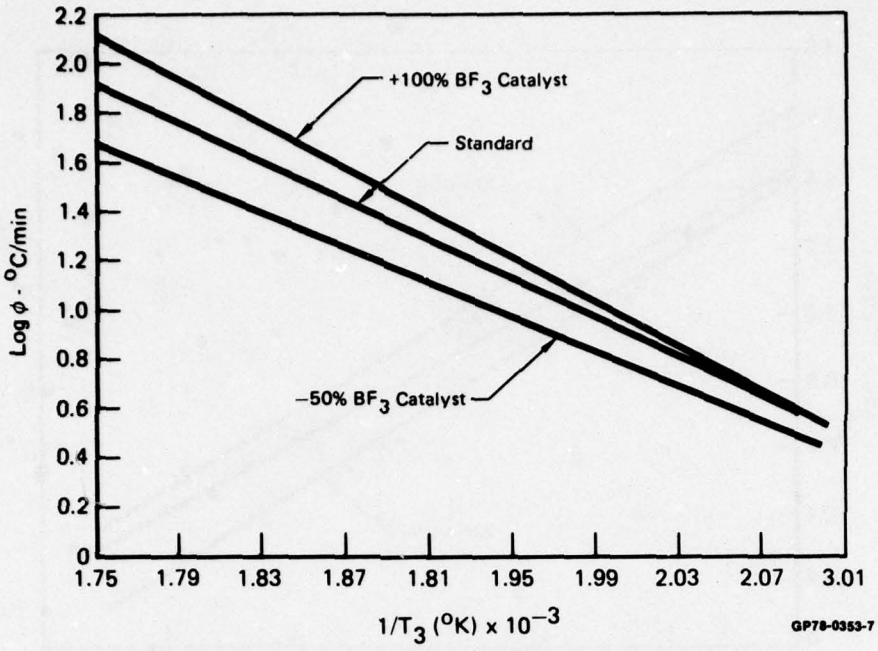

FIGURE 6
DSC DATA PLOTS: ALTERED RESIN BATCHES
(EXOTHERM PEAKS - VARIED CATALYST)

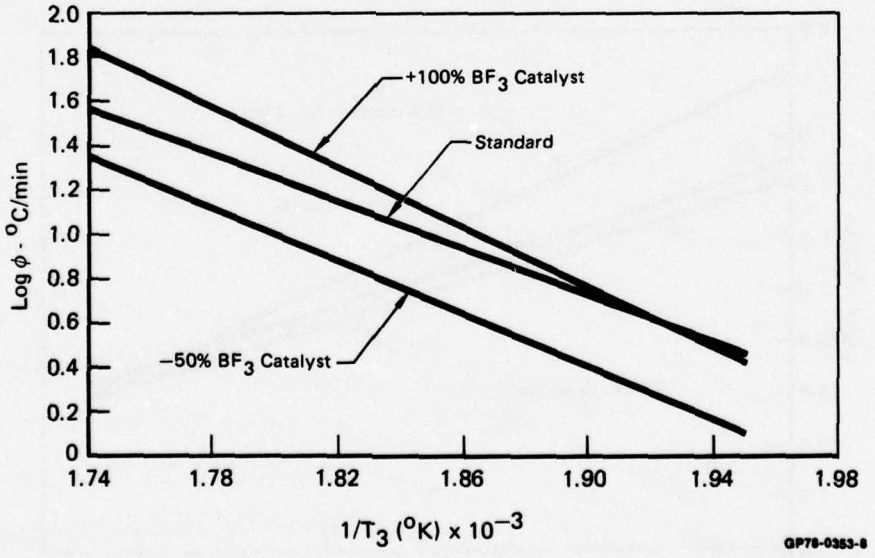

FIGURE 7
DSC DATA PLOTS: ALTERED RESIN BATCHES
(COMPLETE REACTION - VARIED CATALYST)

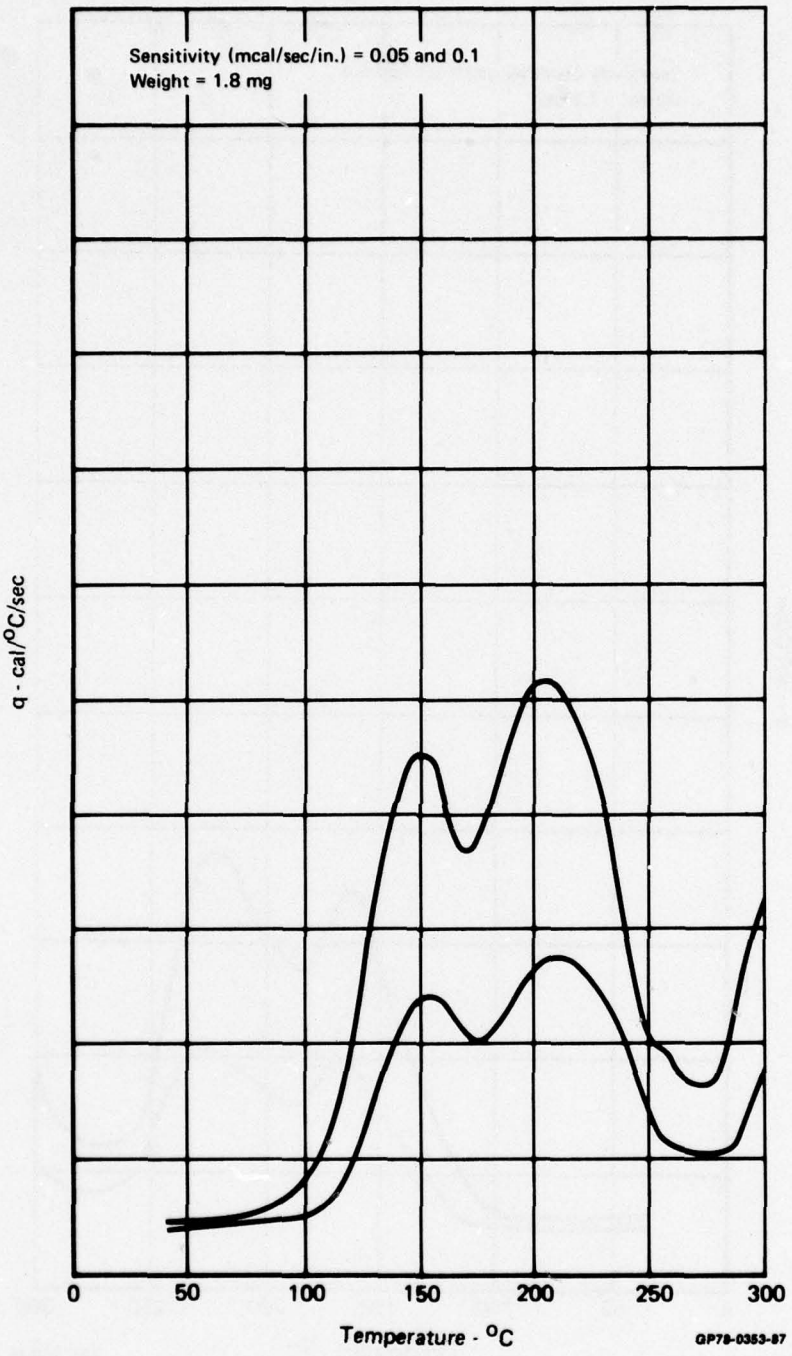

FIGURE 8
DSC THERMOGRAM, 3501-6 BATCH CRT-75-14, 5°C/MIN

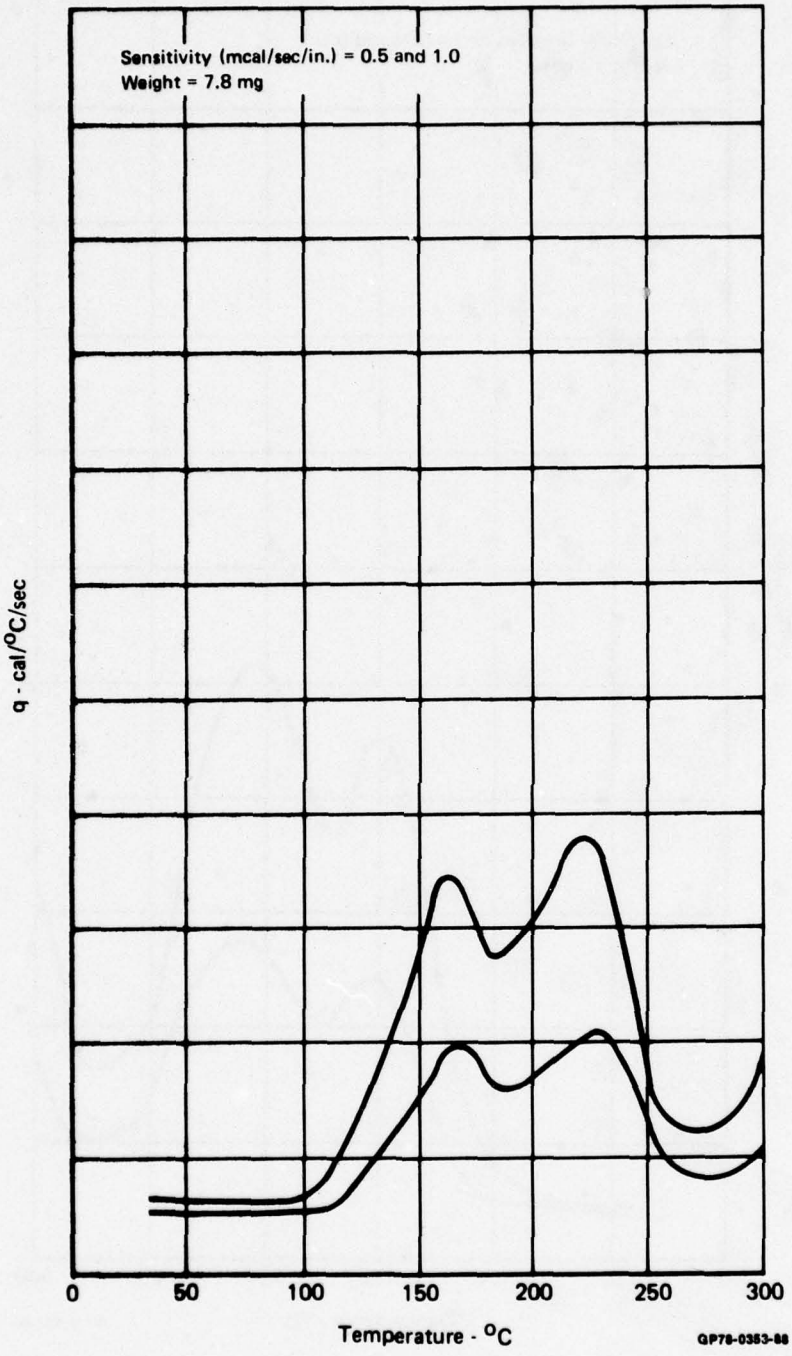

FIGURE 9

DSC THERMOGRAM, 3501-6 BATCH CRT-75-14, 10°C/MIN

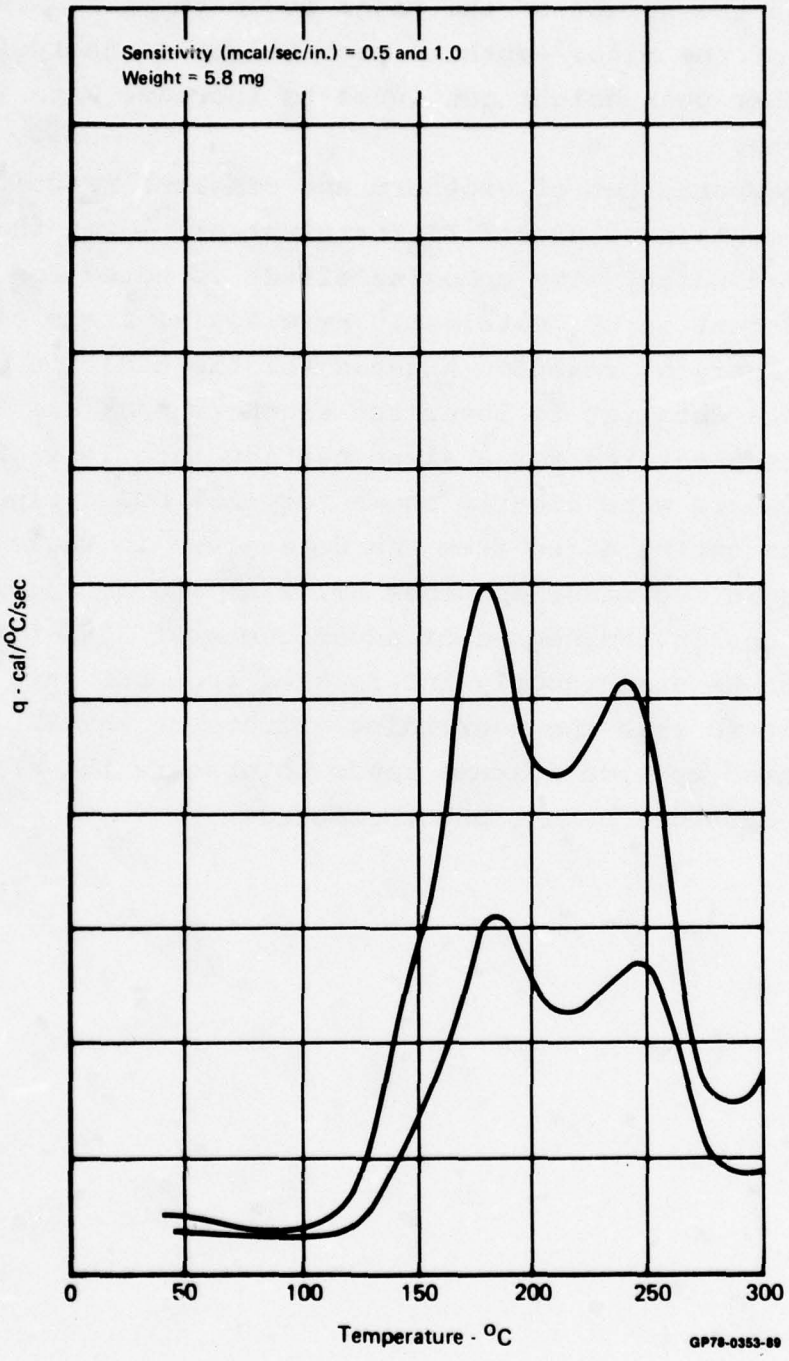

FIGURE 10
DSC THERMOGRAM, 3501-6 BATCH CRT-75-14, 20°C/MIN

causes an increase in the height of the minor exotherm peak relative to the height of the major exotherm peak. Further, the ratio of the minor exotherm peak height to that of the major exother peak height continues to increase with increased heating rate.

The temperatures of exotherm and complete reaction for the batch containing excess BF_3 catalyst are lower than for the standard batch. The opposite effect is noted for the batch deficient in BF_3 catalyst. Here again, it is consistent with the theory of reaction kinetic for the addition of greater amounts of a catalyst to lower the exotherm peak and complete reaction temperatures for a given heating rate (ϕ). Similar DSC differences were clearly shown for $\pm$20% DDS curing agent. However, as can be noted from the data given in Table IV, variations in the minor epoxides No. 2(H) and No. 3(H) and small changes in the degree of advancement of 3501-6 formulations cannot be unambigously interpreted from DSC data alone. It is believed that the overriding effects of the BF_3 on diamine cured epoxide systems tends to obscure the effect of the minor epoxides on the DSC thermogram.

3.1.3 Dynamic Mechanical Properties and Moisture Sensitivity of Special Resins - Cured neat resin coupons were prepared from the special batches of 3501-6 resin. One set of coupons were tested by Dynamic Mechanical Analysis (DMA). Another set of coupons were examined for moisture sensitivity.

3.1.3.1 Dynamic Mechanical Analysis - The Rheovibron Viscoelastometer, Model DDV-II-C (Toyo Baldwin Co. Ltd.) was used to study the dynamic mechanical properties of cured neat resin specimens prepared from the special batches of off-specification 3501-6. The neat resin specimens were prepared for DMA by first vacuum degassing the resin melt at 240°F. The deaired melt was then poured into a stainless steel mold preheated to 250°F and again vacuum degassed. Shims and a cover plate were used to provide the desired specimen thickness and surface characteristics. The temperature was held at 250°F for 60-90 minutes, after which the temperature was increased to 350°F and held for 120 minutes. The cured specimens of 0.02 inch thickness were removed and cut to approximately 2.5 inches in length and 0.2 inches wide. A final width of 0.15 inches was obtained by sanding to remove any edge flaws. Each specimen was post cured 8.5 hours at 350°F, just prior to the DMA run.

A schematic diagram of the Rheovibron instrument is shown in Figure 11.

For the Rheovibron, a sinusoidal strain is applied at one end of the test specimen and the stress response is measured at the other. For a perfectly elastic material, the stress and strain would be "in phase", that is stress would be a maximum when strain is a maximum. For viscoelastic materials, such as the cured epoxy resins, the stress is out of phase with the strain. The extent that stress is out of phase with strain is measured as the phase angles (δ). The value for TAN δ is read directly from the instrument. TAN δ is referred to as the loss tangent. It is the ratio of viscous to elastic response and is directly proportional to the damping or energy absorption in an oscillating deformation. The value of (E^*) is calculated

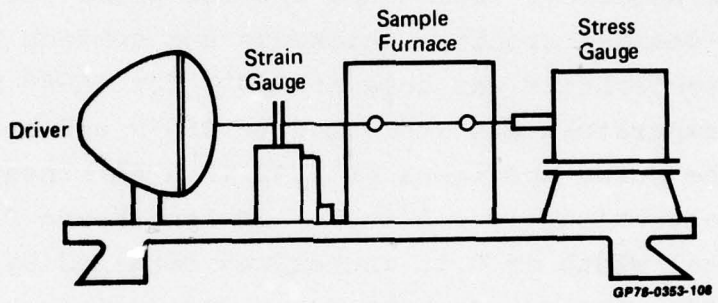

FIGURE 11
SCHEMATIC DIAGRAM OF THE RHEOVIBRON INSTRUMENT

from specimen dimensions and instrument readings representing the force (D) and the amplitude factor (A). E* is the ratio of maximum stress to maximum strain. Dynamic mechanical measurements were made at 100 Hz from room temperature to 270°C at a scan rate of 1° C/minute. The plots for log TAN δ and log E* vs temperature are given in Figure 12 to 27.

The temperature for the peak of the TAN δ curve is referred to as the dynamic glass transition temperature (Tg). Since crosslinking of the polymer restricts the mobility of the polymer segments, higher dynamic Tg's are associated with more efficient crosslinking for a given system. The dynamic Tg's for the special batches of 3501-6 are given in Table 9.

The differences between dynamic Tg values of the off-specification batches and the standard formulation of 3501-6 were smaller than expected, considering the relatively large compositional changes. The highest dynamic Tg was obtained for batch CRT-79-4 containing the highest amount (+20%) of curing agent and the lowest Tg was obtained for batch CRT-79-5, having the lowest amount (-20%) of the curing agent. The batch with the highest amount of curing agent is closer to equimolar amounts of DDS and Epoxide No 1(H) than the standard formulation and thus may have a higher crosslink density under the cure cycle used. The increased dynamic Tg for batch CRT-78-9 (-40% Epoxide No. 2(H) may be due to the fact that Epoxide No. 2(H) has the lowest viscosity and epoxide functionality of the three epoxies in the formulation and thus may have a plasticizing effect; however, increase amounts of Epoxide No. 2(H) did not lower the Tg. The reason for the lower dynamic Tg for batch CRT-76-12 (+100% Epoxide No. 3(H) is not clear.

As noted from the plots (Figures 12 to 27), (E*) begins to drop approximately 30-40°C ahead of the dynamic Tg's obtained using the peak of the TAN δ curves. The temperature associated with this drop in E* is probably a better indicator of the highest possible use temperature of a particular resin formulation, than the dynamic Tg. The dynamic Tg has also been reported to run considerably higher than the glass transition

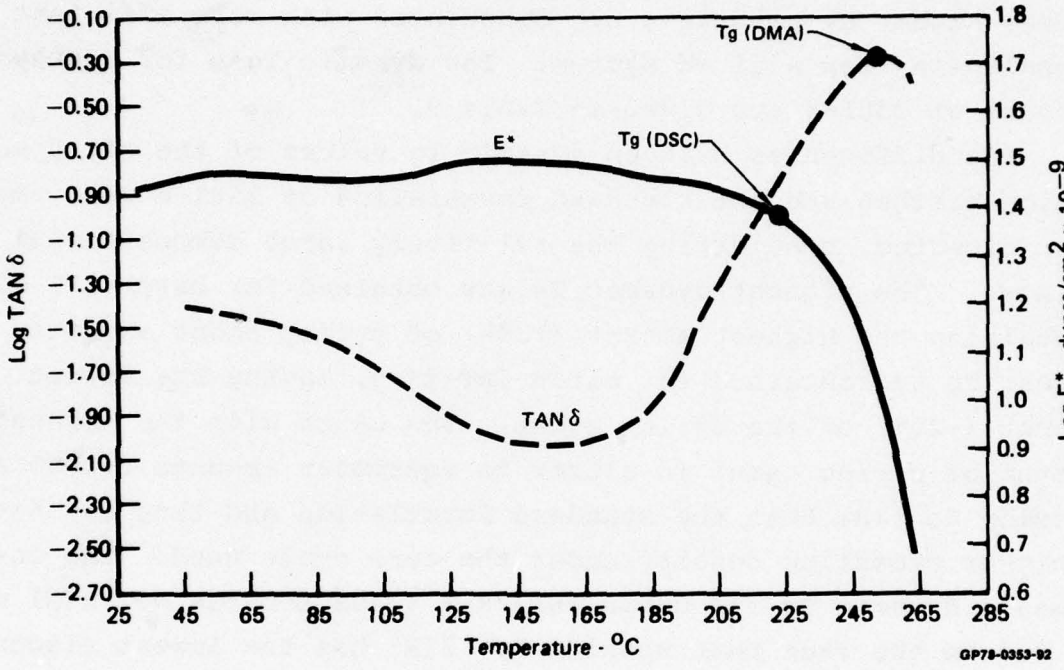

FIGURE 12
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-76-1
(STANDARD FORMULATION)

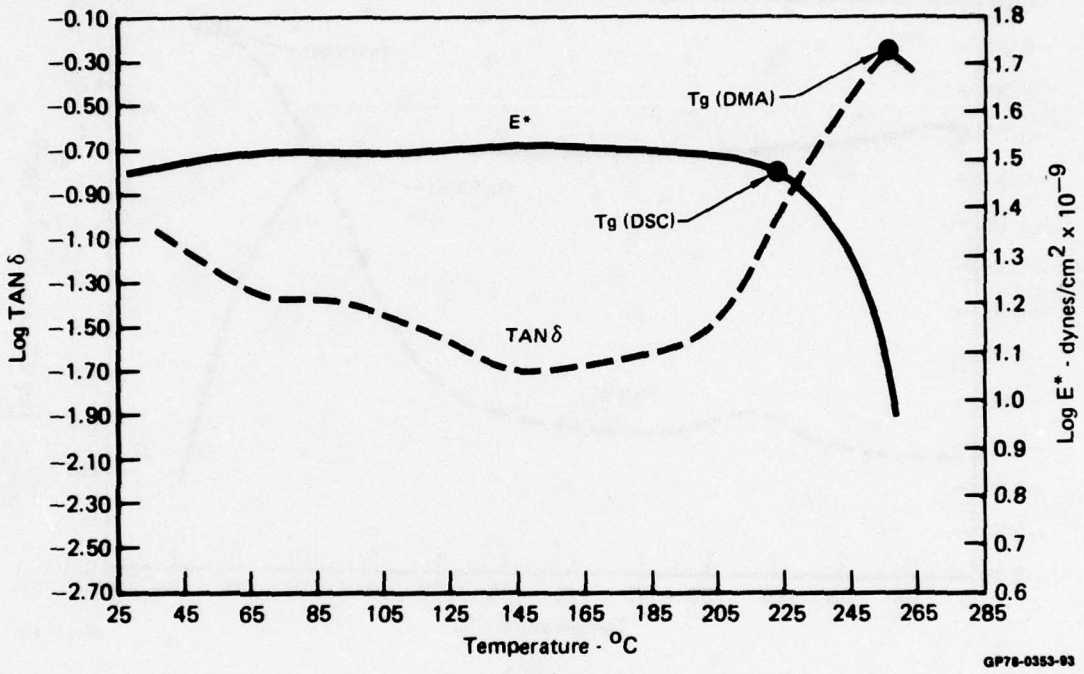

FIGURE 13
TAN AND E* vs TEMPERATURE FOR BATCH NO. CRT-77-2
(+10% Curing Agent)

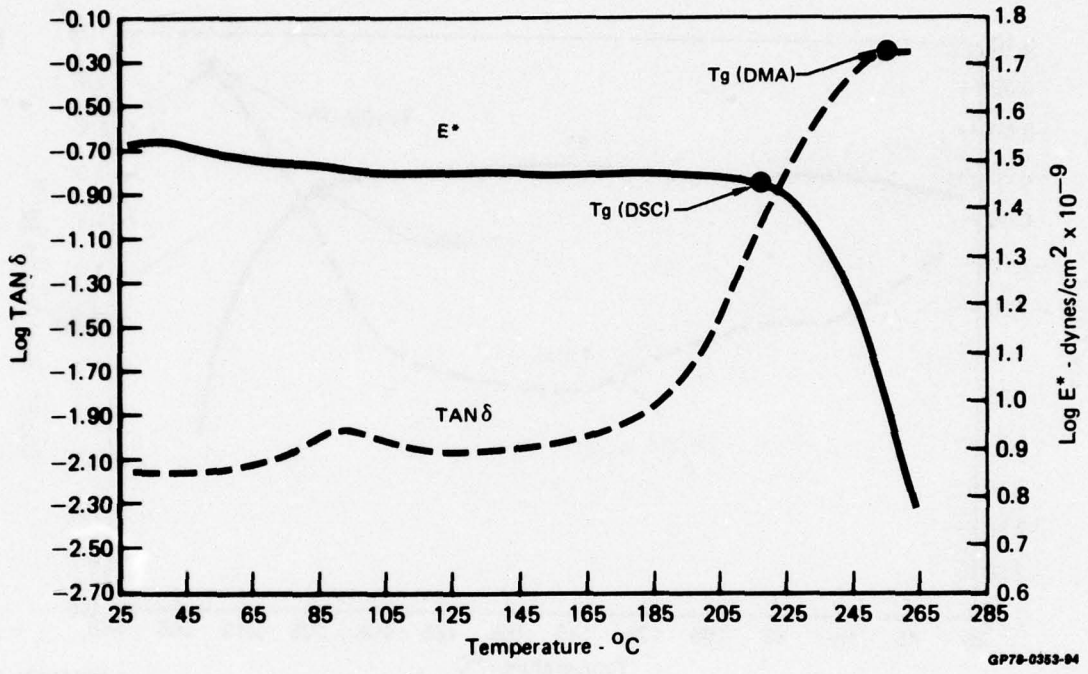

FIGURE 14
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-77-3
(—10% Curing Agent)

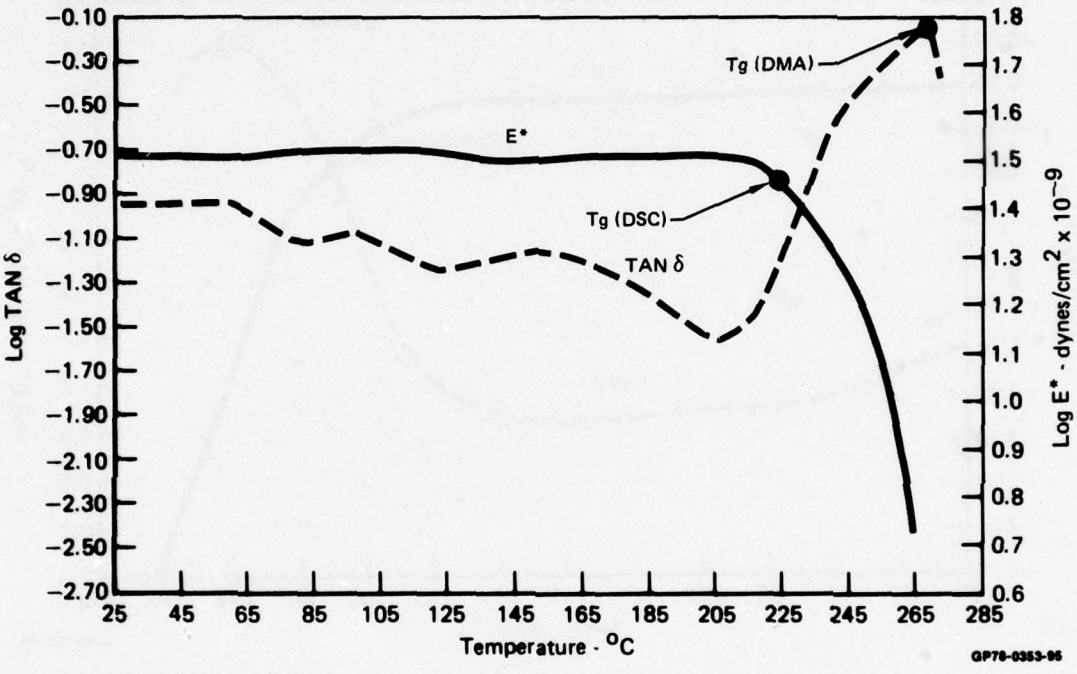

FIGURE 15
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-79-4
(+20% Curing Agent)

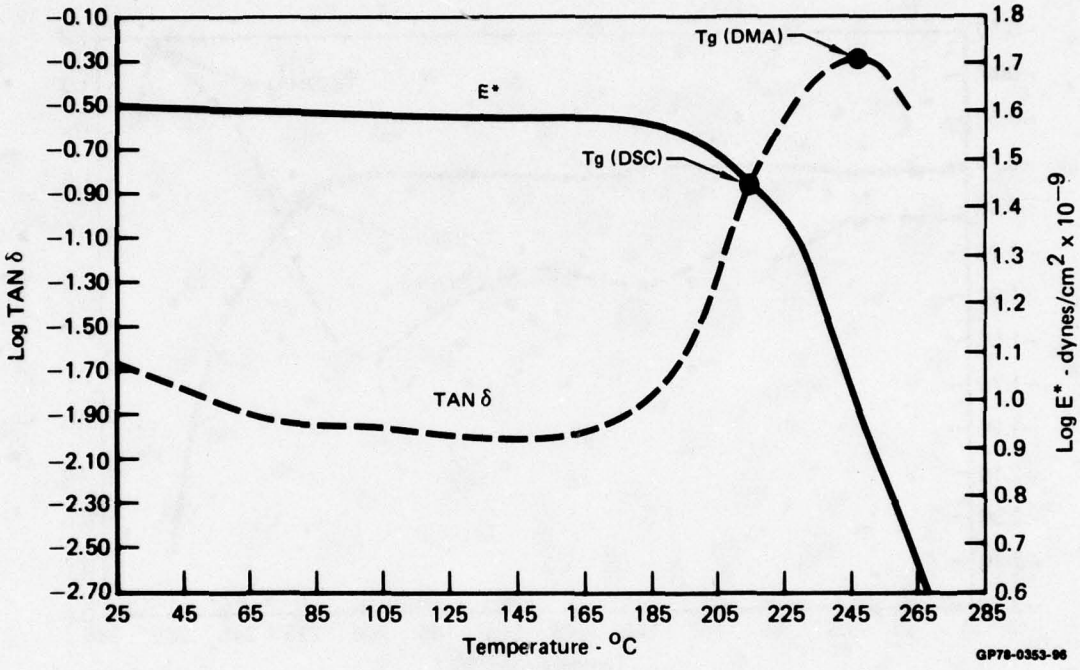

FIGURE 16
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-79-5
(—20% Curing Agent)

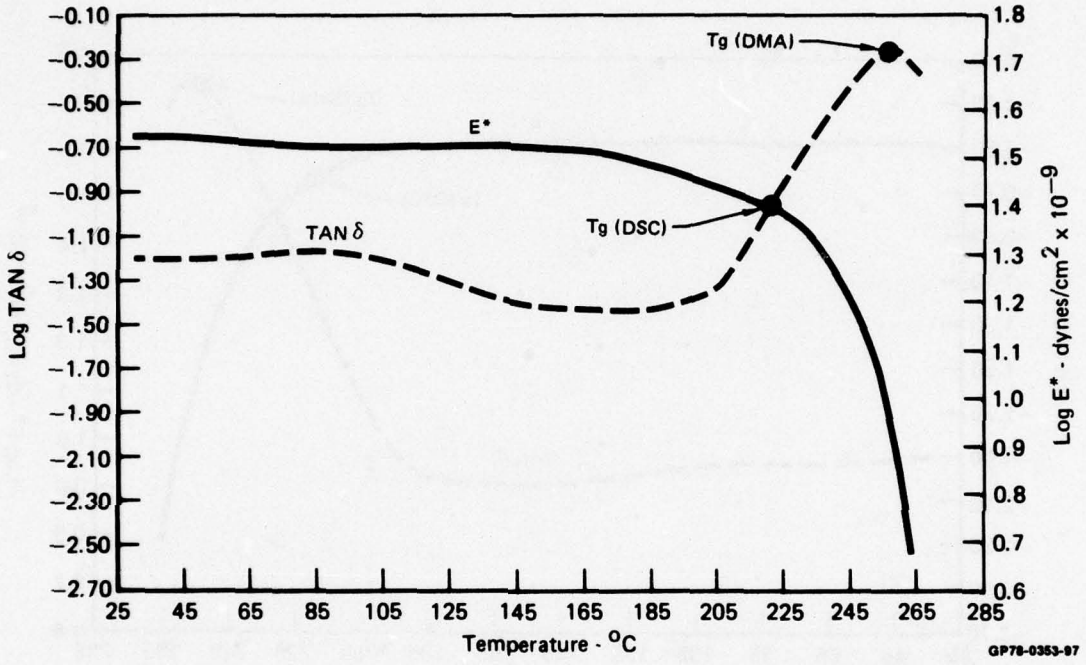

FIGURE 17
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-77-6
(+20% Epoxide No. 2(H))

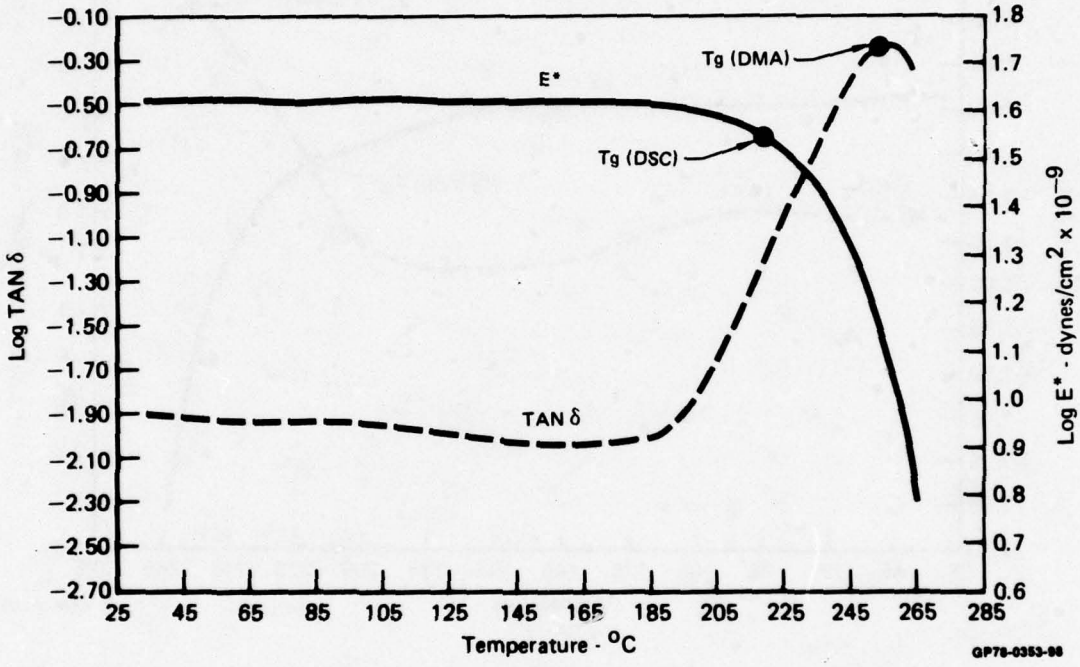

FIGURE 18
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-77-7
(—20% Epoxide No. 2(H))

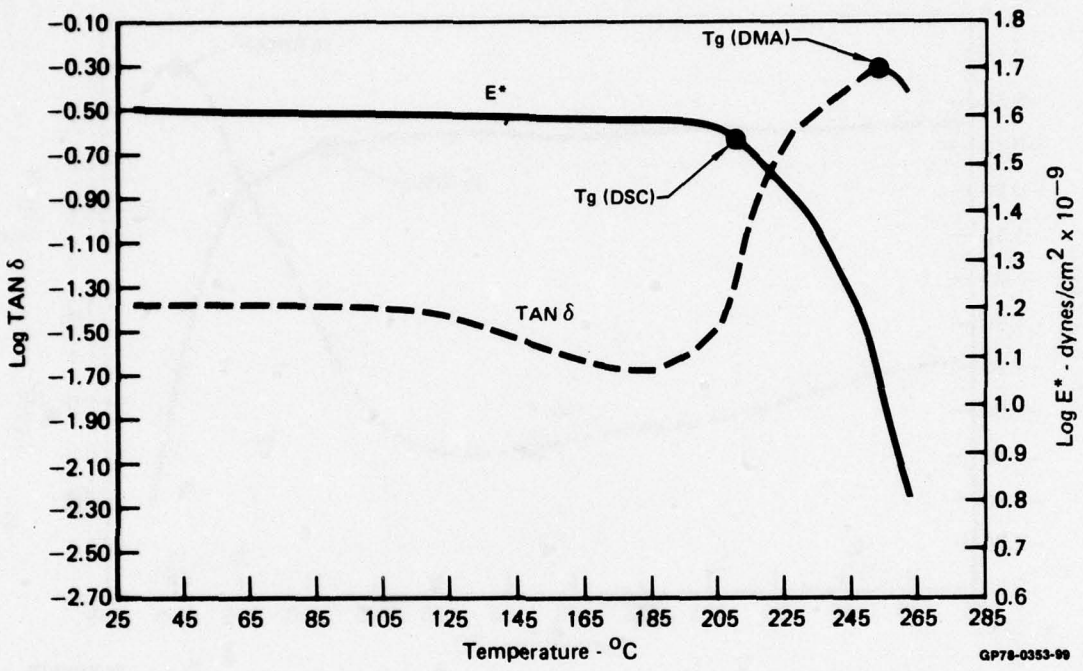

FIGURE 19
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-77-8
(+ 40% Epoxide No. 2(H))

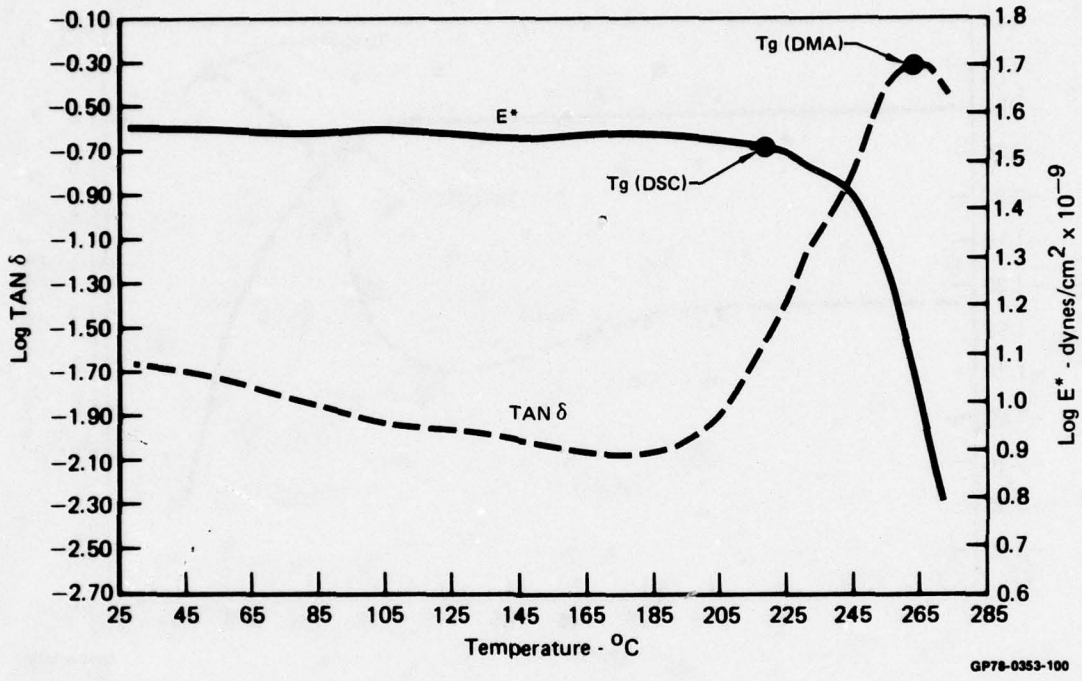

FIGURE 20
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-78-9
(—40% Epoxide No. 2(H))

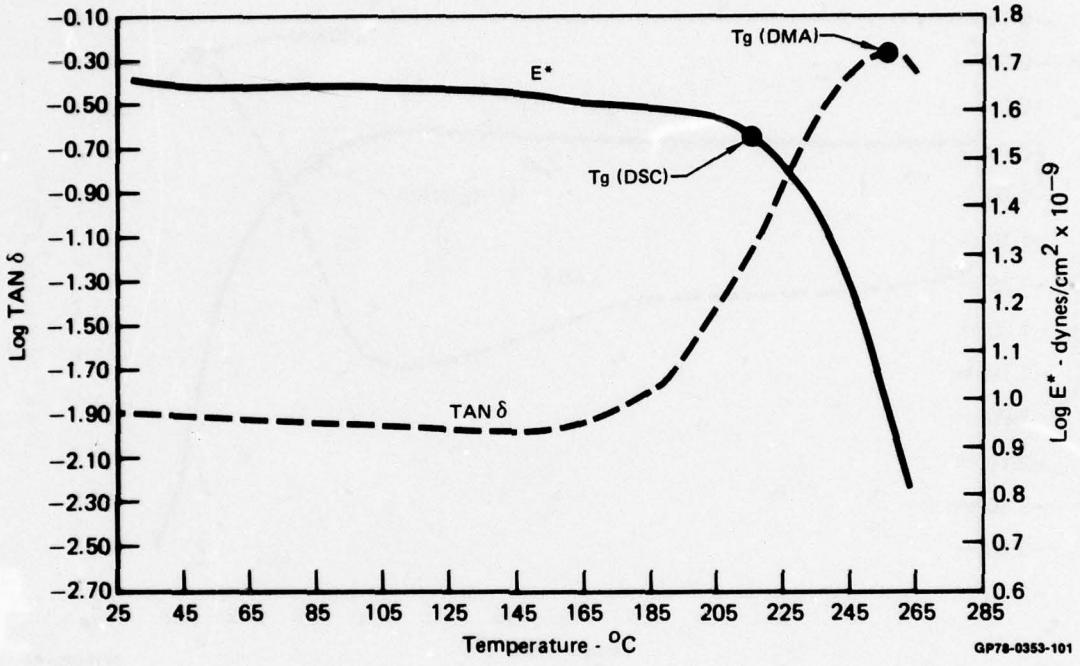

FIGURE 21
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-76-10
(+50% Epoxide No. 3(H))

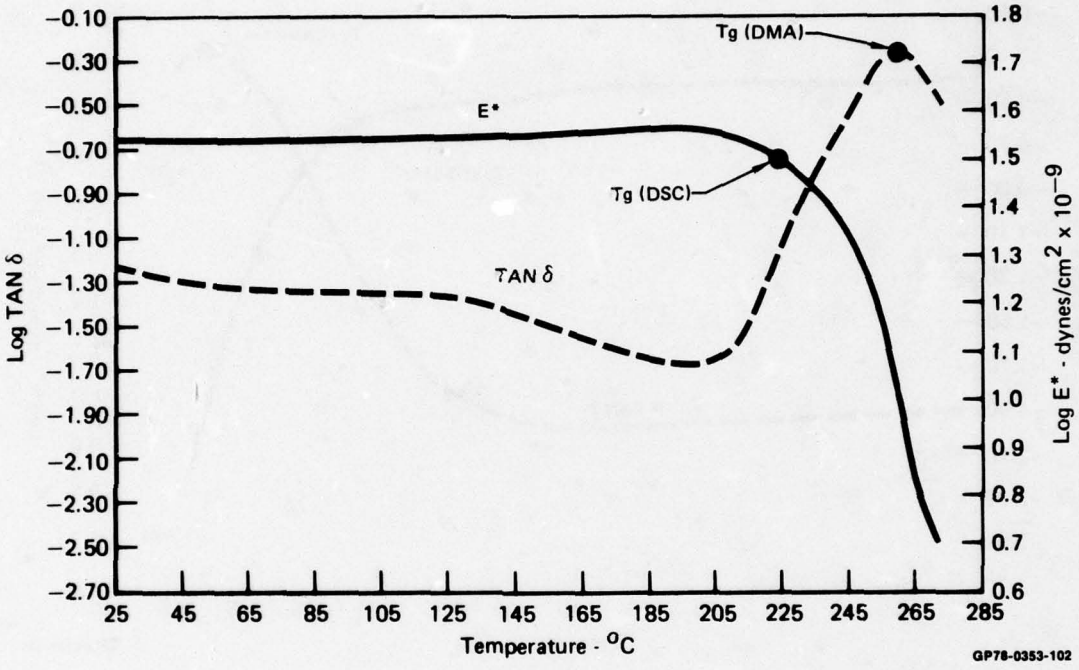

FIGURE 22
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-79-11
(—50% Epoxide No. 3(H))

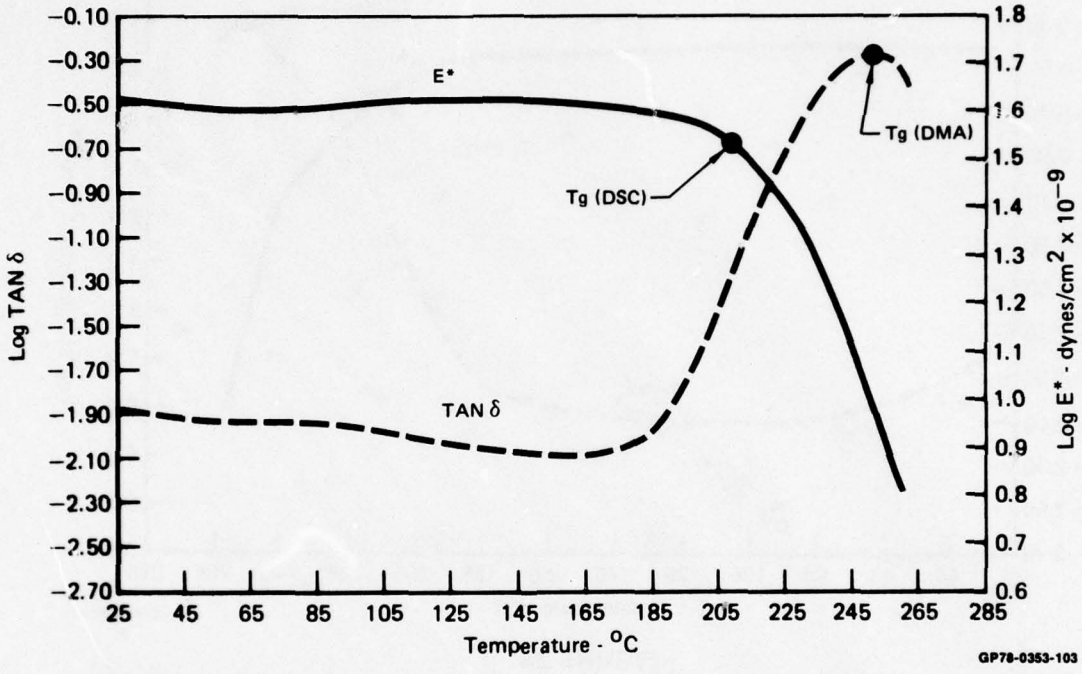

FIGURE 23
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-76-12
(+ 100% Epoxide No. 3(H))

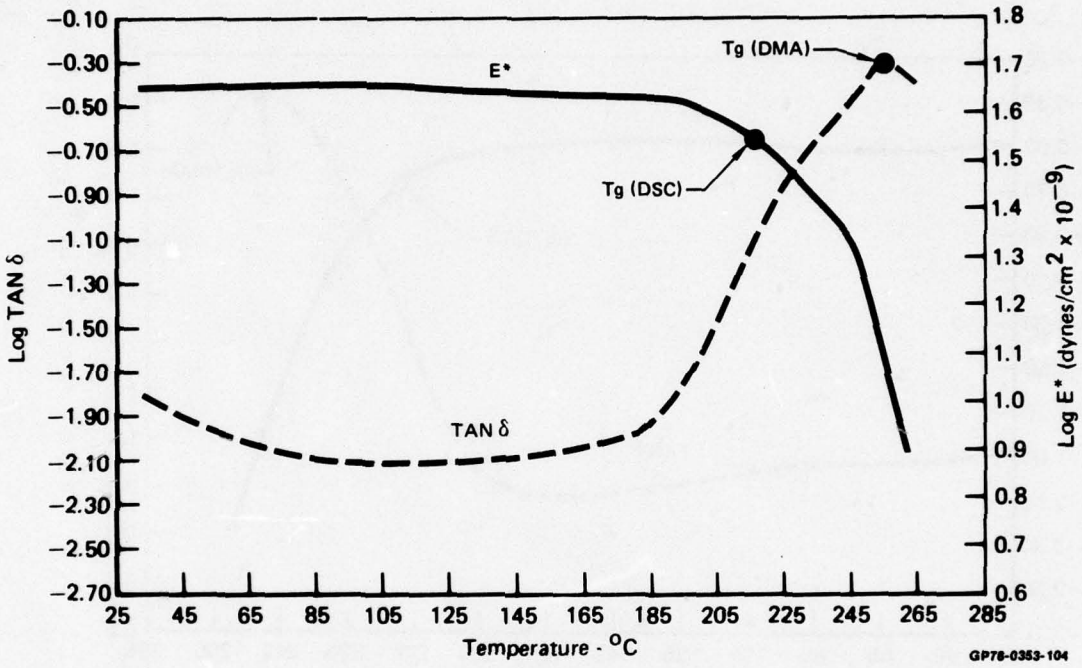

FIGURE 24
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-75-13
(—50% BF_3 Catalyst)

