②

AFWAL-TR-84-4174

POLYMERIC COATINGS DEGRADATION PROPERTIES

The Sherwin-Williams Company
10909 S. Cottage Grove Avenue
Chicago, IL 60628

February, 1985

Final Report for Period September 1981 - September 1984

Approved for public release; distribution unlimited.

MATERIALS LABORATORY
AF WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AFB, OHIO 45433

NOTICE

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

MICHAEL J. HALLIWELL, Proj Engr
Nonstructural Materials Branch
Nonmetallic Materials Division
Materials Directorate

Kent J. Eisentraut
KENT J. EISENTRAUT, Chief
Nonstructural Materials Branch
Nonmetallic Materials Division
Materials Directorate

George F. Schmitt for
CHARLES E. BROWNING, Chief
Nonmetallic Materials Division
Materials Directorate

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER AFWAL-TR-84-4174	**2. GOVT ACCESSION NO.**	**3. RECIPIENT'S CATALOG NUMBER**
4. TITLE (and Subtitle) POLYMER COATINGS DEGRADATION PROPERTIES		**5. TYPE OF REPORT & PERIOD COVERED** Final September 1981 - September 198
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) T. K. Rehfeldt		**8. CONTRACT OR GRANT NUMBER(s)** F33615-81-C-5091
9. PERFORMING ORGANIZATION NAME AND ADDRESS Sherwin-Williams Research Center 10909 S. Cottage Grove Ave. Chicago, IL 60628		**10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS** 24220206
11. CONTROLLING OFFICE NAME AND ADDRESS		**12. REPORT DATE** February 1985
		13. NUMBER OF PAGES 162
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		**15. SECURITY CLASS. (of this report)** Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Coating
Degradation
Weathering
Urethane
Accelerated Weathering
Analysis

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

An evaluation of standard paint tests and physical and chemical analysis for natrually and artifically weathered aircraft coatings is reported. Most standard paint tests such an pendulum hardness have little ability to predict coating failure. Physical tests of bulk properties such as dynamic mechanical analysis have little ability to predict coating failure. Surface analysis techniques such as XPS, photoacoustic spectroscopy, and contact angle when used with property data analysis such as Box-Jenkins time series analysis do have predictive and mechanistic utility.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

FOREWORD

This report was prepared by T. K. Rehfeldt of the Research Center - Coatings, The Sherwin-Williams Company, Chicago, Illinois, under Contract No. F33615-81-C-5091. This research project is entitled Polymeric Degradation Coatings Properties. The program was administered under the direction of the Coatings and Thermal Protection Materials Brance (MLBT), Nonmetallic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, with Mr. M. Halliwell as the project engineer.

The report describes work by C. P. Chiang, D. C. Rich, R. W. Scott, D. T. Smith, M. L. Harrison, B. J. Hofbauer, M. D. Pankau and J. E. Pierre, all of the Sherwin-Williams Research Center-Coatings staff. The principal investigator was the author of this report, T. K. Rehfeldt. The work was conducted under the supervision of S. G. Croll, group leader for contract research.

The electron spin resonance work was graciously conducted by J. Gerlock of the Ford Motor Company Research Center in Dearborn, Michigan.

The measurements of water vapor transmission were made for us by the service laboratory of Modern Controls Instrument Co., Minneapolis, Minnesota.

The XPS measurements were conducted at the University of Wisconsin at Milwaukee, Department of Material Science.

Claude Luchessi and R. Haidle of the Department of Chemistry at Northwestern University, Evanston, Illinois provided invaluable consultation throughout this investigation.

This report covers research performed from September 1981 through September 1984.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

List of Illustrations (concluded)

LIST OF TABLES

SECTION I

INTRODUCTION

The objective of this program is to develop methods to characterize coating property degradation during weathering to provide an understanding of performance failures during service which can be used to improve future aircraft coatings systems, and to predict lifetimes of current coatings systems.

Coatings for Air Force aircraft are constantly being developed and improved due to limitations of current coating systems and changing requirements. Many changes have been made to additives and pigments while the basic polymers and solvents have been unchanged. Losses in service life have been noticed even with these limited changes. Further, developments coatings compliant with EPA and OSHA requirements may require completely new and radically different coatings systems, such as water based and high solids coatings. The service life of these water borne and high solids coatings is historically less than the service life of current aircraft coatings, which have excellent but less than optimum service life.