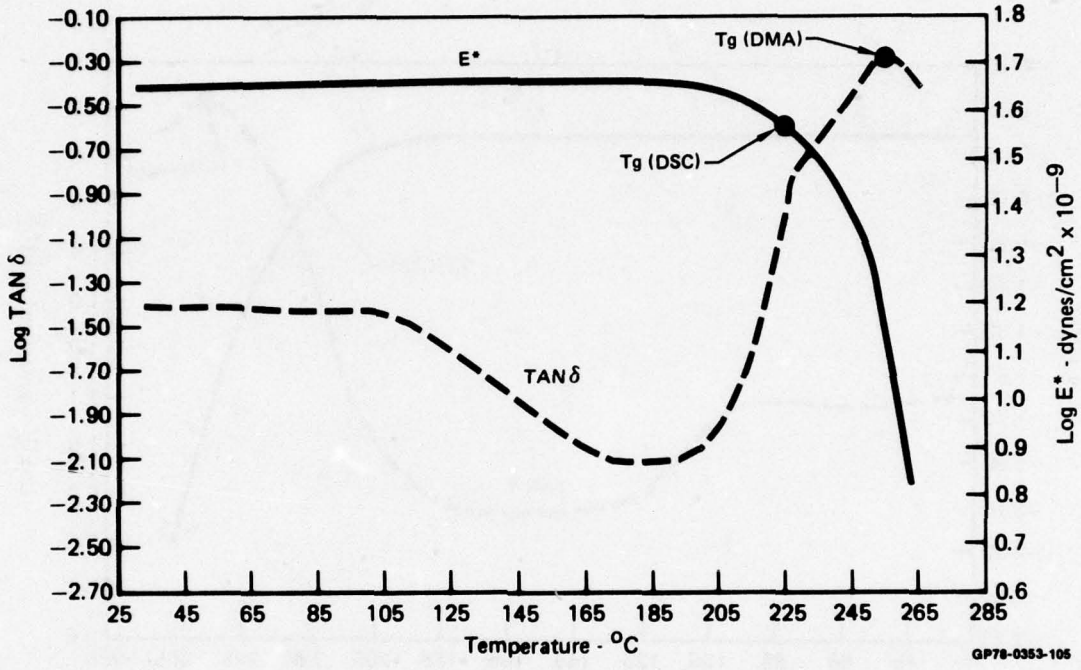

FIGURE 25
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-77-14
(+100% BF_3 Catalyst)

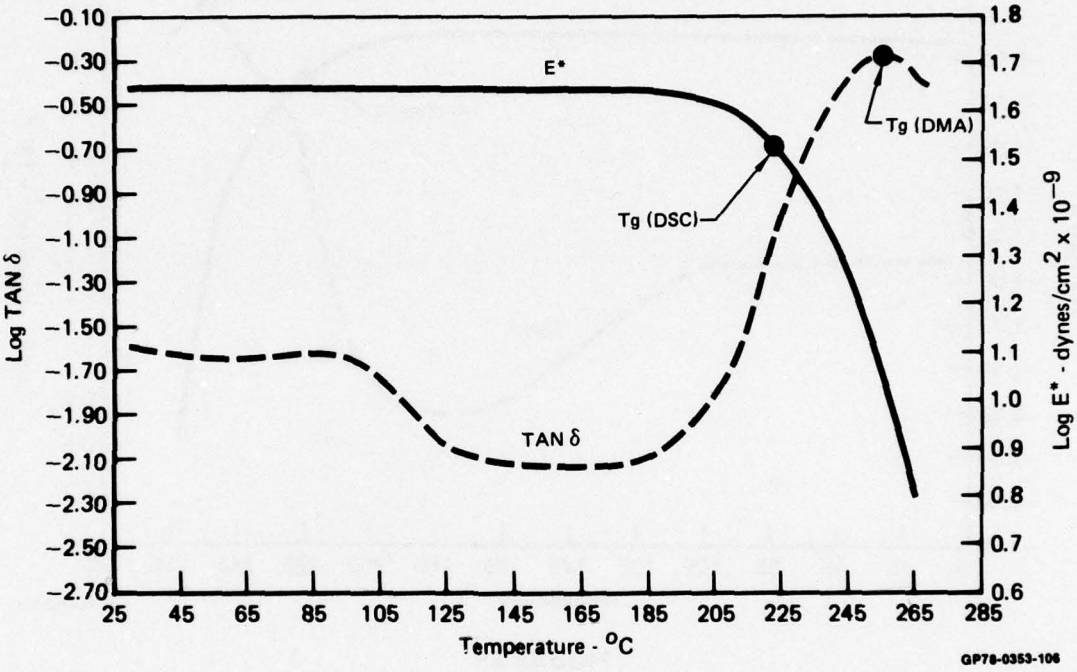

FIGURE 26
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-75-15
(Understaged)

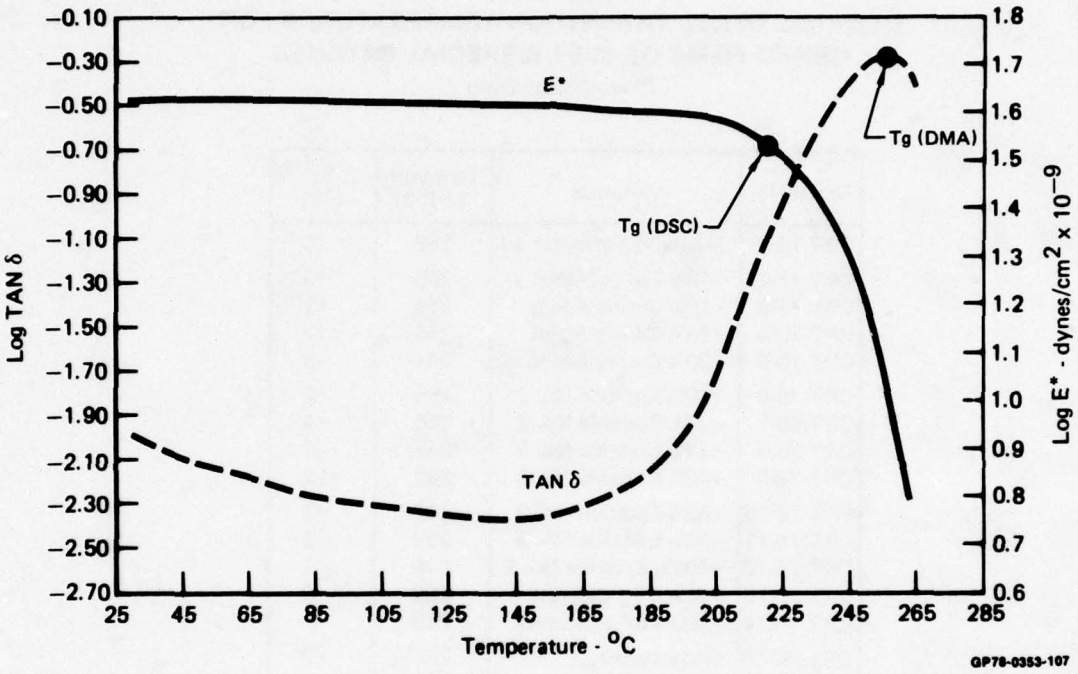

FIGURE 27
TAN δ AND E* vs TEMPERATURE FOR BATCH NO. CRT-75-16
(Overstaged)

TABLE 9
DYNAMIC GLASS TRANSITION TEMPERATURES FOR CURED FILMS OF 3501-6 SPECIAL BATCHES
Rheovibron Data

Batch No.	Variation	Dynamic Tg (°C)	Δ Tg(1) (°C)
CRT-76-1	Standard Formulation	252	0
CRT-77-2	+10% Curing Agent	255	+3
CRT-77-3	−10% Curing Agent	253	+1
CRT-79-4	+20% Curing Agent	265	+13
CRT-79-5	−20% Curing Agent	244	−8
CRT-76-6	+20% Epoxide No. 2	255	+3
CRT-78-7	−20% Epoxide No. 2	256	+4
CRT-76-8	+40% Epoxide No. 2	252	0
CRT-78-9	−40% Epoxide No. 2	262	+12
CRT-76-10	+50% Epoxide No. 3	254	+2
CRT-79-11	−50% Epoxide No. 3	258	+6
CRT-76-12	+100% Epoxide No. 3	245	−7
CRT-75-13	−50% BF_3 Catalyst	255	+3
CRT-75-14	+100% BF_3 Catalyst	253	+1
CRT-75-15	Understaged	255	+3
CRT-75-16	Overstaged	253	+1

(1) ΔTg is [Tg (Varied Batch) - Tg (Standard Batch)]

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temperature obtained under static conditions, such as the thermal analysis techniques of differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) measurements based on the change in coefficient of expansion, Reference (2).

DSC Determination of Tg - The "static" Tg values were determined by DSC and the data points are shown on the complex modulus curves for the DMA plots (Figures 12-27). In most cases the Tg by DSC is very close to the temperature where the complex modulus begins to drop rapidly with increased temperature. The DSC data for glass transition is given in Table 10. The values obtained for the "dynamic" Tg range from 30 to 50°C higher than the "static" Tg values determined by DSC. The differences among batches for Tg values, as determined by DSC, is quite small. As with the dynamic Tg's, the DSC Tg's show a trend of increasing values as the percent curing agent is increased from 20.9 to 28.4 percent (wt/wt). Contrary to Rheovibron results, the Tg measured by DSC increases with increasing BF_3 catalyst.

3.1.3.2 Moisture Sensitivity - Absorption of moisture was determined using the cast film specimens prepared for the determination of dynamic mechanical properties by Rheovibron. Moisture pickup was monitored during exposure to elevated temperature and humidity (140°F, 95% RH) over a period of 44 days. The data is compiled in Table 11. These thin films, of approximately 0.02 inch thickness, reached saturation rapidly. Most of the specimens were moisture saturated in 18 to 22 days. Since most specimens had absorbed more than 60% of the total saturation amount of moisture prior to the first days measurement, accurate diffusion coefficients for company rate of moisture pickup could not be measured. It can be seen from inspection of the data however, that the rates of moisture absorption are quite similar. It does appear that the rate of moisture absorption increases with increasing amount BF_3 catalyst. The total moisture absorbed by all specimens ranged from 5-6% by weight over the initial 28 day exposure. Again, the only trend noted is an increase in total moisture absorbed with increased percent of BF_3 catalyst. As noted above, saturation was complete in about 18 days and the

TABLE 10
STATIC GLASS TRANSITION TEMPERATURES FOR CURED FILMS OF 3501-6 SPECIAL BATCHES
DSC Data

Batch No.	Variation	Static Tg (°C)	ΔTg(1) (°C)
CRT-76-1	Standard Formulation	219	0
CRT-77-2	+10% Curing Agent	220	+1
CRT-77-3	−10% Curing Agent	215	−4
CRT-79-4	+20% Curing Agent	220	+1
CRT-79-5	−20% Curing Agent	213	−6
CRT-76-6	+20% Epoxide No. 2	218	−1
CRT-78-7	−20% Epoxide No. 2	217	−2
CRT-76-8	+40% Epoxide No. 2	211	−8
CRT-78-9	−40% Epoxide No. 2	214	−5
CRT-76-10	+50% Epoxide No. 3	213	−6
CRT-79-11	−50% Epoxide No. 3	225	+6
CRT-76-12	+100% Epoxide No. 3	213	−6
CRT-75-13	−50% BF_3 Catalyst	216	−3
CRT-75-14	+100% BF_3 Catalyst	225	+6
CRT-75-15	Understaged	221	+2
CRT-75-16	Overstaged	220	+1

(1) ΔTg is [Tg (Varied Batch) - Tg (Standard Batch)]

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TABLE 11
MOISTURE ABSORPTION (PERCENT BY WEIGHT) OF SPECIAL BATCHES (3501-6)

Batch Code	Description	Thick-ness (in.)	Time - days															
			1	2	3	4	8	9	10	11	15	16	18	22	23	24	25	28	44
CRT 76-1	Standard Formulation	0.0287	4.22	4.29	4.44	4.61	4.85	4.96	5.02	5.07	5.04	5.09	5.27	5.51	5.77	5.41	--	5.42	7.10
CRT 79-5	−20% Curing Agent	0.0235	3.77	3.96	4.17	4.22	4.51	4.54	4.81	4.86	4.86	4.91	5.13	5.1	5.12	5.12	4.9	4.98	6.61
CRT 77-3	−10% Curing Agent	0.0270	3.64	4.11	4.42	4.51	4.74	4.77	4.96	5.04	4.75	5.15	5.13	5.08	5.52	5.35	5.17	5.23	6.55
CRT 77-2	+10% Curing Agent	0.0205	4.04	4.19	4.41	4.52	4.74	4.90	4.99	5.04	4.96	5.36	5.28	5.43	5.64	5.58	5.40	5.45	6.69
CRT 79-4	+20% Curing Agent	0.0242	3.74	4.15	4.38	4.52	4.82	4.82	5.0	5.1	5.13	5.18	5.51	5.39	5.79	5.51	5.29	5.42	6.73
CRT 78-9	−40% Epoxide No. 2(H)	0.0246	3.79	4.09	4.26	4.31	4.59	4.68	4.88	4.97	4.92	5.06	5.47	5.29	5.33	5.29	5.35	5.35	5.75
CRT 78-7	−20% Epoxide No. 2(H)	0.0240	3.80	4.14	4.36	4.40	4.76	4.76	5.04	5.09	5.09	5.07	5.43	5.25	5.44	5.51	5.19	4.97	6.71
CRT 76-6	+20% Epoxide No. 2(H)	0.0357	2.98	3.75	4.23	4.78	5.18	5.21	5.44	5.5	5.55	5.56	5.29	5.23	5.34	5.39	5.29	5.28	6.32
CRT 76-8	+40% Epoxide No. 2(H)	0.0260	3.63	3.94	4.19	4.27	4.60	4.58	4.83	4.93	5.01	4.92	5.30	5.20	5.27	5.35	5.34	5.49	6.46
CRT 79-11	−50% Epoxide No. 3(H)	0.0221	4.19	4.41	4.59	4.64	4.94	5.02	5.26	5.28	5.21	5.39	5.74	5.80	5.78	5.84	5.64	5.60	6.74
CRT 76-10	+50% Epoxide No. 3(H)	0.0223	3.74	3.92	4.06	4.13	4.44	4.36	4.69	4.73	4.69	4.82	5.26	5.36	5.39	5.36	5.06	5.12	6.05
CRT 76-12	+100% Epoxide No. 3(H)	0.0218	3.81	4.07	4.21	4.27	4.51	4.62	4.76	4.77	4.75	4.92	5.28	5.29	5.04	5.29	4.92	4.80	5.76
CRT 75-13	−50% Accelerator	0.0216	3.76	3.55	4.02	4.06	4.41	4.46	4.63	4.67	4.58	4.78	5.36	5.22	5.12	5.27	5.03	5.18	6.11
CRT 75-14	+100% Accelerator	0.0217	4.43	4.62	4.84	4.81	5.23	5.26	5.58	5.52	5.41	5.68	6.18	6.08	5.95	6.14	5.92	5.88	7.36
CRT 75-15	Understaged	0.0217	4.11	4.23	4.29	4.31	4.77	4.81	5.02	5.02	5.02	5.07	5.76	5.61	5.42	5.71	5.47	5.34	6.82
CRT 75-16	Overstaged	0.0221	4.01	4.32	4.38	4.42	4.84	4.90	5.17	5.12	5.06	5.24	5.77	5.81	5.69	5.91	5.70	5.70	6.96

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percent moisture remained constant through 28 days. The jump in percent moisture values reported after the longest exposure, i.e., 44 days, is believed due to microcracking on long exposure under elevated conditions of temperature and humidity. This phenomenon has been noted frequently by other investigations, Reference (3). Dynamic mechanical analysis of the moisture saturated specimen for the control batch, CRT-76-1, showed very little difference from the DMA data for the dry control. Calculations, using a previously determined diffusion coefficient for the standard formulation, showed that the moisture had diffused away from the wet specimen during the DMA heat up at 1°C/minute. Since the thin Rheovibron specimens dry before reaching a temperature critical to the modulus or Tg, and the instrument could not be equipped to operate at elevated humidities, no further DMA runs were attempted. The attempt to test wet specimens did confirm that moisture degradation is reversible in that absorption and subsequent desorption had not significantly changed the dynamic mechanical properties.

A determination of "wet" Tg's was attempted by pressurized DSC. The moisture saturated control specimen was hermetically sealed in the small aluminum specimen dish. Attempts to match the increased vapor pressure of water inside the dish with externally applied argon pressure was not workable since early application of full argon external pressure crushed the dish and late application would allow the dish to blow out the hermetically sealed crimped top. Stainless steel dishes have reportedly been used for DSC measurements involving retaining moisture in tissue specimens. Stainless steel dishes were not available in time for trial.

3.1.4 Processability of Special Resins - Viscosity data for the neat resins were determined as a means of assessing effects of chemical variations on processability. Viscosity profiles, as a function of time and temperature, were determined under both isothermal conditions and dynamic conditions (controlled linear heating rate). All data was obtained using a laboratory assembled apparatus employing a Brookfield Rheolog viscometer designed to

provide a continuous recording of viscosity as a function of temperature and time. Data for the standard formula resin viscosity profiles for isothermal runs at 225, 250, 260 and 275° are shown in Figures 28, 29, 30, 31. Viscosity runs for the standard formula under dynamic conditions of constant heating rate for 1.8, 3.9 and 9.0°F/minute are shown in Figures 32, 33, 34, 35.

The data can be reduced to give the following relationships for gel under isothermal and dynamic heating:

$$(1) \quad t_{gel} = 1.48 \times 10^{-14} \, T^2 \, 10^{4180.7/T}$$

$$(2) \quad \log \phi = \frac{-4180.7}{T_{gel}} + 9.847344$$

Equation (1) can be used to the gel time (t_{gel}) for any isothermal temperature (T, °K). Equation (2) can be used to calculate the temperature of gel, under dynamic conditions, for any linear heating rate (ϕ, °C/MIN). By the methods outlined in Reference 4, these two equations can be used to calculate the occurrence of gel under the parameters of any selected cure cycle. Gellation, particularly under isothermal conditions, is not a sharp well-defined point. We have selected a viscosity of 100, 000 centapoise (about the consistency of a cold grease) as representative of gel. From an engineering standpoint, it is imperative that full autoclave pressure be applied ahead of the gel point for a given cure cycle to assure good interlaminar properties in the cured laminate.

Viscosity profiles for the experimental resin batches were determined. Gel time (t_{gel}), was determined under isothermal conditions for each of the 16 special batches. The data is given in Table 12. The best straight line fit for: log $[t_{gel}/T^2]$ vs $1/T$ was determined by linear regression. From the slope and intercept points for these plots the time to gel (t_{gel}) can be expressed in the form:

$$t_{gel} = c \, T^2 \, 10^{A/T}$$

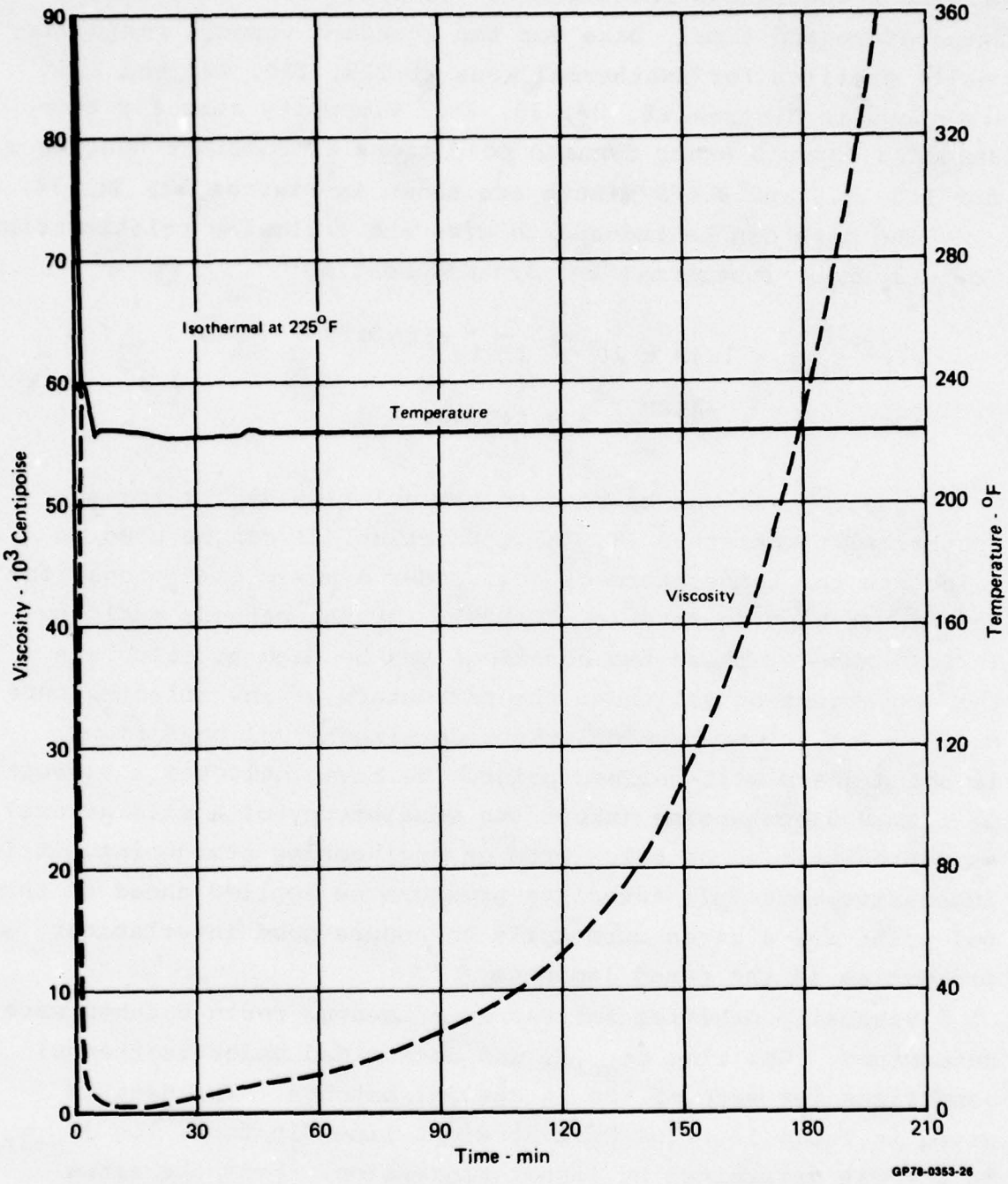

FIGURE 28
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

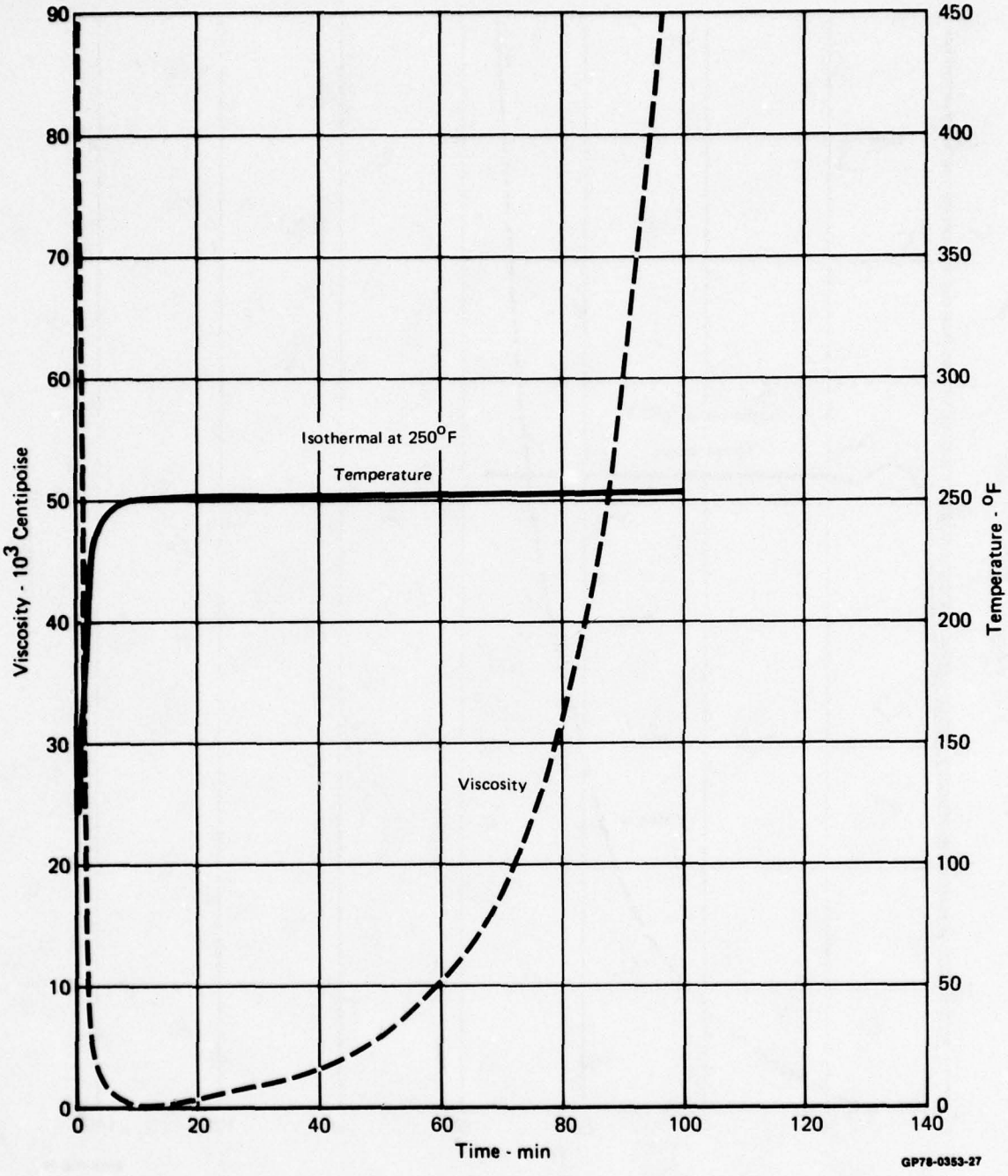

FIGURE 29
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

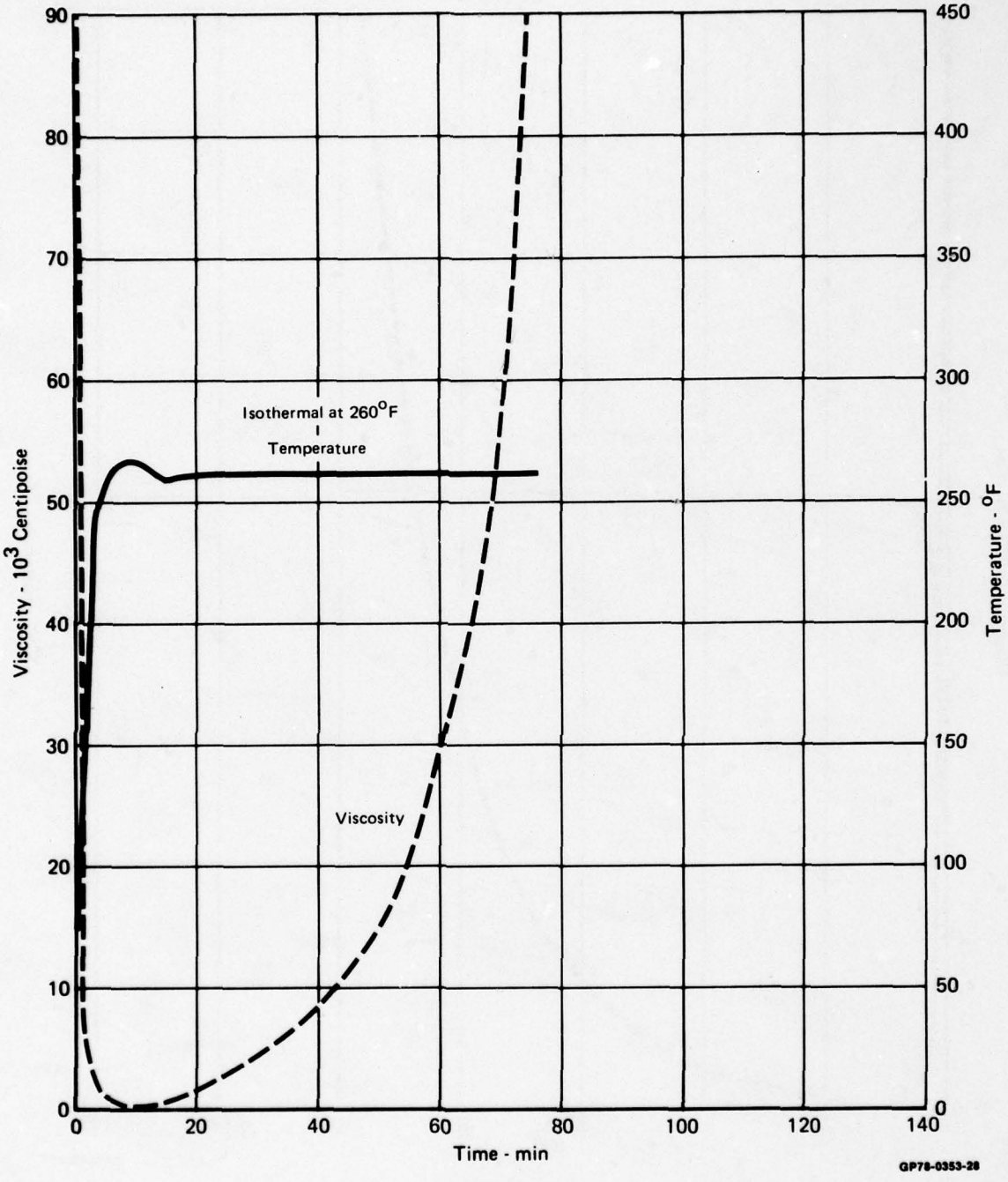

FIGURE 30
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

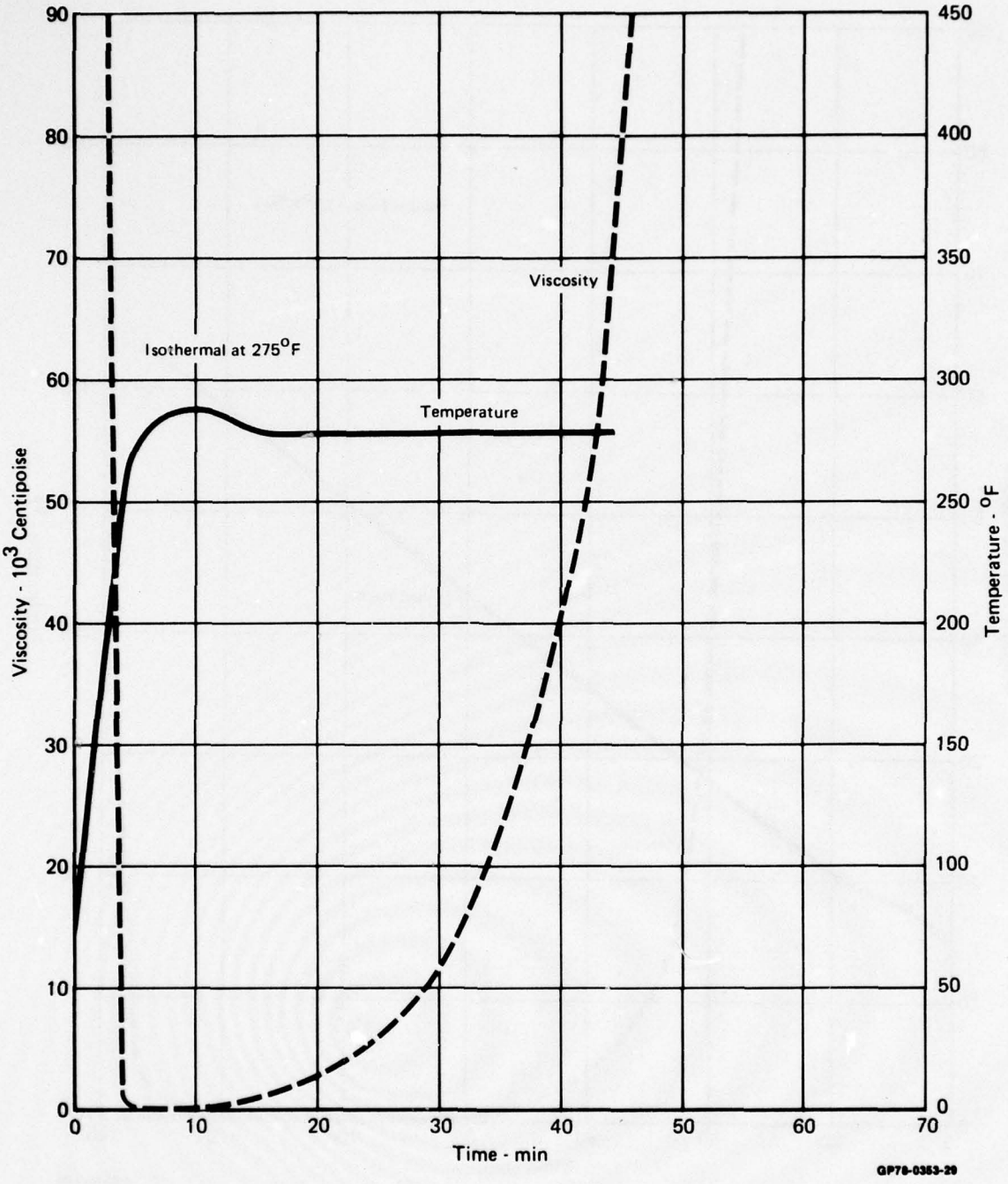

FIGURE 31
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

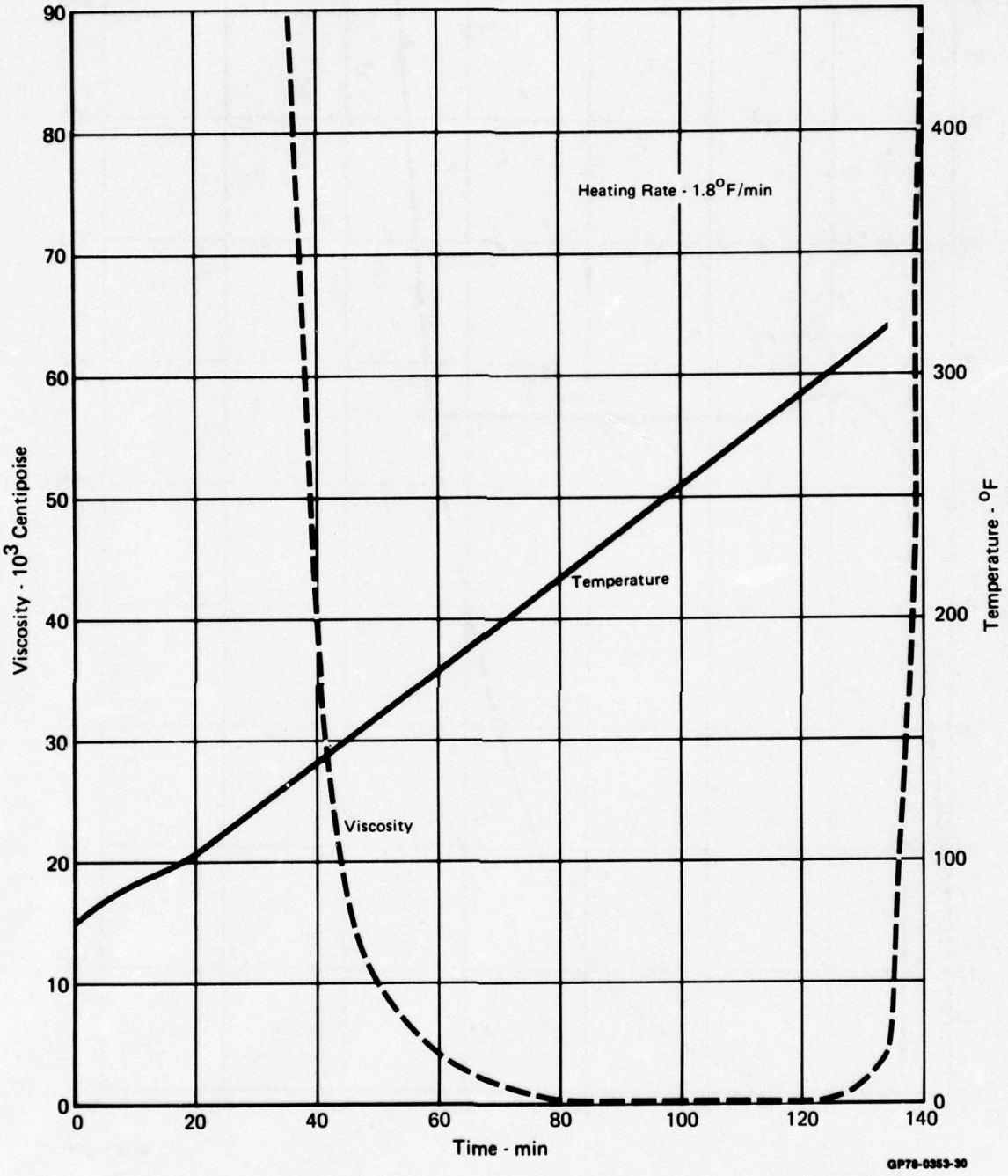

FIGURE 32
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

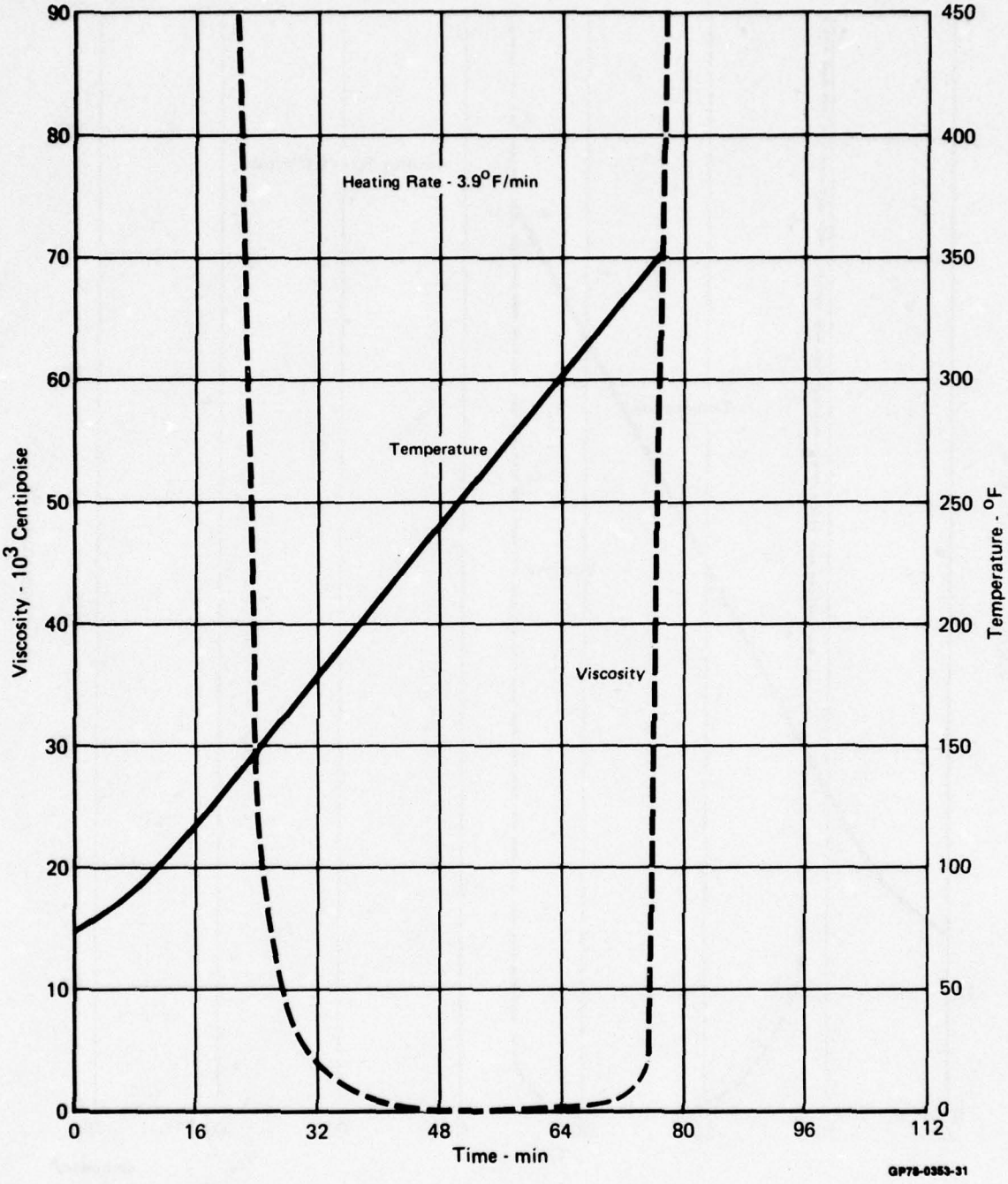

FIGURE 33
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

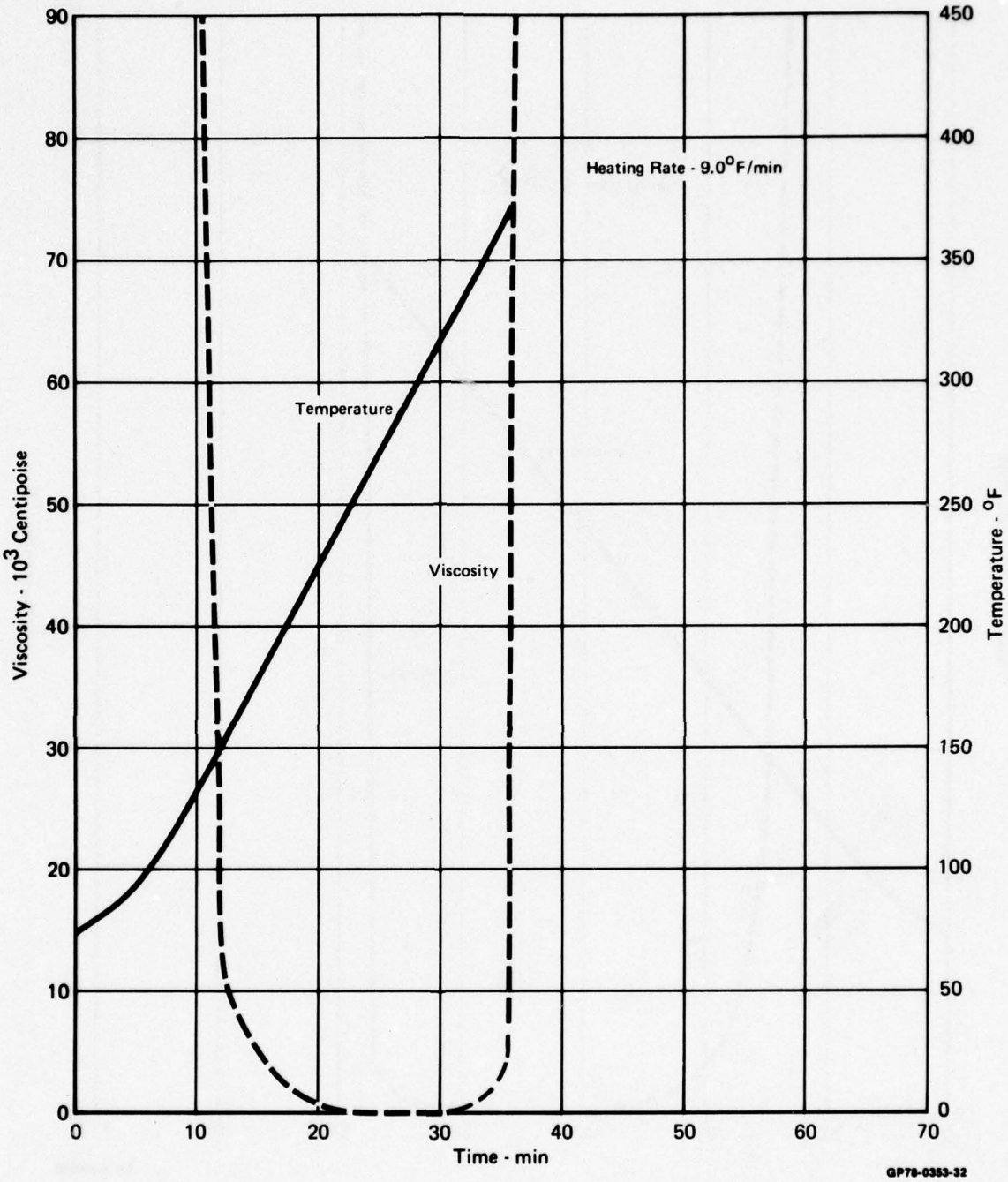

FIGURE 34
VISCOSITY vs TEMPERATURE/TIME FOR 3501-6 RESIN

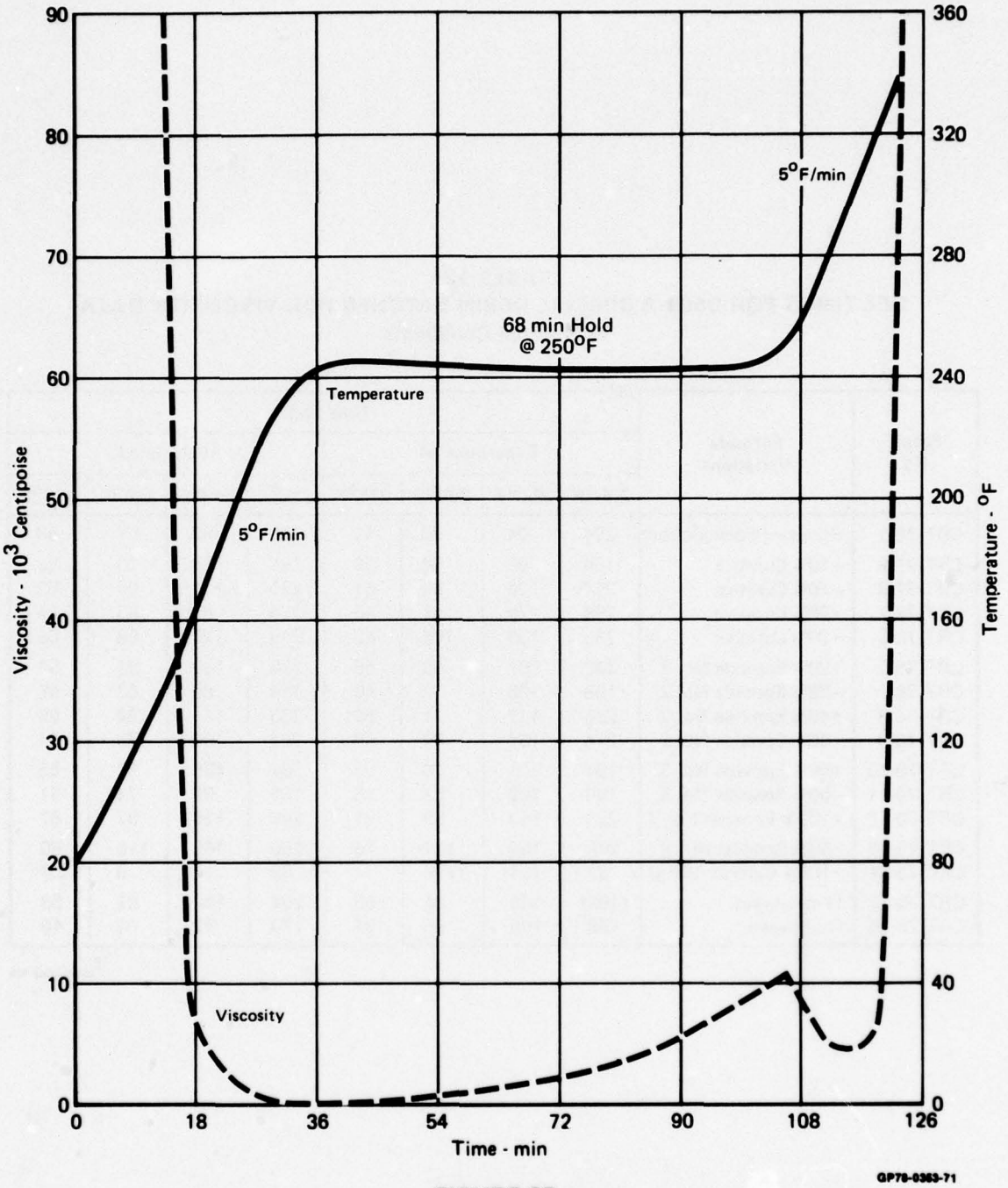

FIGURE 35
VISCOSITY vs TEMPERATURE/TIME 3501-6 BATCH CRT-76-1
(STANDARD FORMULA)

TABLE 12
GEL TIMES FOR 3501-6 SPECIAL RESIN BATCHES FOR VISCOSITY DATA
Isothermal Conditions

Batch No.	Formula Variations	Time (min)							
		Experimental				Calculated			
		225°F	250°F	260°F	275°F	225°F	250°F	260°F	275°F
CRT-76-1	Standard Formulation	204	94	70	41	209	92	67	43
CRT-77-2	+10% Curative	164	90	68	50	164	88	70	50
CRT-77-3	−10% Curative	214	126	85	61	221	114	89	62
CRT-79-4	+20% Curative	158	79	61	46	155	81	63	44
CRT-79-5	−20% Curative	235	133	104	62	249	127	98	68
CRT-76-6	+20% Epoxide No. 2	232	107	80	55	230	108	82	54
CRT-78-7	−20% Epoxide No. 2	168	103	70	40	184	89	67	45
CRT-76-8	+40% Epoxide No. 2	236	117	71	60	233	111	84	56
CRT-78-9	−40% Epoxide No. 2	274	104	60	50	262	104	73	44
CRT-76-10	+50% Epoxide No. 3	194	121	76	53	207	105	81	55
CRT-79-11	−50% Epoxide No. 3	190	103	63	55	189	96	74	51
CRT-76-12	+100% Epoxide No. 3	220	163	89	61	246	125	97	67
CRT-75-13	−50% Catalyst (BF_3)	276	162	114	76	290	149	115	80
CRT-75-14	+100% Catalyst (BF_3)	82	(21)	(7.5)	–	89	17	9	3.6
CRT-75-15	Understaged	(198)	106	84	53	204	104	81	56
CRT-75-16	Overstaged	158	100	65	34	179	82	61	40

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where "A" is the slope, "c" is a constant equal to the inverse logarithim of the intercept and T is in the absolute temperature in °K. The formulas for calculating t_{gel} are given in Table 13 and were used to give the calculated valves for t_{gel} given in Table 12. The isothermal data can also be used to calculate dynamic data, i.e., the temperature of gel (T_{gel}, °K) for any heating rate (ϕ, °C/Min) by the integrative procedures derived in-house and reported in Reference 4. The formulas for T_{gel} as a function of ϕ are also given in Table 13.

The viscosity of the standard formulation 3501-6 as a function of time and temperature for a typical cure cycle is shown in Figure 35. The resin was heated at 5°F/Min to 250°F and held at 250°F for approximately 70 minutes and then heated at 5°F/Min to gel ($\geq$100,000 CPS). The resin begins to melt after 13 minutes (130°F). The viscosity had dropped below 1000 CPS (about the viscosity of fine machine oil) after about 27 min. (220°F). The minimum viscosity was reached after about 36 minutes (250°F). During the 68 minute hold the viscosity remains low, but slowly rises to about 10,000 CPS (about the viscosity of syrup) mainly from linear chain lengthening polymerization. The second temperature ramp causes an initial drop in viscosity due to the temperature rise. The polymerization, with the on-set of more extensive crosslinking taking place near gel and quickly overrides the effect of temperature rise. The viscosity rapidly then rose to gel (>100,000) after a total time of 120 minutes at a temperature of 340°F.

For the special batches, the variations in amounts of BF_3 complex catalyst caused large changes in gel time for any given temperature. This is shown in Figure 36 by plotting log t_{gel} vs. 1/T (°K). A program was written for a computer/plotter whereby the formula for t_{gel} given in Table 13 can be used to show the point of gellation of the various resin formulations under any set of cure cycle parameters, i.e., varied heating rates and varied set of parameters, Figure 37, shows that the high catalyst resin batch (2.2% BF_3 complex) would gel early during the 250°F hold. Gellation ahead of the application of full autoclave

TABLE 13
FORMULAS FOR CALCULATING GEL TIMES AND TEMPERATURES FOR ISOTHERMAL AND DYNAMIC HEATING OF SPECIAL BATCHES OF 3501-6

Batch No.	Gel Time (Minutes) (Isothermal Hold to Gel) $t = c\,T^2\,10^{A/T}$		Gel Temperature (^oK) (Linear Heating Rate to Gel) $\log \phi = A/T + B$	
	c	A	A	B
CRT-76-1	1.48×10^{-14}	4180.7	−4180.7	9.847344
CRT-77-2	3.25×10^{-12}	3250.0	−3250.0	7.620164
CRT-77-3	1.48×10^{-12}	3427.4	−3427.4	7.931042
CRT-79-4	1.42×10^{-12}	3375.7	−3375.7	7.954966
CRT-79-5	1.07×10^{-12}	3500.4	−3500.4	8.064509
CRT-76-6	1.15×10^{-13}	3855.0	−3855.0	8.986107
CRT-78-7	1.60×10^{-13}	3764.4	−3764.4	8.855446
CRT-76-8	1.42×10^{-13}	3823.6	−3823.6	8.902328
CRT-78-9	9.58×10^{-16}	4667.9	−4667.9	10.985926
CRT-76-10	7.27×10^{-13}	3533.8	−3533.8	8.227800
CRT-79-11	7.72×10^{-13}	3509.4	−3509.4	8.204348
CRT-76-12	9.86×10^{-13}	3512.6	−3512.6	8.098190
CRT-75-13	1.50×10^{-12}	3469.5	−3469.5	7.919425
CRT-75-14	2.74×10^{-25}	8118.5	−8118.5	20.291112
CRT-75-15	9.31×10^{-13}	3491.0	−3491.0	8.126047
CRT-75-16	4.14×10^{-14}	3983.2	−3983.2	9.419842

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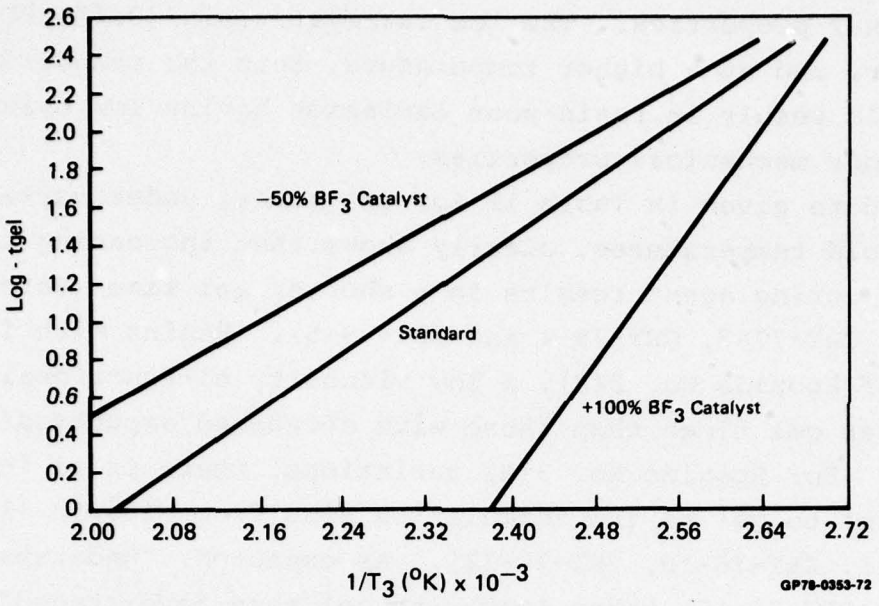

FIGURE 36
GEL TIME AS A FUNCTION OF TEMPERATURE
(FROM VISCOSITY MEASUREMENTS)

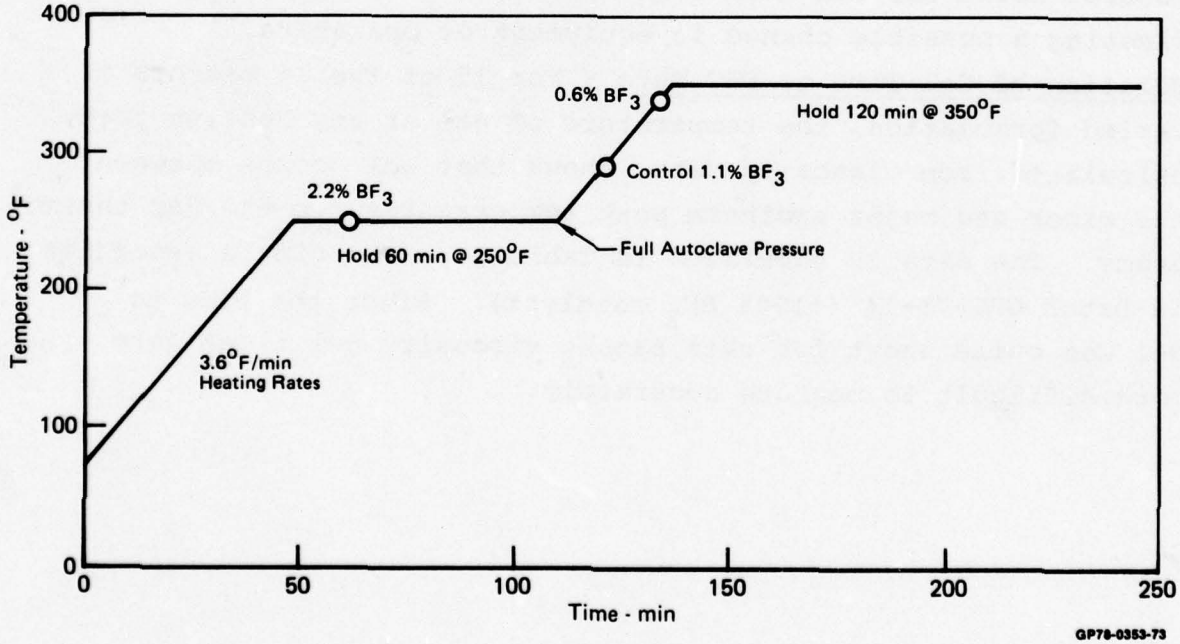

FIGURE 37
GEL POINTS OF 3501-6 WITH VARIED BF_3 CATALYST CONCENTRATION
DURING A TYPICAL CURE CYCLE

pressure could result in resin-rich, porous laminates with poor interlaminar properties. The low catalyst resin (0.67% BF_3 complex) gels later, and at a higher temperature, than the standard formula which could result in resin-poor laminates having low thickness/ply and poor mechanical properties.

The data given in Table 12 for gel times, under varied isothermal hold temperatures, clearly shows that increasing the amount of curing agent results in a shorter gel time (Batches CRT-77-2, CRT-77-3, CRT-79-4 and CRT-79-5). Resins with increased amounts of Epoxide No. 2(H), a low viscosity bi-functional epoxy, gave longer gel times than those with decreased amounts of Epoxide No. 2(H). For Epoxide No. 3(H) variations, there is an increase in the time to gel as the formulation goes from -50% to +100% (CRT-79-11, CRT-76-10, CRT-76-12). As expected, "understaged" material (CRT-75-15) takes longer to gel than "overstaged" resin (CRT-75-16). The control batch (CRT-76-1) does not always fit in a central position between plus and minus variations of each of the various components. This may be due to the fact that the control batch was run much earlier than the other batches, reflecting a possible change in equipment or operators.

Relation of Gel Time to DSC Data - For 15 of the 16 batches of varied formulation, the temperature of gel at any heating rate, calculated from viscosity data, shows that gel occurs between the minor and major exotherm peak temperatures for the DSC thermograms. The data is tabulated in Table 14. The single exception is Batch CRT-75-14 (+100% BF_3 catalyst). Since the time to gel was quite short for this batch, viscosity gel times were more difficult to measure accurately.

TABLE 14
GEL POINT FROM VISCOSITY DATA RELATED TO DSC DATA

Batch No.	Heating Rate (°C/min)	Temperature (°C)		
		DSC (Minor EXO)	Gel (By Viscosity)	DSC (Major EXO)
CRT-76-1	5	149	184	213
	10	162	200	232
	20	171	216	252
CRT-77-2	5	149	197	207
	10	162	219	227
	20	176	241	247
CRT-77-3	5	144	201	210
	10	160	222	232
	20	176	244	252
CRT-79-4	5	147	192	205
	10	165	212	225
	20	175	235	244
CRT-79-5	5	149	202	217
	10	160	222	237
	20	173	244	257
CRT-76-6	5	149	192	213
	10	160	210	233
	20	174	229	250
CRT-78-7	5	147	188	210
	10	160	206	228
	20	172	225	247
CRT-76-8	5	140	193	215
	10	165	211	237
	20	172	230	250
CRT-78-9	5	150	181	211
	10	162	194	232
	20	172	209	249
CRT-76-10	5	152	196	219
	10	164	216	237
	20	177	237	254
CRT-79-11	5	150	195	214
	10	165	214	234
	20	175	235	250
CRT-76-12	5	153	202	221
	10	165	222	235
	20	175	244	255
CRT-75-13	5	138	207	219
	10	153	228	243
	20	175	251	265
CRT-75-14	5	146	(141)	212
	10	166	(148)	230
	20	177	(154)	245
CRT-75-15	5	152	197	215
	10	165	217	235
	20	178	238	253
CRT-75-16	5	149	184	212
	10	165	200	232
	20	172	218	252

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3.2 Phase II - Development of Advanced Test Methods

Advanced test method development emphasized work with liquid-liquid chromatography.

3.2.1 Selection and Refinement of Methods - From in-house efforts, work completed under NASC Contract No. N00019-C-76-0138, Reference 1, and discussions with workers active in the field of polymer analysis, References 5-8, it was decided to concentrate the program method-development effort on refinement and utilization of reverse phase liquid-liquid chromatography (RPLLC). Liquid-liquid chromatography (LLC) is generally used to separate components of resin that have differences in solubility and polarity. The epoxy resins and curing agent components in the 3501-6 resin system fit nicely into this category. In normal-phase liquid-liquid chromatography (NPLLC), a stationary solid support surface is coated (or bonded) with a second liquid (the stationary phase) which is quite polar and immiscible in the nonpolar mobile phase. However, in reverse-phase LLC (RPLLC), the stationary phase is nonpolar, and a polar solvent mixture (usually a mixture of a nonpolar solvent and water) is used as the mobile phase. In effect, the RPLLC would appear to provide the best LC technique for adequately separating the components in the 3501-6 resin system which vary only slightly in polarity and solubility. For example, Epoxide No. 3(H) is a high-molecular weight novalac resin, that is slightly less polar than Epoxide No. 1(H) which is the major epoxy in 3501-6. The curing agent, diaminodiphenyl sulfone (DDS), is quite polar. Thus, due to its slightly lower polarity, Epoxide No. 3(H) could be expected to elute from the RPLLC column after both DDS and Epoxide No. 1(H).

Isocratic RPLLC - In establishing the applicability of the RPLLC method to the 3501-6 resin, each of the individual components were run separately to establish instrumental and solution parameters. This was followed by runs in which the B-stage reaction product for each epoxide with DDS curing agent was examined for relative location and identification of peaks. The best wave length setting to achieve maximum detector sensitivity was determined.

Initially, each of the components and prepared reaction adducts were examined under the following conditions using a Waters ALC/GPC-301 instrument.

- Column - 30 cm of Waters Associates C_{18} - Bondapak
- Elution Solvent - 40% THF/60% H_2O (vol/vol)
- Solvent Flow - 0.7 ml/min @ 1000 PSI
- Sample Size - 5µl (contains approx. 40µg resin)
- Detector - Schoeffel variable wavelength ultraviolet unit, operated at 230, 254, or 280 nm. Setting 0.1 absorbance units, full scale.

Chromatograms for Epoxide No. 1(H) are shown in Figure 38. Either 254 or 230 nm gives satisfactory sensitivity for the Epoxide No. 1(H) component. It is immediately apparent, from the large number of separated peaks that the major epoxy component for 3501-6 is not a single pure compound, but also contains a number of by-product impurities originating in its synthesis.

Epoxide No. 3(H), as run individually at three wavelengths, is shown in Figure 39. There is no doubt that the major peaks for the component are best detected at 230 nm. Chromatograms for 3501-6 resin system and 3501-6 spiked with Epoxide No. 3(H) are shown in Figure 40. The concentration of Epoxide No. 3(H) was determined from spiked samples of a production batch of 3501-6 by the method of standard addition. The values obtained for three replicate runs were 7.4, 8.1 and 8.7% by weight, giving an average value of 8.1% free component. The standard formula concentration requires the addition of 8.5% of this component. The method of standard addition gives a fair quantitative estimate for Epoxide No. 3(H); however, the precision is too poor for consideration as a viable control method.

The chromatograms for the diaminodiphenyl sulfone (DDS) curing agent is shown in Figure 41. There is only one detectable impurity of any significance peak Ⓐ and the concentration of this unidentified impurity is quite low. DDS has major response at 280 and 254 nm, but also has adequate response at the 230 nm wavelength found best for Epoxide Numbers 1(H) and 3(H).

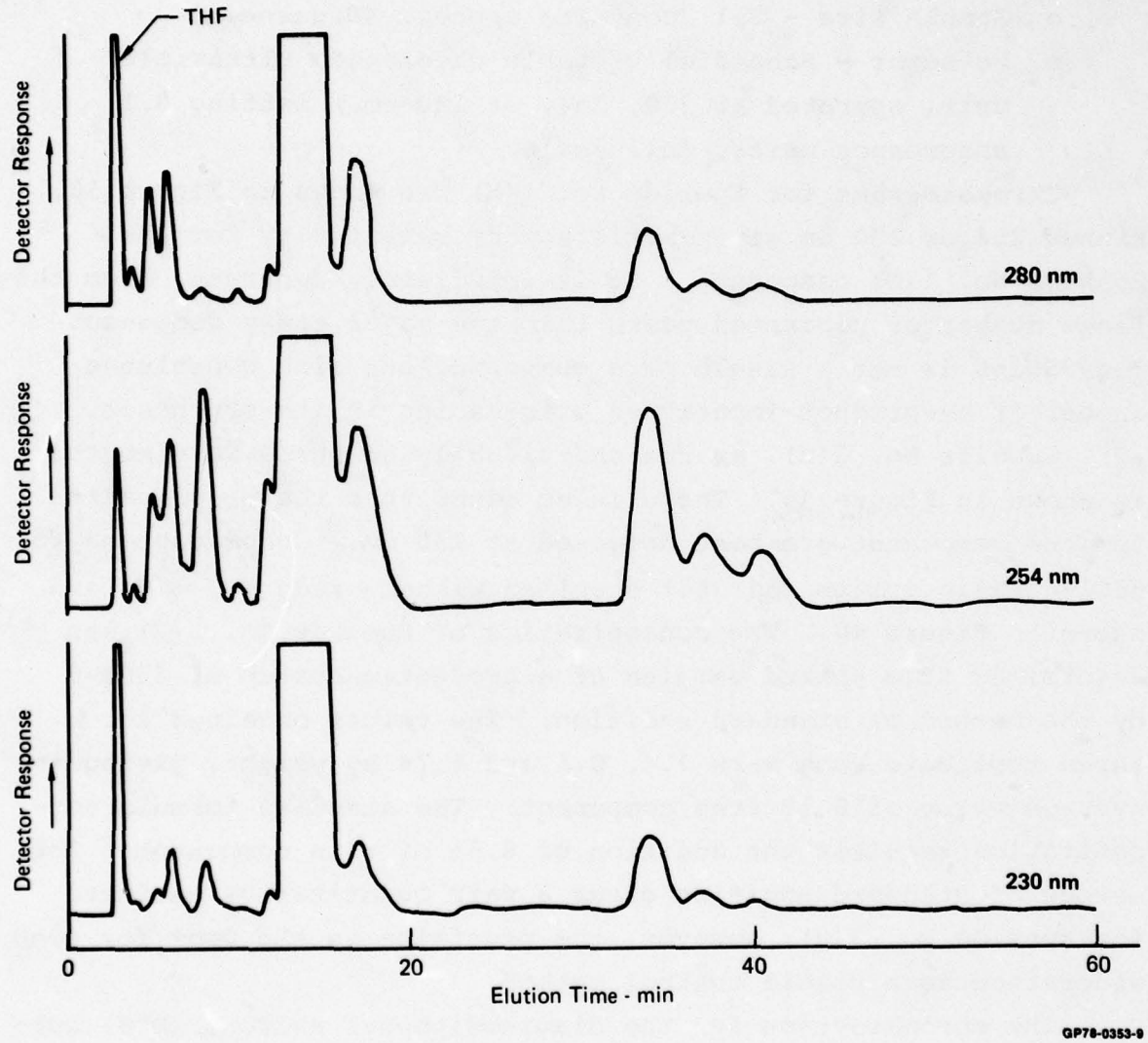

FIGURE 38
RPLLC FOR EPOXIDE NO. 1(H) COMPONENT

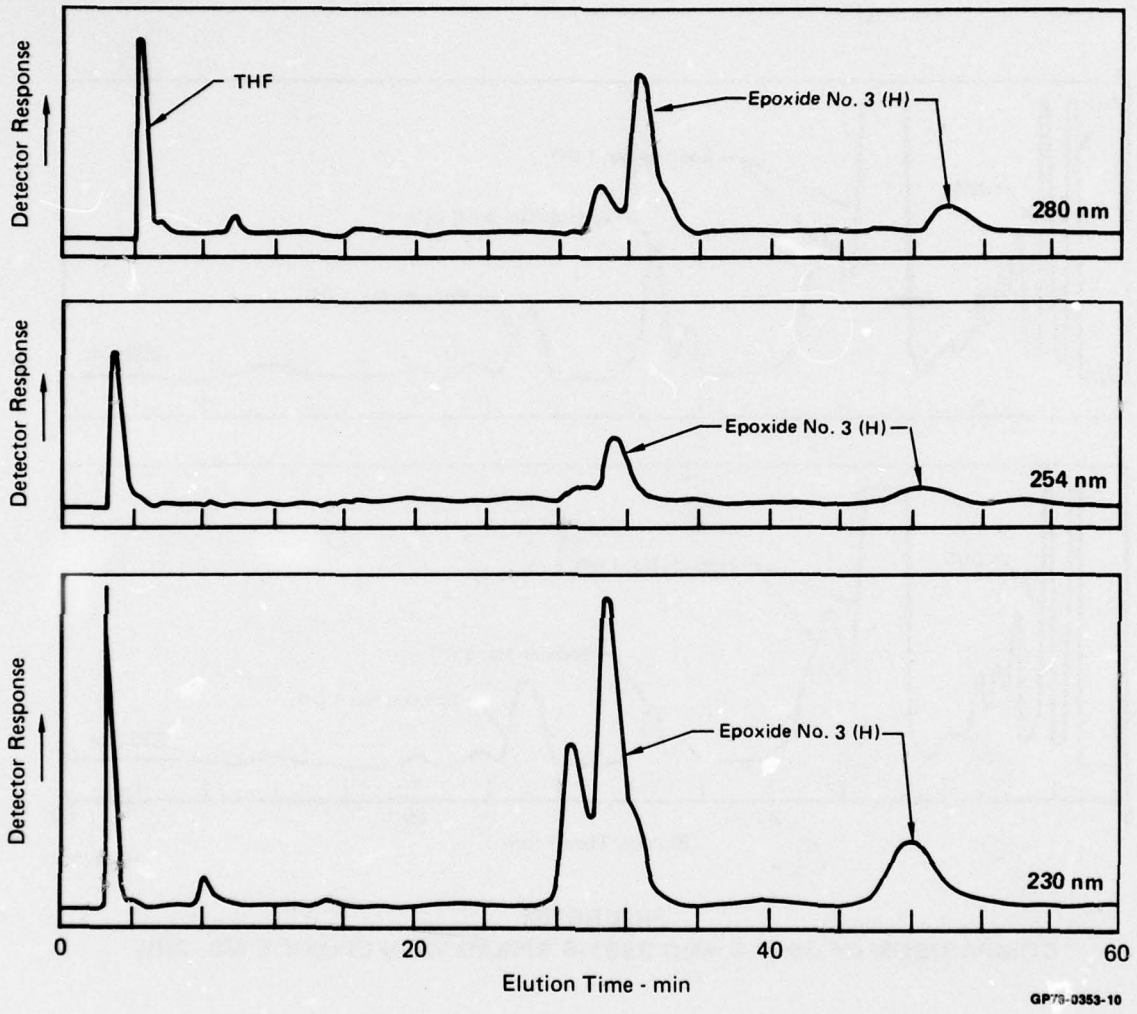

FIGURE 39
RPLLC FOR EPOXIDE NO. 3(H) COMPONENT

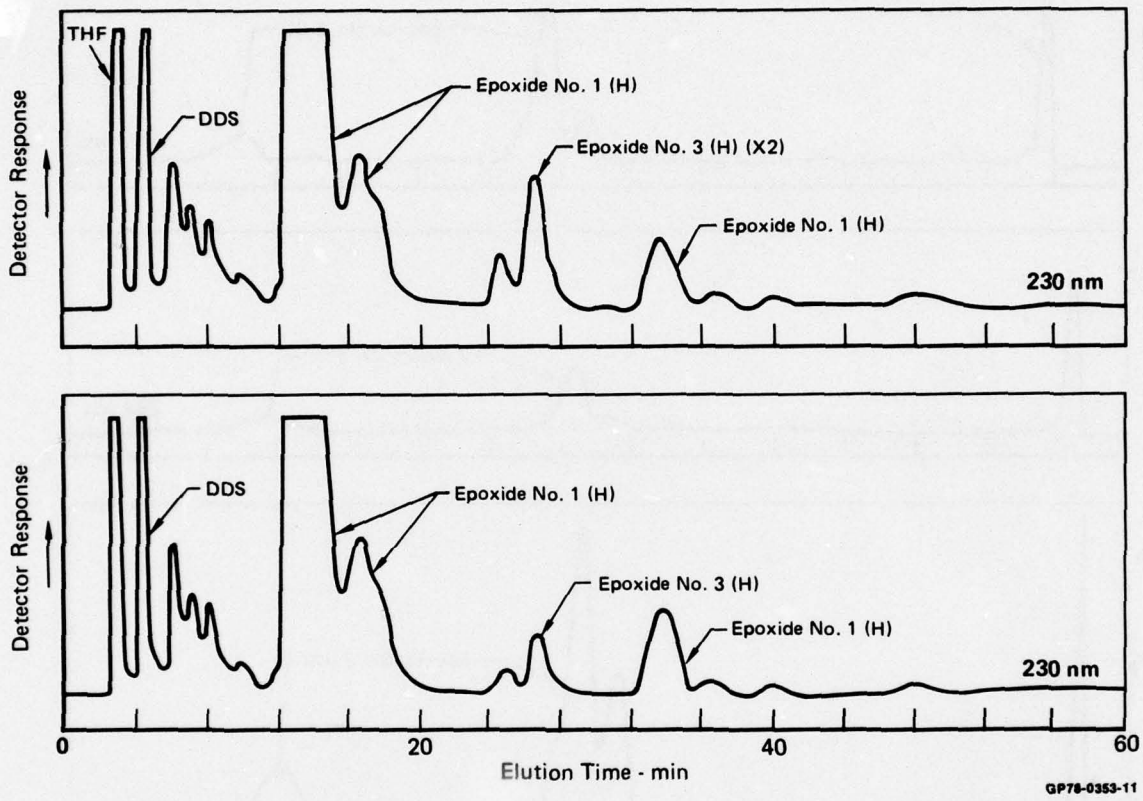

FIGURE 40
COMPARISON OF 3501-6 AND 3501-6 SPIKED WITH EPOXIDE NO. 3(H)

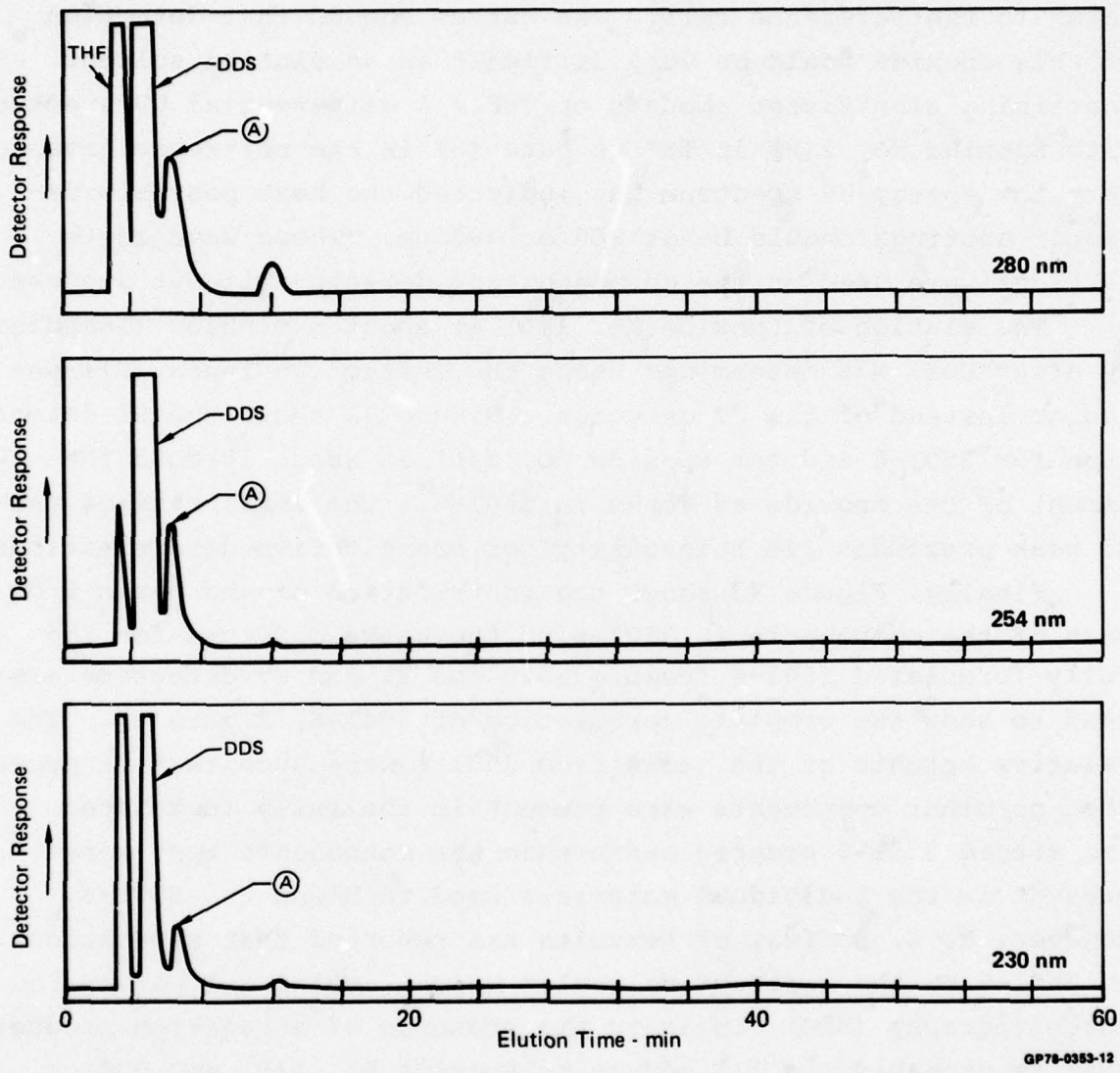

FIGURE 41
RPLLC FOR CURING AGENT (DDS)

Epoxide No. 2(H) was not detected at any of the three wavelengths (230, 254 and 280 nm) and was not detected at 310 nm, which should be an area of maximum UV absorbance for material with the molecular structure of Epoxide No. 2(H). UV absorbance specta were obtained for Epoxide No. 2(H) and for THF solvent vs water in the reference cell. The curves showed that detection of this epoxide would be very difficult in an elution solvent containing significant amounts of THF. A differential UV spectrum with Epoxide No. 2(H) in THF vs pure THF in the reference gave a very low energy UV spectrum but indicated the best possible detector settings should be at 260 or 300 nm. These wavelength settings were used on the chromatograph detector without success.

The elution of Epoxide No. 2(H) at about 6 minutes (immediately after DDS) was determined using the refractive index (RI) detector instead of the UV detector. Figure 42 shows the RI detector runs for 3501-6 and for Epoxide No. 2(H) at about 10-fold the amount of the epoxide as found in 3501-6. The small size of the RI peak precludes its suitability for quantitative determinations.

Finally, Figure 43 shows the contribution of the peaks from each of the components in 3501-6 to the peaks observed for the fully formulated 3501-6 resin. Both the RI and UV detectors are used to show the complete formulation of 3501-6, Figure 44. The relative heights of the peaks from 3501-6 were such that it appears that no other components were present in the fully formulated and staged 3501-6 prepreg resin than the components that were present in the individual materials used to blend the 3501-6. However, R. E. Hoffman of Hercules has reported that separations of 3501-6 on the basis of molecular weight, using gel permeation chromatography (GPC), indicate the presence of a reaction product that is probably the 1:1 adduct of Epoxide No. 1(H) and DDS, Reference 6. For RPLLC, reaction products were probably masked under the large-area peak of Epoxide No. 1(H) for the isocratic runs at 40% THF/60% H_2O.

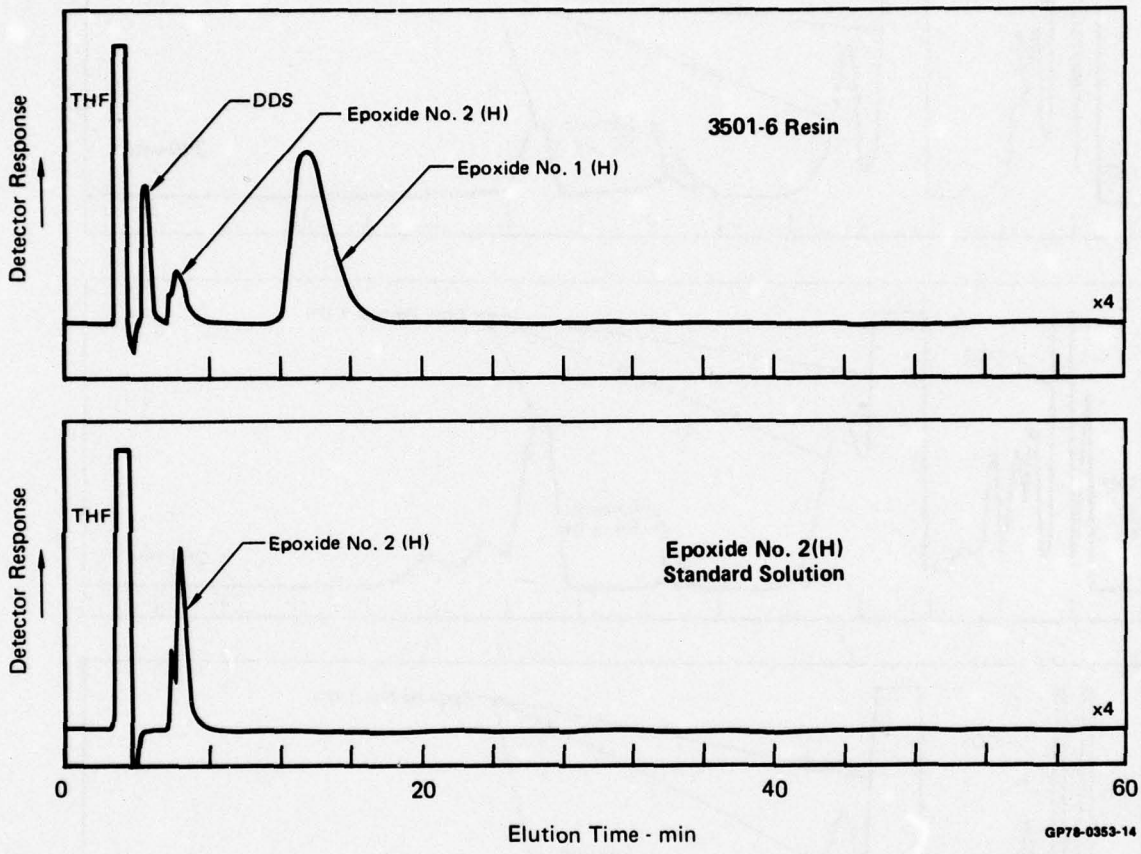

FIGURE 42
DETECTION OF EPOXIDE NO. 2(H) WITH THE REFRACTIVE INDEX DETECTOR

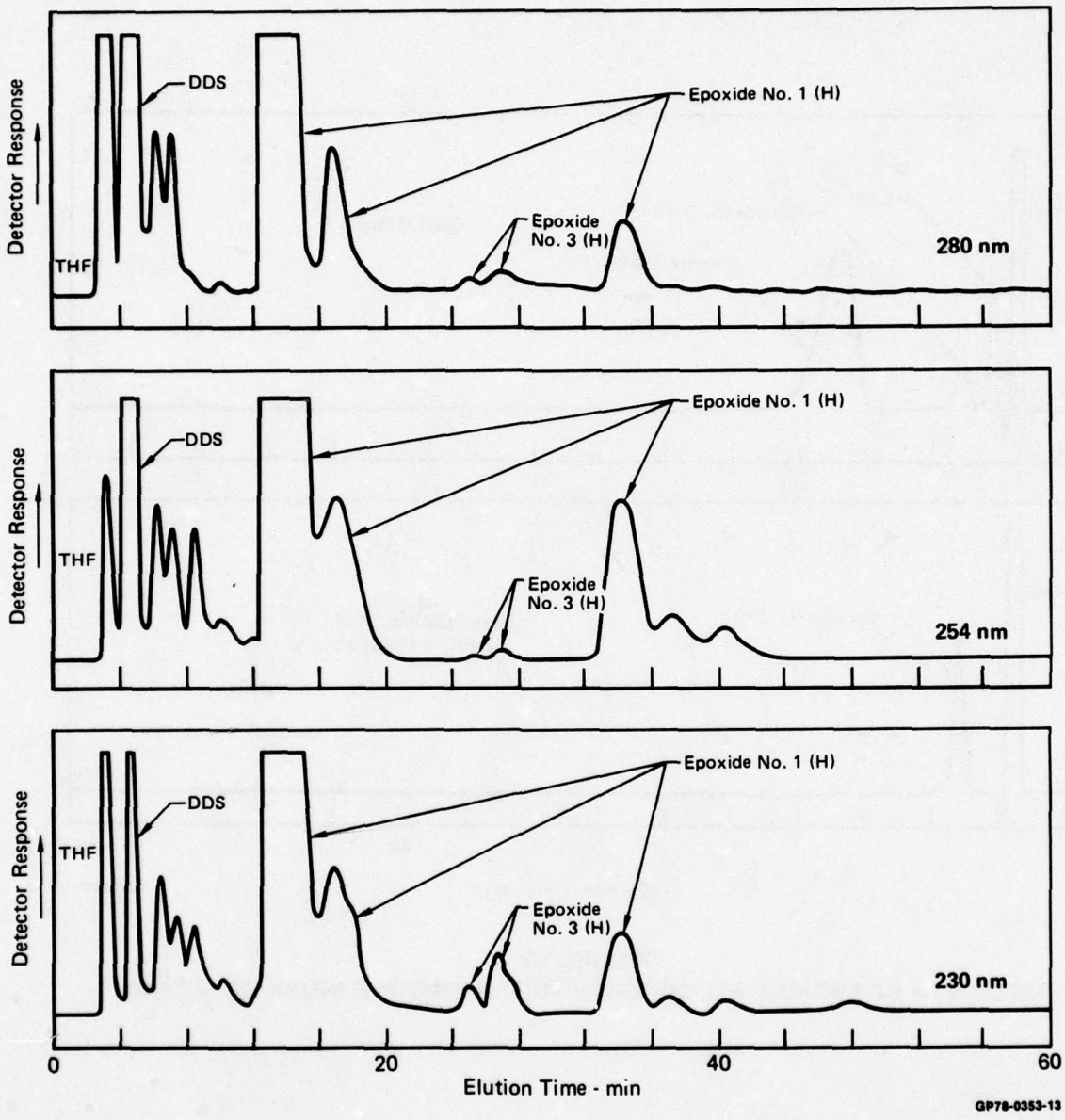

FIGURE 43
RPLLC FOR 3501-6 RESIN SYSTEM

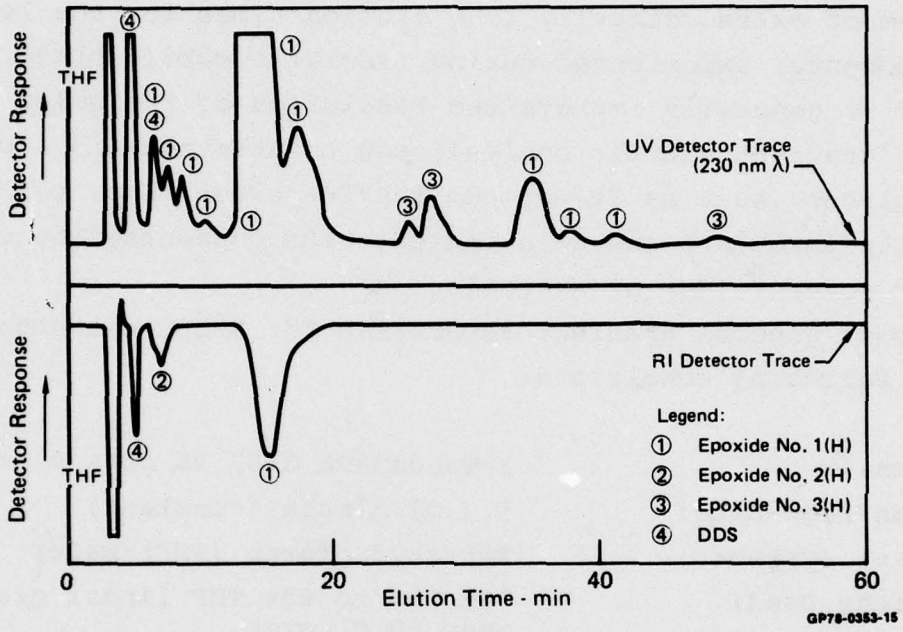

FIGURE 44
ORIGINS OF PEAKS IN UV AND RI CHROMATOGRAMS OF 3501-6

Gradient Elution RPLLC - Gradient-elution chromatography is simply a programmed changing of the polarity of the elution solvent during the course of the analysis and can be used to good advantage in the reverse phase mode. For example, an RPLLC column commonly used for the detailed separation of epoxy systems components is C_{18} Bondapak. This column has a nonpolar stationary phase (C_{18}) that allows the more polar components to elute first. The more polar the solvent, the longer the time required for nonpolar compounds to elute from the column. To circumvent the problem of extraordinarily long elution times for the less polar components, experienced during isocratic mobile phase operation, and to generally improve the resolution of the polar components, a gradient elution analysis can be started with a polar elution solvent (such as 30-percent THF/70-percent H_2O, vol/vol, or acetonitrile/water) and then increase the concentration of the less polar solvent (THF or acetonitrile).

The best general gradient separation for RPLLC was obtained using the following conditions:

Column:	μ Bondapack C18, 30 cm x 4 mm I.D.
Column Flow-Rate:	1.2 ml/minute (constant)
Solvent System:	Tetrahydrofuran (THF)/water
Gradient Used:	20% THF to 60% THF linear gradient over 60 minutes.
Analytical Wavelength:	254 nm @ 0.4 or 1.0 AUFS.
Sample Size:	6.0 μℓ of THF/resin solution
Sample Concentration:	20 mg 3501-6/ml THF (both unknowns and standards

In order to obtain good gradient-elution operation, ultraviolet (UV) grade uninhibited tetrahydrofuran (THF) was used to minimize any UV background from the solvent.

A gradient elution chromatogram for an old batch of Hercules 3501-6 (Batch B263) is shown in Figure 45. A graph of the increasing solvent concentration (gradient) is superimposed on the chromotogram to show the relationship between resolution and elution time with the changing composition of the elution solvent.

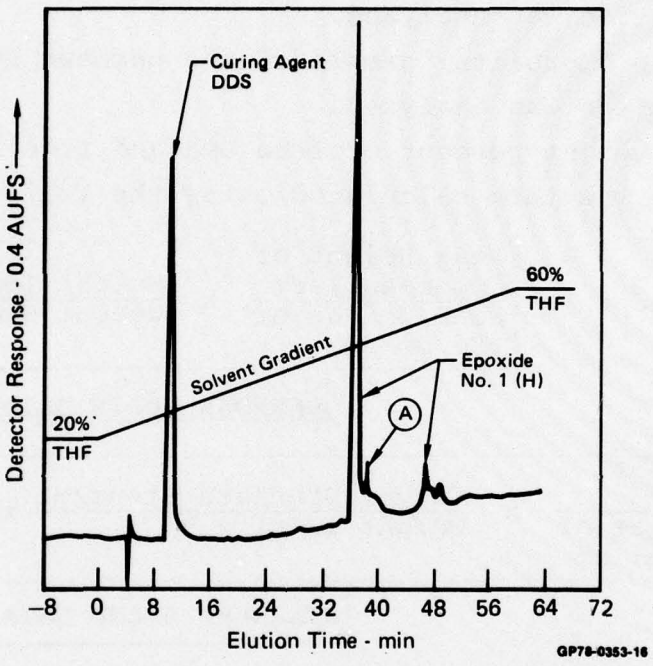

FIGURE 45
GRADIENT ELUTION ANALYSIS OF HERCULES 3501-6
(Batch 263)

THF. The known blends were prepared by weight from DDS, Epoxide No. 1(H), Epoxide No. 2(H) and Epoxide No. 3(H). These blends were prepared by adding each individual component directly into THF to assure no reaction occurred between DDS and the epoxides. For quantitative analysis, the following procedure was used:

(a) Solutions of the known standard and the unknown resin were prepared in the THF with the IS (containing one part by weight resin and nine parts by weight IS).

(b) A 6.0 microliter sample of the standard blend + IS solution was analyzed.

(c) A 6.0 microliter sample of the unknown resin + IS solution was analyzed.

(d) The weight percent of free DDS and free Epoxide No. 1(H) was then calculated using the following equation:

$$\%w\ \text{Component} = \underbrace{\left[\frac{\text{Peak Height of Component, cm}}{\text{Peak Height of IS, cm}} \times \frac{\text{Weight IS/ml} \times 9}{\text{Weight Sample/ml}}\right]}_{\text{UNKNOWN RESIN DATA}} \times \underbrace{\left[\frac{\text{Peak Height of IS, cm}}{\text{Peak Height of Component, cm}} \times \frac{\text{Weight Standard Blend/ml}}{\text{Weight IS/ml} \times 9} \times \text{Weight Percent Component in Standard Blend}\right]}_{\text{STANDARD BLEND DATA}}$$

The difference in the sensitivity between the IS and the materials in the resins is not of significance as long as the weight ratio of resin/IS is accurately known.

Figure 46 is a chromatogram of known Blend No. 1 plus the IS. The analysis through elution of the IS was completed in about 66 minutes. The weight percent of DDS and Epoxide No. 1(H) in Blend No. 1 is shown on the chromatogram, 19.7% wt/wt DDS and 56.5% wt/wt Epoxide No. 1(H). After completion of the analysis, 15 minutes were allowed for a reverse-gradient program to the initial solvent condition of 20% THF/80% water and an additional 5-10 minutes allowed for the system to equilibrate before another sample could be injected. Thus, a new sample could be analyzed

Good separation of components and excellent retention time repeatabilities were obtained under these conditions in less than one hour of analysis time. At the completion of an analysis, a 15-minute reverse program was run to re-establish the initial conditions and ready the system for the start of the next run. The analyses were conducted at sensitivity settings of 0.4 or 1.0 Absorbance Units Full Scale (AUFS) in order to keep the DDS and Epoxide No. 1(H) peaks on scale. At these ranges of AUFS, some of the minor components that eluted between DDS and Epoxide No. 1(H) are now only visible as very small peaks above the baseline. The new generation of LLC instrumentation would have been of great value at this point, since microprocessor integration of data, available with the newer units, does not require on-scale readings and allows stronger concentrations to bring out major and minor components in a single run.

The peak marked (A) in Figure 45 was found to be the major advancement peak from 3501-6 and is attributable to the formation of the 1:1 adduct for the major epoxide and the curing agent.

To allow the quantitative determination of DDS and Epoxide No. 1(H) in a 3501-6 resin system, an internal standard and standard blends of known composition were used. The alkyl-phenyl ester, phenyl laurate, was used as the internal standard (IS). This compound was chosen because it had enough alkyl-character to be somewhat retarded by the C_{18} liquid phase in the column and a phenyl group to impart a reasonable sensitivity in the UV between 230-280 nm, and more specifically, at the analytical wavelength of 254 nm that was used. The phenyl laurate eluted in a clear area of the chromatogram, 16 minutes after the last resin component peak under the analysis conditions used.

In order to do quantitative work with the known blends and the IS, it was determined from sensitivity measurements under the chosen analytical conditions that the resin components were about nine times more sensitive than an equal weight of the internal standard. So, all blends for quantitative analyses were made up at one part by weight resin to nine parts by weight IS in THF, based on 0.02 grams resin and 0.18 grams IS per 50 milliliters of

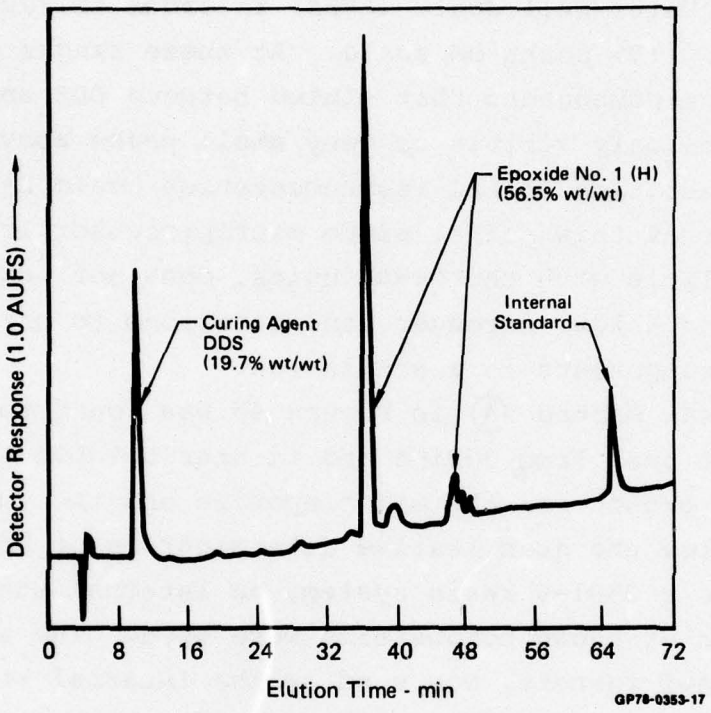

FIGURE 46
KNOWN BLEND NO. 1 PLUS THE INTERNAL STANDARD

about every 1.5 hours. For this run, the ratio of weight IS/ weight Blend No. 1 equalled 7.23. Figure 47 is a chromatogram of known Blend No. 2 plus the IS. This blend contained 30.9% wt/wt DDS and 45.3% wt/wt Epoxide No. 1(H). When comparing Figures 46 and 47, the differences in the peak heights (and thus, the concentrations) for DDS and Epoxide No. 1(H) are quite evident. For this analysis, the ratio of Weight IS/Weight Blend No. 2 equalled 9.06. Figure 48 is the chromatogram obtained for known Blend No. 3 plus the IS, which contained 24.2% wt/wt DDS and 58.6% wt/wt Epoxide No. 1(H). The ratio of Weight IS/Weight Blend No. 3 equalled 8.41.

The actual weight percent composition of known Blends 1, 2 and 3 that are shown in Figures 46-48 and the known compositions were compared with those obtained by duplicate analyses of each blend. These comparisons were made to determine an approximate quantitative accuracy for the technique. To analyze each of the known blends, another of the known blends was used as the standard blend.