Current coating tests do not provide much information about the changes to the coating system during weathering which lead to coating failure. It was felt that there are methods of characterization of aircraft coatings which would relate to changes in performance during exposure and, hence, could provide information which could be used to extend the service life.

The scope of work reported here; under contract to the Air Force Materials Laboratory, at Wright-Patterson Air Force Base, Ohio; is to provide a better understanding of the changes which occur in a coating during weathering. This would include development of the ability to forecast coating lifetime by accelerated tests. Thus, better judgments of when to strip and recoat aircraft would become possible.

In order to provide as much information as possible about changes to the coating polymer during weathering a large number of sample coatings were prepared. Two commercial aliphatic poly(urethane) aircraft coatings which meet MIL-83286 in combination with several primers were selected. The coating/primer combinations are specified in Table I. A prototype high solids coating system, currently under further development, was also added to the study. In addition, one of the commercial coatings, which also served as the primary basis for comparison, was selected for testing with four different u.v. stabilizers. Both clear and pigmented coatings were prepared for all tests. Coatings were exposed to natural weathering in south Florida and included orientations of 45 deg. south and 5 deg. black box. Standard accelerated weathering included QUV weatherometer and the twin-arc weatherometer. One series of the selected standard coating was prepared over tin-foil to provide for free film tests where needed. In order to provide all the combinations of topcoat/ primer, clear/pigmented, natural/ artificial weathering, stabilized/ unstabilized, and the two different substrates, almost 1000 coated panels were prepared for testing.

Standard physical paint tests were to be made on all coatings. An objective of this investigation was to try to use these tests as a measure of coating degradation and to find objective tests which would be representative of the changes in the polymer during weathering and which, at the same time, would correlate with standard paint tests. If this could be done we could find out what is occurring in the coating and have simple tests which would relate to the extent of the changes. These objective tests may or may not be more sophisticated than standard coatings tests.

The standard physical tests investigated included pencil hardness, gloss, pendulum hardness, reverse impact, cross hatch adhesion, and contact angle of water. Each of these tests are useful to measure the suitability of a coating for specific uses or application. However, when used as a measure of the degradation of a coating or as a correlate to other techniques it was found that most of these had very limited utility.

SECTION II

GENERAL WORK DESCRIPTION

Photo-oxidation Chemistry

The most important cause of degradation in poly(urethane) coatings is taken to be photo-oxidation since the thermal degradation is important only at greater than normal ambient temperatures [1].

A proposed general pathway for the photo-oxidation of polymer, P, is illustrated by the following sequence [2,3].

Initiation: $PH \rightarrow P^* + H^*$

Propagation: $P^* + O{:}O \rightarrow POO^*$

$POO^* + PH \rightarrow POOH + P^*$

Chain branching: $POOH \rightarrow PO^* + {}^*OH$

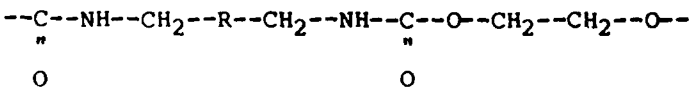
$PO^* + PH \rightarrow POH + P^*$

$HO^* + PH \rightarrow HOH + P^*$

Termination: Whenever two radicals interact

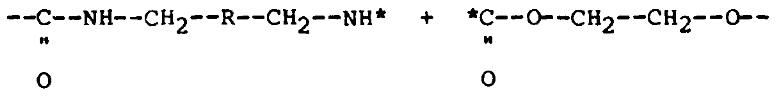
The photodegradation mechanism of poly(urethanes) is not known in detail, however, much has been added to our understanding. The presence of peroxide compounds in irradiated poly(urethanes) has been established [4]. Oxygen consumption and the presence of activated compounds which are the precursors of color body formation has been shown [5]. The effect of singlet oxygen reactions on the accelerated degradation of poly(urethanes) was demonstrated [6].