The absolute quantitative accuracy of the technique appears to be acceptable. DDS and Epoxide No. 1(H) can be reported to approximately $\pm$1% wt/wt. Not enough data was collected to allow a meaningful statistical treatment of the accuracy of the method.

Figure 49 shows the chromatogram of an old batch of Hercules 3501-6, B239, with the IS added to allow quantitative determination of free DDS and free Epoxide No. 1(H). Notice the height of Peak (A) in this batch, which had been warmed to room temperature and opened several times. Figure 50 shows the chromatogram of an old batch of Hercules 3501-6, B247, with the IS added for quantitative determination. This material contained some cured resin that was insoluble in THF suggesting that it had been more advanced by setting at room temperature for longer periods of time than batch B239 shown in Figure 49. The height of Peak (A) in this obviously advanced material relative to the size of Peak (A) in B239 that contained no material insoluble in THF. Also, the peak heights for DDS and Epoxide No. 1(H) are much lower relative to the IS than found for B239, indicating a considerable

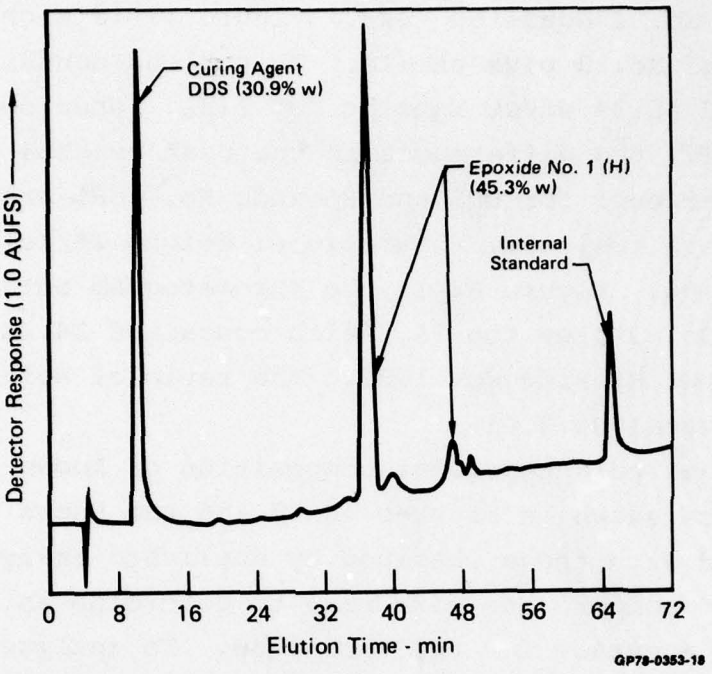

FIGURE 47
KNOWN BLEND NO. 2 PLUS THE INTERNAL STANDARD

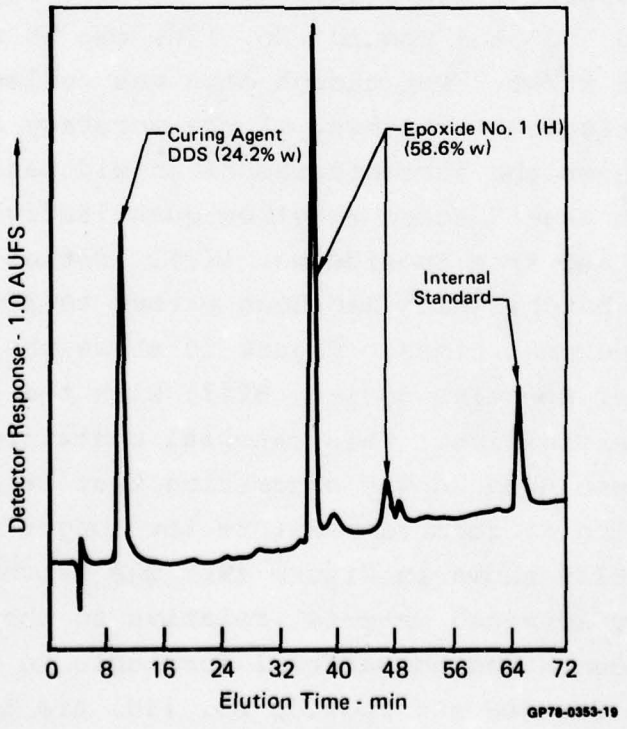

FIGURE 48
KNOWN BLEND NO. 3 PLUS THE INTERNAL STANDARD

283 MCDONNELL AIRCRAFT CO ST LOUIS MO F/G 11/9
TEST PROGRAM EVALUATION OF HERCULES 3501-6 RESIN.(U)
MAY 78 J F CARPENTER N00019-77-C-0155
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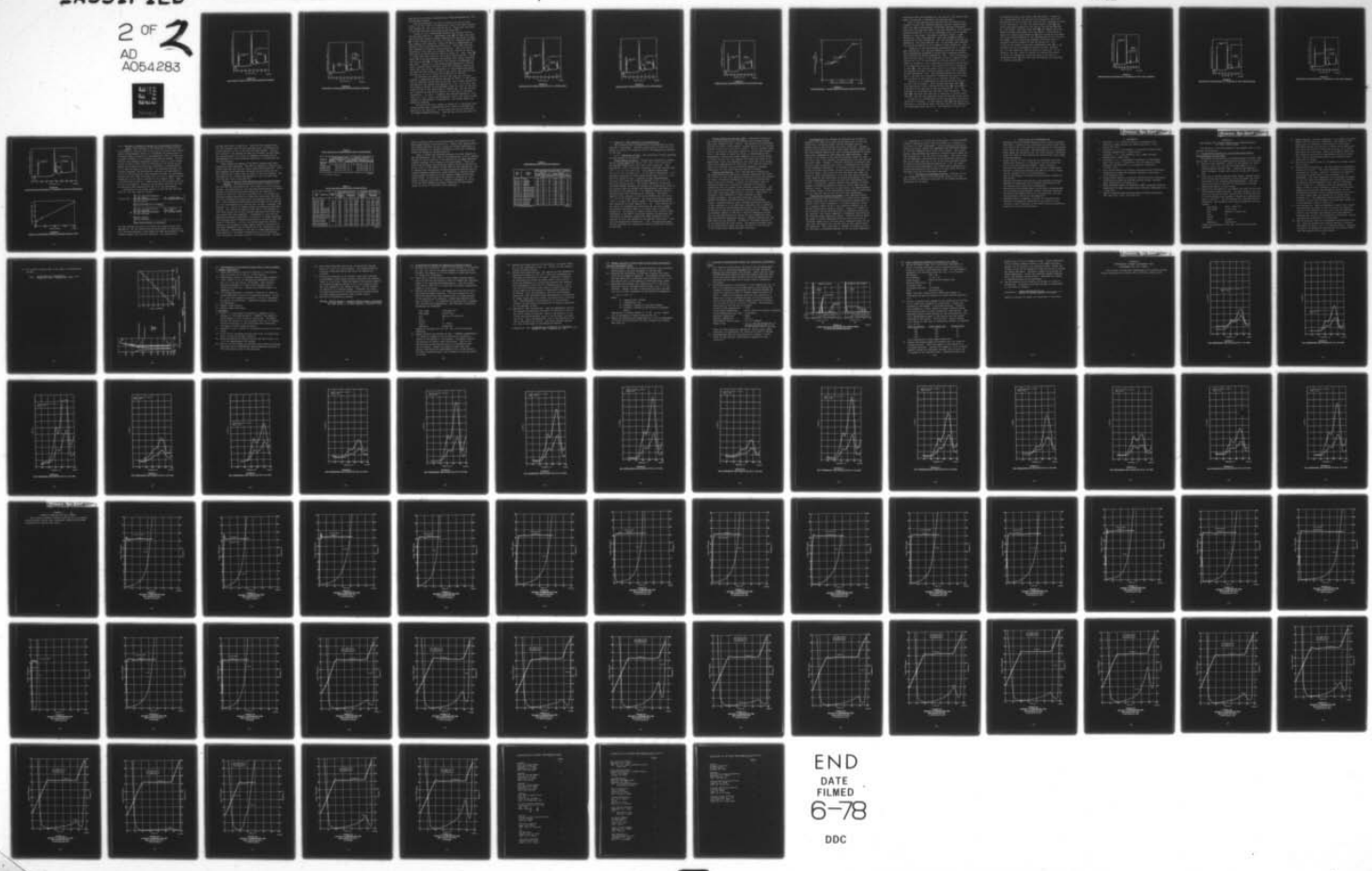

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DATE
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6-78
DDC

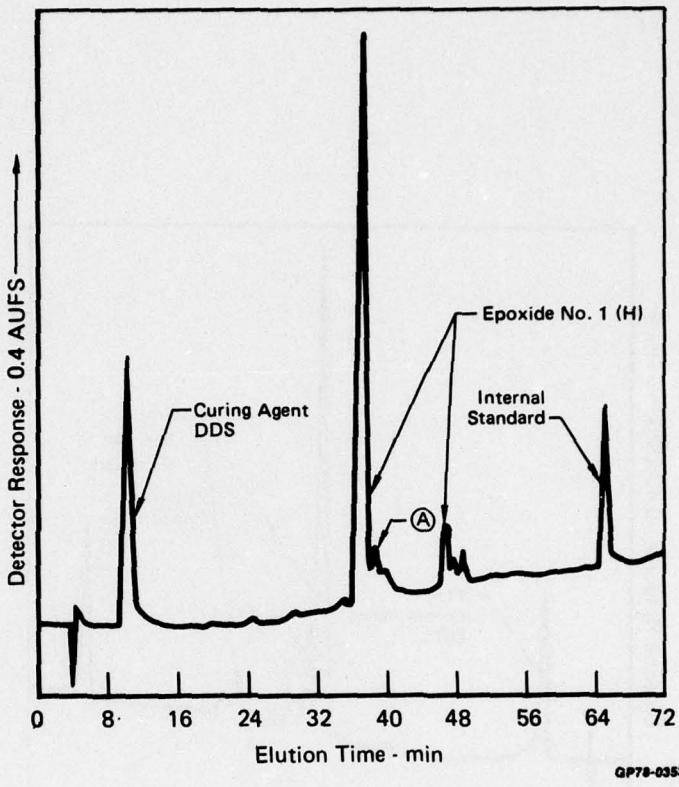

FIGURE 49
BATCH B239 OF HERCULES 3501-6 PLUS INTERNAL STANDARD

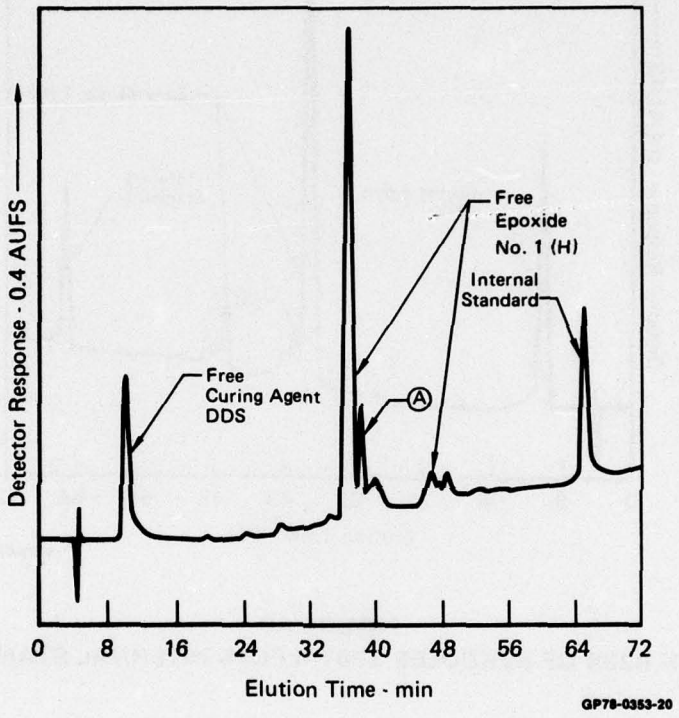

FIGURE 50
BATCH B247 OF HERCULES 3501-6 PLUS INTERNAL STANDARD

portion of the original concentration of DDS and Epoxide No. 1(H) had probably reacted.

The weight percent free DDS in Batches 239 and 247 were found to be 12.7% and 6.2% respectively, while the weight percent free Epoxide No. 1(H) was 37.9% and 28.1%. These data very definitely show that B247 had advanced more than B239.

Figure 51 is a chromatogram obtained for Hercules 3501-6, control batch CRT-76-1. Advancement Peak (A) is small and since this batch was properly staged, comparison of the height of Peak (A) in B239 (Figure 49) with that for CRT-76-1 suggested that B239 was slightly more advanced. Figure 52 shows a chromatogram of Hercules 3501-6, Altered Batch CRT-76-16. Batch CRT-75-16 had been purposely overstaged during production. Both the DDS and Epoxide No. 1(H) peaks are slightly smaller relative to the IS than those for batch CRT-76-1 shown in Figure 51. Also, Peak (A) is larger than that found for the control batch CRT-76-1. Since batch CRT-75-16 was purposely overstaged, this further indicated the size of Peak (A) is related to the degree of advancement of the resin. Figure 53 is the chromatogram obtained for Hercules 3501-6, Special Batch CRT-79-4, which was blended to contain an extra 20% wt/wt of DDS. Examination of this chromatogram shows the peak for DDS relative to the IS was larger than the DDS peak relative to the IS in either batch CRT-76-1 or CRT-79-4.

To determine the amount of total DDS that was initially blended in preparing the special batches of 3501-6, it was necessary to develop a method that would take into account how much of the material had reacted with Epoxide No. 1(H). To do this, the plot shown in Figure 54 was prepared, where the ratio of the peak height of DDS to the peak height of Epoxide No. 1(H) was plotted as a function of the weight percent of total DDS in the known Blends Nos. 1, 2, and 3. Assuming that DDS and Epoxide No. 1(H) react on a 1 to 1 molar (stoichiometric) basis, the ratio of peak heights for DDS relative to Epoxide No. 1(H) should remain essentially constant.

The use of the curve, shown in Figure 54, to determine total weight percent DDS in Batches CRT-76-1, CRT-75-16 and CRT-79-4 were 20.9, 20.6 and 24.6. In all cases this was 4% lower than the vendor-formulated amount. This was due to the fact that the

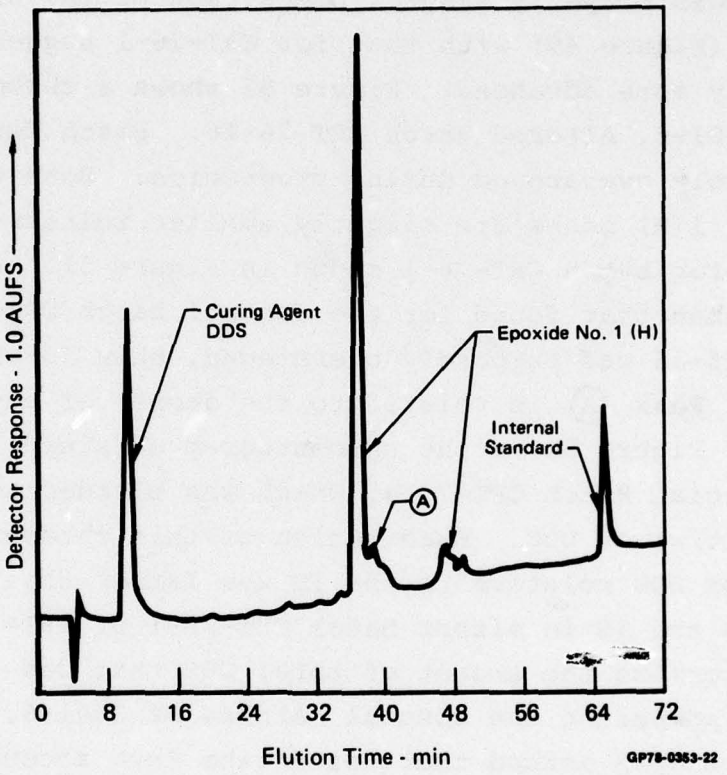

FIGURE 51
HERCULES 3501-6 SPECIAL BATCH CRT-76-1 (CONTROL BATCH)

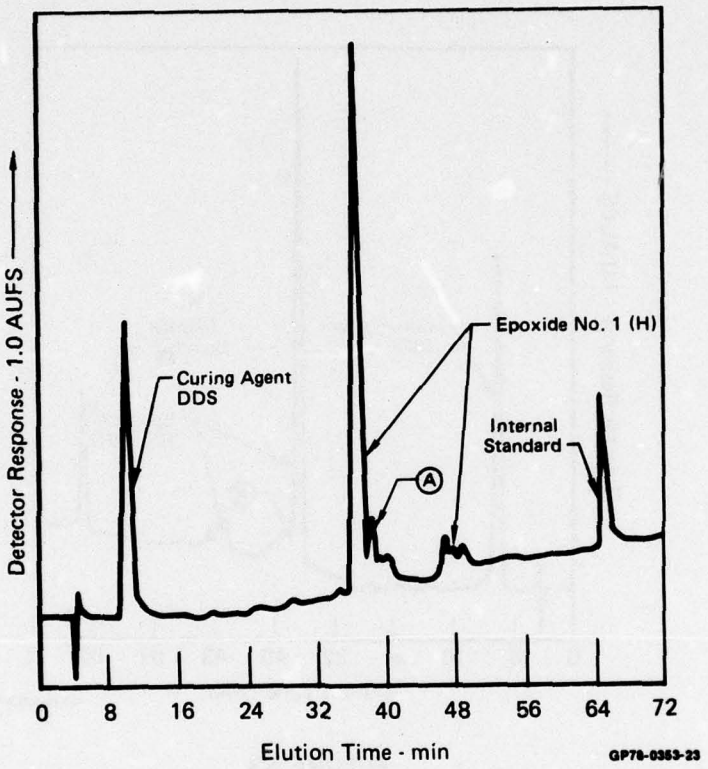

FIGURE 52
HERCULES 3501-6 SPECIAL BATCH CRT-75-16 (OVERSTAGED)

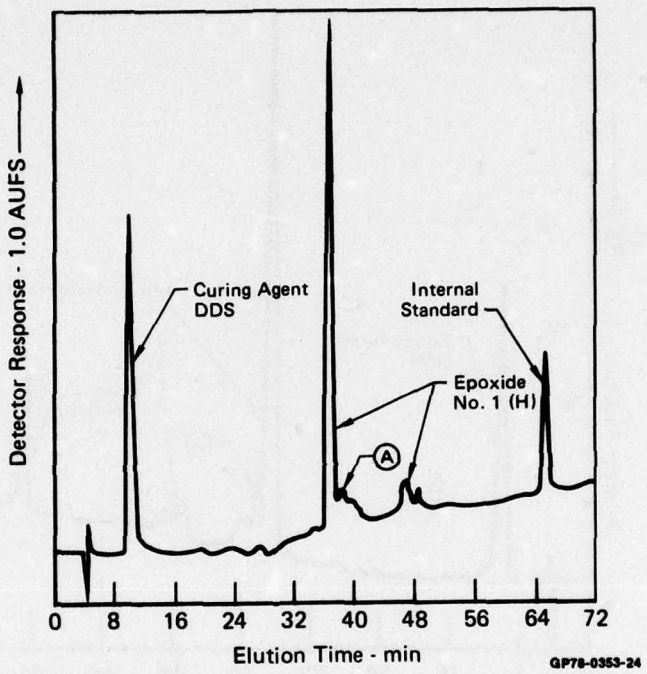

FIGURE 53
HERCULES 3501-6 SPECIAL BATCH CRT-79-4 (PLUS 20%w DDS)

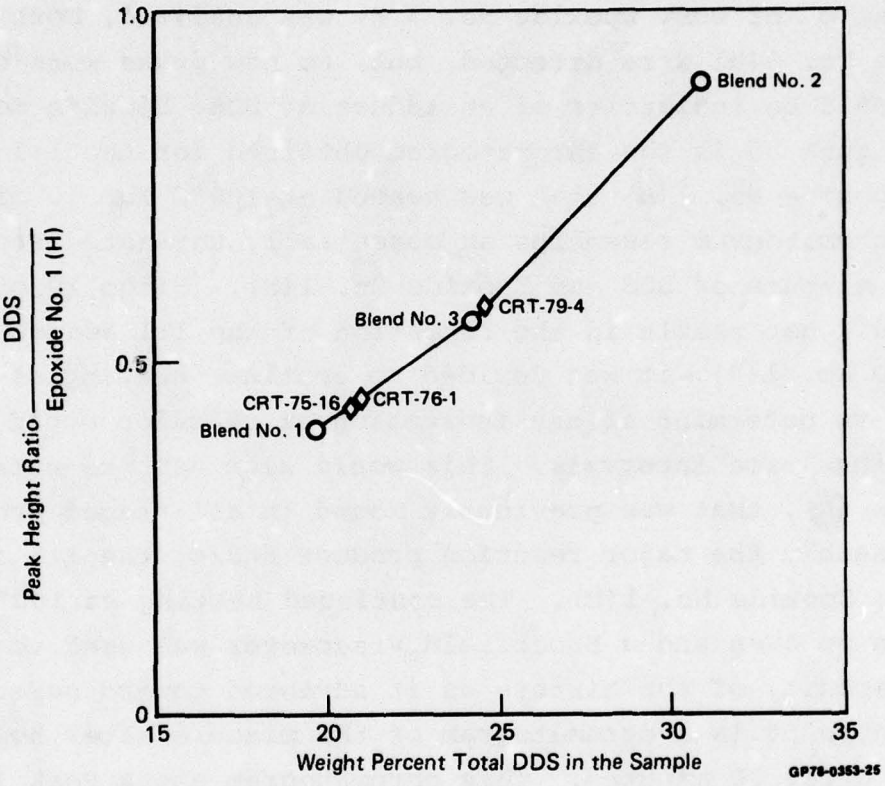

FIGURE 54
DDS/EPOXIDE NO. 1 (H) PEAK HEIGHTS vs WEIGHT PERCENT TOTAL DDS

reaction of DDS with Epoxides No. 2(H) and No. 3(H) had not been taken into account in preparing the working curve.

Each of the epoxides was mixed with DDS and heated in an attempt to detect and identify possible reaction product peaks. Under the same chromatographic conditions employed throughout this work, only DDS was found in the DDS: Epoxide No. 2(H) mixture because Epoxide No. 2(H) is not detectable with this UV system. However, no new peaks, indicating a possible adduct of DDS: Epoxide No. 2(H), were observed. When the attempted adduct preparation of DDS: Epoxide No. 3(H) was analyzed, both DDS and Epoxide No. 3(H) were detected, but, no new peaks were observed that would be indicative of an adduct of DDS: Epoxide No. 3(H).

Figure 55 is the chromatogram obtained for the 1:1 adduct of DDS: Epoxide No. 1(H) that was heated at 100°C for 10 minutes. This chromatogram resembles an essentially unreacted stoichiometric mixture of DDS and Epoxide No. 1(H). Since 10 minutes at 100°C did not result in the formation of the 1:1 adduct of DDS: Epoxide No. 1(H), it was decided to continue heating of this sample to determine if any indication of reaction could be seen at various time intervals. This would also help to establish if Peak (A), that was previously found in all staged products, was possibly the major reaction product and/or the 1:1 adduct of DDS: Epoxide No. 1(H). The continued heating at 100°C was done in an oven and a Brookfield Viscometer was used to follow the viscosity of the mixture as it advanced toward cure.

Figure 56 is a chromatogram of the mixture after heating at 100°C for 20 minutes. This chromatogram shows Peak (A) just beginning to form, indicating that Peak (A) was probably a product of the reaction of DDS and Epoxide No. 1(H). The viscosity at 20 minutes was less than 1,000 centipoise. Also, Peak (A) was about the same size as observed in control batch CRT-76-1, and the old production batch of Hercules 3501-6 B239.

Figure 57 is a chromatogram of the mixture after heating at 100°C for 70 minutes. In this sample, Peak (A) has gained considerably in size and is about the same size as was observed for the overstaged batch CRT-75-16. The viscosity of the mix at

70 minutes was still less than 1,000 centiposie. Figure 58 is a chromatogram of the mixture after heating at 100°C for 390 minutes, at which point the viscosity had increased to about 30,000 centipoise. In this 390 minute sample, Peak (A) was quite large when compared to the size of the DDS and Epoxide No. 1(H) peaks, confirming that Peak (A) was indeed the major reaction product detectable with our system. Also, notice in Figure 58 a second peak marked at (A) that eluted at 40 minutes, which has become prominent in the chromatogram of this 390 minute sample. This second peak probably was indicative of a secondary reaction product of DDS and Epoxide No. 1(H).
A plot of the height of the major advancement Peak (A) vs the minutes that the stoichiometric mixture of DDS: Epoxide No. 1(H) was heated at 100°C is shown in Figure 59. As is shown by the plot, after 20 minutes of heating the mixture at 100°C, an essentially linear increase in the size of advancement Peak (A) with the time the mixture was maintained at 100°C was observed.

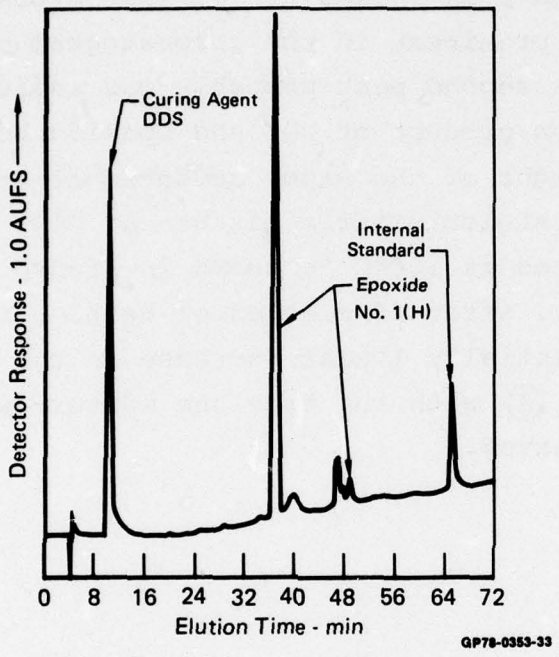

FIGURE 55
MOLAR MIX OF DDS/EPOXIDE NO. 1 (H) HEATED AT 100°C FOR 10 MINUTES

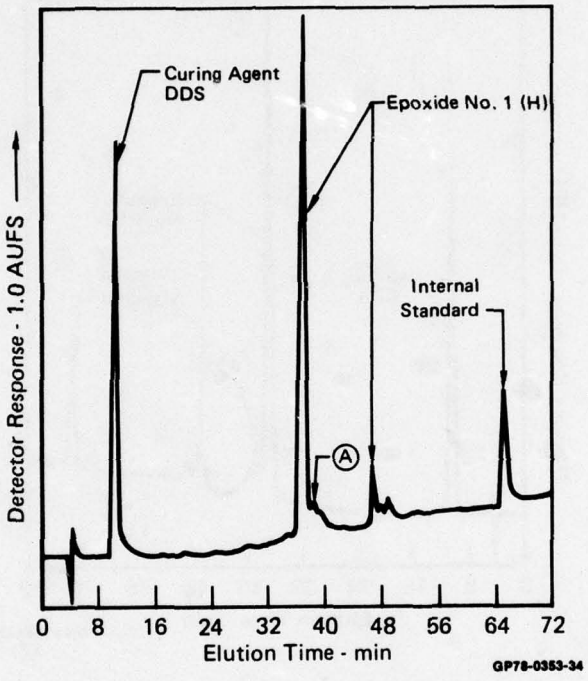

FIGURE 56
MOLAR MIX OF DDS/EPOXIDE NO. 1 (H) HEATED AT 100°C FOR 20 MINUTES

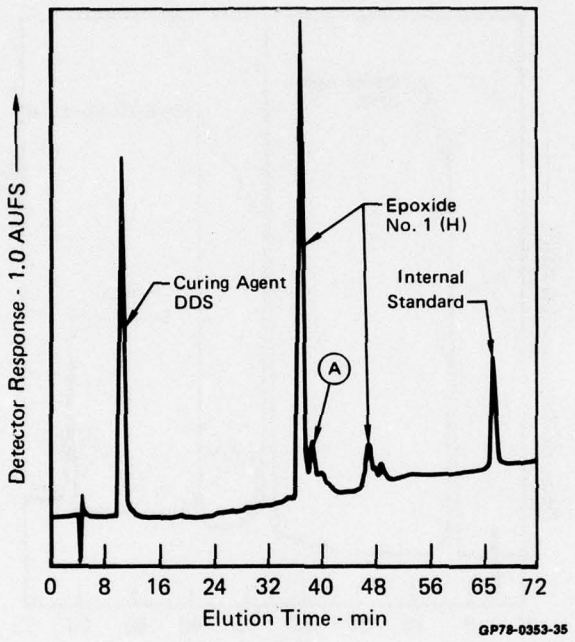

FIGURE 57
MOLAR MIX OF DDS/EPOXIDE NO. 1 (H) HEATED AT 100°C FOR 70 MINUTES

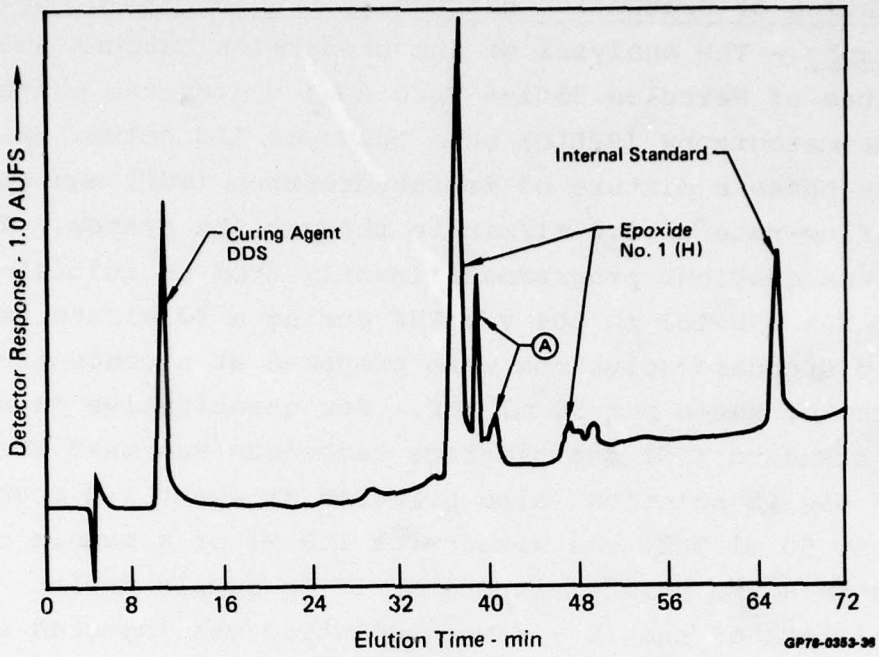

FIGURE 58
MOLAR MIX OF DDS/EPOXIDE NO. 1 (H) HEATED AT 100°C FOR 390 MINUTES

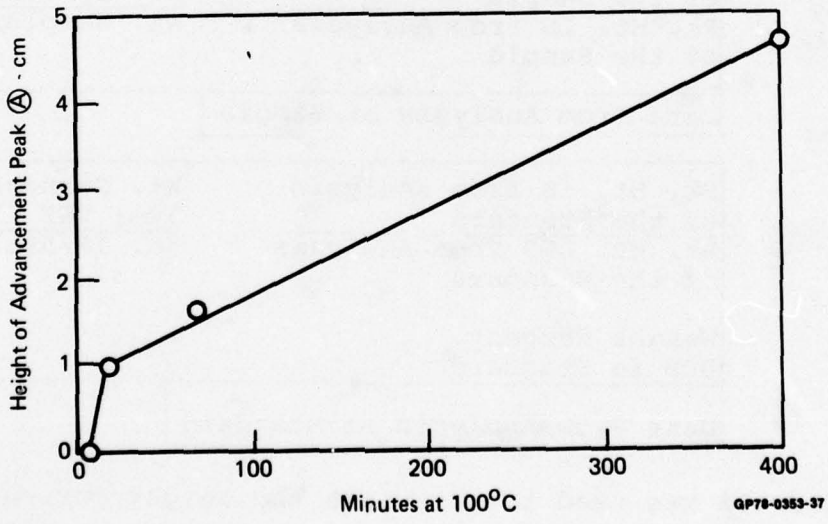

FIGURE 59
HEIGHT OF ADVANCEMENT PEAK Ⓐ vs MINUTES HEATED AT 100°C

3.2.2 Testing of Production Batches by Liquid-Liquid Chromatography - The analyses of the production batches and special batches of Hercules 3501-6 were done by reverse phase liquid-liquid chromatography (RPLLC) on a Bondapak C18 column using as the mobile phase a mixture of tetrahydrofuran (THF) and water at a steady flow-rate of 1.2 ml/minute through the system. The solvent mix was gradient programmed linearly from an initial composition of 20% v/v THF to 60% v/v THF during a 60 minute period. Sample and standard solutions were prepared at a concentration of 1.0 gram of resin per 50 ml THF. For quantitative data, the internal standard (IS) quantitative technique was used wherein 9.0 ml of the IS solution (also prepared at about 1.0 gram phenyl laurate per 50 ml THF) was mixed with 1.0 ml of a sample solution, resulting in a 9/1 wt/wt, mixture of IS to sample resin. Then, 5.0 microliters of the IS - sample solution was injected into the LC unit for analysis. Blends of the standard solutions and sample solutions were analyzed with the IS in the same manner.

Calculation of the weight percent of free DDS and free Epoxide No. 1(H) were done as follows:

$$\%\ \text{wt/wt DDS} = \left[\frac{\text{Pk. Ht. DDS from Analysis of the Sample}}{\text{Pk. Ht. IS from Analysis of the Sample}} \times \frac{\text{Wt. IS/50ml THF}}{\text{Wt. Sample/50ml THF}}\right]_{\text{Data From Analysis of Sample}} \times \left[\frac{\text{Pk. Ht. IS from Analysis of the Standard}}{\text{Pk. Ht. DDS from Analysis of the Standard}} \times \frac{\text{Wt. Standard/50ml THF}}{\text{Wt. IS/50ml THF}} \times \text{Weight Percent DDS in Standard}\right]_{\text{Data From Analysis of Standard}}$$

The same formula was used to calculate the weight percent free Epoxide No. 1(H) by substituting the peak height for Epoxide No. 1(H) from the analysis of the sample and from the analysis of the standard sample into the above equation. All quantitative

analyses were done in duplicate. Each day that analyses were run, the standard solution was analyzed first, followed by duplicate analysis of two of the special blend samples. Usually, this regime of five samples per day was followed, as each analysis required about 1-1/2 hours to complete, including the re-establishment of initial gradient conditions in preparation for the next analysis.

Three production batches of AS/3501-6 prepreg resin were analyzed by this technique. The data is compiled in Table 15 together with data for the neat resin control batch CRT-76-1. This data suggests that additional B-staging occurs during the hot melt application of neat resin to fiber to form the prepreg. The concentration of curative and Epoxide No. 1(H) are both lower than the neat resin, batch CRT-76-1.

3.2.3 Testing of Special Resin Batches by Liquid-Liquid Chromatography - Duplicate analyses are shown in Table 16 for the free DDS and free Epoxide No. 1(H) found in the 16 variation batches. The repeatability for duplicate determinations of weight percent free DDS was quite good except for the analyses of CRT-79-11, CRT-76-12, CRT-75-13 and CRT-75-14. The larger differences between duplicates for these four blends may have been due to an intermittant problem with the pumping system of the LC unit. The difference between duplicate analyses for the Epoxide No. 1(H) was essentially as good as that for DDS, although a few batches, e.g., CRT-76-12 showed greater differences between duplicates. The results for percent free DDS or free Epoxide No. 1(H) found versus the percent blended represents the weight percent reacted for that component. Consistency is good and the method has adequate sensitivity to variation in either component. The technique clearly indicates variations in curative from -20% wt/wt to +20% wt/wt. In fact, the method shows the relative changes in curing agent or major epoxy caused by variations of the other components such as Epoxide No. 2(H), Epoxide No. 3(H) and catalyst. Furthermore in the case of understaged material, batch CRT-75-15, the higher concentration of free Epoxide No. 1(H) indicated a very small percent of the Epoxide No. 1(H)/DDS

TABLE 15
RPLLC ANALYSES FOR PRODUCTION AS/3501-6 PREPREG RESIN

Batch No.	DDS Curing Agent (% wt/wt)			Epoxide No. 1 H (% wt/wt)		
	Hercules Formula	Amount Found (Free)	Δ(1) (Reacted)	Hercules Formula	Amount Found (Unreacted)	Δ (Reacted)
CRT-76-1 (Control)	24.9	20.1 (19.8, 20.4)	4.8	56.5	53.0 (53.7, 52.3)	3.5
B-586 Prepreg		16.8 (17.0, 16.5)	8.1		44.7 (45.1, 44.2)	11.8
B-605 Prepreg		18.1 (18.5, 17.7)	6.8		46.2 (46.9, 45.5)	10.3
B-703 Prepreg		16.2 (16.7, 15.6)	8.7		41.5 (41.6, 41.4)	15.0

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(1) Δ = Total amount - free amount

TABLE 16
RPLLC ANALYSES OF SPECIAL 3501-6 RESIN BATCHES

Batch No.	Description	Variation (phr)	DDS Curing Agent (% wt/wt)		Epoxide No. 1 (H) (% wt/wt)	
			Hercules Formulation (Total)	MCAIR Analysis (Unreacted)	Hercules Formulation (Total)	MCAIR Analysis (Unreacted)
CRT-76-1	Control	–	24.9	20.1 (19.8) (20.4)	56.5	53.0 (53.7) (52.3)
CRT-79-5	DDS	−20%	20.9	16.8 (16.7) (16.9)	59.4	53.5 (53.4) (53.6)
CRT-77-3	DDS	−10%	22.9	19.1 (19.1) (19.0)	57.9	52.8 (53.2) (52.4)
CRT-77-2	DDS	+10%	26.7	23.8 (23.8) (23.8)	55.1	51.7 (51.9) (51.5)
CRT-79-4	DDS	+20%	28.4	24.1 (23.8) (24.4)	53.8	51.6 (51.5) (51.7)
CRT-78-9	Epoxide 2 (H)	−40%	25.8	20.0 (19.9) (20.1)	58.6	54.3 (54.5) (54.3)
CRT-78-7	Epoxide 2 (H)	−20%	25.3	19.2 (18.9) (19.5)	57.8	47.8 (47.9) (47.6)
CRT-76-6	Epoxide 2 (H)	+20%	24.4	19.6 (19.3) (19.8)	55.5	50.0 (49.3) (50.5)
CRT-76-8	Epoxide 2 (H)	+40%	24.0	18.8 (19.1) (18.3)	54.5	51.2 (50.0) (52.4)
CRT-79-11	Epoxide 3 (H)	−50%	26.0	22.4 (23.4) (21.4)	59.0	56.6 (57.7) (55.4)
CRT-76-10	Epoxide 3 (H)	+50%	23.8	19.7 (19.5) (19.8)	54.2	51.5 (51.0) (52.0)
CRT-76-12	Epoxide 3 (H)	+100%	22.9	18.8 (20.4) (17.4)	52.1	49.8 (51.4) (48.2)
CRT-75-13	Catalyst	−50%	25.0	22.4 (23.4) (21.4)	56.8	53.9 (53.5) (54.2)
CRT-75-14	Catalyst	+100%	24.6	19.2 (18.1) (20.2)	55.9	49.9 (49.5) (50.3)
CRT-75-15	Understaged	–	24.9	20.7 (20.3) (21.0)	56.5	54.8 (55.5) (54.0)
CRT-75-16	Overstaged	–	24.9	19.9 (20.0) (19.7)	56.5	50.1 (49.4) (50.7)

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adduct formation while a low concentration was observed in the overstaged material, batch CRT-75-16. Hence, data obtained from this method provides the user a means to observe variations in resin advancement of incoming raw material, and also a possible method for detecting overage material.

Table 17 shows the difference between the total amounts of DDS and Epoxide No. 1(H) used in the preparation of the 16 special batches of 3501-6 relative to the amounts of the free components found by analysis (the average of the duplicates). Since the analytical procedure was previously shown to have an accuracy of ±1.0%, wt/wt, of the amount of free DDS and free Epoxide No. 1(H), it appears that the special batches prepared by Hercules had all reacted somewhat differently, which resulted in varying differences between the amount of each component added and the free amount found. In the case of the amount of Epoxide No. 1(H) found in special batch CRT-78-7, where a difference of -10.0% wt/wt was found between the amount added and the free amount found, an error in formulation was suspected.

TABLE 17
COMPARISON OF RPLLC ANALYTICAL RESULTS

Batch No.	Variation (phr)	DDS Curing Agent (% wt/wt)			Epoxide No. 1 H (% wt/wt)		
		Hercules Formula	Amount Found (Free)	Δ(1) (Reacted)	Hercules Formula	Amount Found (Free)	Δ(1) (Reacted)
CRT-76-1	Control	24.9	20.1	4.8	56.5	53.0	3.5
CRT-77-2	+10% DDS	26.7	23.8	2.9	55.1	51.7	3.4
CRT-77-3	−10% DDS	22.9	19.1	3.8	57.9	52.8	5.1
CRT-79-4	+20% DDS	28.4	24.1	4.3	53.8	51.6	2.2
CRT-79-5	−20% DDS	20.9	16.8	4.1	59.4	53.5	5.9
CRT-76-6	+20% Epoxide 2(H)	24.4	19.6	4.8	55.5	50.0	5.5
CRT-78-7	−20% Epoxide 2(H)	25.3	19.2	6.1	57.8	47.8	10.0
CRT-76-8	+40% Epoxide 2(H)	24.0	18.8	5.2	54.5	51.2	3.3
CRT-78-9	−40% Epoxide 2(H)	25.8	20.0	5.8	58.6	54.3	4.3
CRT-76-10	+50% Epoxide 3(H)	23.8	19.7	4.1	54.2	51.5	2.7
CRT-79-11	−50% Epoxide 3(H)	26.0	22.4	3.6	59.0	56.6	2.4
CRT-76-12	+100% Epoxide 3(H)	22.9	18.8	4.1	52.1	49.8	2.3
CRT-75-13	−50% Catalyst	25.0	22.4	2.6	56.8	53.9	2.9
CRT-75-14	+100% Catalyst	24.6	19.2	5.4	55.9	49.9	6.0
CRT-75-15	*Understaged*	24.9	20.7	4.2	56.5	54.8	1.7
CRT-75-16	Overstaged	24.9	19.9	5.0	56.5	50.1	6.4

(1) Δ = Total amount - free amount

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3.3 Phase III - Data Analysis and Interpretation

The evaluation and interpretation of program data are summarized in this phase. Detailed correlations of data were presented in tabular and graphical form in the appropriate sections of the text.

3.3.1 Evaluation of Data - The evaluation of data generated by this program is as follows:

Physiochemical Analysis - Intentional variations in weight percent curing agent were (20.9, 22.9, 24.9, 26.7, and 28.4). Our analysis found (21.2, 22.3, 24.1, 25.8 and 29.0). For Epoxide No. 2 (H), intentional variations in weight percent were (5.6, 7.4, 9.0, 10.6 and 12.2). Our analysis values were (6.1, 6.9, 9.5, 9.8 and 11.0). In the case of Epoxide No. 3 (H), Hercules variations in total amounts added were (4.4, 8.5, 12.2 and 15.6) weight percent. Analysis by gas chromatography gave only the "free" or unreacted amounts as (3.3, 5.6, 8.3, and 11.5) weight percent. The latter comparison of Hercules and MCAIR values indicated the changes in concentration to be in the correct order and showed that approximately one-quarter to one-third of the Epoxide No. 3 (H) added by Hercules had prereacted during their processing or B-staging. The actual amounts of BF_3 catalyst in the varied formulations were (0.57, 1.13 and 2.23) weight percent. Our analytical results showed (0.64, 1.24 and 2.44) weight percent. No suitable method has been developed for total Epoxide No. 1 (H). Since Epoxide No. 1 (H) cannot be independently determined, We use total weight per epoxide equivalent (WPE) as a control test in receiving inspection. All batches of special resins were tested for WPE. Variations in the WPE of individual epoxide raw materials and variations in Hercules staging precluded assessment of the accuracy of this test method for the special resin mixes. Thus, with the exception of Epoxide No. 1 (H), our analytical test results confirmed the intentional chemical variations reported by Hercules.

Dynamic Mechanical Analysis (DMA) - Rheovibron testing of the cured films from each of the special resin batches showed only minor changes in Tan δ and E*. The dynamic Tg's determined from the loss Tan δ peaks showed a maximum spread for all altered batches of only 25°C (from 244 to 265°C). The two extreme values were for the lowest and highest amounts of curing agent respectively. The spread in static Tg values, as determined by DSC measurements, showed even lesser changes, with a maximum spread in values of only 14°C. The dynamic Tg values were close to the temperatures which corresponding to the rapid drop in E* values. These lower temperatures for rapid loss in E* and the static Tg values are believed to more accurately represent a maximum temperature for the resin than the dynamic Tg values.

Moisture Sensitivity - Cast film specimens prepared for DMA measurements were exposed to elevated temperature and humidity (140°F, 95% RH) until moisture saturation levels were reached. The rates of moisture absorption for all special batches were found to be quite similar. A minor, but consistent trend in moisture pickup rate, indicated an increase in diffusion coefficient with an increase in BF_3 catalyst concentration. The total equilibrium moisture under the exposure conditions showed only minor variations ranging from 5 to 6 wt%. Here again, an increase in BF_3 resulted in a small increase in total moisture absorbed. The specimen containing +100% BF_3 showed the greatest moisture pickup of all the specimens tested. Extended exposure under elevated conditions resulted in what appeared to be an additional secondary rise in moisture pickup, beyond the established equilibrium. This secondary rise in moisture pickup was attributed to microcracking. Attempts to determine changes in DMA due to moisture absorption failed. The thin specimens dried out during the slow temperature scan rate required for Rheovibron testing. Humidity control with the Rheovibron was not feasible. Attempts to determine changes in Tg by pressurized DSC also failed. The external pressure could not be controlled to match the vapor pressure of the moisture in the hermetically sealed specimen containers.

Processability was assessed by measuring the viscosity changes of the resin melt under varied conditions of time and temperature, including changes during isothermal heating, dynamic heating and simulated cure cycle conditions. Batches containing low precents of DDS curing agent exhibit greater flow than the standard formulation, while increased amounts of curing agent show a decrease in flow under the same conditions. Variations in the amount of BF_3 have the greatest effect on flow and time to gel, with high BF_3 concentrations giving low flow and short gel times. Changes in flow are important in laminate fabrication since an optimum cure cycle is established on the basis of the standard formulation. An increase in flow will manifest itself by excess resin bleed, giving a resin-poor laminate. On the other hand, a resin with low flow and short gel times can result in resin-rich laminates, or in the case where gellation occurs ahead of the application of autoclave pressure, the result is poor consolidation of plies and very low interlaminar properties. Fortunately, current chemical test methods are shown capable of affording adequate control of curing agent and BF_3 catalyst levels. Though not as quantitative, an added dimension of quality control is the demonstrated relationships established for gel time and the critical points of DSC thermograms.

Advanced Test Method Development which emphasized RPLLC demonstrated the value and potential of liquid-liquid chromatogrpahic techniques for rapid and simultaneous determination of several 3501-6 resin components in a single operation. While not a panacea, RPLCC can be a cost effective addition to improved physiochemical quality control. Operation of RPLLC in the isocratic elution mode detected all components except the BF_3 catalyst, the latter component is adequately controlled by the existing atomic absorption method. Gradient-elution RPLLC was shown to afford advantages over isocratic elution by an increased resolution of the more polar components while at the same time, decreasing the time per test by more rapid elution of components. This techniques is capable of analyzing 3501-6 for the free or uncombined amounts of the two major components,

i.e., Epoxide No. 1 (H) and the curing agent. It also provides a means of measuring their reaction product as a function of the degree of resin advancement. Three production batches of prepreg resin were tested and reasonable and consistent amounts of the free components were found to be present. The sixteen special resin batches were tested by gradient elution RPLLC for free Epoxide No. 1 (H) and free curing agent. This data could not be adequately interpreted due to the possible reaction of the curing agent with any or all of the three epoxides present. In order to bring both DDS and Epoxide No. 1 (H) "on scale" for quantitative measurement, our present RPLLC equipment required that sensitivity be reduced to a point where the minor epoxides could not be effectively measured.

3.3.2 Revision of Acceptance Criteria - Revision of current acceptance limits is not warranted, based on the very small effects of chemical variations on the dynamic mechanical properties of the resin.

4. CONCLUSIONS AND RECOMMENDATIONS

- Previously developed physiochemical quality control methods, Reference 1, quantitatively confirmed the vendor-stated chemical variations in off-specification batches for curing agent, major epoxy, and catalyst. The determination of a uncombined minor epoxy was consistent with the total amounts, indicating about one third of this epoxide had reacted with curing agent during processing.
- Vendor batches of resin supplied as overstaged and understaged were difficult to distinguish from one another by any of the physiochemical methods. Resin viscosity profiles did indicate less flow for the over staged batch.
- Changes in amounts of catalyst and amounts of curing agent had the greatest effect on processability.
- None of the changes in chemistry significantly changed the DMA results.
- Moisture diffusion rates and the total percent of moisture absorbed at saturation did not change significantly with the compositional variations investigated.
- Gradient-elution reverse phase liquid-liquid chromatography is a promising physiochemical quality assurance technique and method development should be continued using the new, microprocessor controlled instrumentation.
- Improved quality acceptance criteria for prepreg resins should be continued by investigating the effect of variations in resin chemistry on the matrix-critical mechanical properties of the cured laminates.

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5. REFERENCES

1. Carpenter, J. F., "Quality Control of Structural Non-metallics," NASA Contract No. N00019-76-C-0138. Final report June 1976.
2. Carpenter, J. F., with Kaelble, D.,Rockwell Science Center, Personal Communication, January 1978.
3. Carpenter, J. F., with Browning, C.E., AFML, Personal Communication, March 1978.
4. Carpenter, J. F., "Instrumental Techniques for Developing Epoxy Cure Cycles," Presented at the 21st National SAMPE Symposium and Exhibition at Los Angeles, California, 6-8 April 1976.
5. First Annual Meeting on Chemical Characterization Techniques, Cosponsored by AFML and Lockheed, Sunnyvale, California, 24-25 February 1976.
6. Second Annual Meeting on Chemical Characterization Techniques, Cosponsored by AFML and Rockwell Science Center, Thousand Oaks, California, 8-10 March 1977.
7. Naval Advisory Council on Materials (NMAC) Technical Standing Committee on Polymer Characterization Meeting, Washington, D.C., 17 May 1977.
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APPENDIX A

TEST METHODS FOR CHEMICAL ANALYSIS AND CHARACTERIZATION OF 3501-6 RESIN SYSTEM

The details of the physiochemical test methods used in this program are presented.

A.1 IR Quantitative Method for Curing Agent-Ciba Eporal, Diaminodiphenyl Sulfone (DDS)

The method for determining the diaminodiphenyl sulfone (DDS) curing agent in AS/3501-6 graphite/epoxy prepregs is as follows:

(1) Working curve procedure: Weigh (to the nearest 0.1 milligram) 50, 100, 150, and 200 milligram samples of 4, 4, diaminodiphenyl sulfone (DDS). Transfer the samples to 100ml volumetric flasks and dilute to volume with chloroform.

(2) Place two 1.0 mm KBr precision path length, matched liquid cells filled with chloroform in both the sample and reference beams of the infrared spectrophotometer. Scan the region from 1000 to 1200 cm^{-1} to insure that no solvent absorptions appear in this region.

(3) Replace the chloroform in the sample cell with the 50 milligram standard sample solution. For best results, the cell should be emptied and then flushed with 2-3 fresh portions of the solutions to be analyzed. Record the spectrum from 1000 to 1200 cm^{-1}. For the Beckman IR-9 infrared spectrophotometer, the following instrumental parameters are suggested:

Scan Range	1000 - 1200 cm^{-1}
Scan Speed	40 cm^{-1}/min
Slit	Routine (2 times std.)
Gain	3%
Period	2
Scale	0-100% T
Reference	Chloroform

Repeat the analysis for the 100, 150 and 200 milligram standards.

(4) Sample analysis for DDS: Transfer 1.5 of prepreg to approximately 50 milliliters of chloroform. The weight of the sample shall be measured to the nearest 0.1 milligram. Thoroughly agitate the solution to assure resin dissolution. This can be achieved by placing the solution in an ultrasonic bath for 15 minutes. Remove the graphite fiber from this solution and wash with approximately 40 ml of chloroform. Add this chloroform wash to the volumetric flask and dilute to volume.

(5) Analyze the liquid portion of the sample in a manner identical to Step 3.

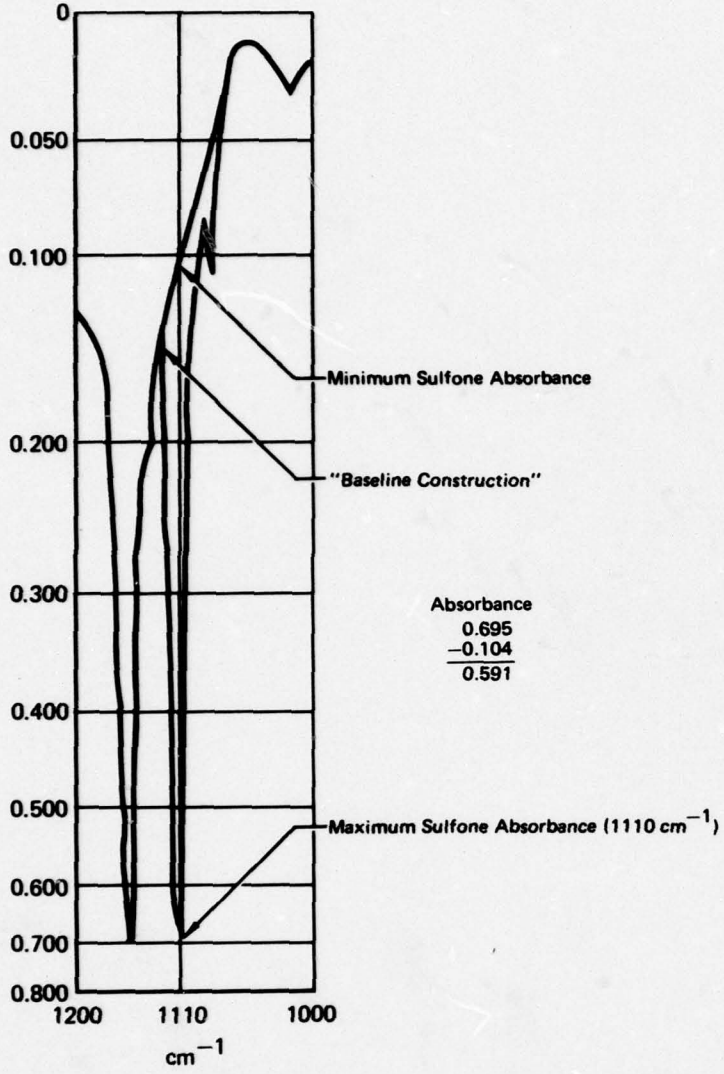
(6) Working Curve Construction: The DDS exhibits an absorption maximum at 1110 cm^{-1}. The total absorbance of this band is calculated as follows: Construct a baseline by connecting the minima on either side of the very sharp 1110 cm^{-1} absorbance. The total absorbance is the maximum absorbance at 1110 cm^{-1} minus the absorbance of a point which bisects the baseline and corresponds to the 1110 cm^{-1} frequency point, Figure A-1. A working curve for determining the amount of DDS in actual samples of prepreg is constructed graphically by plotting the absorbance values for the standard DDS solutions versus concentrations in mg./100 ml on linear graph paper and connecting the points with a straight line. The absorbance values should be on the ordinate (y-axis) and the amount of curing agent should be on the abscissa (x-axis), Figure A-1.

(7) DDS Calculation: Take the absorbance value of the samples and determine the amount of DDS in the 100 ml sample by drawing a line parallel to the x-axis from the absorbance value to the straight line working curve and dropping a perpendicular line to the mg DDS/100 ml chloroform. Record the value as mg DDS/100 ml in chloroform.

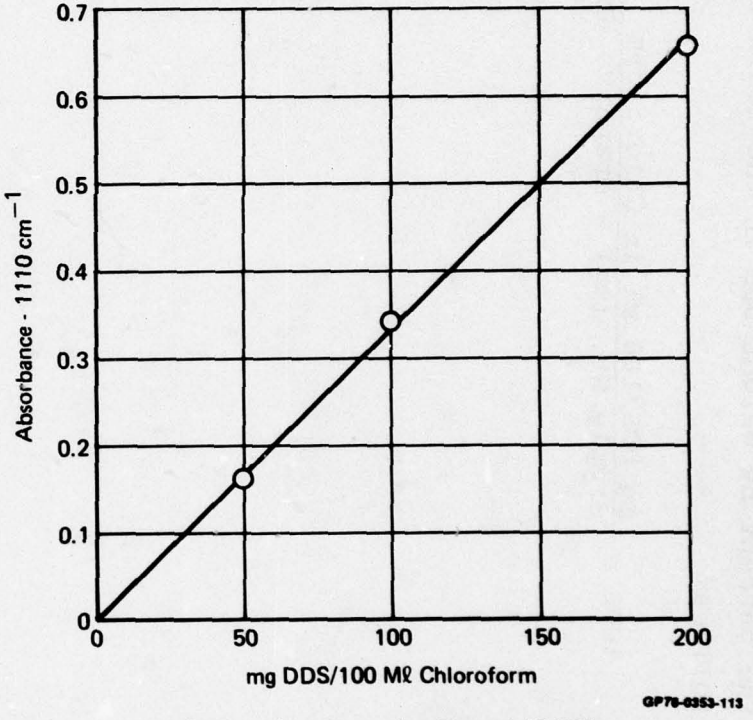
(8) Add the graphite fiber to a preweighed fritted glass crucible. Wash the graphite with copious amounts of acetone followed by drying at 100° C to constant weight. Determine the amount of graphite by subtracting the crucible weight from the graphite plus crucible weight.

(9) The percent by weight DDS in the resin is calculated as follows:

$$\%DDS = \frac{\text{mg DDS/100 ml in Chloroform}}{\text{Sample Wt. (mg) - Graphite Wt. (mg)}} \times 100$$



IR Measurement of Sulfone Absorbance



Calibration Curve for Eporal (DDS)

FIGURE A-1
DETERMINATION OF EPORAL (DDS) CONCENTRATION

A.2 Determination of the Epoxide Content WPE in 3501-6 Prepreg

o Reagent Preparation

(1) Cresol Red indicator solution: Dissolve 0.1 gram sodium salt of cresol red in 100 ml. of 50% ethanol.

(2) Hydrochloric Acid in 1,4 Dioxane Solution (approximately 0.2N): pipet 1.6 ml. of concentrate hydrochloric acid (sp. gr. 1.19) per 100 ml. of dioxane. This solution should be prepared in a dark bottle equipped with a Teflon-line screw cap. Prepare only enough reagent for immediate use.

(3) 0.1N Sodium Hydroxide in Methanol: Dissolve 4.0 grams of sodium hydroxide in 200 ml. of anhydrous methanol. Dilute to 1 liter with anhydrous methanol. Filter if necessary, to remove any insolubles. Standardize against potassium acid phthalate.

(4) Reagent grade acetone.

(5) Reagent grade chloroform.

o Procedure

(1) Weigh a 1.5 gram sample of prepreg or adhesive to the nearest 0.1 milligram accuracy. Transfer this sample to approximately 75 milliliters of chloroform. Thoroughly agitate the solution in an ultrasonic bath for 15 minutes. Dilute the solution to 100 milliliters with chloroform and shake to assure adequate mixing.

(2) Transfer a 50 ml. aliquot of the sample solution to a 250-ml. flask.

(3) To the 50 ml. of sample solution add 10-ml of acetone and, 20-ml. of the HCL-dioxane solution.

(4) Swirl the mixture to effect solution and then allow it to stand for approximately 90 minutes.

(5) Add 1-ml of the cresol red indicator and titrate the excess acid with the 0.1N methanolic sodium hydroxide solution to the first violet color of the end point.

(6) Run a blank titration with 50 ml. of chloroform through steps 3, 4, and 5 of the procedure. Two blanks should be titrated, preferable before and after the samples are titrated.

(7) Filter the remainder of the solution from step 1 through a preweighed fritted glass crucible, retaining the graphite fiber or scrim cloth. Wash the support with copious amounts of acetone followed by drying at 50° C for graphite fiber and room temperature for adhesive scrim. Dry the supporting material to a constant weight. Determine the amount of supporting material by substracting the crucible weight from the supporting material plus crucible weight.

(8) The WPE is calculated as follows:

$$WPE = \frac{500 \text{ (Sample Weight. - Graphite Weight)/100ml. chloroform}}{\text{[ml NaOH (Blank) - ml NaOH (Sample)] x Normality NaOH}}$$

A.3 IR Quantitative Method for Epoxide No.2(H)(3501-6 Resin)

(1) Working Curve Procedure: Weigh (to the nearest 0.1 milligram) 50, 100, 150, and 200 milligram samples of Epoxide No.2(H). Transfer the samples to 100 ml volumetric flasks and dilute to volume with chloroform.

(2) Place two 1.0 mm KBr precision path length matched liquid cells filled with chloroform in both the sample and reference beams of the infrared spectrophotometer. Scan the region from 1600 to 1800 cm^{-1} to insure that no solvent absorptions appear in this region.

(3) Replace the chloroform in the sample cell with the 50 milligram standard sample solution. For best results the cell should be emptied and then flushed with 2-3 fresh portions of the solution to be analyzed. Record the spectrum from 1600 to 1800 cm^{-1}. If recording the spectrum with a Beckman IR-9 infrared spectrophotometer, the following instrumental parameters are suggested:

Scan range	1600-1800 cm^{-1}
Scan speed	40 cm^{-1}/min
Slit	Routine (2 times std)
Gain	3%
Period	2
Scale	0 - 100% T
Reference	Chloroform

Repeat the analysis for the 100, 150, and 200 milligram standards.

(4) Sample analysis for Epoxide No.2(H): Transfer approximately 2.75 grams of prepreg to 50 milliliters of chloroform. (Weigh to the nearest 0.1 milligram). Thoroughly agitate the solution to assure resin dissolution. This can be achieved by placing the solution in an ultrasonic bath for 15 minutes. Remove the graphite fiber from this solution and wash with approximately 40 ml of chloroform. Add this chloroform wash to the volumetric flask and dilute to volume.

(5) Analyze the liquid portion of the sample in a manner identical to that described in step (3). Filter off the graphite fibers and obtain weight.

(6) Working Curve Construction: The Epoxide No.2(H) exhibits an absorption maximum at 1730 cm^{-1}. The total absorbance of this band is calculated as follows: Construct a baseline by connecting the minima on either side of the 1730 cm^{-1} minus the abosrbance of a point which bisects the baseline and corresponds to the 1730 cm^{-1} frequency point. A working curve for determining the amount of Epoxide No.2(H) in actual samples of the prepreg is constructed graphically as follows. Plot the absorbance value for the standard Epoxide No. 2(H) solutions versus concentration in mg/100 ml on linear graph paper and connect the points with a straight line. The absorbance values should be on the ordinate (y-axis) and the amount of Epoxide No. 2(H)/100 ml should be on the abscissa (x-axis).

(7) Epoxide No. 2(H) calculations: Take the absorbance value of the samples and determine the amount of Epoxide No. 2(H) in the 100 ml sample as follows: Draw a line parallel to the x-axis from the absorbance value to the straight line working curve. Drop a perpendicular line to the Epoxide No.2(H) 100 ml chloroform and record. The weight percent Epoxide No. 2(H) in the resin is calculated as follows:

$$\% \text{ Epoxide No. 2(H)} = \frac{\text{mg Epoxide No.2(H)/100 ml in chloroform}}{\text{sample wt (mg) - graphite wt. (mg)}} \times 100$$

A.4 Thermal Analysis of 3501-6 Resin System Using Differential Scanning Calorimetry (DSC)

(1) Use the DuPont 990 Thermal Analysis System or the equivalent Perkin-Elmer or Mettler equipment in the DSC mode.

(2) Generate DSC thermograms in 20ml/min nitrogen flow using 10-15 mg of prepreg or adhesive. Satisfactory sensitivity for the DuPont 990 is obtained using settings of 0.1 to 1.0 mcal/sec/in and a scale setting of 50°C/inch chart speed.

(3) Determine the exotherm peak temperatures for a series of three DSC runs at different heating rates, e.g. 5, 10 and 20°C/min. Reduce the data by obtaining the best straight line fit by linear regression of the Arrhenius expression:

$$\log \phi = A/T + B$$

Where:

ϕ = Heating rate (°C/Min)

T = Temperature (°K)

A = Constant, related to activation energy

B = Constant, related to the Arrhenius frequency factor

Statistical fit should exceed $r^2 = 0.98$. If not, repeat runs as necessary to improve statistical fit.

(4) Report the exotherm peak temperature in °C for a progression of 5°C/min calculated from the best straight line formula from Step (3).

A.5 Gas-Liquid Chromatographic Method for Epoxide No.3(H)(3501-6) Resin)

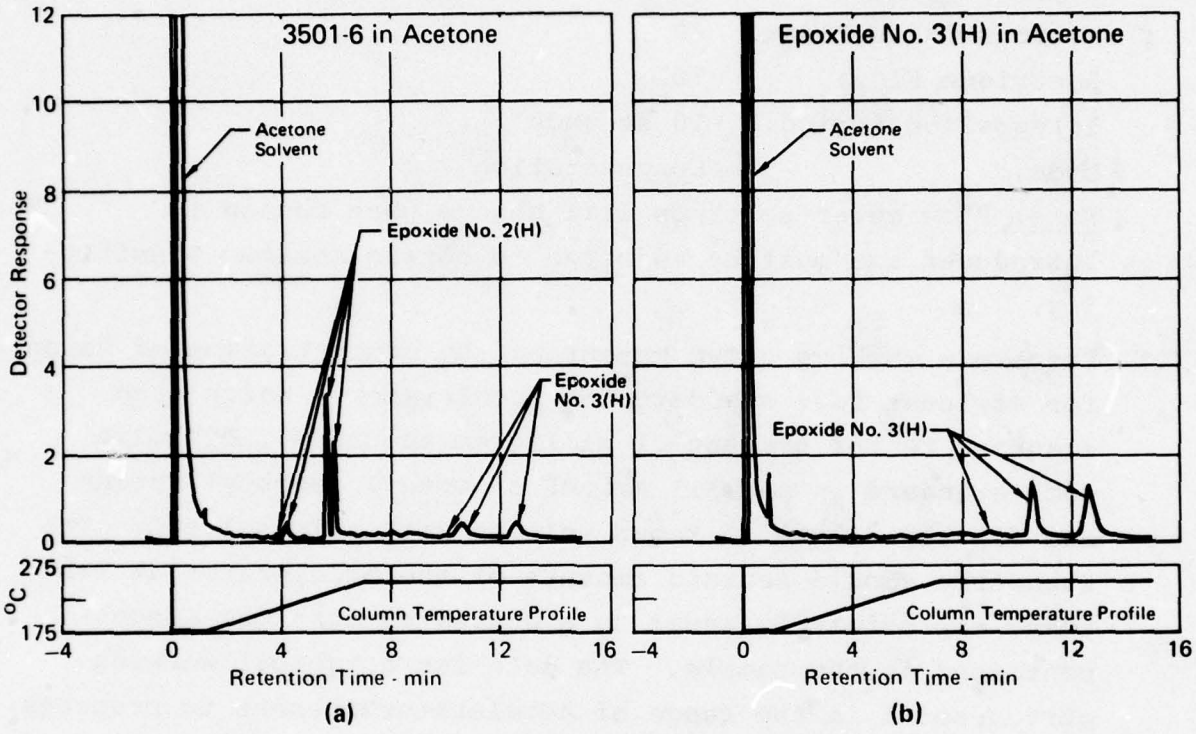
(1) Use a Hewlett-Packard Model 5750 gas-liquid chromatographic (GLC) unit or equivalent equipped with a flame ionization detector and using Dexsil 300 columns. Dexsil 300 is a polycarboranesiloxane material with high thermal stability that can be operated between 50-500°C and can be maintained for sustained periods above 400°C without loss of separation efficiency.

(2) The weight percent of unreacted or "free" Epoxide No.3(H) in 3501-6 is determined by the comparison of peak heights for standard solutions of Epoxide No.3(H) with peak heights obtained for Epoxide No.3(H) in unknown sample solutions of 3501-6. Prepare the standard solutions by dissolving 0.5 grams and 1.0 gram of Epoxide No.3(H) in 25 ml portions of acetone and prepare the unknown sample solution by dissolving 1.0 gram of 3501-6 in 25 ml of acetone. The operating conditions for the GLC are as follows:

Initial Column Temperature	: 175°C
Final Column Temperature	: 300°C (Hold till analysis complete)
Column Temperature Rise Rate	: 15°C/minute
Vaporizer Temperature	: 280°C
Detector Temperature	: 250°C
Electrometer Current Range	: 8×10^{-9} amperes
Sample Sizes	: 2.0 μ l for the Epoxide No.(3) standard solutions and 5.0 μℓ of the unknown 3501-6 solution

Under the above operating conditions, the two major peaks indicative of Epoxide No.3(H) elute at 8.6 and 9.5 minutes

(3) Chromatograms used for the analysis are similar to those shown for the original identification Epoxide No.3(H), Figure A-2.



GP78-0353-112

FIGURE A-2
IDENTIFICATION OF EPOXIDE NO. 3(H) IN 3501-6 RESIN BY GAS PHASE CHROMATOGRAPHY

A.6 Atomic Absorption Method for Accelerator in 3501-6

(1) Set up the Perkin Elmer 503 or equivalent instrument to obtain a maximum absorbance with an aqueous solution of boron in a nitrous oxide-acetylene flame. The instrumental parameters for the Perkin Elmer 503 unit are as follows:

Wavelength:	249.7 nm
Slit Setting:	0.7 mn (-4)
Light Source:	Boron hollow cathode lamp
Nitrous Oxide Flow:	40
Acetylene Flow:	70
Integration Period:	10 seconds
Mode:	Concentration

Note: Flow meter settings will change when sample is introduced and must be adjusted to obtain maximum sensitivity.

(2) Prepare a working curve measuring the concentration of boron for at least four standards of accelerator. Weigh each standard to the nearest .1 milligram accuracy. Dissolve each standard in a small amount of methyl isobutyl ketone and finally dilute to known volumes with this solvent. The standards should contain amounts of the accelerator at less than, approximately equal to and greater than the amount contained in the sample. The data for a typical working curve useful in the range of accelerator present to prepregs, i.e., 1%, is

Grams Accelerator	Final Volume (ml)	Concentration
.025	100	15
.050	100	30
.075	100	42
.100	100	62

Plot Concentration versus Grams Accelerator

(3) Prepare the prepreg sample by weighing ten (10) grams of prepreg material. Weigh the sample to the nearest 0.1 milligram accuracy. Transfer the sample to 50 ml of methyl isobutyl ketone and thoroughly agitate this solution for 15 minutes in an ultrasonic bath. Completely decant the

solvent into a 100 ml volumetric flask. Add an additional 30 ml of methyl isobutyl ketone to the sample and again agitate for 15 minutes in an ultrasonic bath. Decant the solvent in the 100 ml volumetric flask and dilute to volume and shake thoroughly. Withdraw a sample for analysis by atomic absorption. Filter the remaining support material onto a pre-weighed fritted filter. Determine the weight of supporting material by difference.

(4) Use the working curve to obtain the weight to volume of accelerator. Calculate the weight percent of accelerator in the resin as follows:

$$\text{Accelerator} = \frac{\text{grams accelerator/100 ml}}{\text{Sample wt.(grams)-Graphite wt.(grams)}} \times 10$$

Report as percent by weight of accelerator in the resin.

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APPENDIX B

DIFFERENTIAL SCANNING CALORIMETRY (DSC) THERMOGRAMS FOR 3501-6 RESIN

This section includes DSC thermograms of all sixteen altered batches analyzed by the DuPont 990 at 10°C/min. heating rate.