For poly(urethane) polymer with the general structure



$$--\underset{\overset{\|}{O}}{C}--NH--CH_2--R--CH_2--NH--\underset{\overset{\|}{O}}{C}--O--CH_2--CH_2--O--$$

the degradation is presumed to start between the carbonyl and amino groups,



$$--\underset{\overset{\|}{O}}{C}--NH--CH_2--R--CH_2--NH^{*} \quad + \quad {}^{*}\underset{\overset{\|}{O}}{C}--O--CH_2--CH_2--O--$$

This would initially lead to crosslinking, followed by a period during which the physical properties do not change, followed at a later time by more rapid degradation [7]. The various physical property changes taken together are most often manifested as embrittlement and gloss loss.

The stability of different poly(urethanes) follows the order diphenylmethane diisocyanate < toluene diisocyanate < hexamethylene diisocyanate [2]. The last of these is the isocyanate component in the coatings of this report. The data presented here will be evaluated in light of this mechanism.

Tests Considered

The initial phases of this investigation included three categories of tests, viz.

1.) Standard Physical Paint Tests
2.) Physical Property Measurements
3.) Chemical Property Measurements

The first category includes hardness e.g. pencil and pendulum, gloss, impact, salt spray, adhesion e.g. cross hatch, weight loss, and appearance. The second category includes measurements of water vapor transmission (WVTR), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), contact angle, and scanning laser acoustic micrography (SLAM). The third category includes electron spin resonance (ESR), scanning Auger microscopy (SAM), x-ray photoelectron spectroscopy (XPS), and

Fourier transform infra red spectroscopies (FT-IR). These categories will be discussed in turn.

Materials in Studies

A large number of samples were prepared for natural and artificial weathering and the related testing. We attempted to provide enough material to allow changes in the experiments during the course of the work. The main series of test panels were coated with a commercial DOD aircraft coating, type D. This was a basic aliphatic poly(urethane) coating currently in use by the U.S.A.F. This coating was prepared as both pigmented grey and unpigmented coatings which were sprayed over treated and primed 2024 TO aluminum panels. This formed the primary experimental material for all of the tests. The coating, type D, in clear and pigmented forms was placed over three different primers: 1) epoxy poly(amide) 2) poly(sulphide) and 3) water reducible epoxy. Additionally standard coatings were made over unprimed tin foil to provide samples for free film tests.

In addition to the primary topcoat coating, type D, panels were prepared by using another commercial coating, DS. This was applied over the standard epoxy poly(amide) primer on 2024 TO aluminum.

In order to provide samples for examination of the effect of ultraviolet radiation stabilizers a series of coatings, prepared by using the coating D containing these substances were prepared over standard epoxy poly(amide) primer on 2024 TO aluminum. Samples were prepared which contained an triazine type stabilizer, a hindered-amine type stabilizer, a benzo-phenone type U. V. absorber and a combination of triazine and hindered amine. The coatings were prepared in both clear and pigmented forms and contained stabilizers at 1% of the total polymer weight.

In all cases the coatings were prepared according to manufacturers specifications and were applied by automatic spray equipment to approximately 3 mils dry film thickness. All of the above coating materials were coded and sent to our south Florida exposure station for natural exposure. A summary of the combinations and the sample codes is given in Table 1. These codes will be used consistently throughout this report. Parallel samples were prepared for artificial exposure testing.

One further set of coatings samples was prepared from a prototype high solids urethane coating. This coating was subsequently replaced by a high solids coating which has been developed under a separate contract. However, this coating has not been on exposure long enough to provide useful data as yet. This will be left on exposure for subsequent analysis.