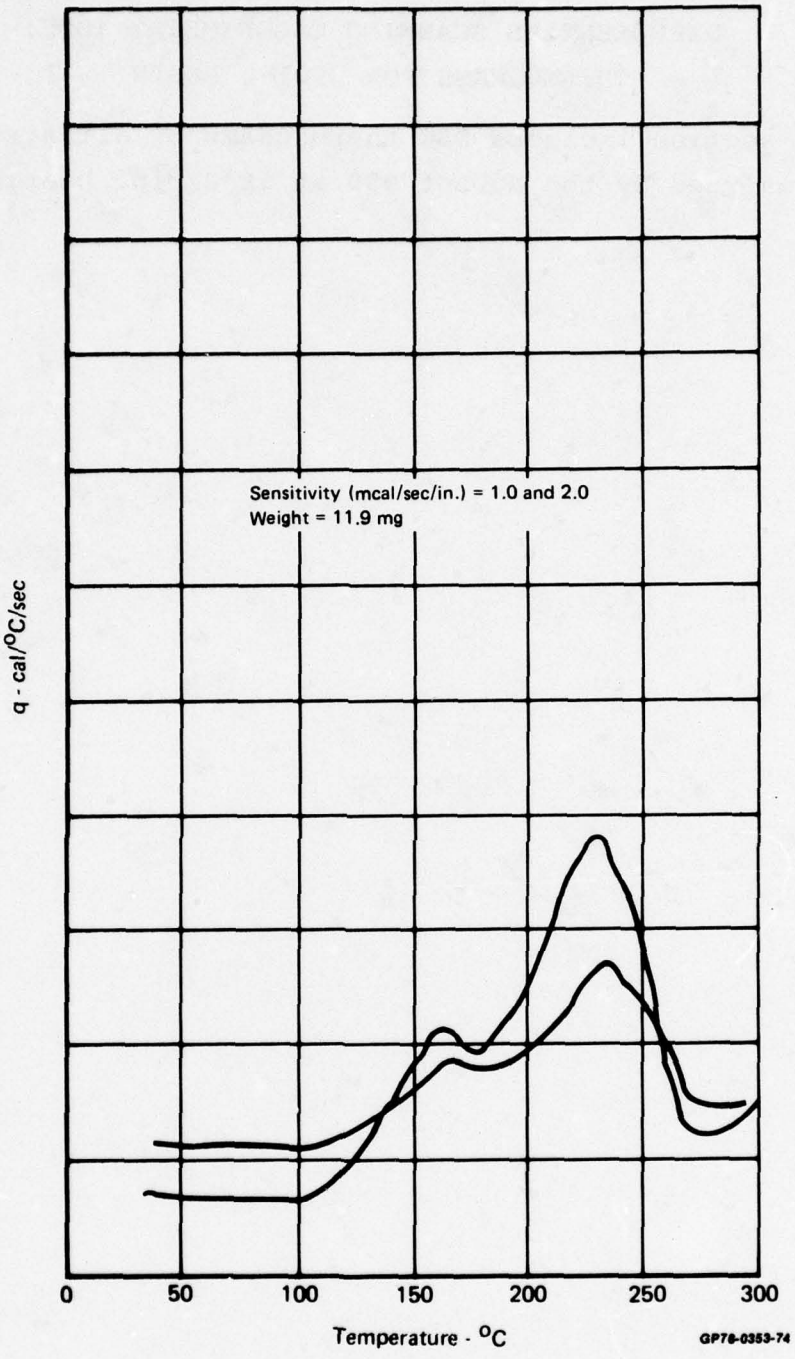

FIGURE B-1
DSC THERMOGRAM, 3501-6 BATCH CRT 76-1, 10°C/MIN

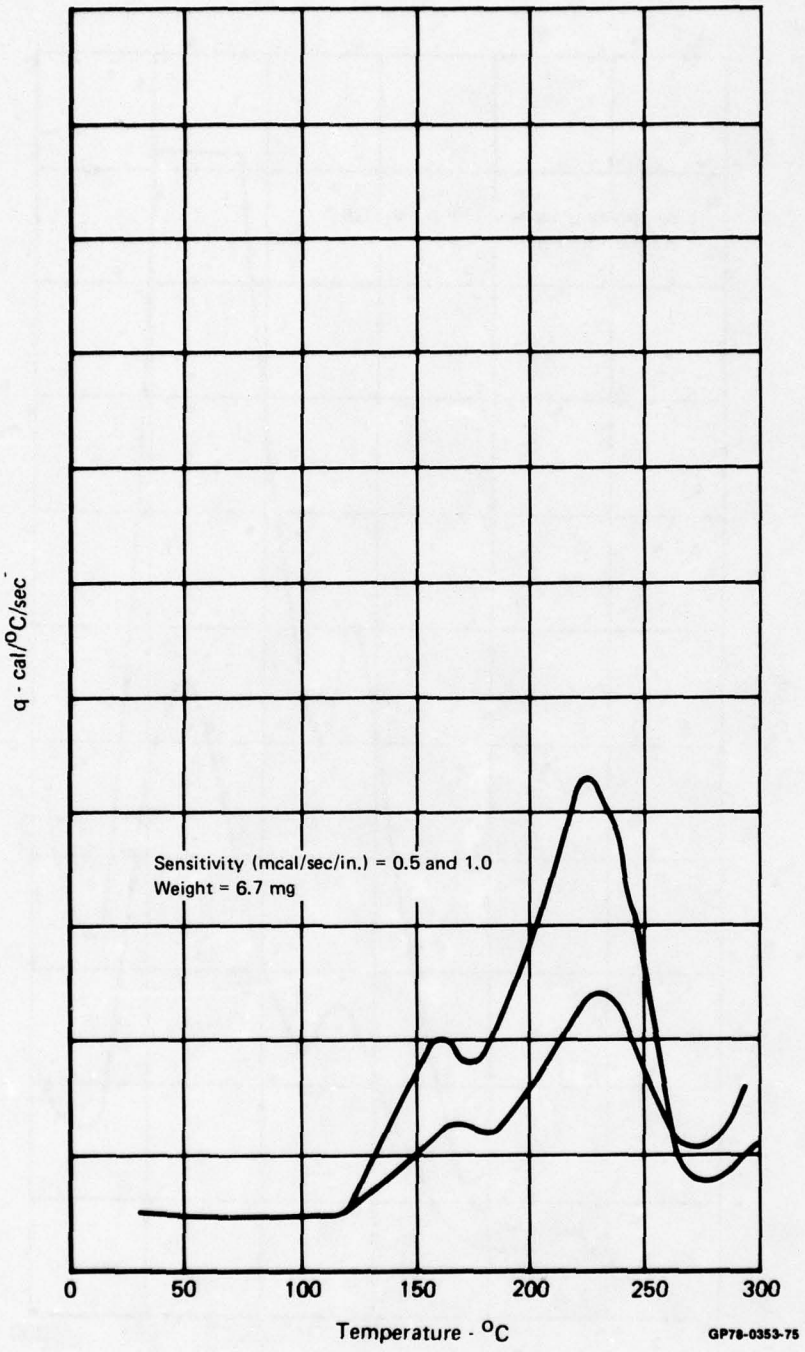

FIGURE B-2
DSC THERMOGRAM, 3501-6 BATCH CRT-77-2, 10°C/MIN

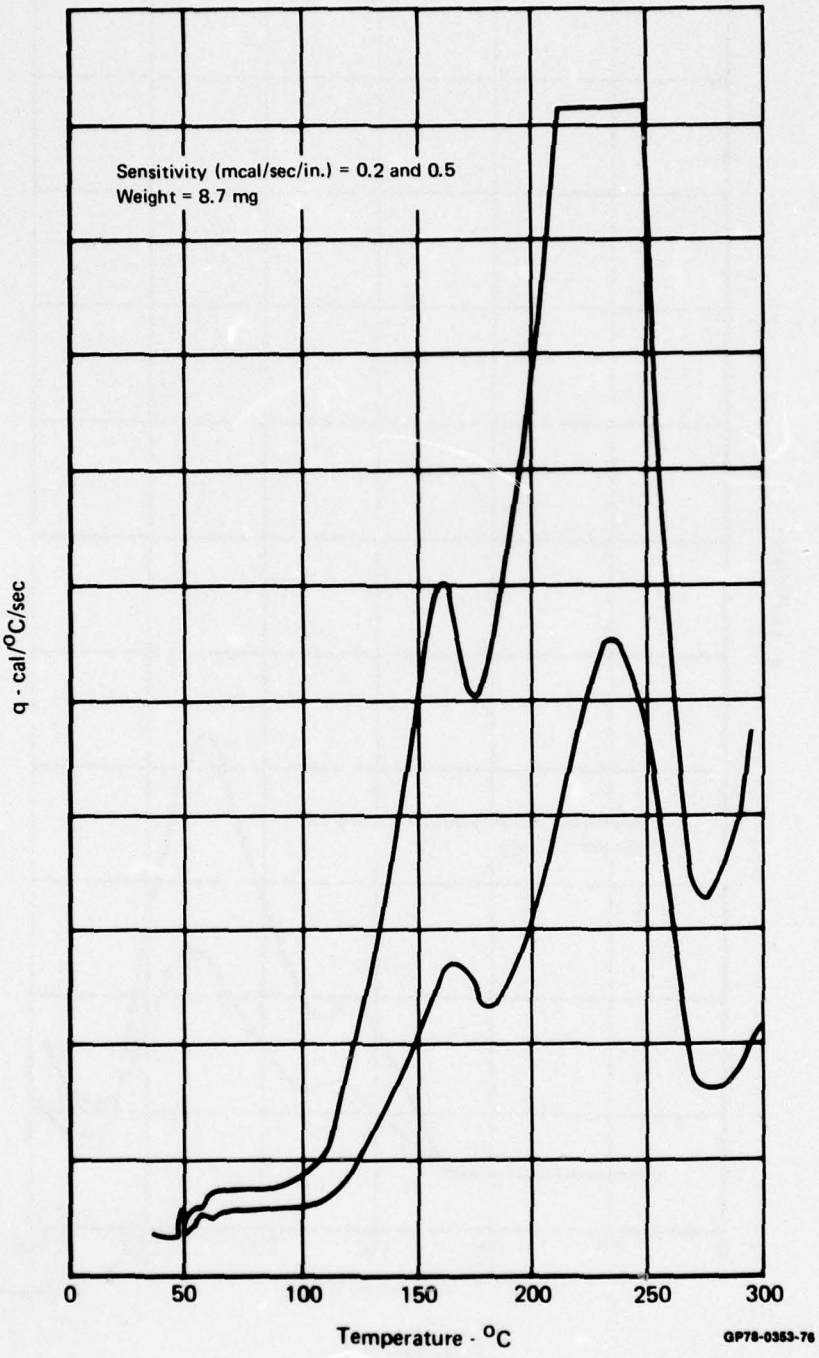

FIGURE B-3
DSC THERMOGRAM, 3501-6 BATCH CRT-77-3, 10°C/MIN

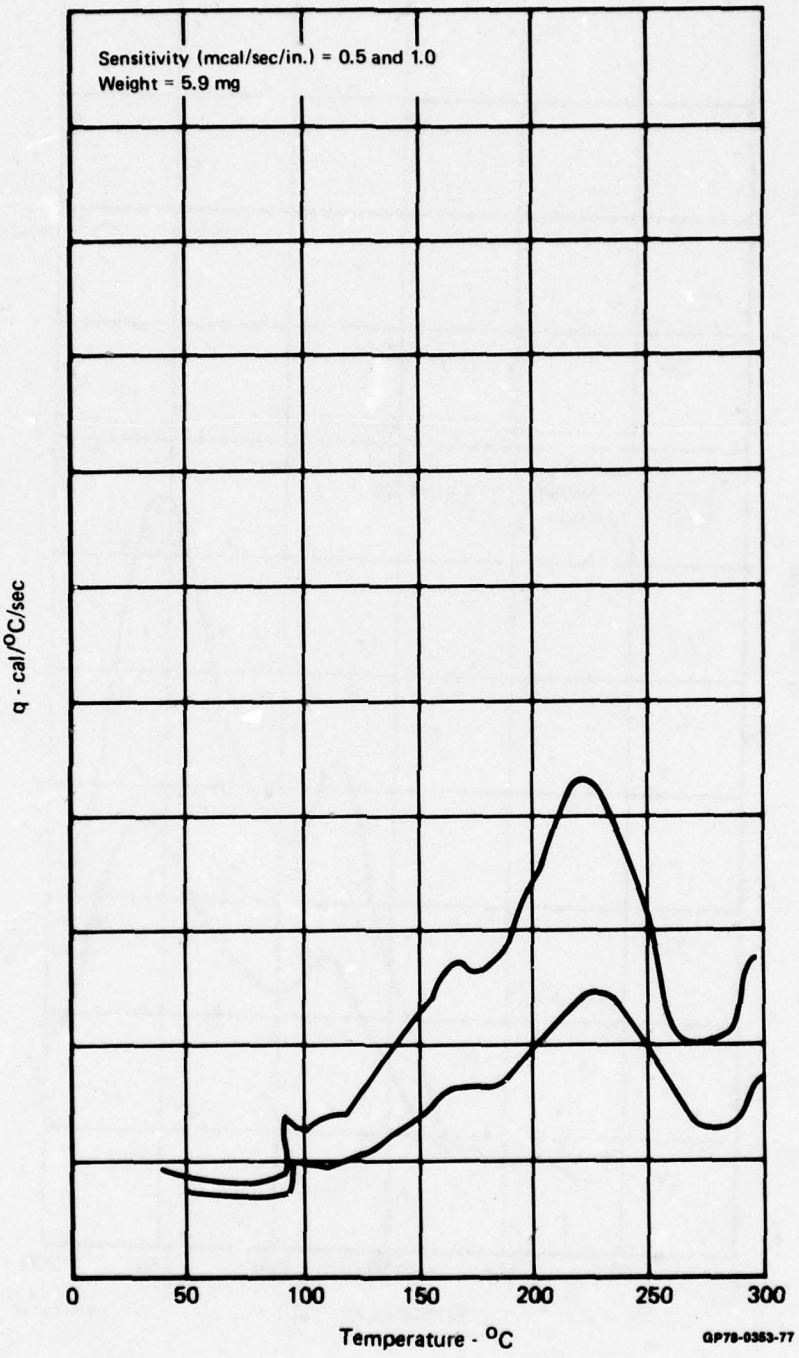

FIGURE B-4
DSC THERMOGRAM, 3501-6 BATCH CRT-79-4, 10°C/MIN

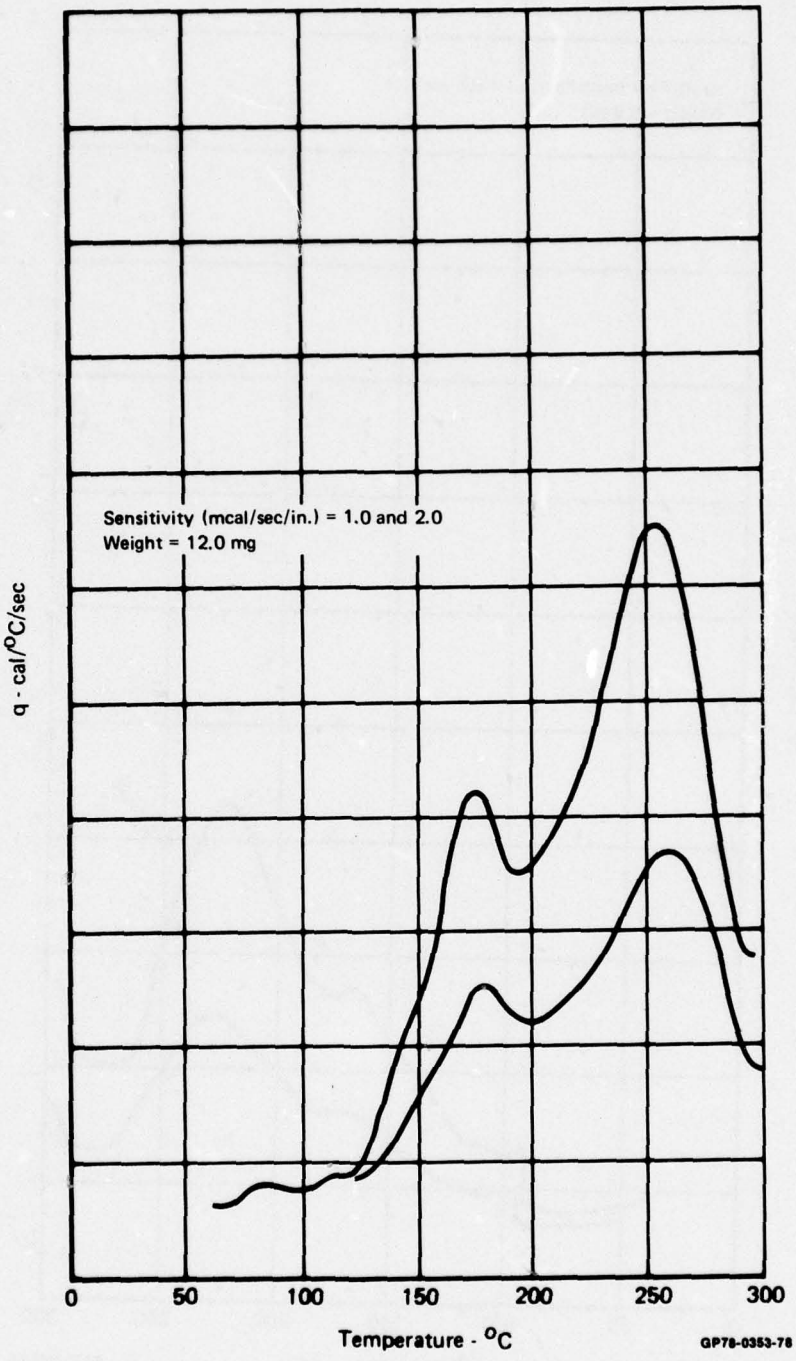

FIGURE B-5
DSC THERMOGRAM, 3501-6 BATCH CRT-79-5, 10°C/MIN

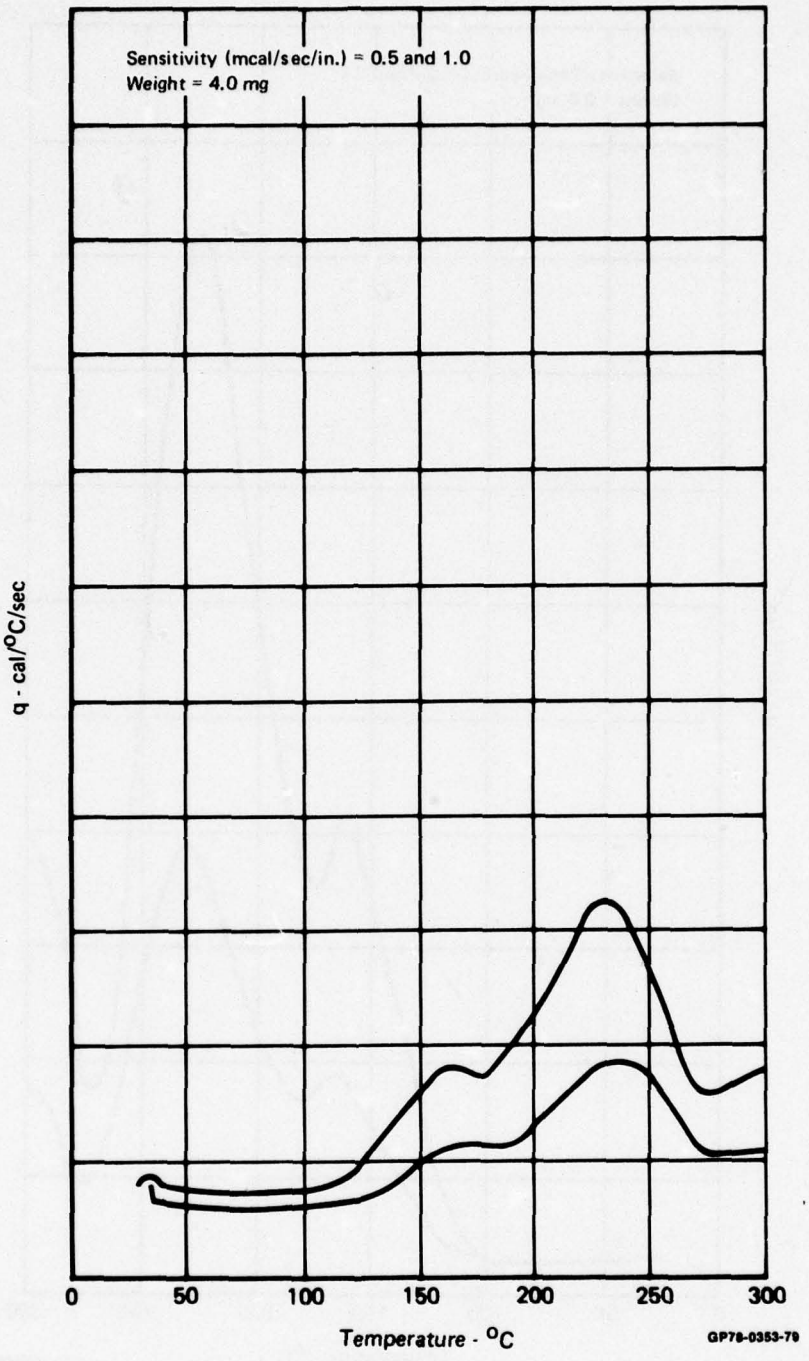

FIGURE B-6
DSC THERMOGRAM, 3501-6 BATCH CRT-76-6, 10°C/MIN

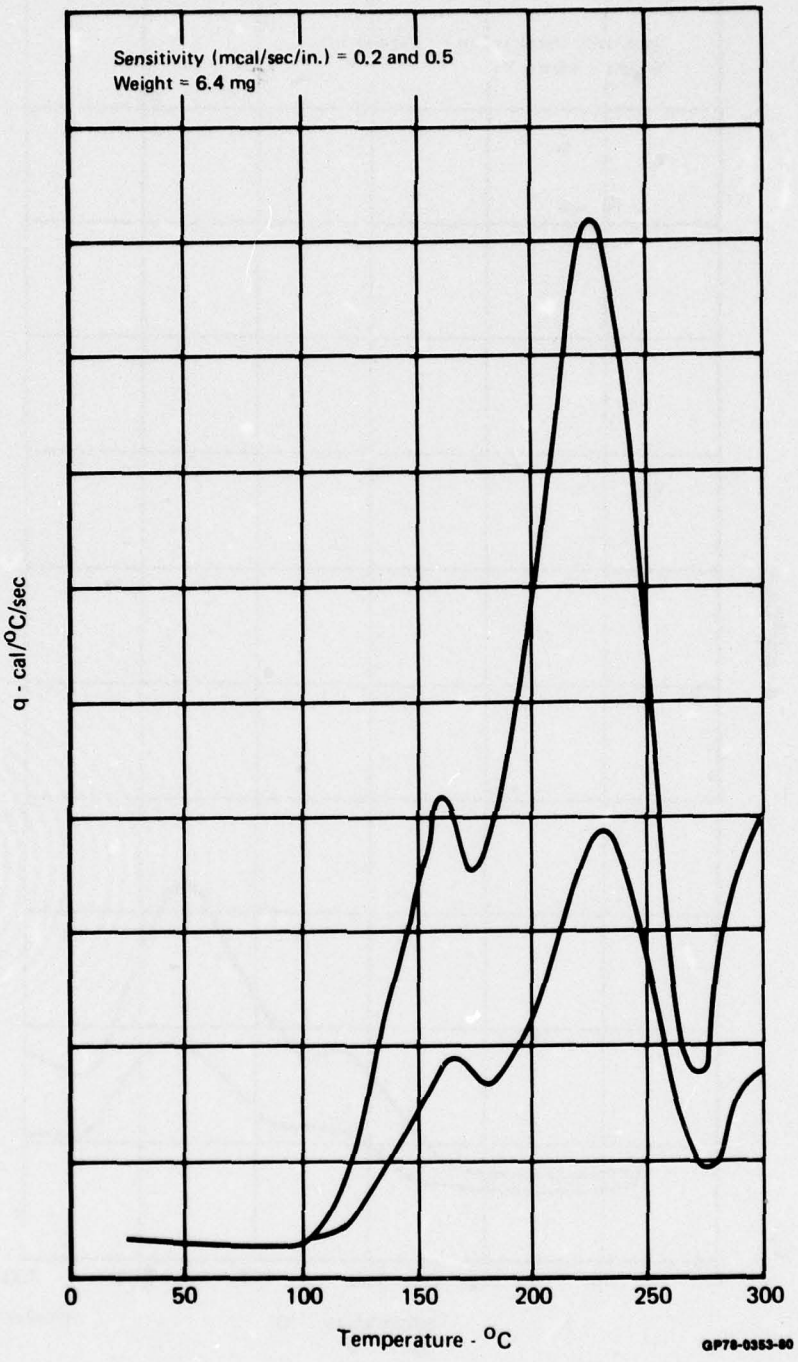

FIGURE B-7
DSC THERMOGRAM, 3501-6 BATCH CRT-78-7, 10°C/MIN

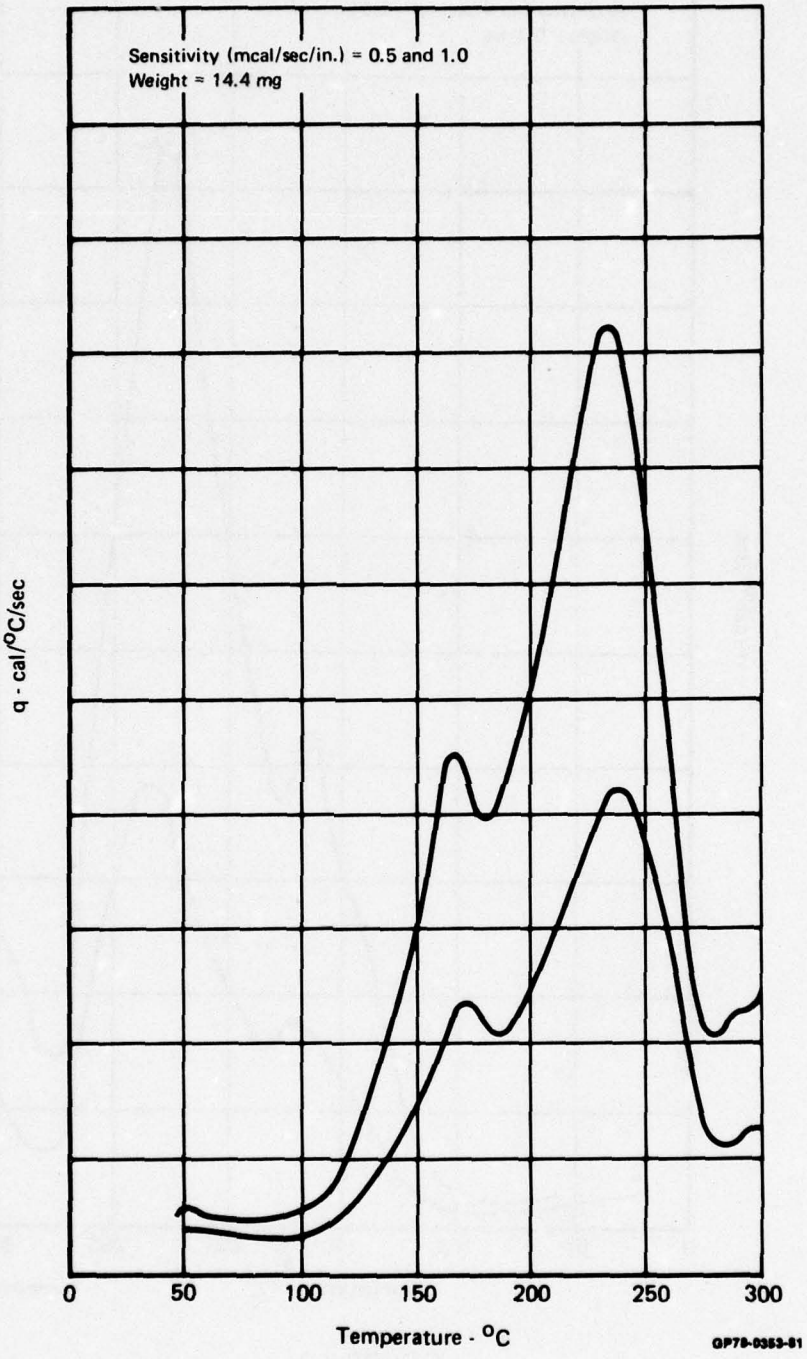

FIGURE B-8
DSC THERMOGRAM, 3501-6 BATCH CRT-76-8, 10°C/MIN

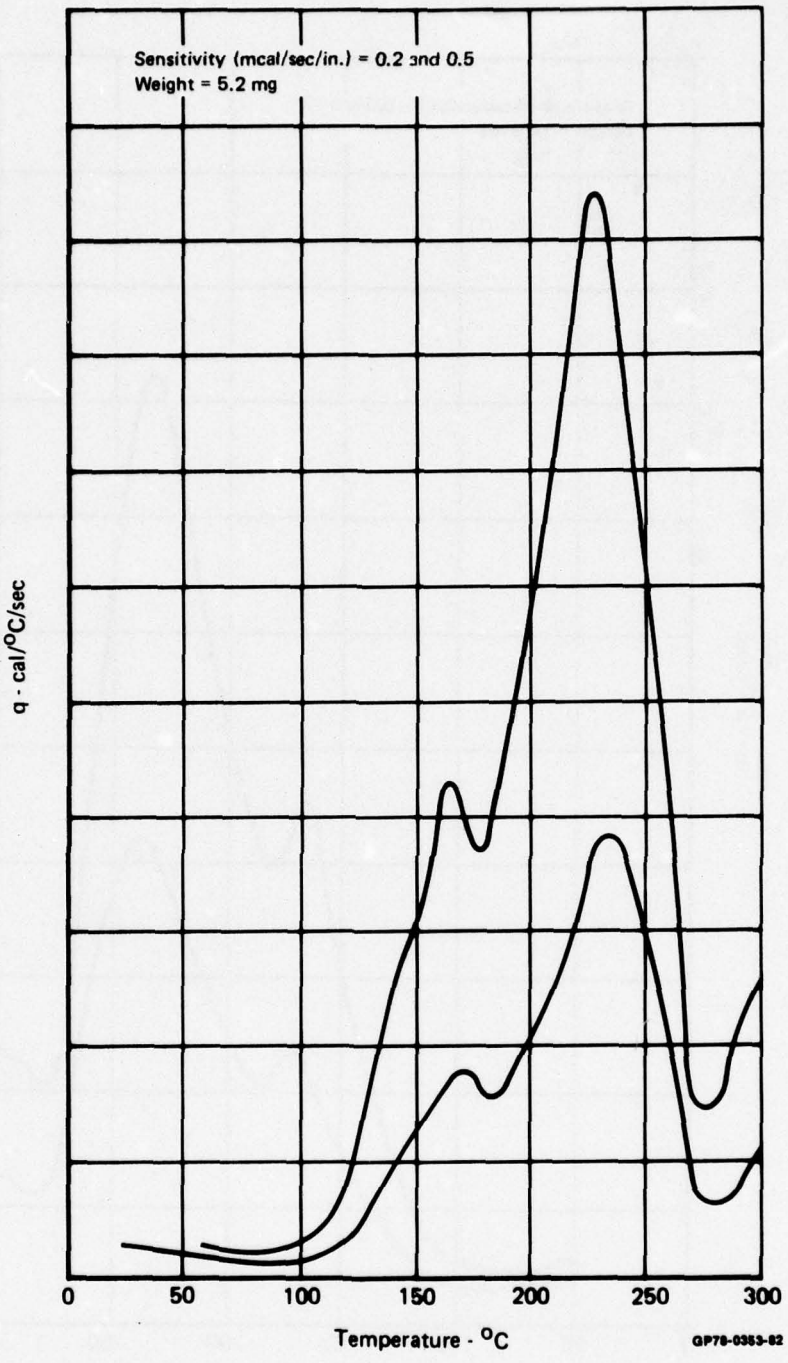

FIGURE B-9
DSC THERMOGRAM, 3501-6 BATCH CRT-78-9, 10°C/MIN

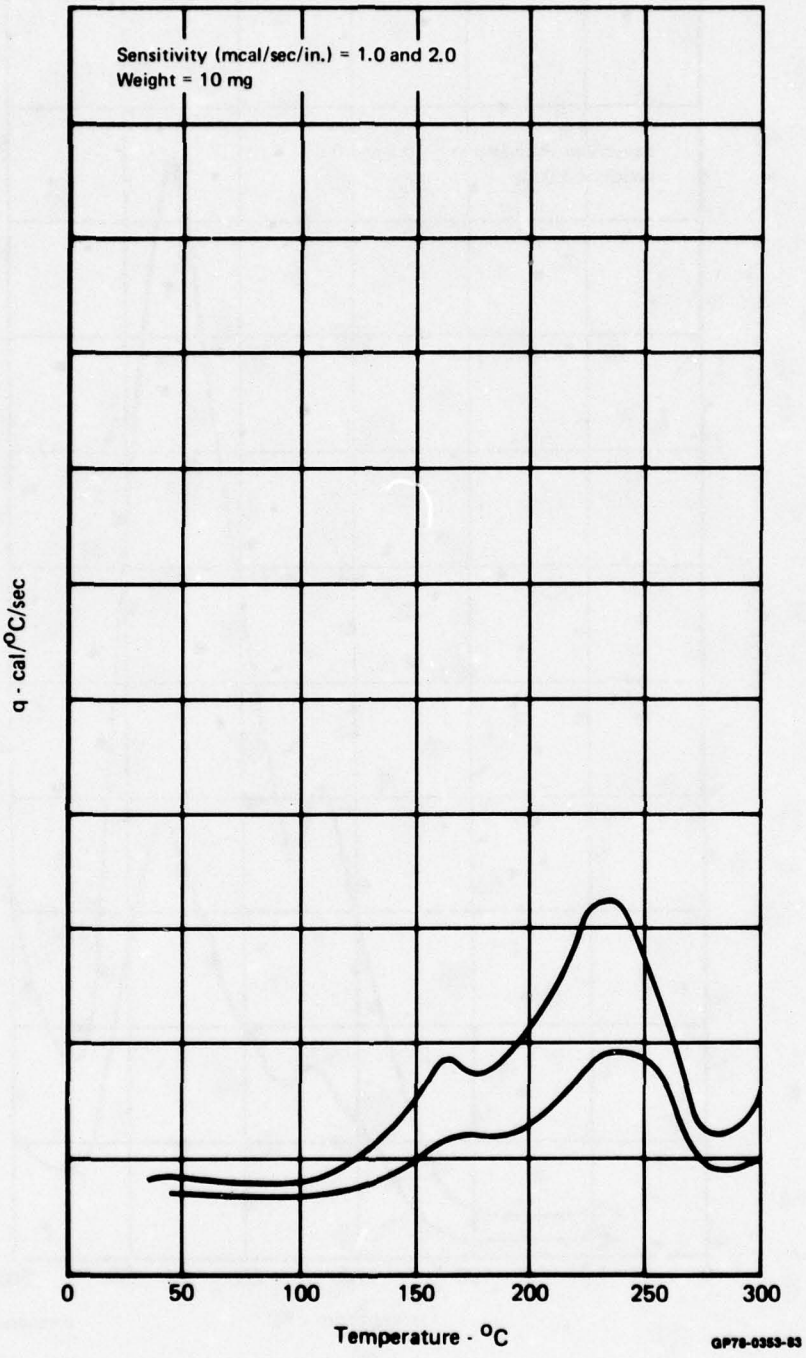

FIGURE B-10
DSC THERMOGRAM, 3501-6 BATCH CRT-76-10, 10°C/MIN

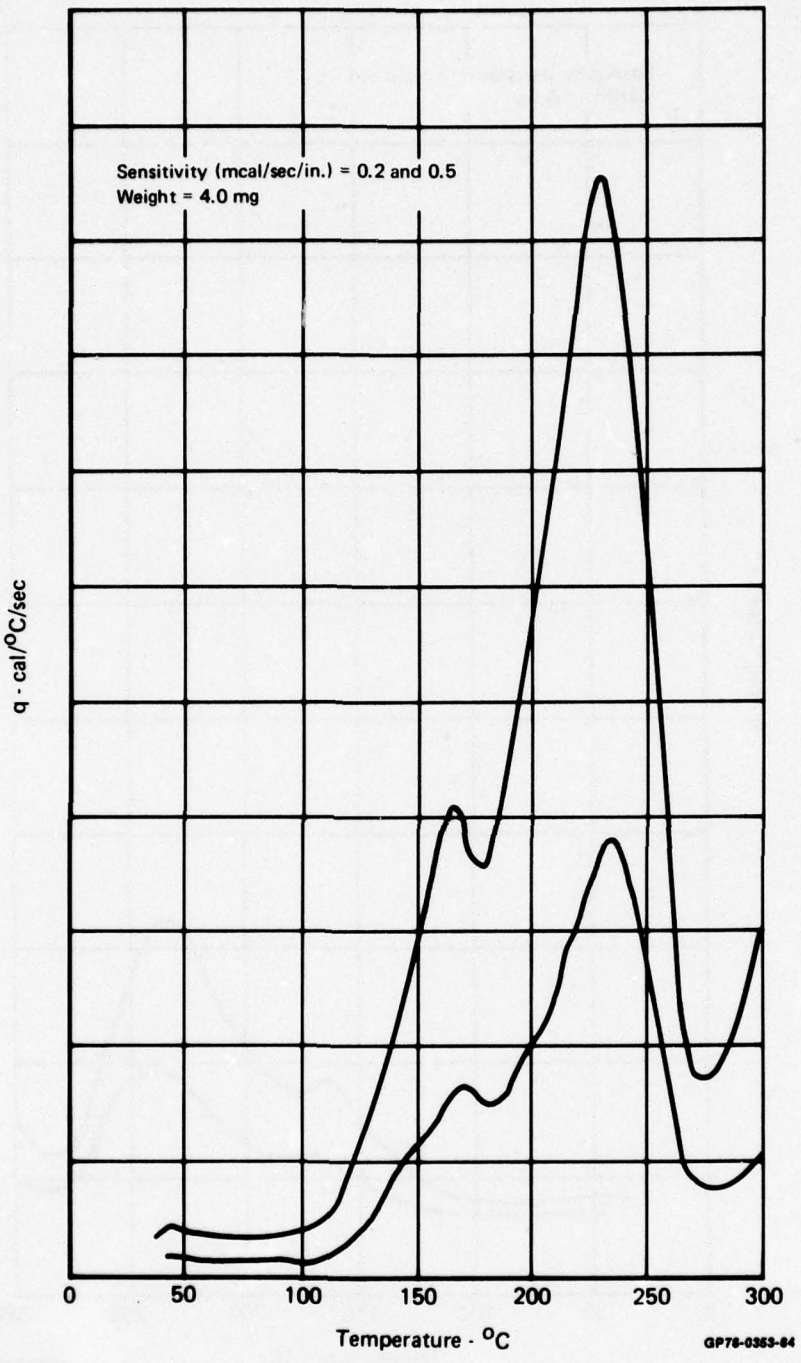

FIGURE B-11
DSC THERMOGRAM, 3501-6 BATCH CRT-79-11, 10°C/MIN

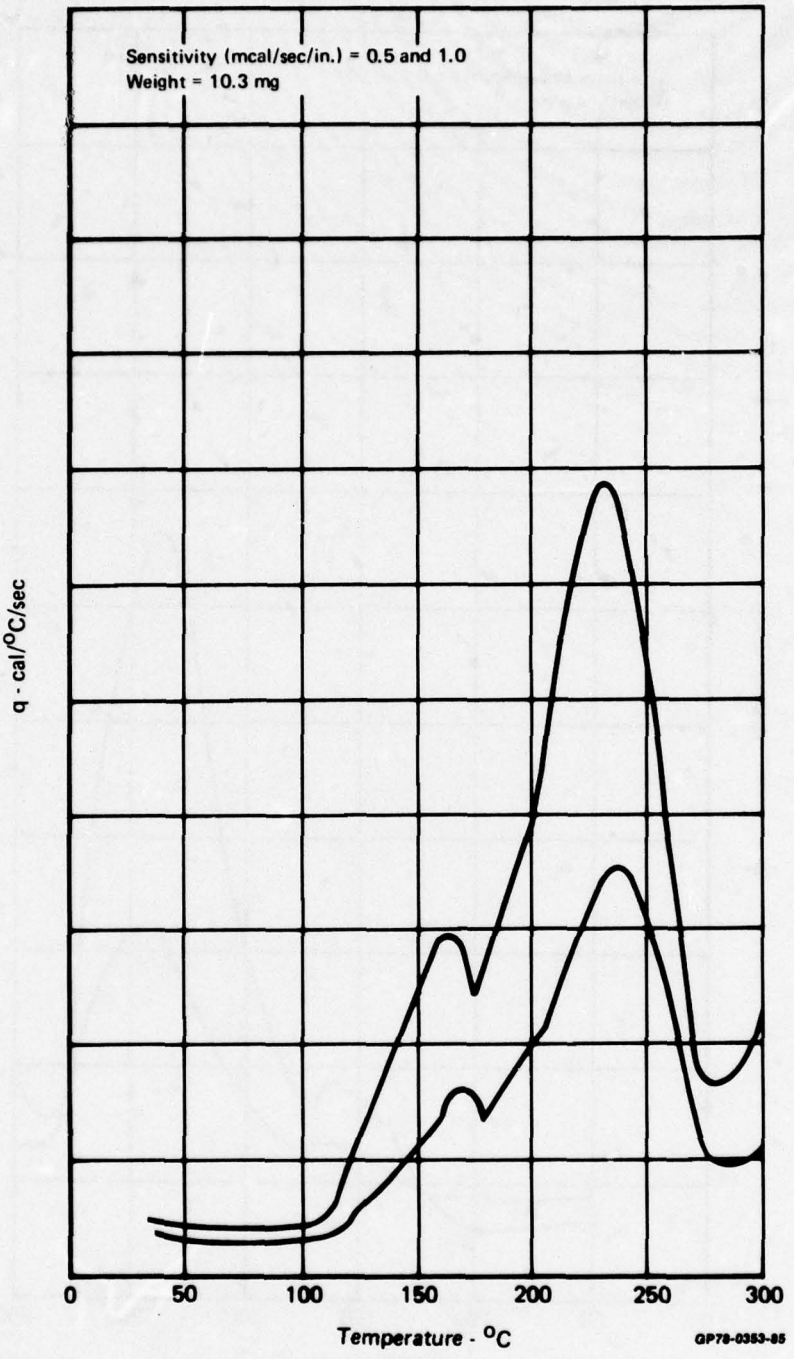

FIGURE B-12
DSC THERMOGRAM 3501-6 BATCH CRT-76-12, 10°C/MIN

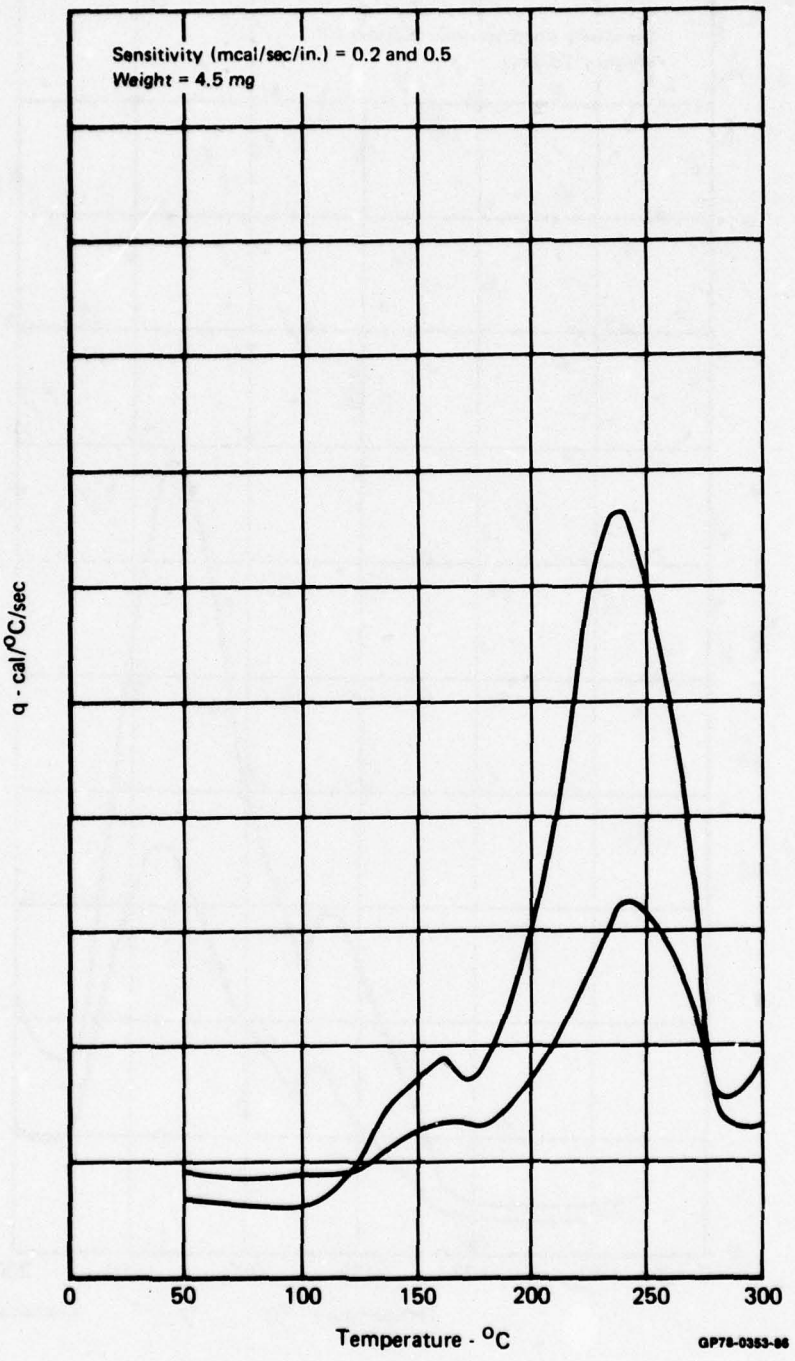

FIGURE B-13
DSC THERMOGRAM, 3501-6 BATCH CRT-75-13, 10°C/MIN

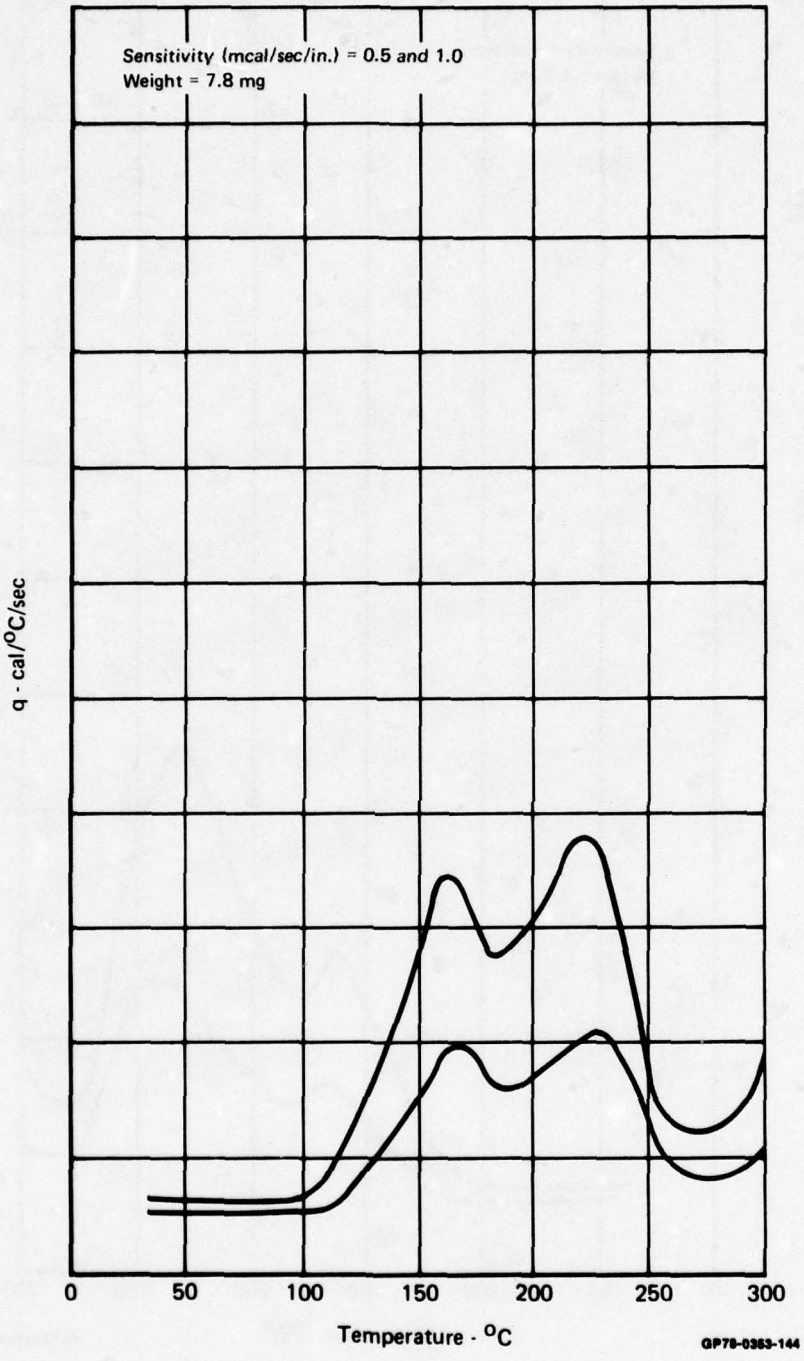

FIGURE B-14

DSC THERMOGRAM, 3501-6 BATCH CRT-75-14, 10°C/MIN

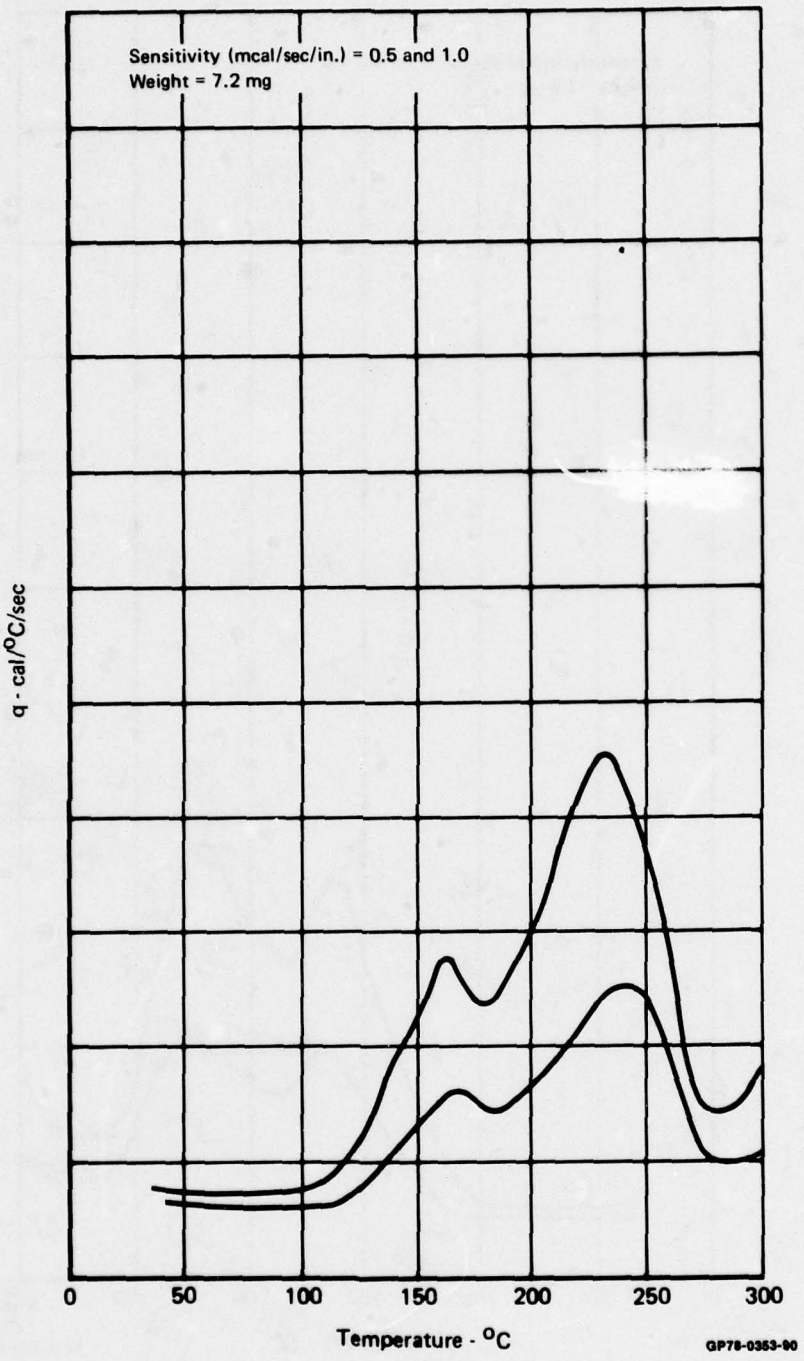

FIGURE B-15
DSC THERMOGRAM, 3501-6 BATCH CRT-75-15, 10°C/MIN

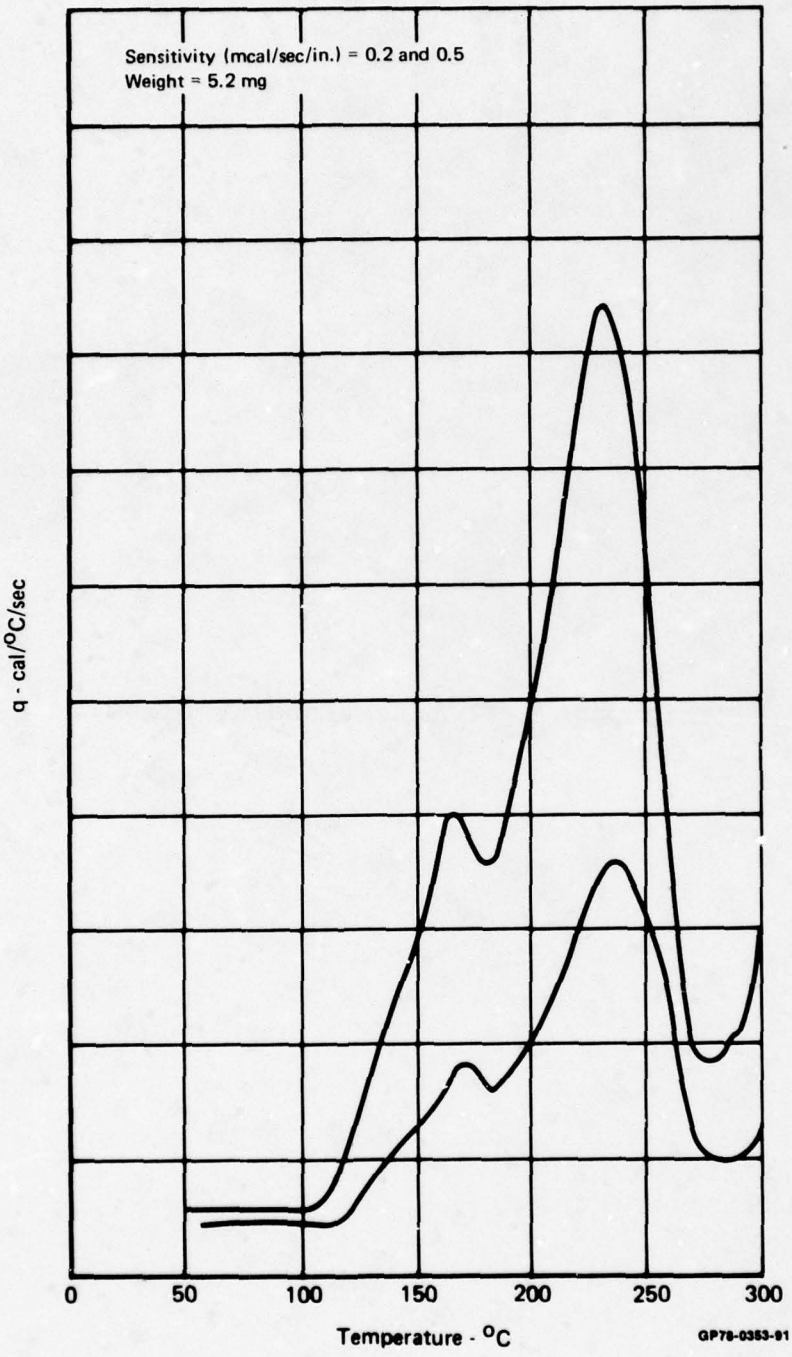

FIGURE B-16
DSC THERMOGRAM, 3501-6 BATCH CRT-75-16, 10°C/MIN

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APPENDIX C

VISCOSITY PROFILES FOR 3501-6 RESIN

This section includes viscosity profiles for all sixteen altered batches tested under isothermal conditions and under conditions of a typical cure cycle.

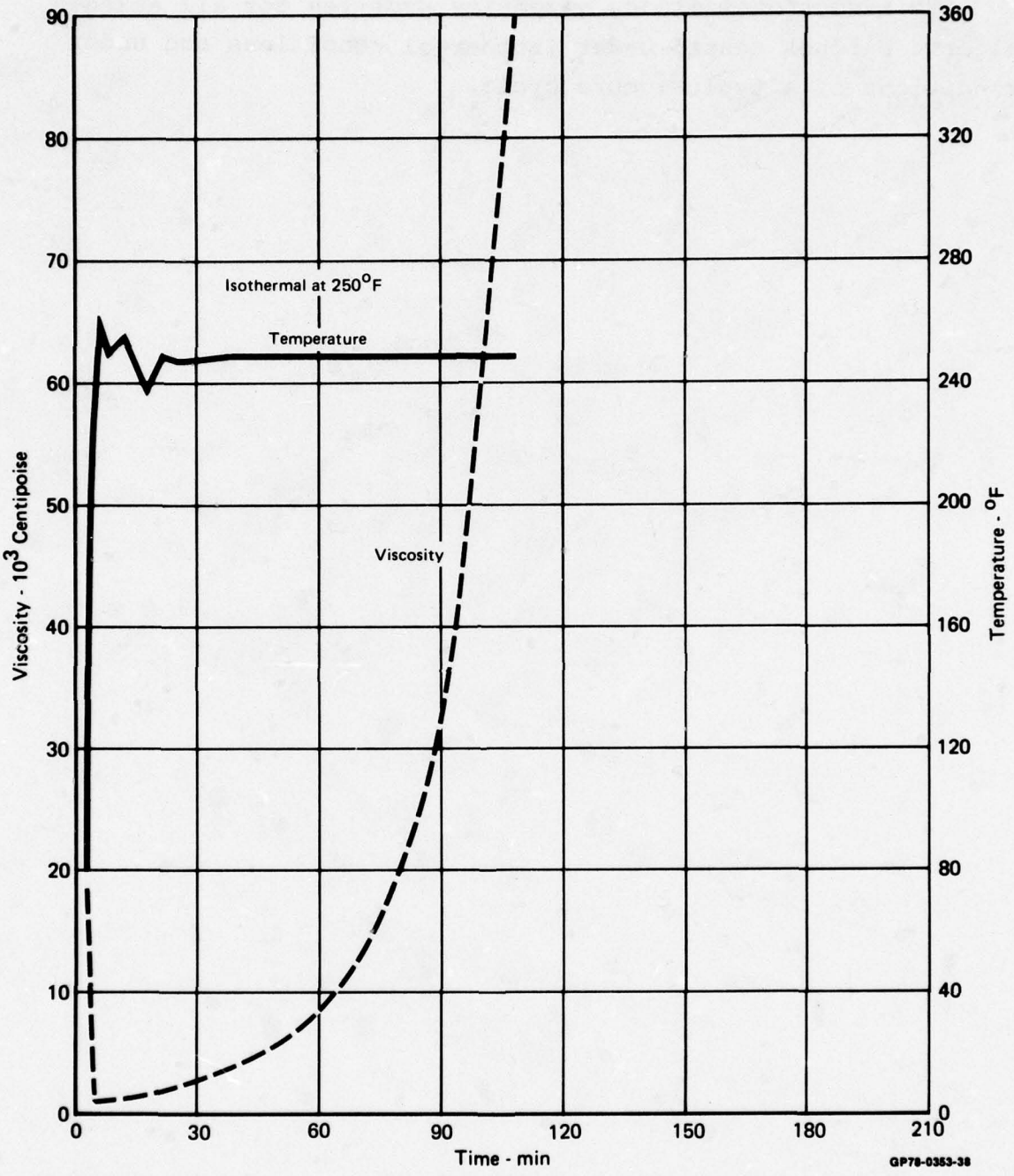

FIGURE C-1
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-1
(Standard Formulation)

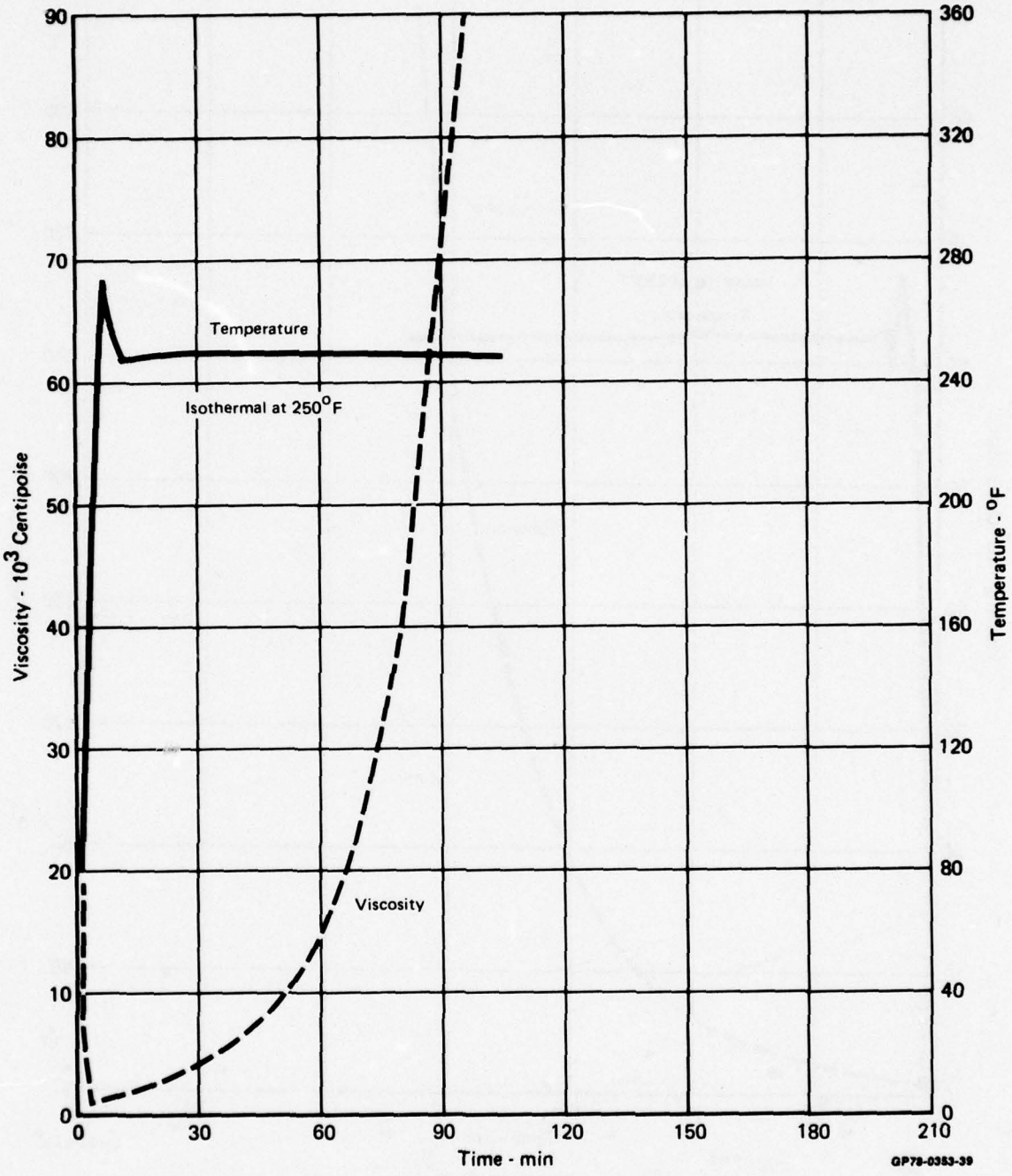

FIGURE C-2
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 77-2
(+ 10% Curing Agent)

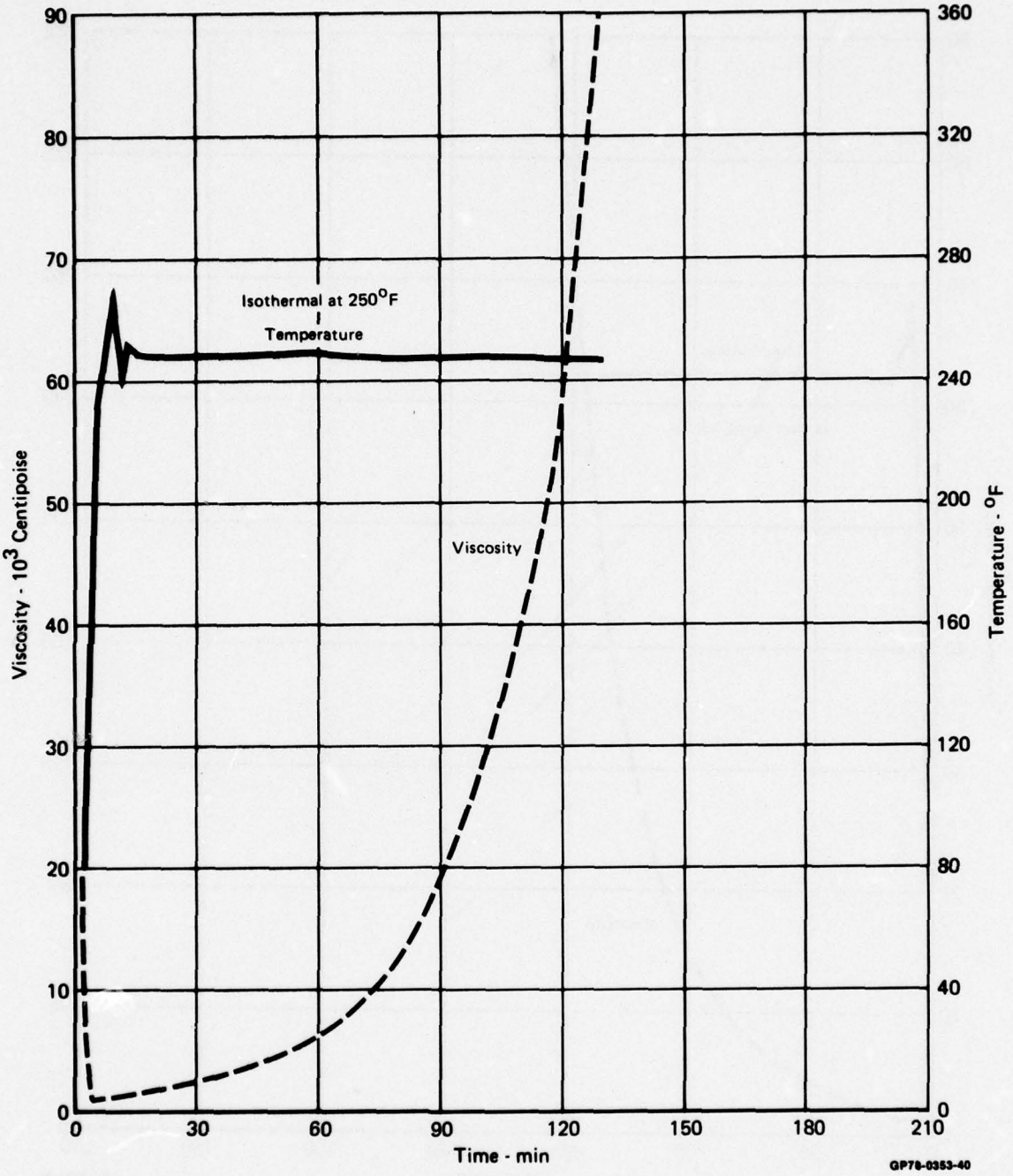

FIGURE C-3
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 77-3
(—10% Curing Agent)

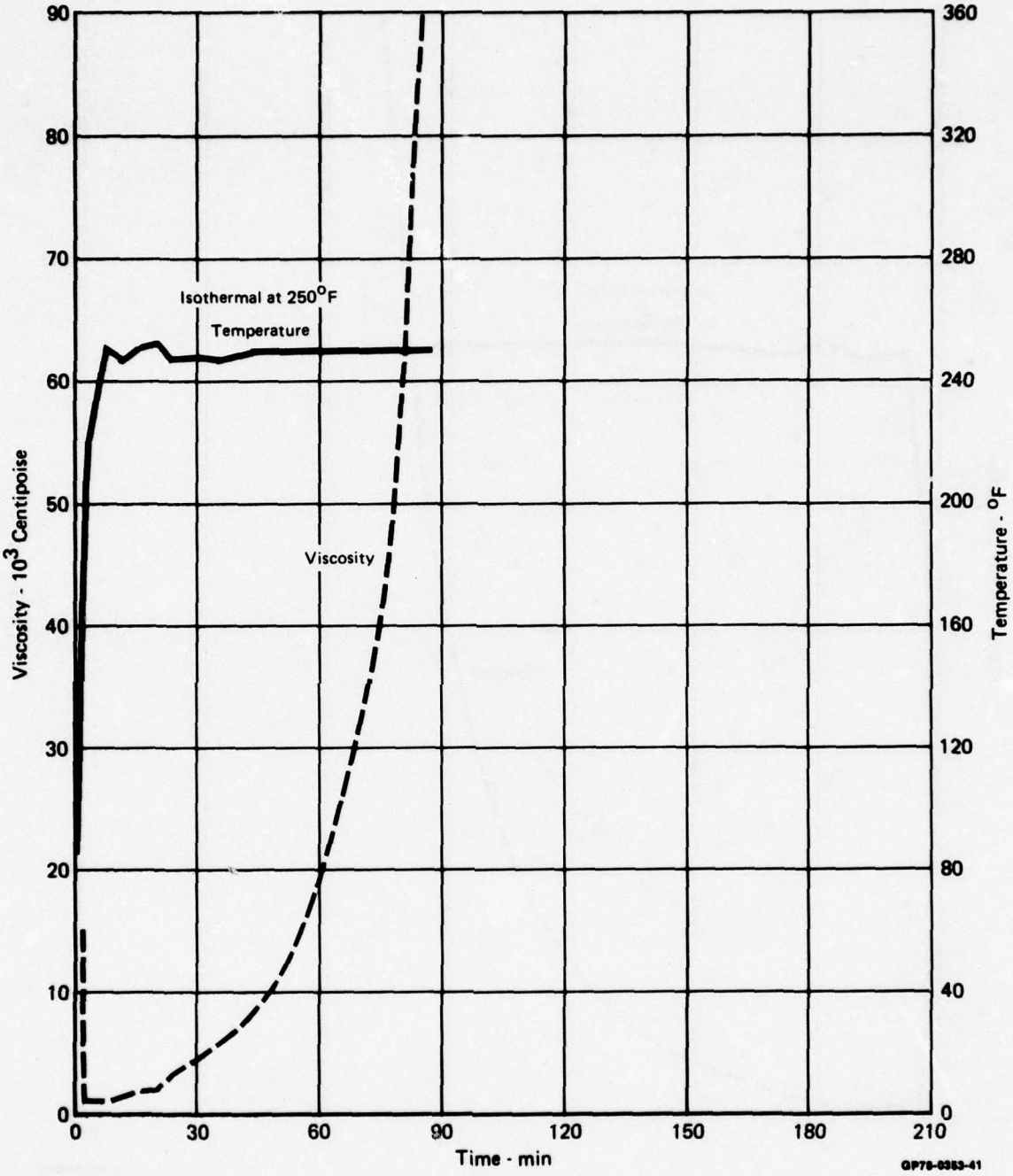

FIGURE C-4
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 79-4
(+ 20% Curing Agent)

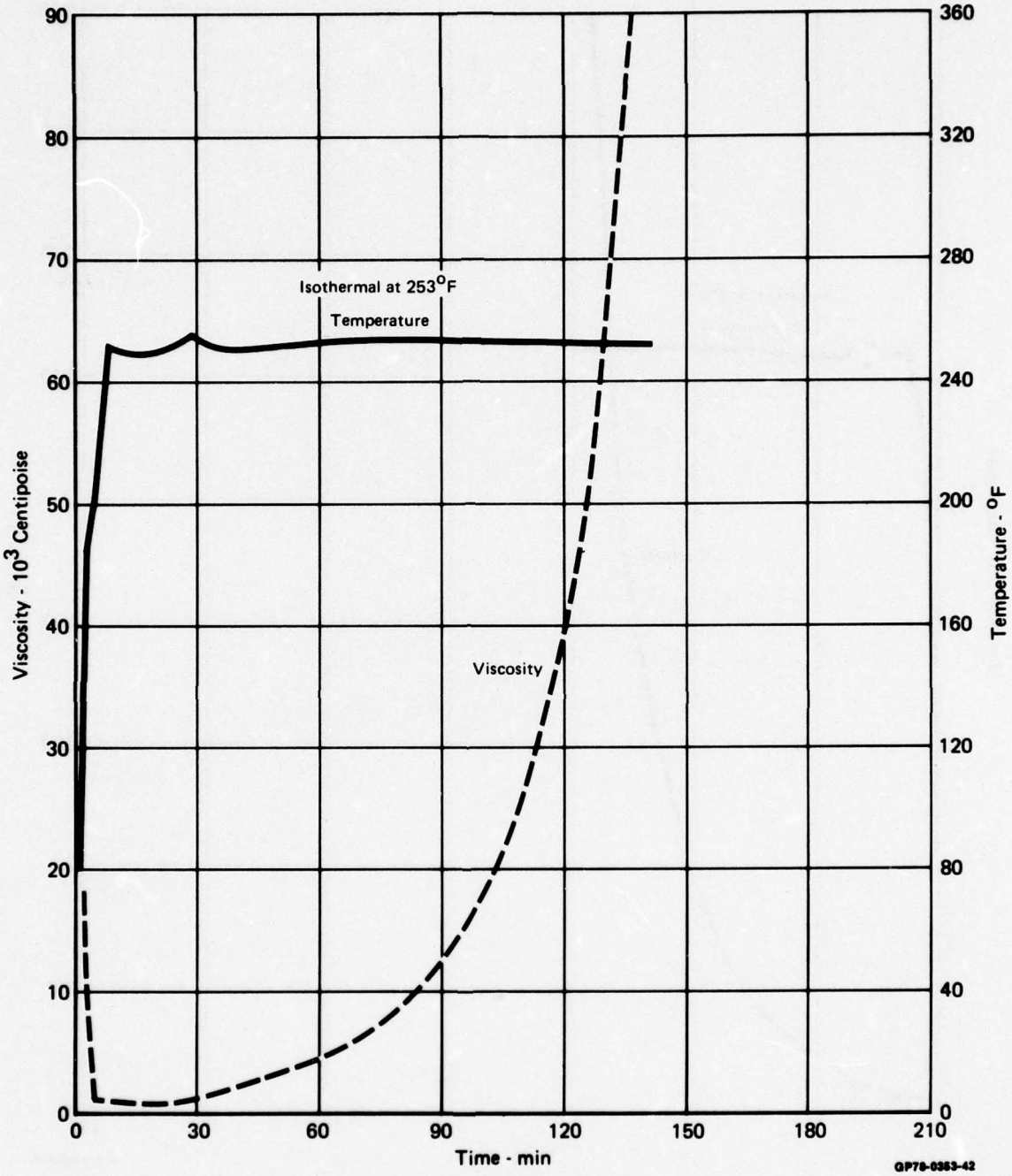

FIGURE C-5
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 79-5
(—20% Curing Agent)

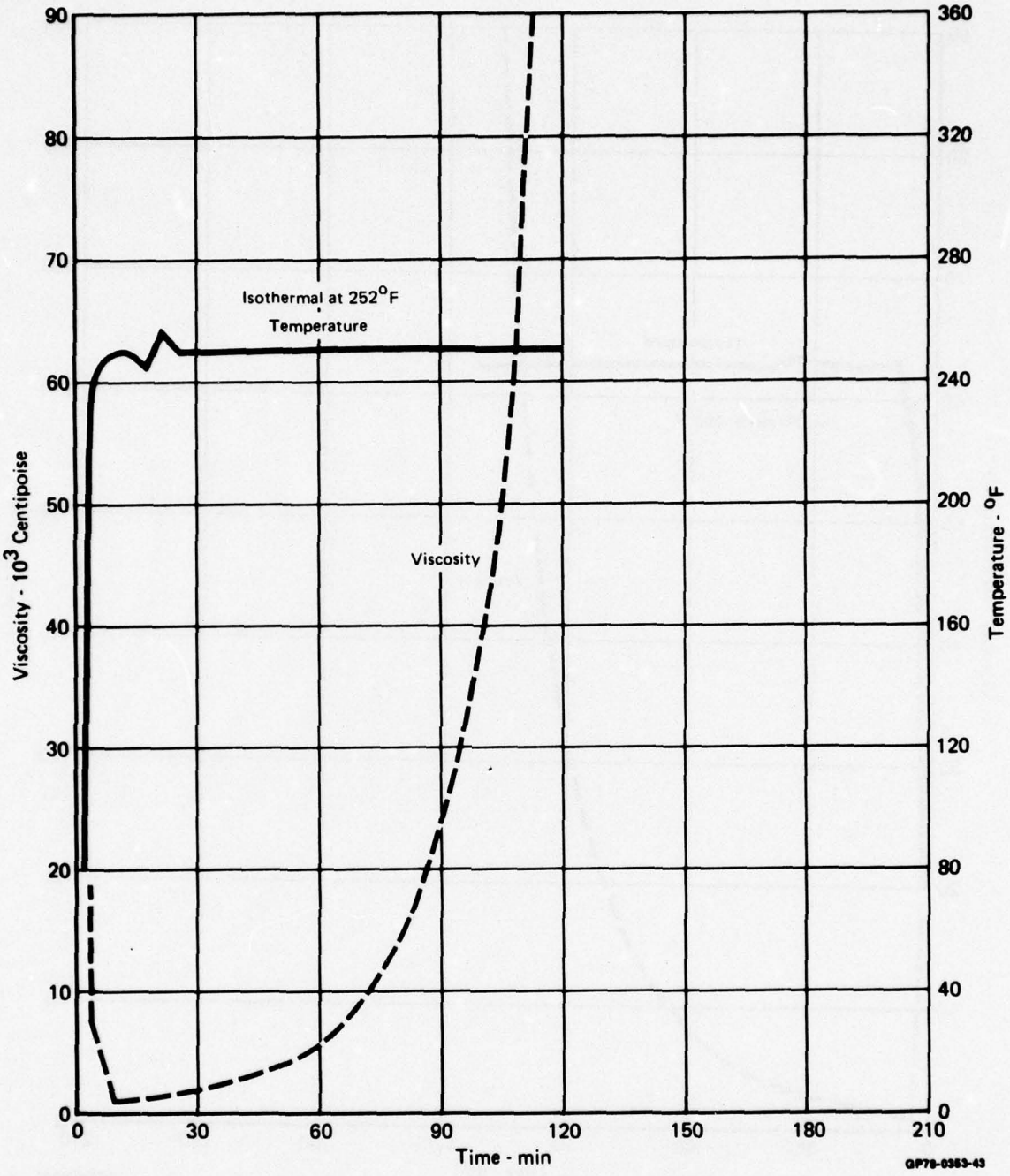

FIGURE C-6
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-6
(+ 20% Epoxide No. 2(H))

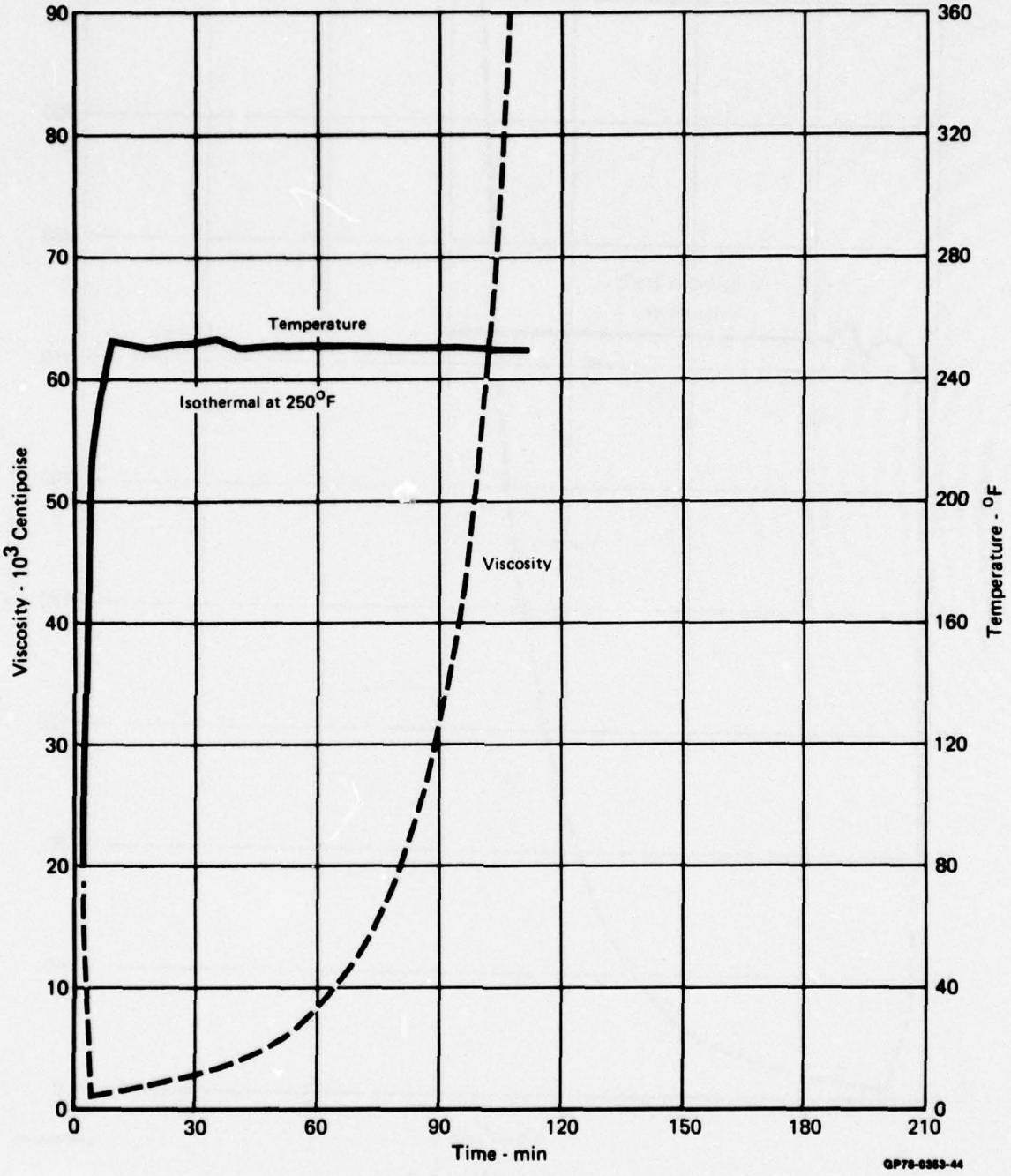

FIGURE C-7
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 78-7
(—20% Epoxide No. 2(H))

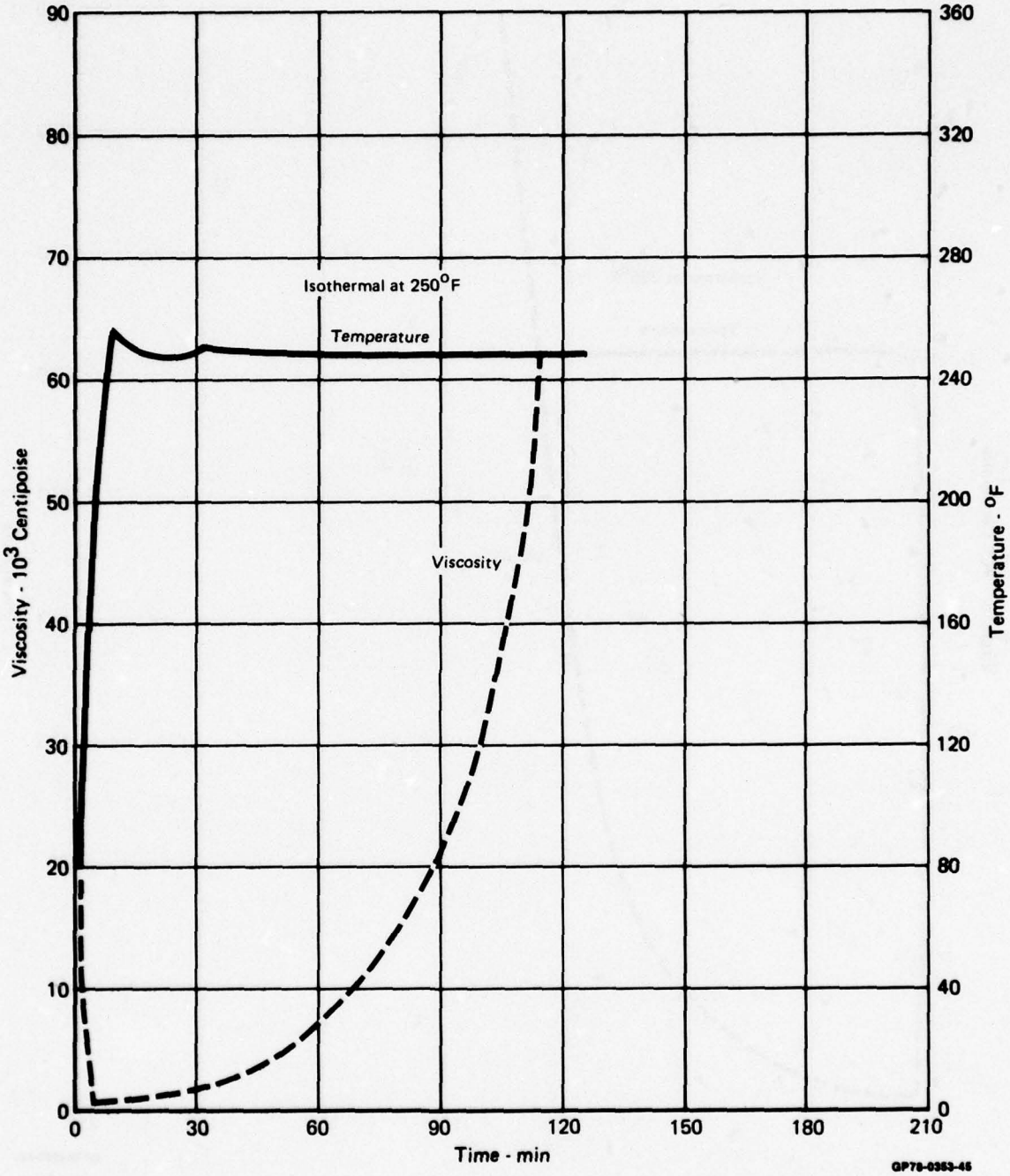

FIGURE C-8
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-8
(+ 40% Epoxide No. 2(H))

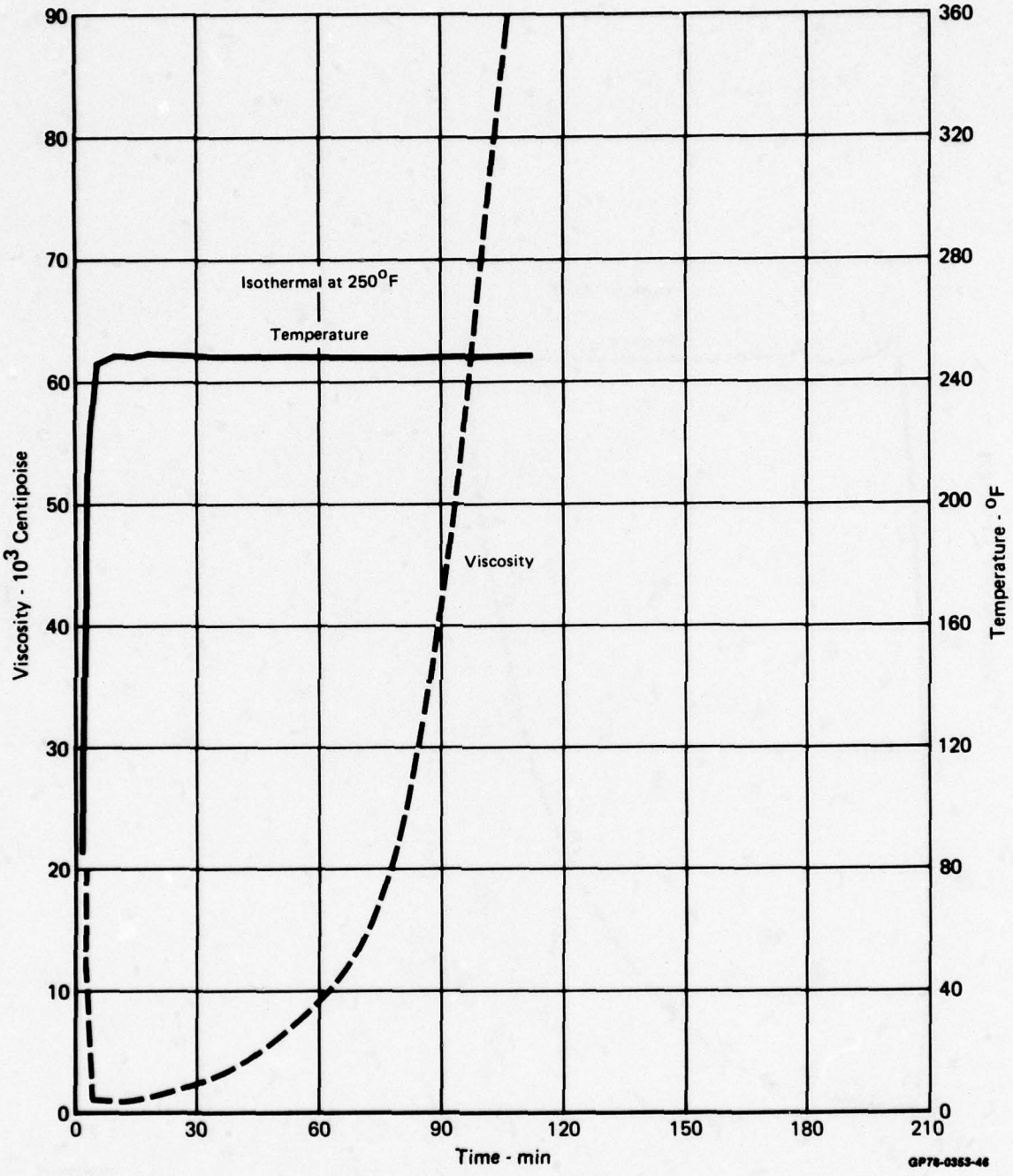

FIGURE C-9
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 78-9
(—40% Epoxide No. 2(H))

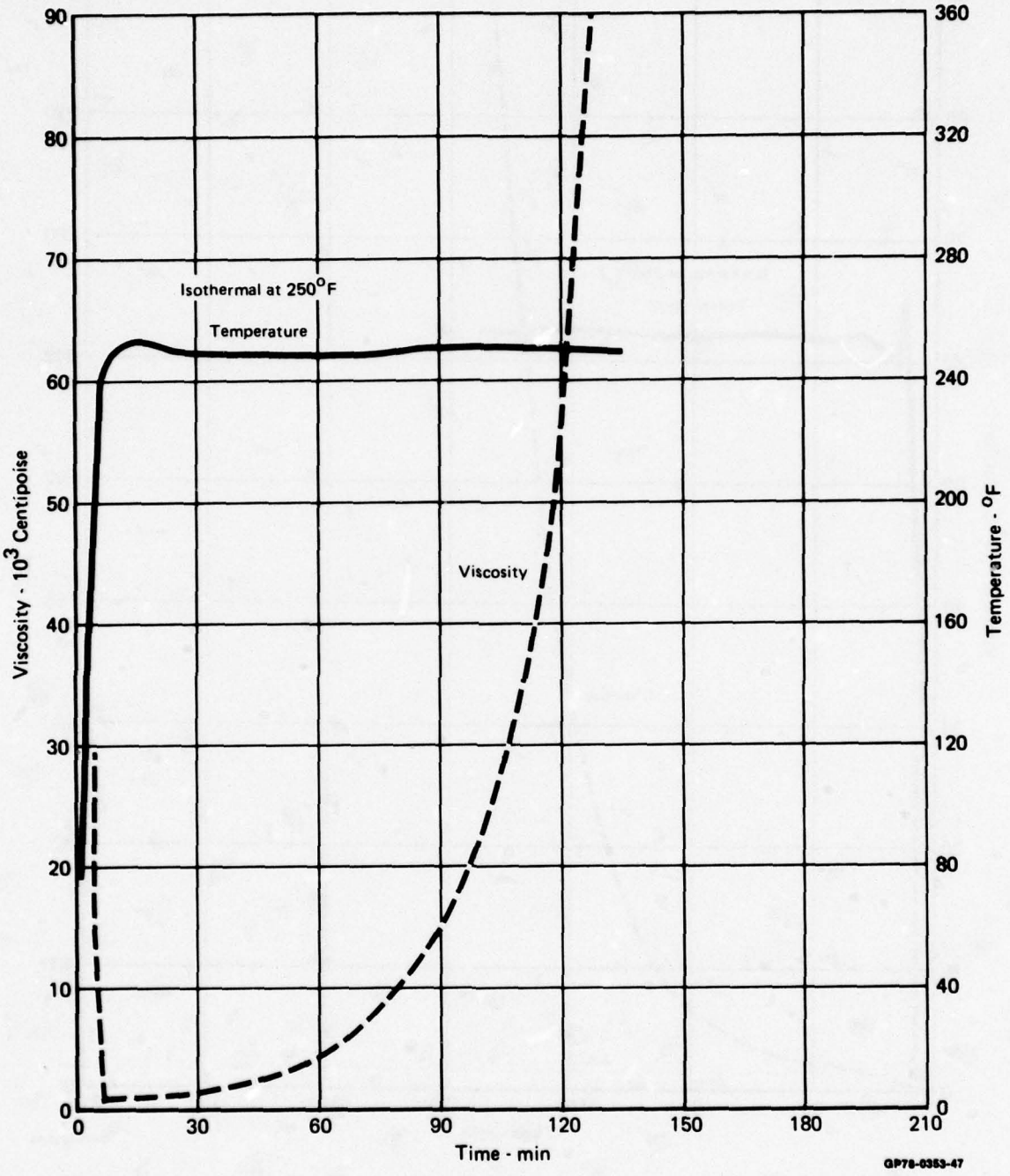

FIGURE C-10
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-10
(+ 50% Epoxide No. 3(H))

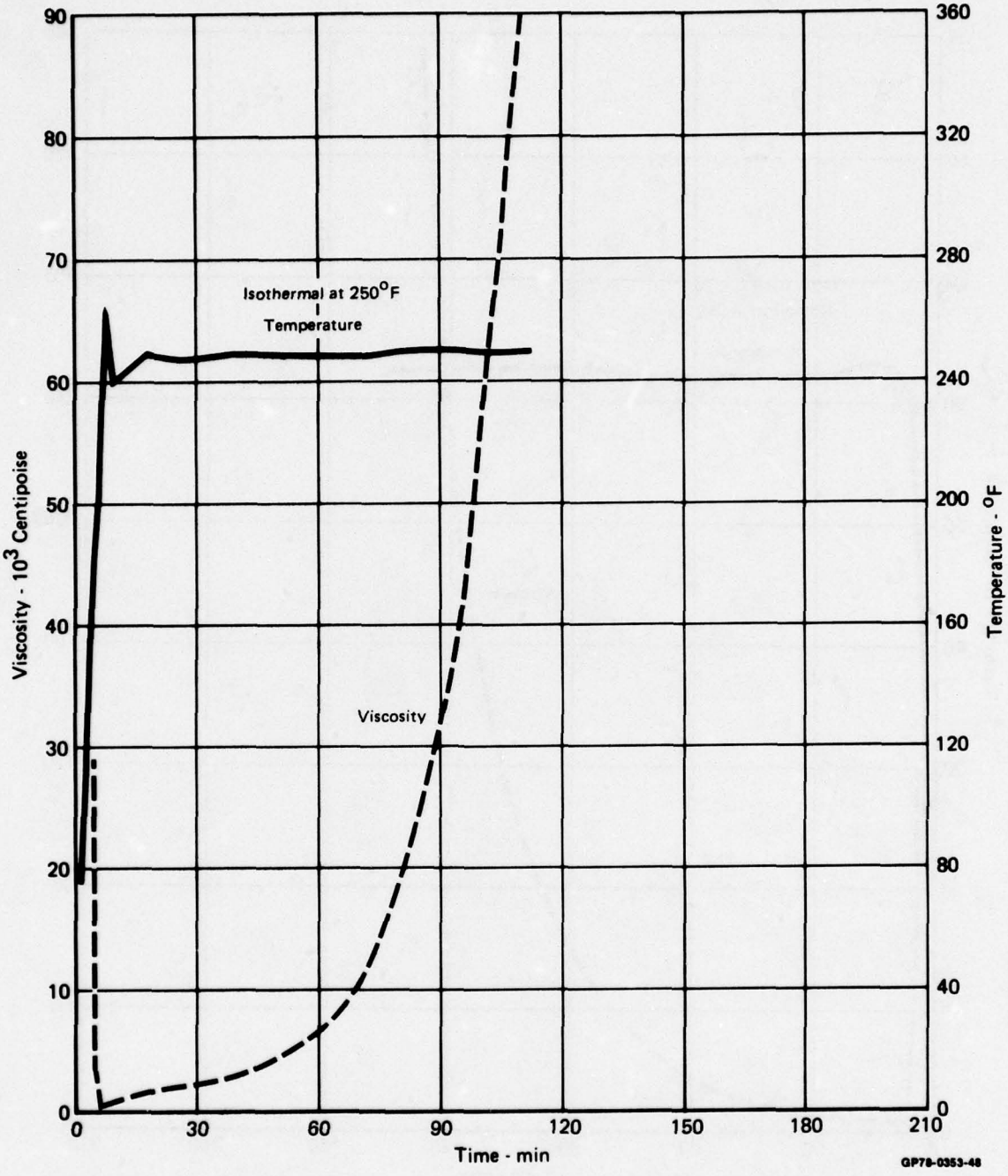

FIGURE C-11
VISCOSITY vs TEMPERATURE TIME
3501-6 BATCH CRT 79-11
(—50% Epoxide No. 3(H))

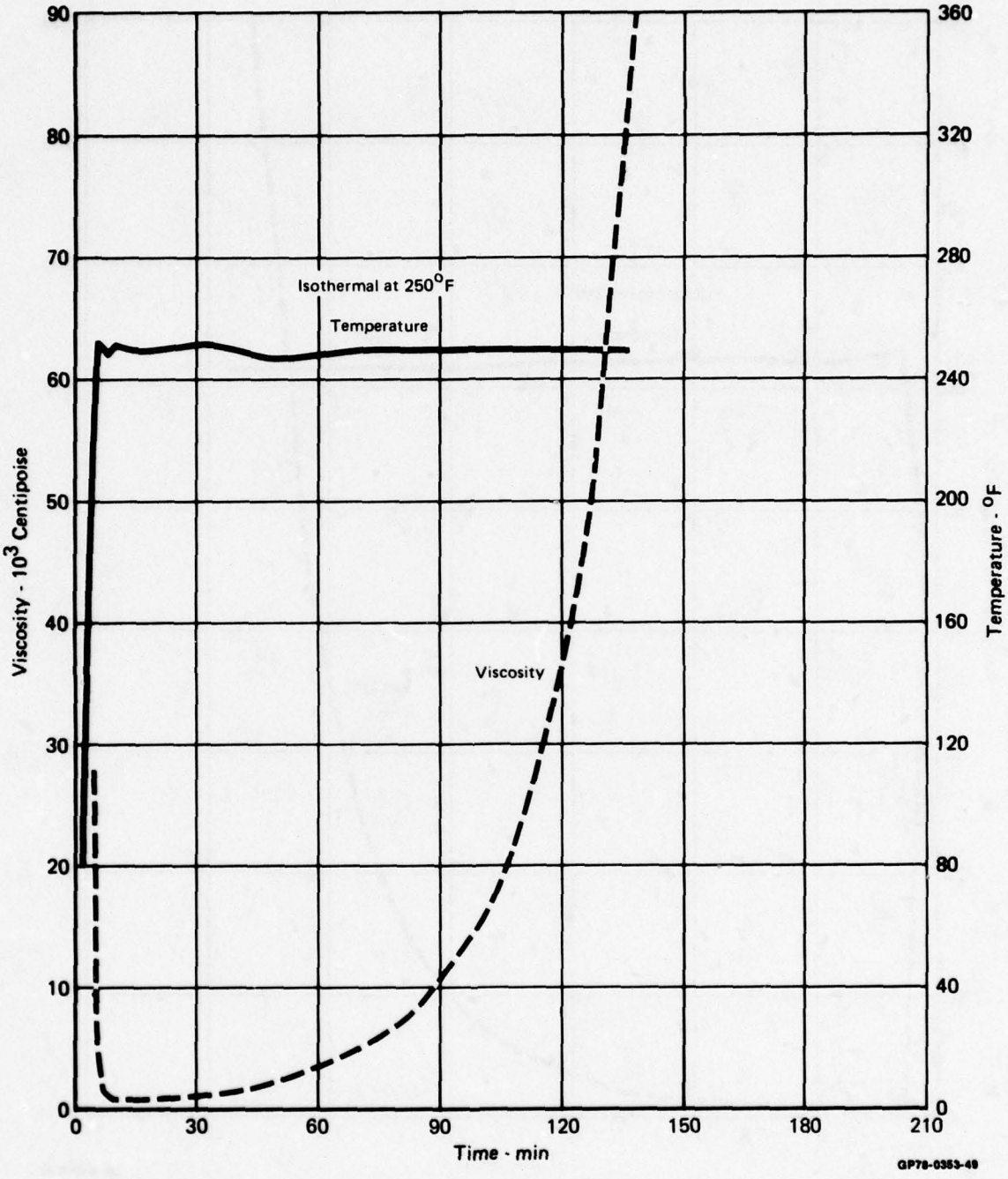

FIGURE C-12
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-12
(+ 100% Epoxide No. 3(H))

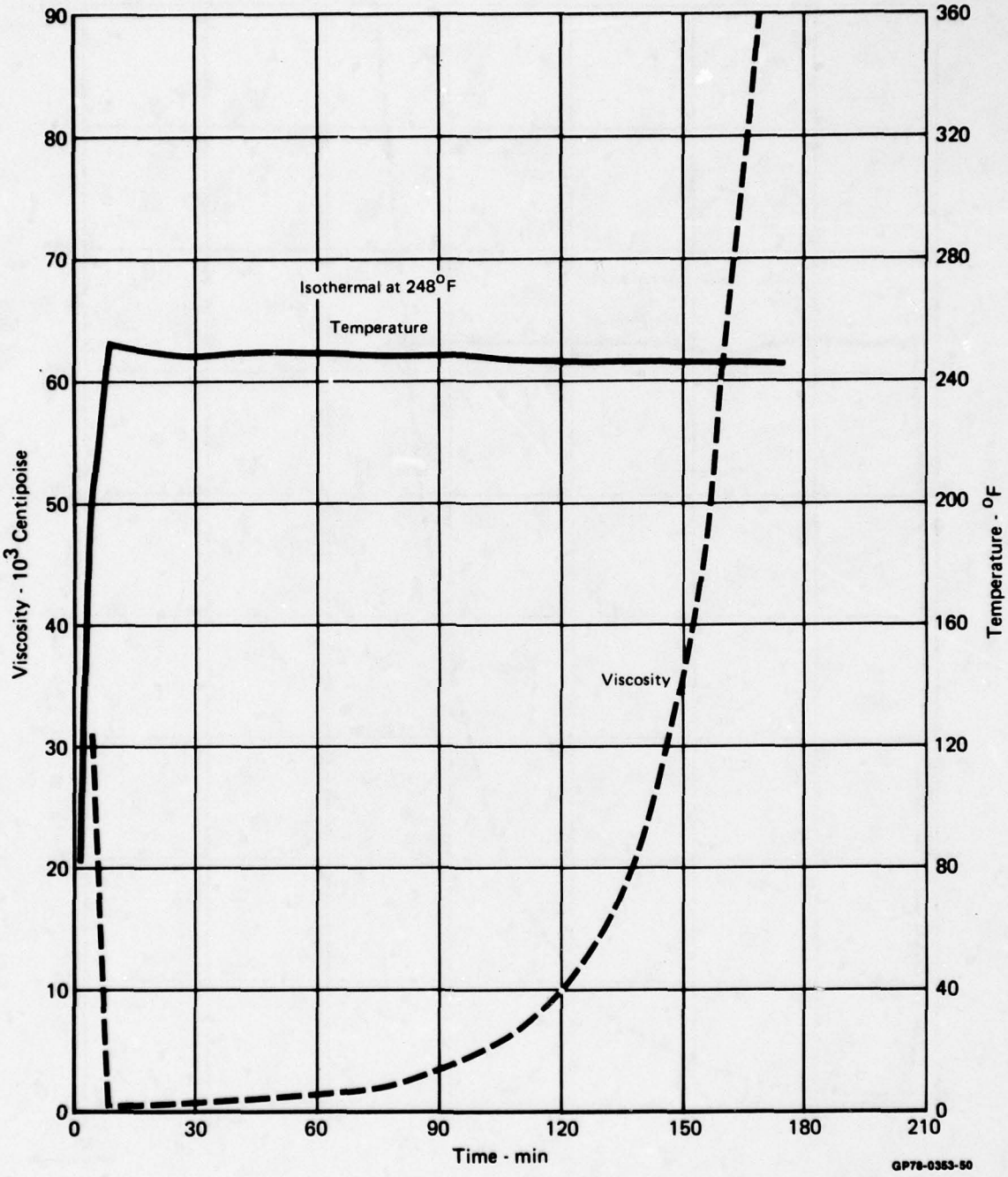

FIGURE C-13
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-13
(—50% Accelerator)

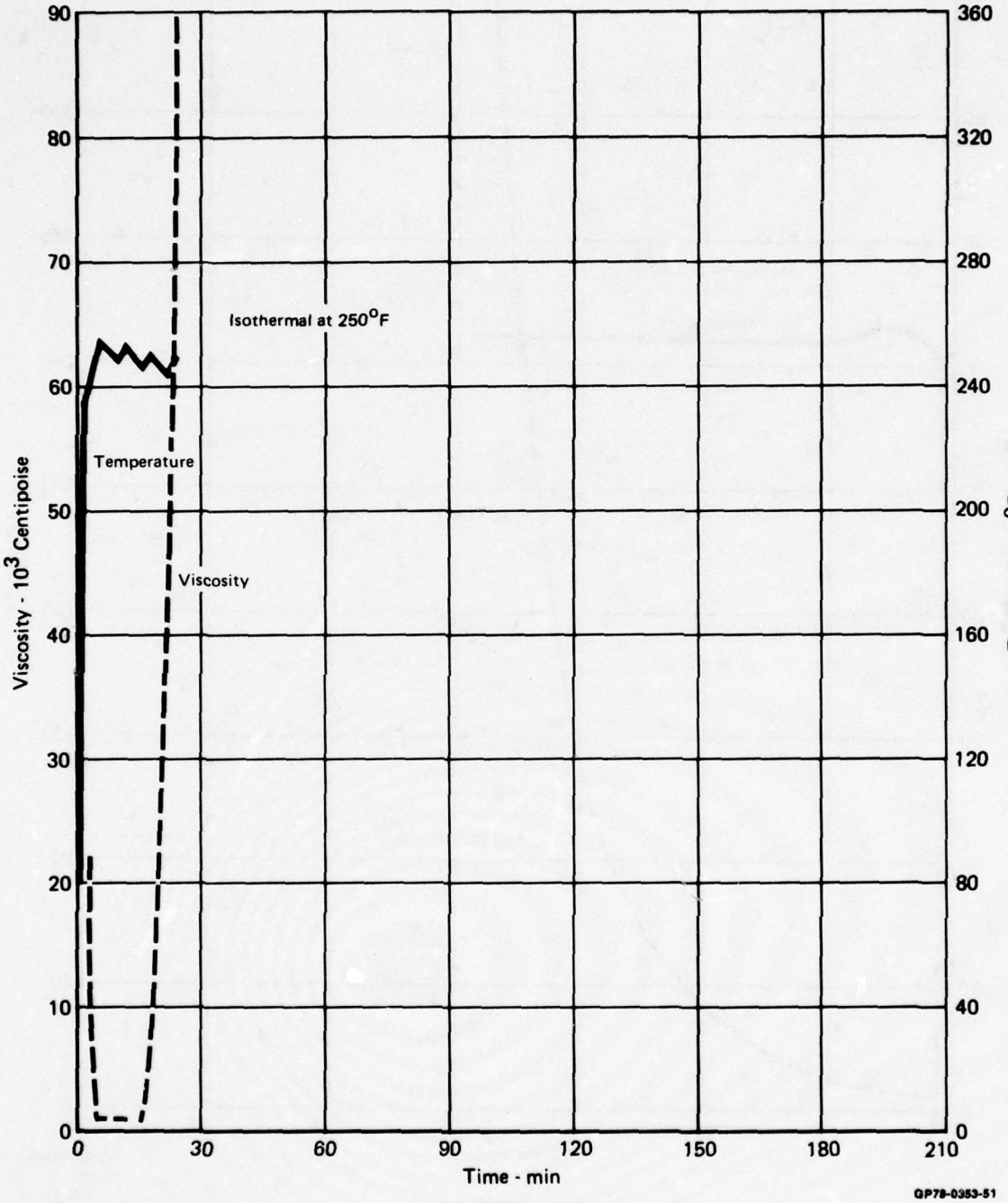

FIGURE C-14
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-14
(+ 100% Accelerator)

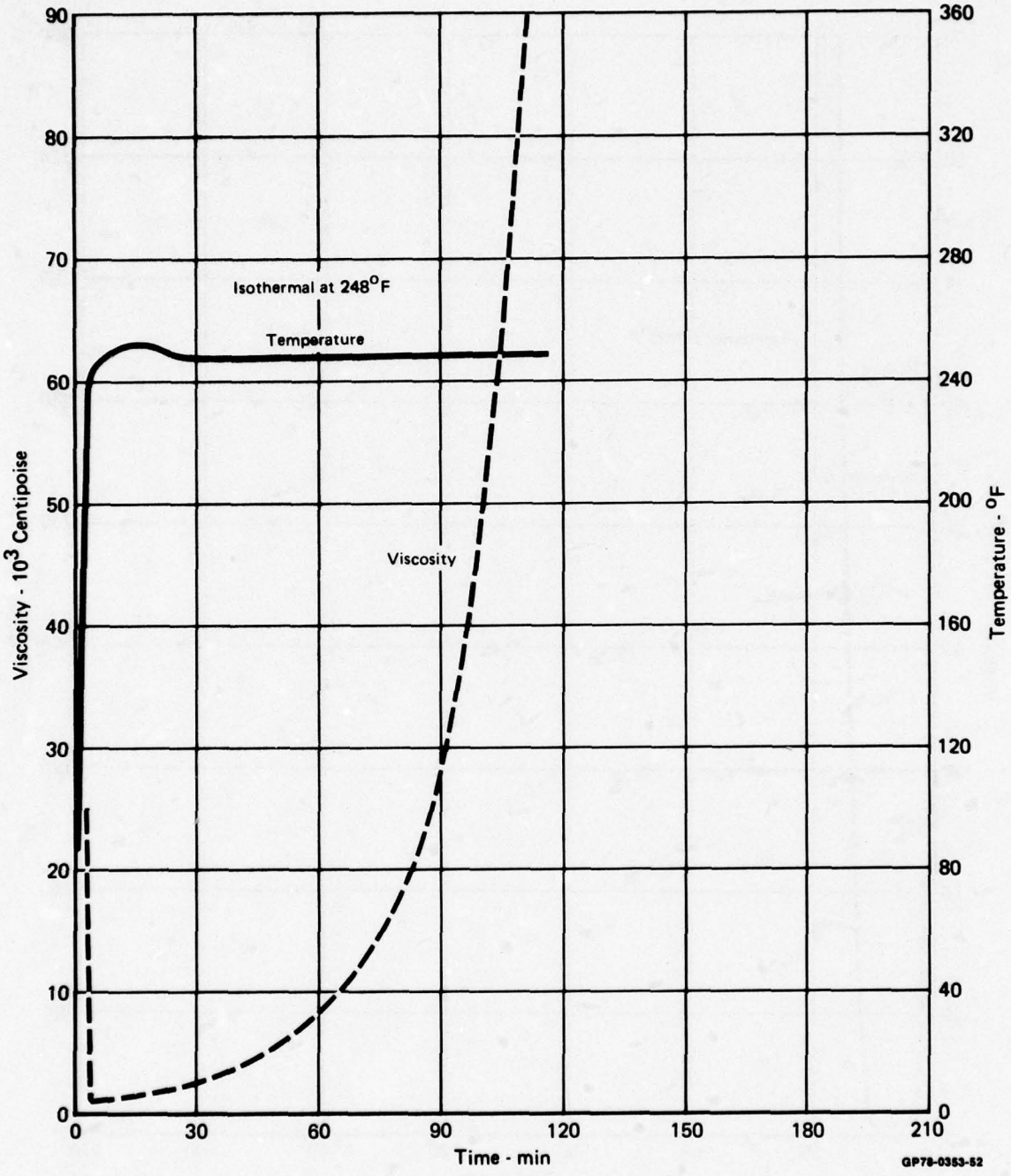

FIGURE C-15
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-15
(Understaged)

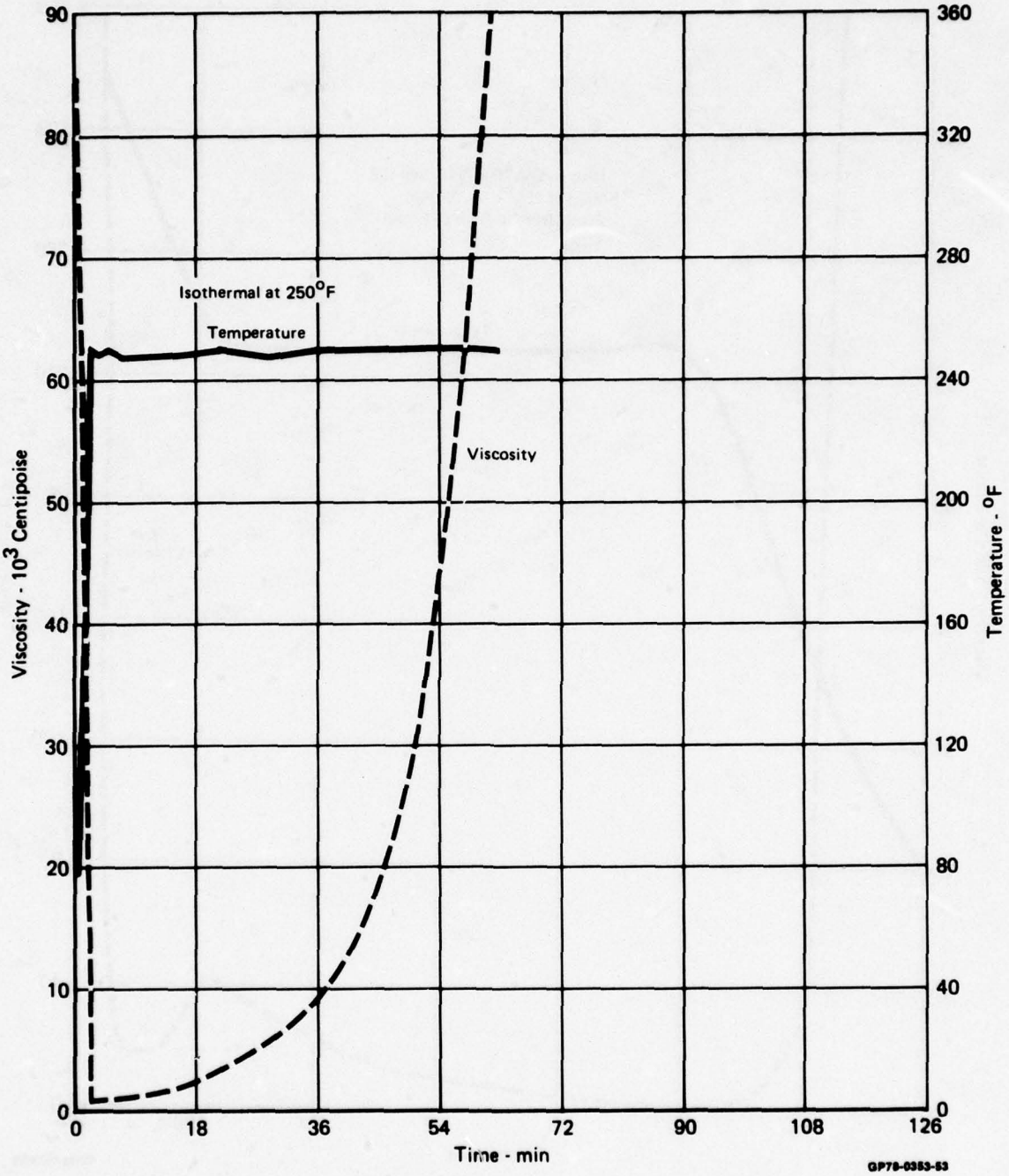

FIGURE C-16
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-16
(Overstaged)

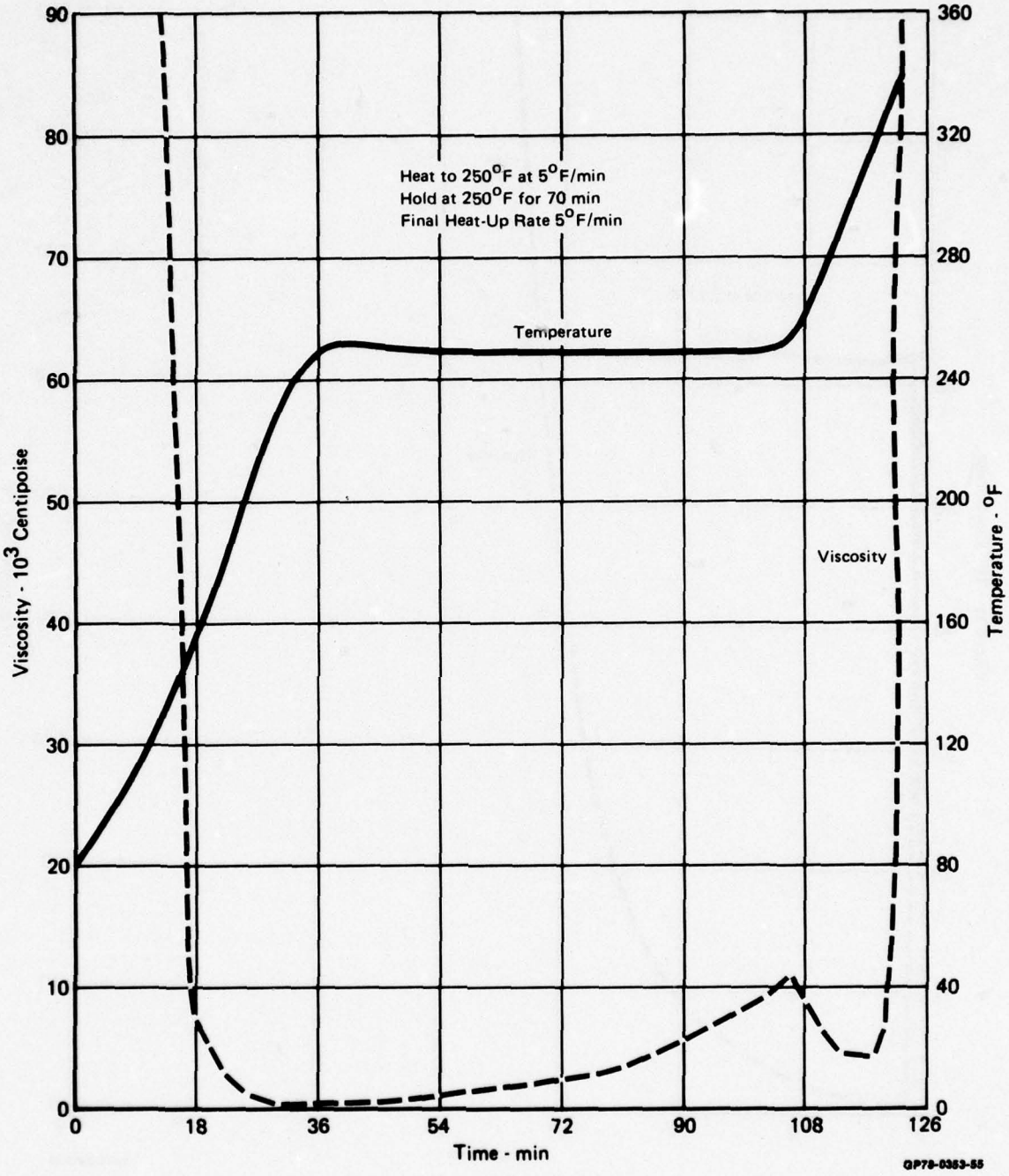

FIGURE C-17
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-1
(Standard Formulation)

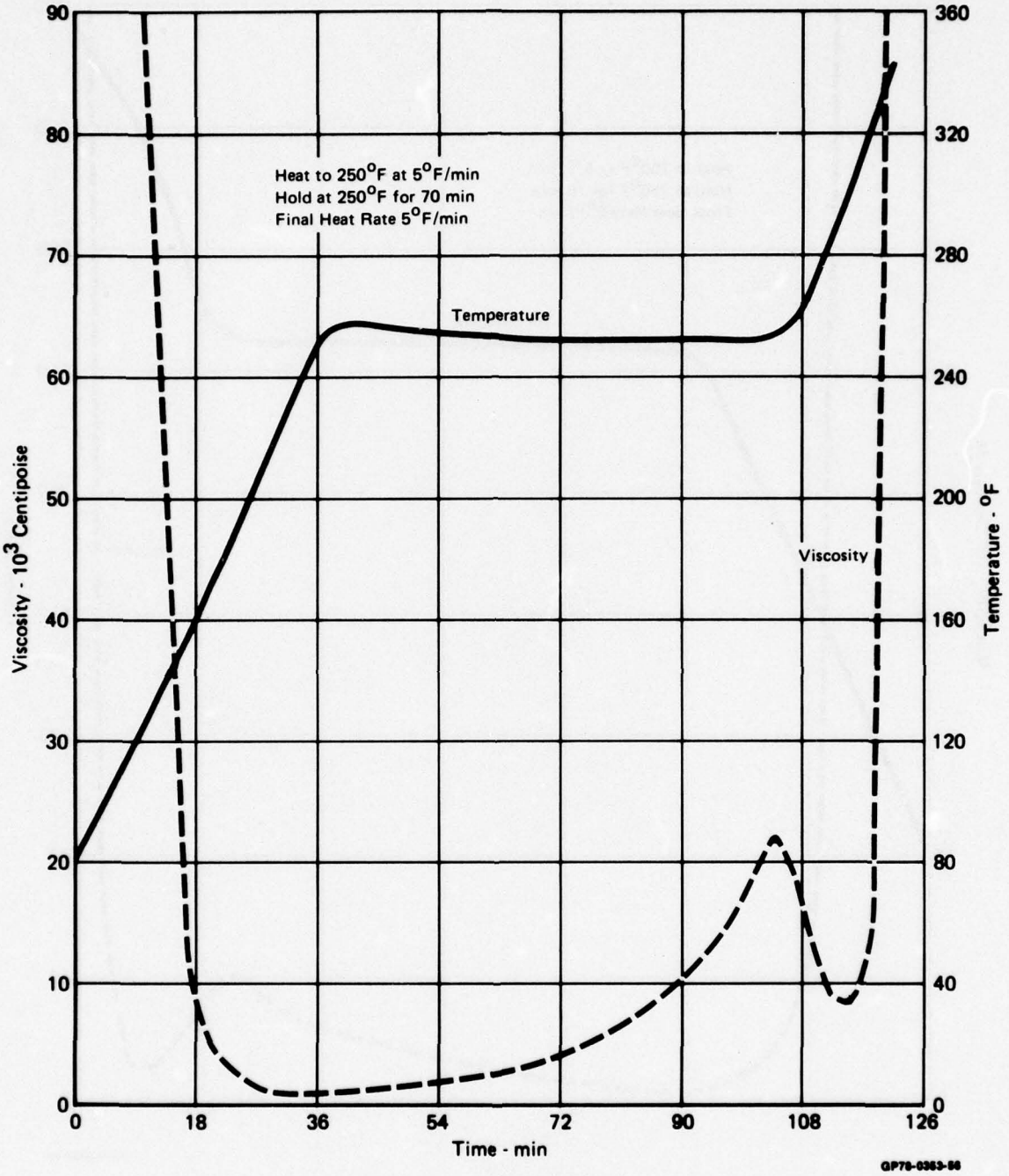

FIGURE C-18
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 77-2
(+ 10% Curing Agent)

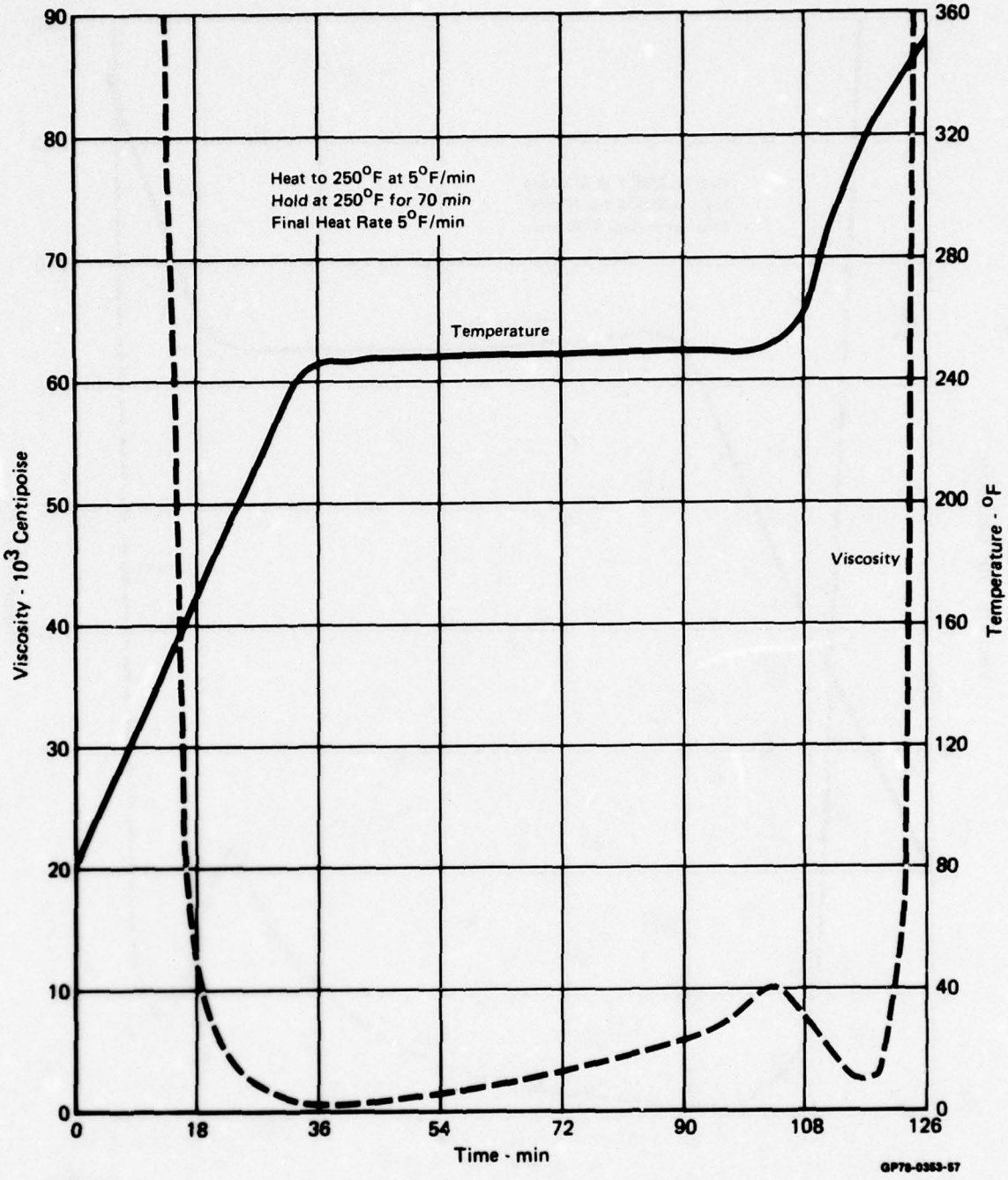

FIGURE C-19
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 77-3
(—10% Curing Agent)

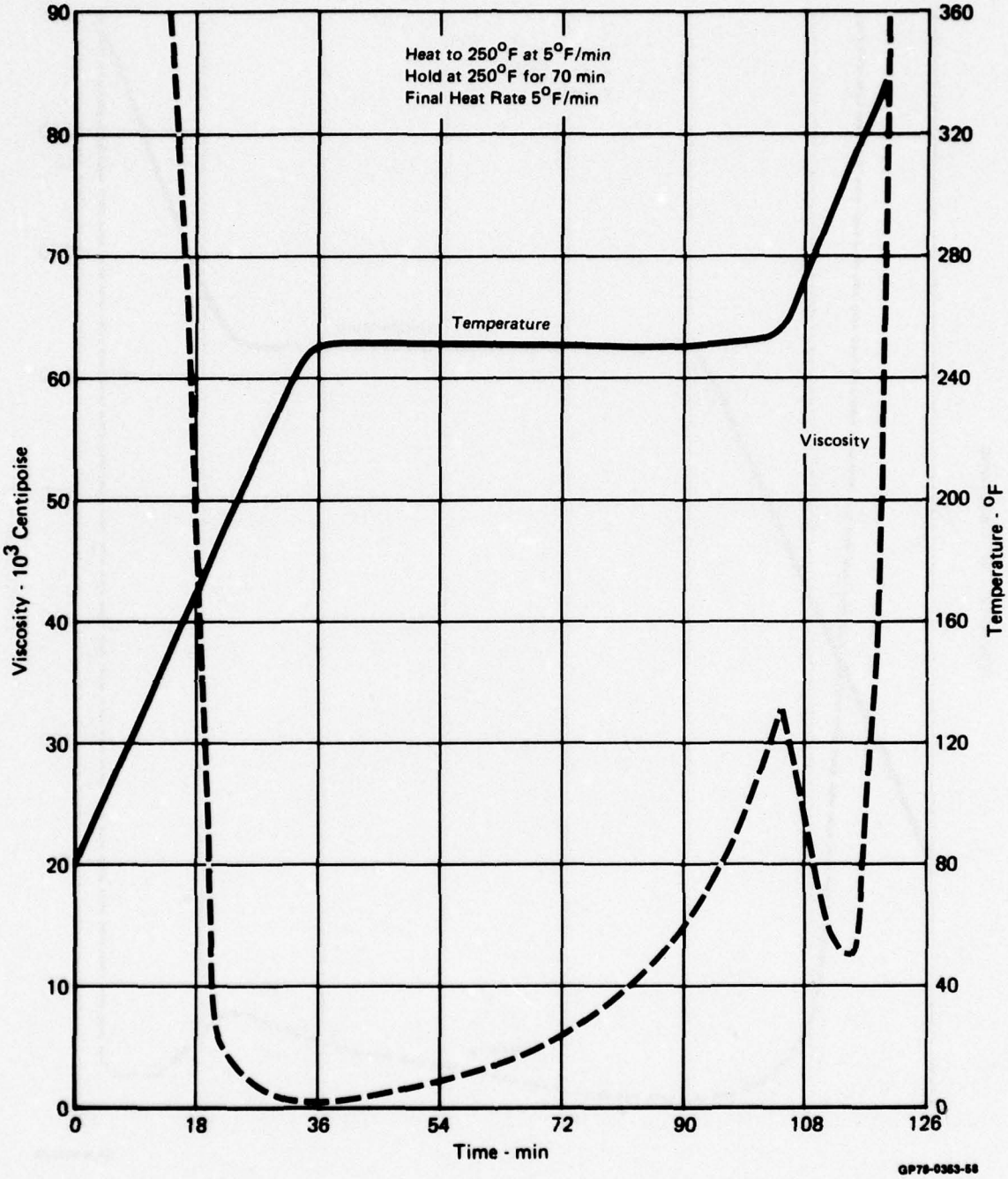

FIGURE C-20
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 79-4
(+ 20% Curing Agent)

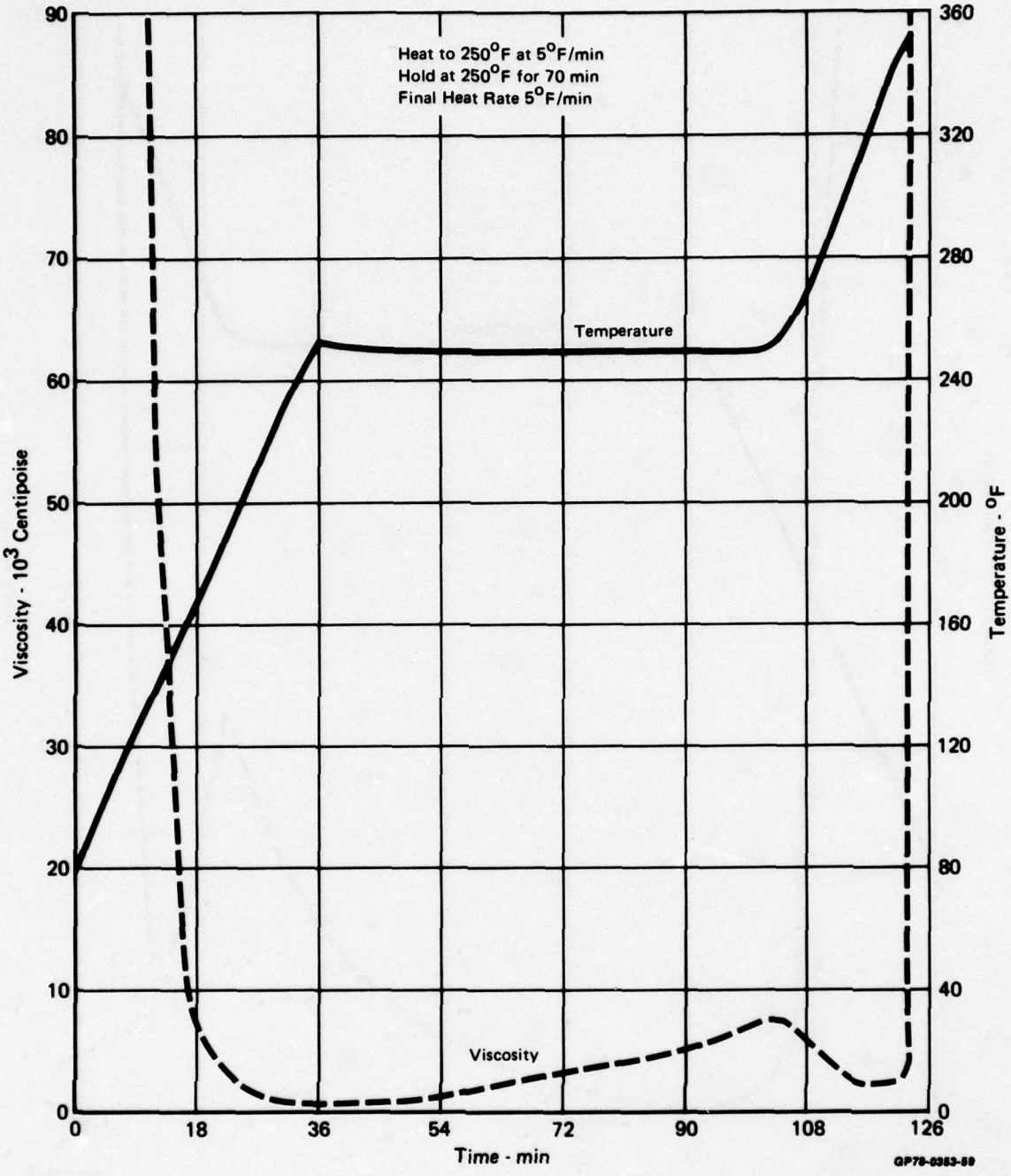

FIGURE C-21
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 79-5
(—20% Curing Agent)

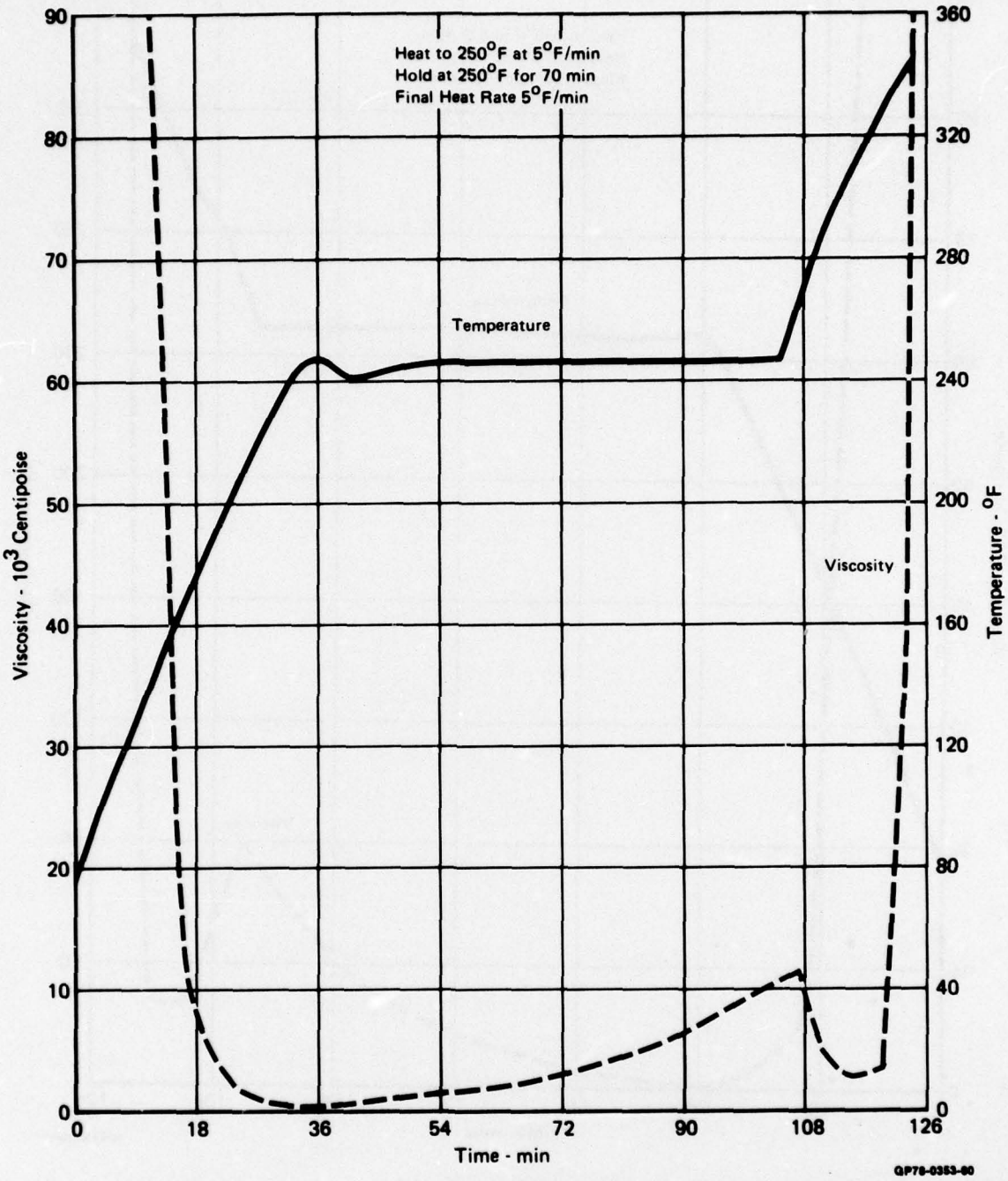

FIGURE C-22
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-6
(+ 20% Epoxide No. 2(H))

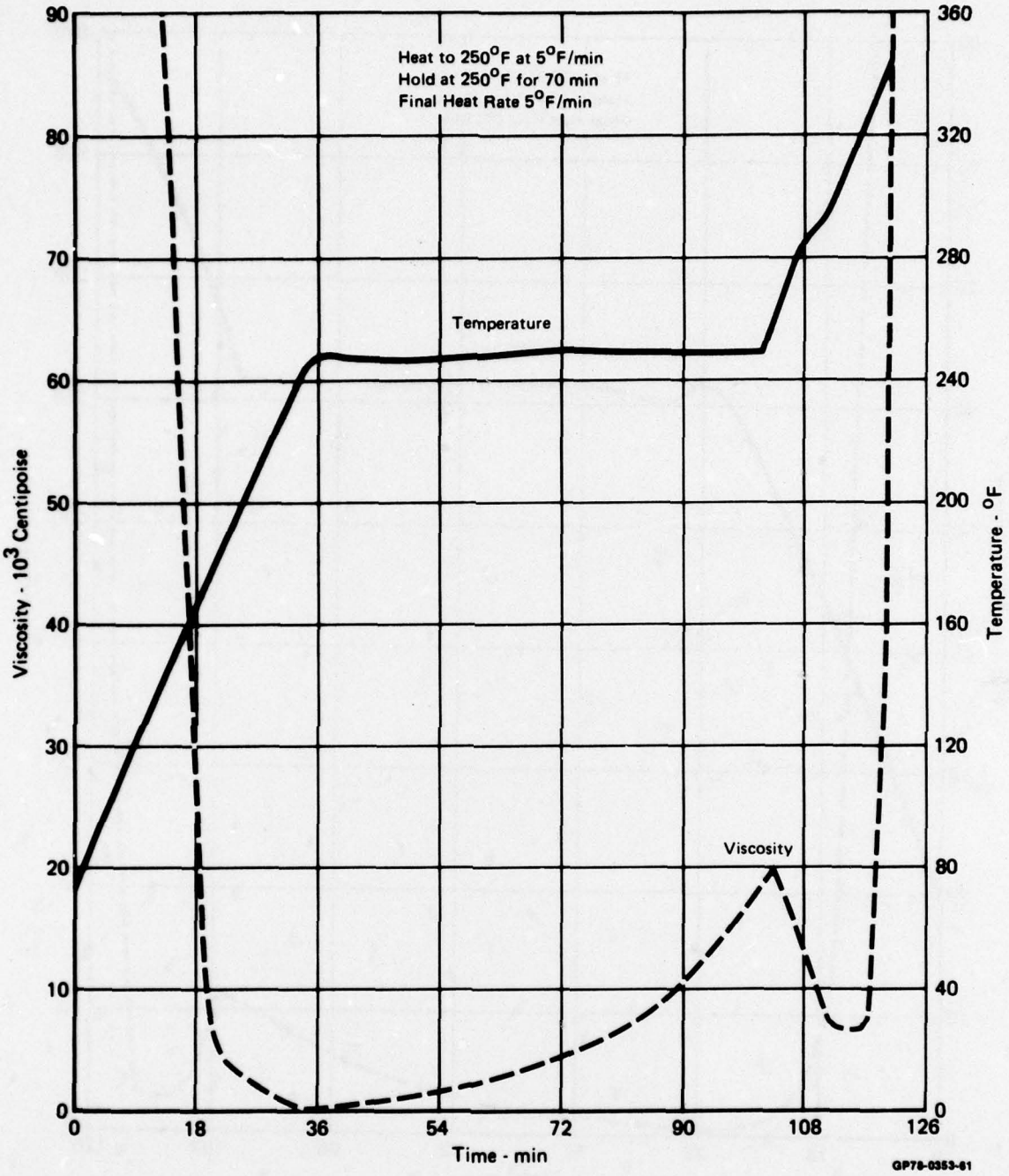

FIGURE C-23
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-7
(—20% Epoxide No. 2(H))

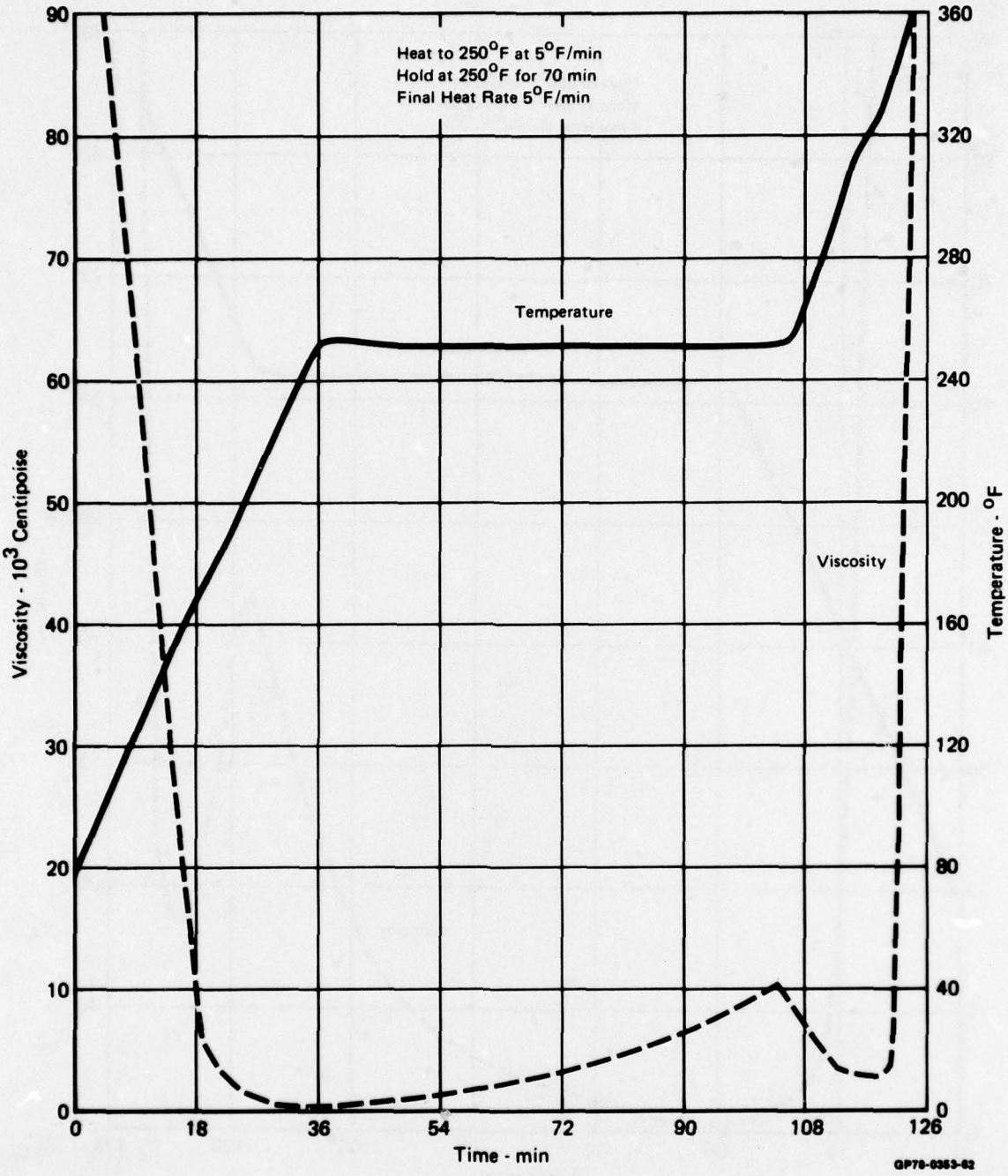

FIGURE C-24
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-8
(+ 40% Epoxide No. 2(H))

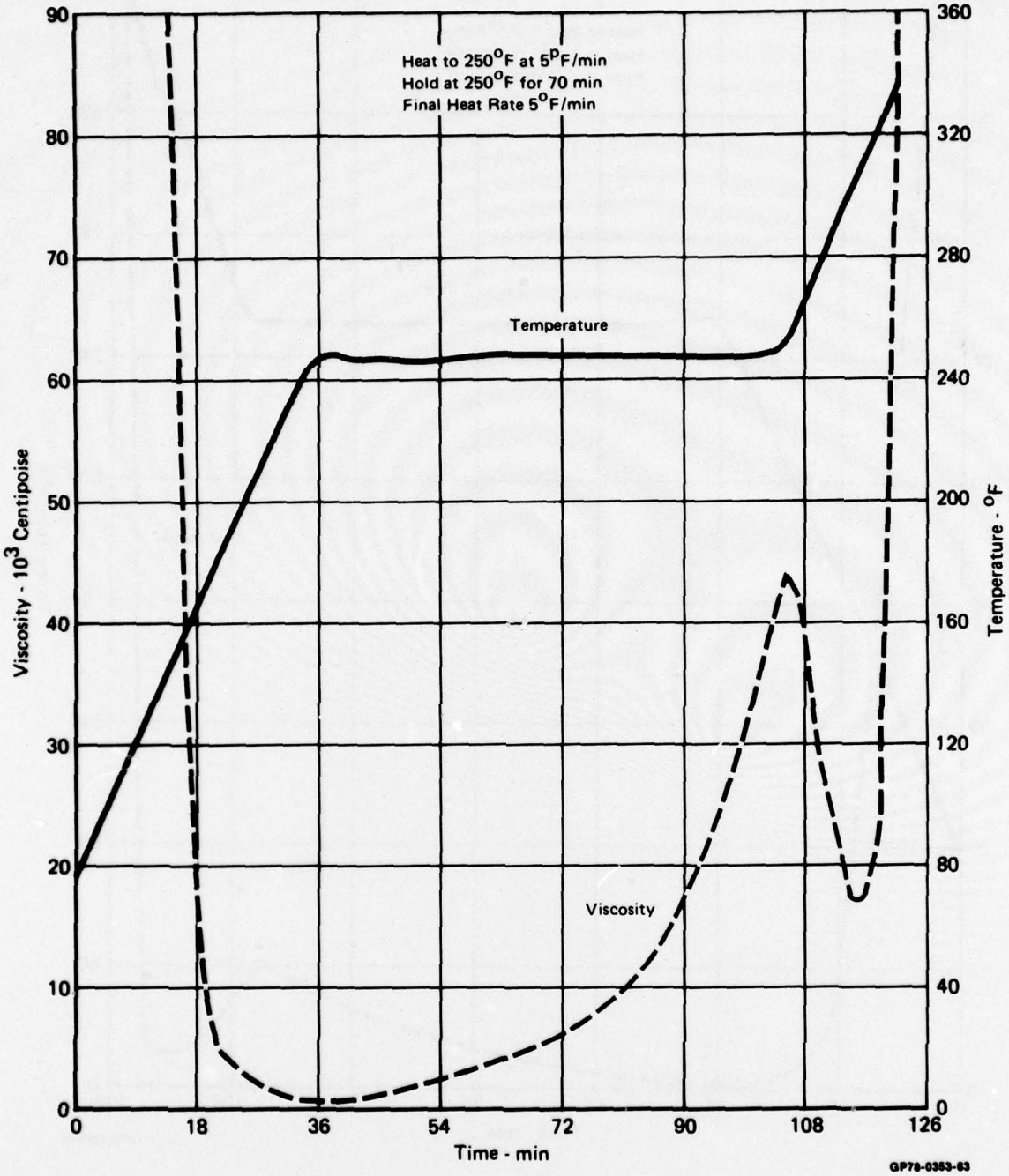

FIGURE C-25
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 78-9
(—40% Epoxide No. 2(H))

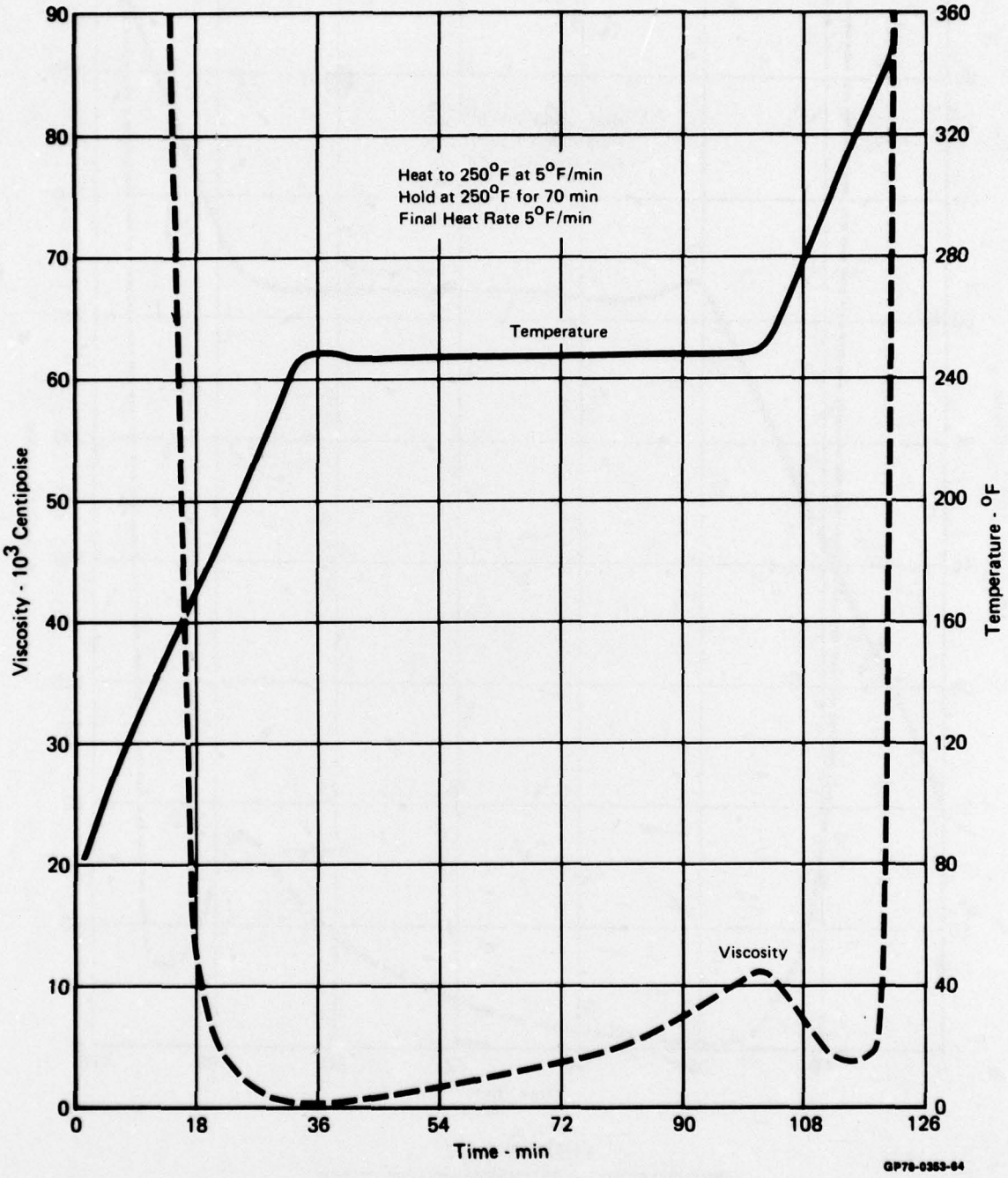

FIGURE C-26
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 78-10
(+ 50% Epoxide No. 3(H))

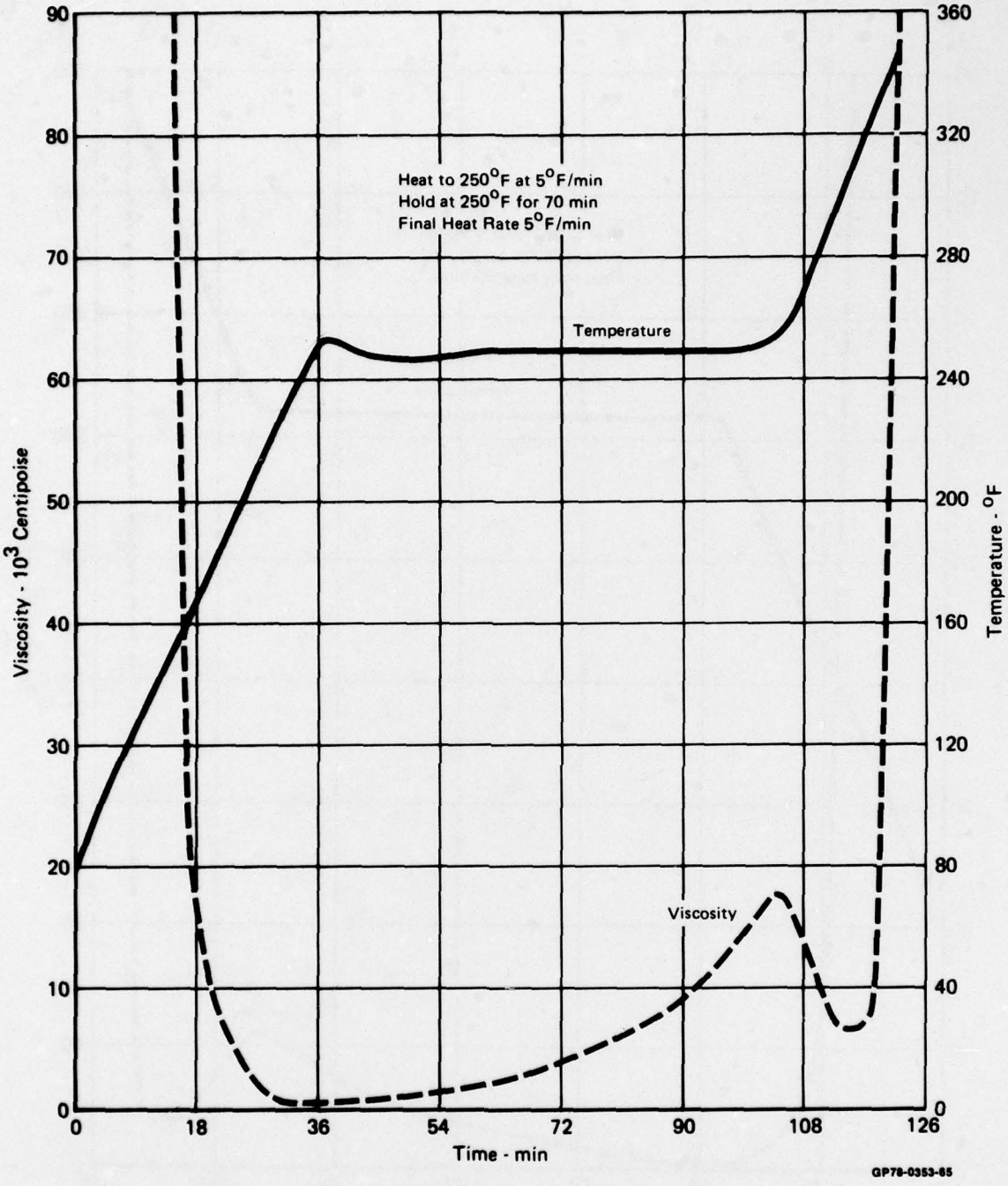

FIGURE C-27
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 79-11
(—50% Epoxide No. 3(H))

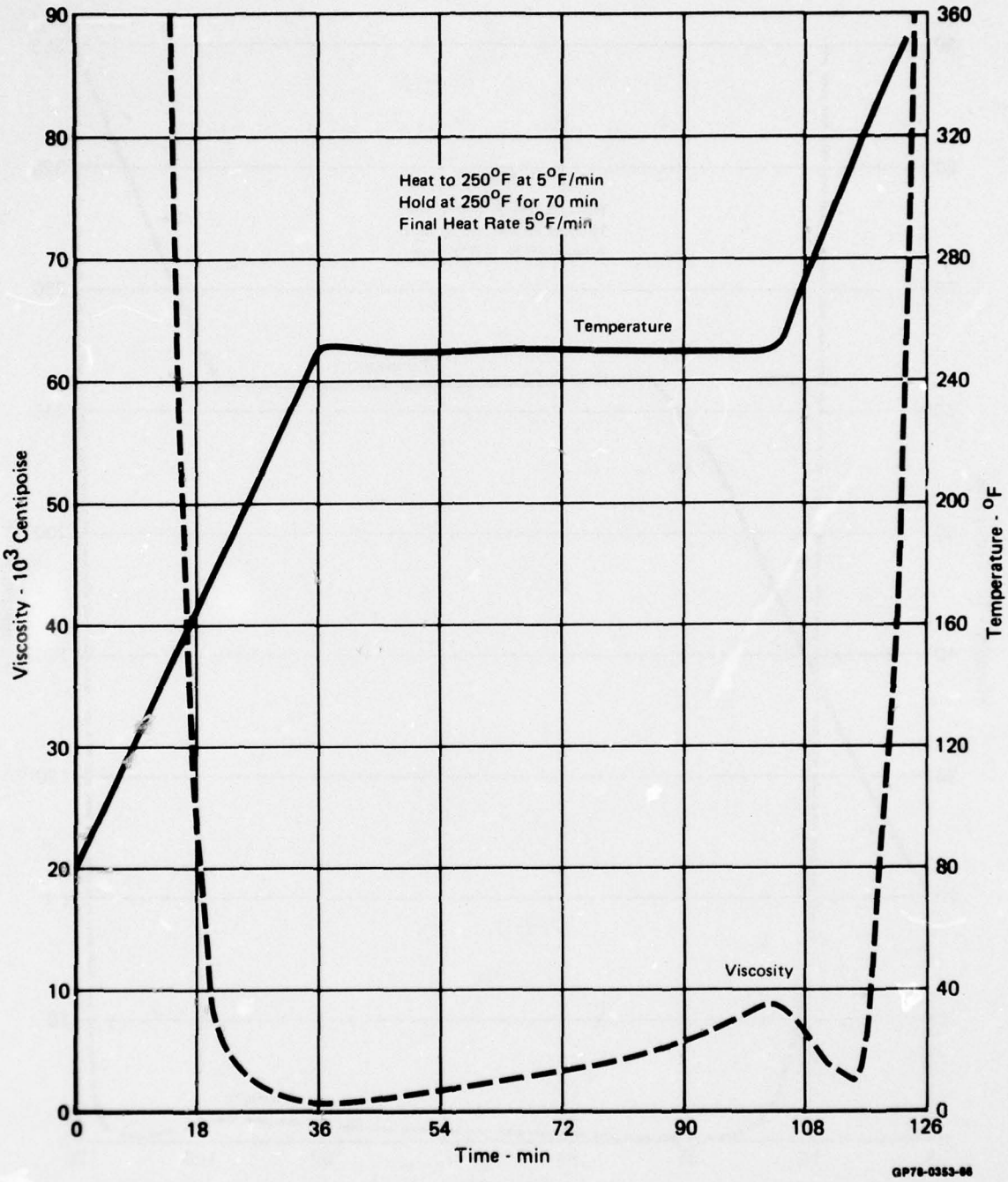

FIGURE C-28
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 76-12
(+ 100% Epoxide No. 3(H))

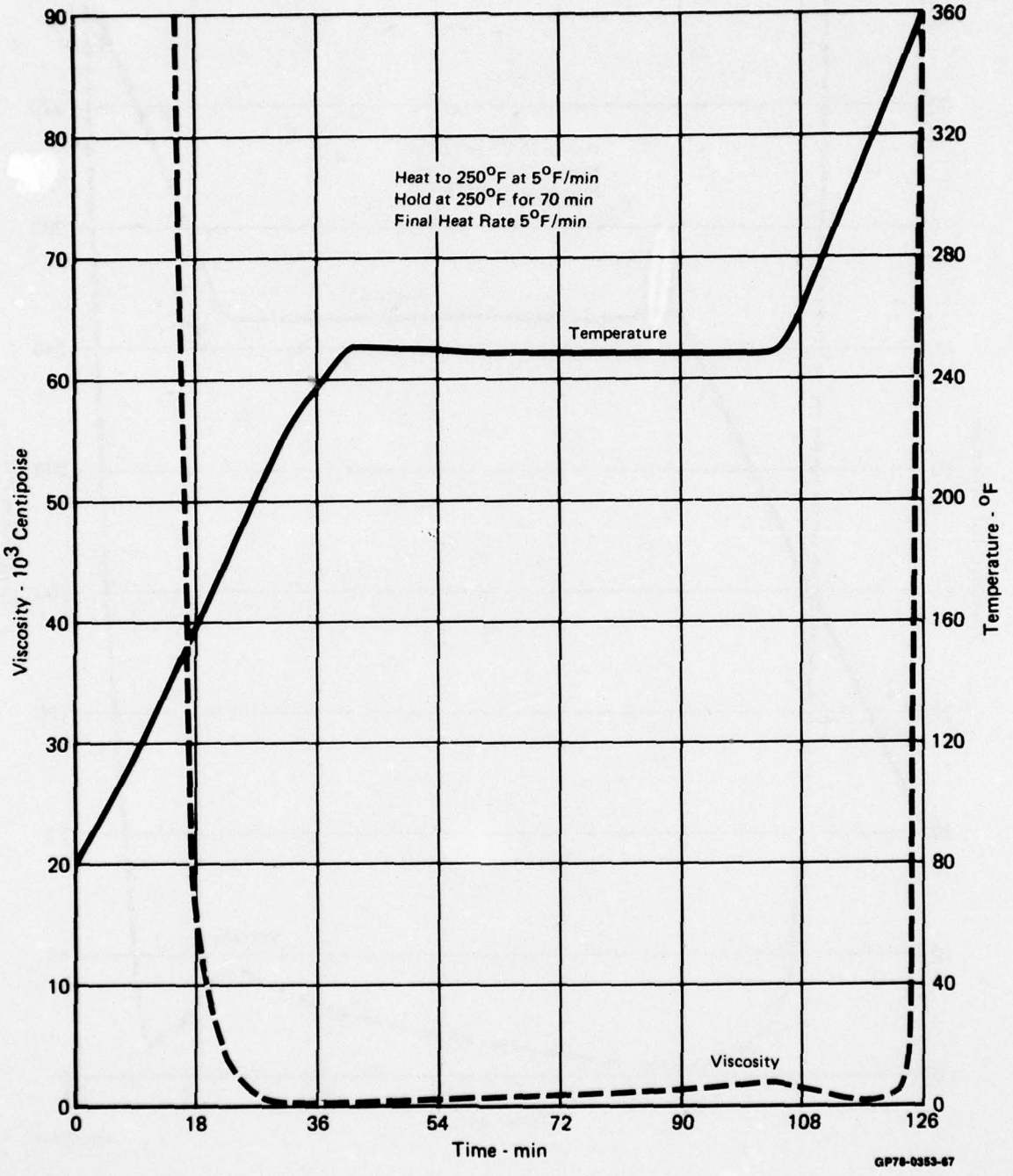

FIGURE C-29
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-13
(—50% Accelerator)

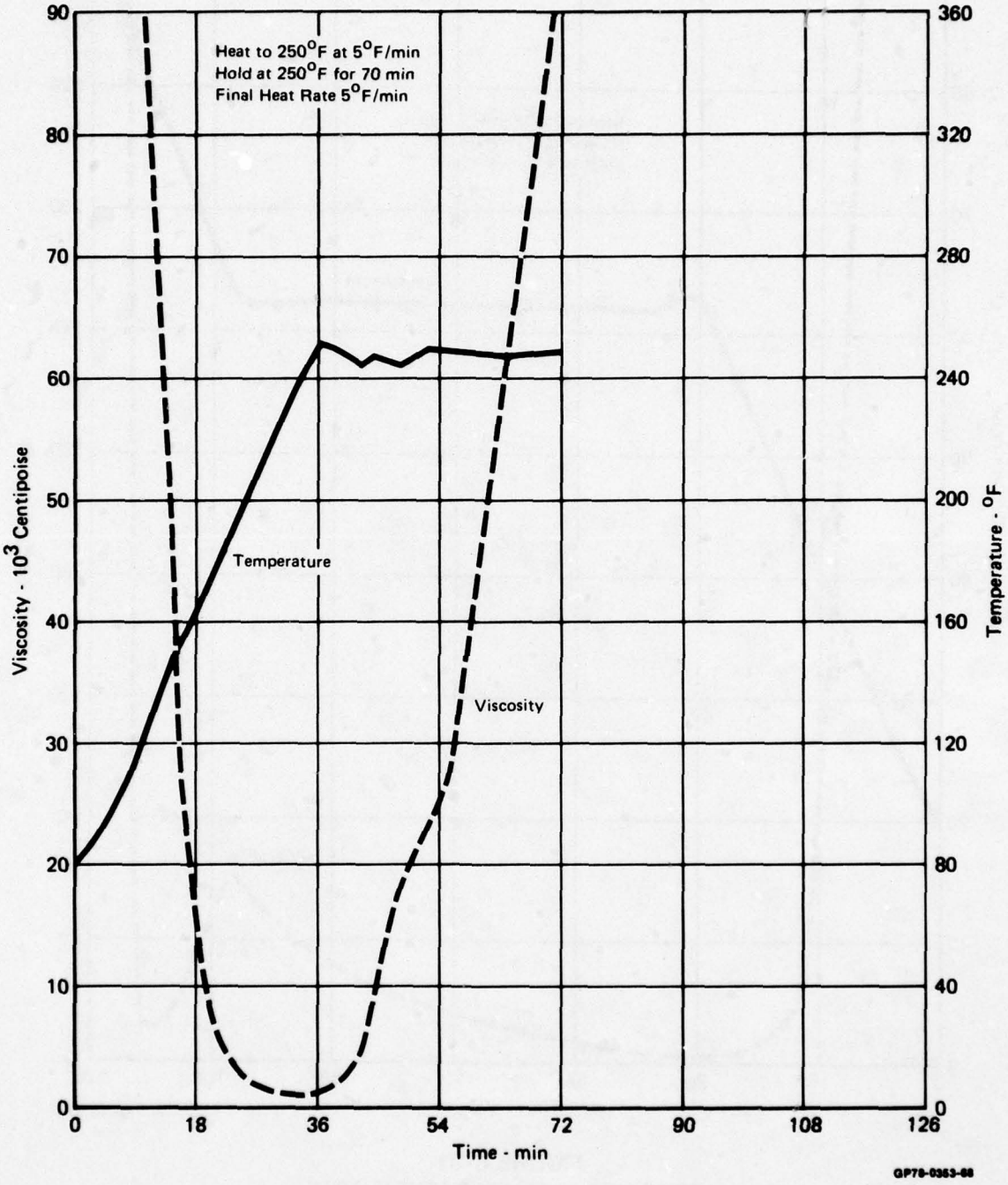

FIGURE C-30
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-14
(+ 100% Accelerator)

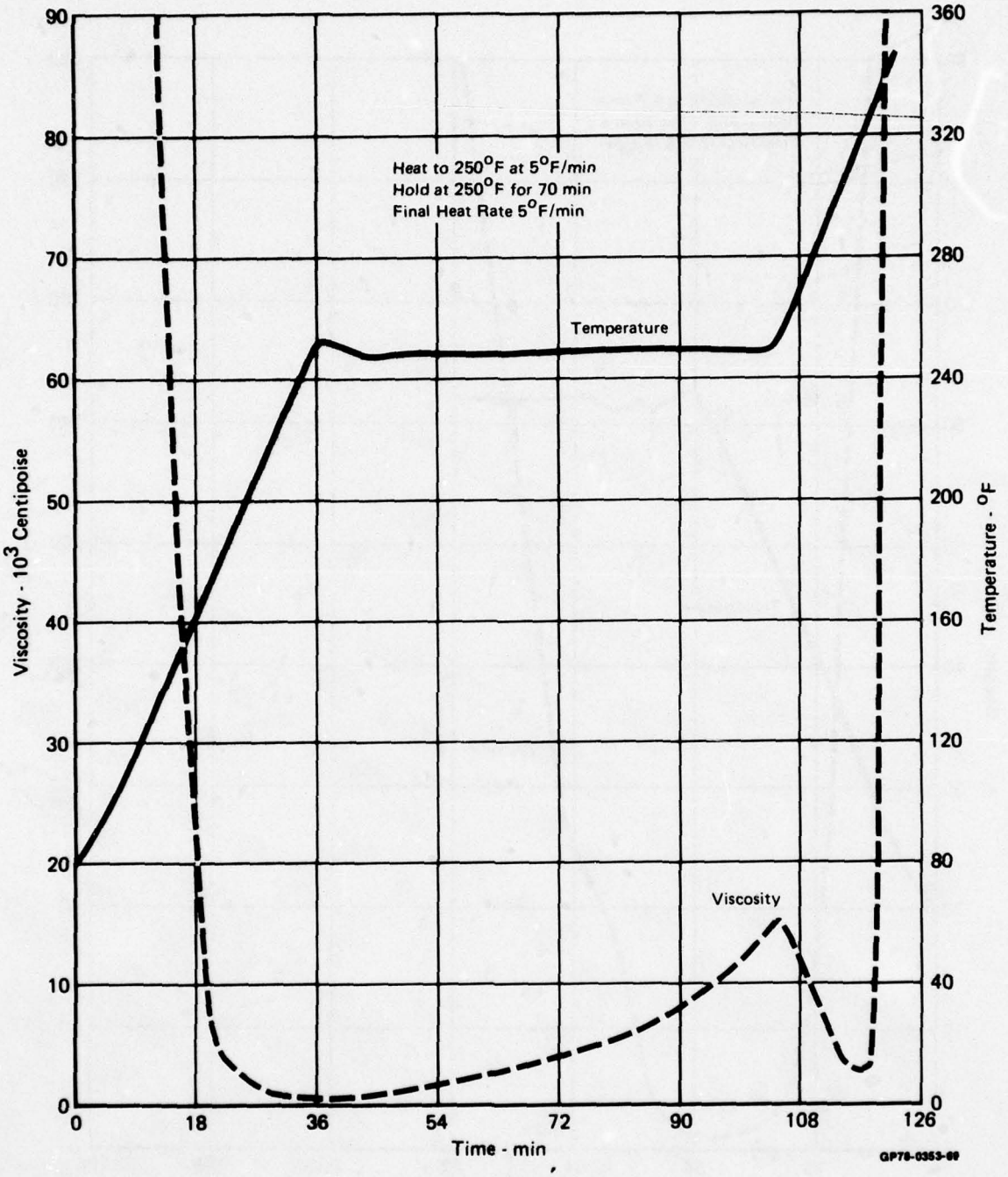

FIGURE C-31
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-15
(Understaged)

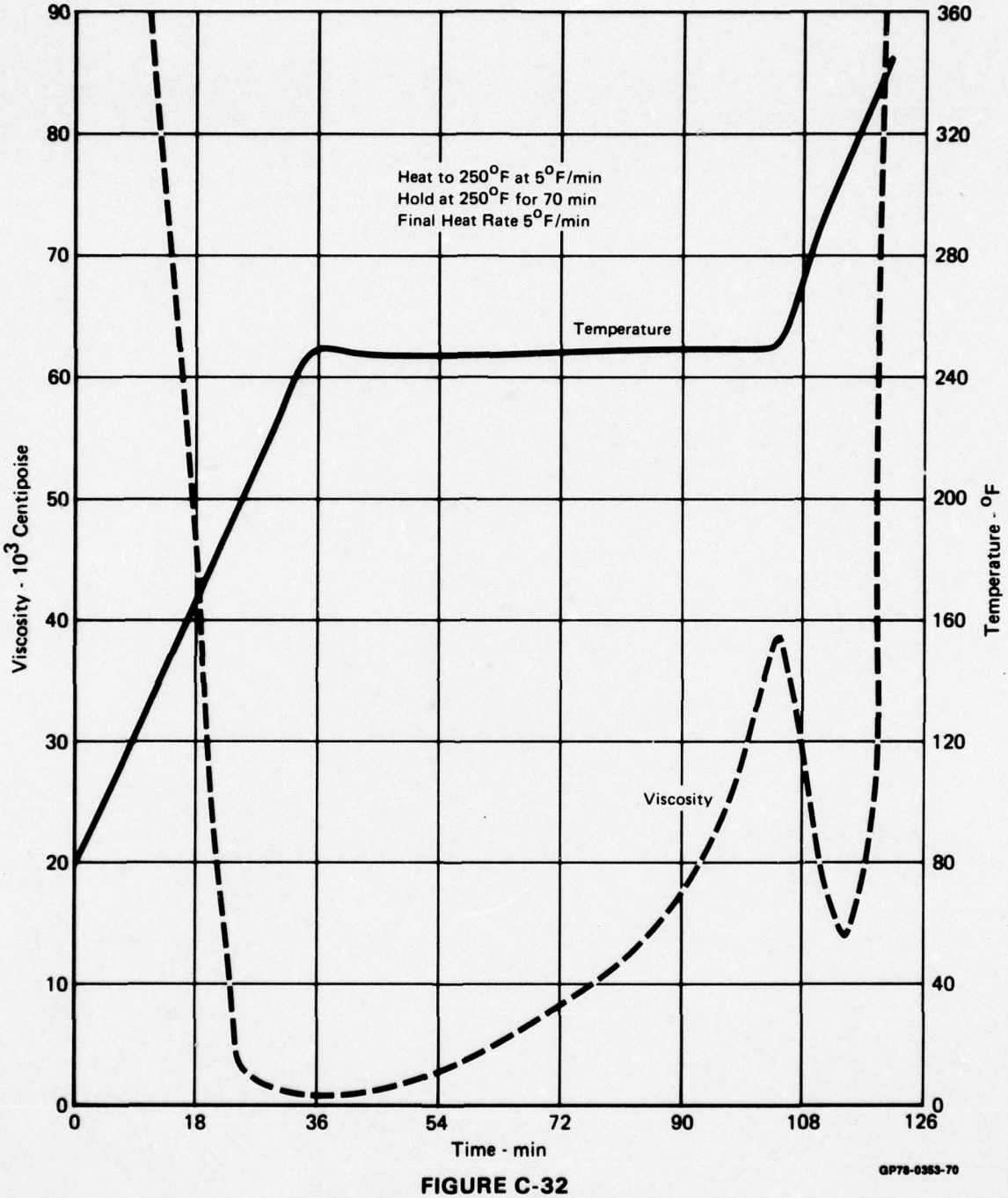

FIGURE C-32
VISCOSITY vs TEMPERATURE/TIME
3501-6 BATCH CRT 75-16
(Overstaged)

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