TABLE 1

SAMPLE CODES AND DESCRIPTIONS AND TEST CONDITIONS

EXTERIOR EXPOSURE SOUTH FLORIDA

Spl.Code	Exposure	Exp.Cond.	U.V.Stab	Top Coat/Primer
Set 1.				
64201	6 mos.(1-6)	45 deg. S	None	D Grey/EPA
64210	6 mos.(1-6)	45 deg. S	None	D Clr/ EPA
64260	6 mos.(1-6)	5 deg. Blk.Box	None	D Grey/EPA
64270	6 mos.(1-6)	5 deg. Blk.Box	None	D Clr/ EPA
64317	6 mos.(1-6)	45 deg. S	None	D Grey/P.S.
64337	6 mos.(1-6)	45 deg. S	None	D Grey/W.R.
64357	6 mos.(1-6)	45 deg. S	None	DS Grey/EPA
64359	6 mos.(1-6)	45 deg. S	None	EPA Primer Only
Set 2.				
64208	6 mos.(7-12)	45 deg. S	None	D Grey/EPA
64218	6 mos.(7-12)	45 deg. S	None	D Clr /EPA
64268	6 mos.(7-12)	5 deg. Blk.Box	None	D Grey/EPA
64278	6 mos.(7-12)	5 deg. Blk.Box	None	D Clr /EPA
64325	6 mos.(7-12)	45 deg. S	None	D Grey/P.S.
64345	6 mos.(7-12)	45 deg. S	None	D Grey/W.R.
64365	6 mos.(7-12)	45 deg. S	None	DS Grey/EPA
64468	6 mos.(7-12)	45 deg. S	None	EPA Primer Only
Set 3.				
64202	12 mos.	45 deg. S	None	D Grey/EPA
64212	12 mos.	45 deg. S	None	D Clr /EPA
64262	12 mos.	5 deg. Blk.Box	None	D Grey/EPA
64272	12 mos.	5 deg. Blk.Box	None	D Clr /EPA
64319	12 mos.	45 deg. S	None	D Grey/P.S.
64339	12 mos.	45 deg. S	None	D Grey/W.R.
64359	12 mos.	45 deg. S	None	DS Grey/EPA
64461	12 mos.	45 deg. S	None	EPA Primer Only

TABLE 1. CONTINUED

Set 4.

65108	6 mos.	45 deg. S	T-328	D Clr/None
65138	6 mos.	45 deg. S	T-770	D Clr/None
65168	6 mos.	45 deg. S	UV-24	D Clr/None
65198	6 mos.	45 deg. S	T-328/T-770	D Clr/None
65228	6 mos.	45 deg. S	T-328	D Grey/None
65258	6 mos.	45 deg. S	T-770	D Grey/None
65288	6 mos.	45 deg. S	UV-24	D Grey/None
65318	6 mos.	45 deg. S	T-770/T-328	D Grey/None

Set 5.

65117	6 mos.(7-12)	45 deg. S	T-328	D Clr/EPA
65147	6 mos.(7-12)	45 deg. S	T-770	D Clr/EPA
65177	6 mos.(7-12)	45 deg. S	UV-24	D Clr/EPA
65207	6 mos.(7-12)	45 deg. S	T-328/T-770	D Clr/EPA
65237	6 mos.(7-12)	45 deg. S	T-328	D Grey/EPA
65267	6 mos.(7-12)	45 deg. S	T-770	D Grey/EPA
65297	6 mos.(7-12)	45 deg. S	UV-24	D Grey/EPA
65327	6 mos.(7-12)	45 deg. S	T-770/T-328	D Grey/EPA

Set 6.

65111	12 mos.	45 deg. S	T-328	D Clr/EPA
65141	12 mos.	45 deg. S	T-770	D Clr/EPA
65171	12 mos.	45 deg. S	UV-24	D Clr/EPA
65201	12 mos.	45 deg. S	T-328/T-770	D Clr/EPA
65231	12 mos.	45 deg. S	T-328	D Grey/EPA
65261	12 mos.	45 deg. S	T-770	D Grey/EPA
65291	12 mos.	45 deg. S	UV-24	D Grey/EPA
65321	12 mos.	45 deg. S	T-770/T-328	D Grey/EPA

Set 7.

64205	18 mos.	45 deg. S.	None	D Grey/EPA
64214	18 mos.	45 deg. S.	None	D Clr/EPA
64265	18 mos.	5 deg Blk.Box	None	D Grey/EPA
64275	18 mos.	5 deg Blk.Box	None	D Clr/EPA
64321	18 mos.	45 deg. S.	None	D Grey/PS
64341	18 mos.	45 deg. S.	None	D Grey/WR
64361	18 mos.	45 deg. S.	None	DS Grey/EPA
64464	18 mos.	45 deg. S.	None	EPA Primer Only

Table 1. CONTINUED

Set 8.

64206	24 mos.	45 deg. S.	None	D Grey/EPA
64216	24 mos.	45 deg. S.	None	D Clr/EPA
64266	24 mos.	5 deg. Blk.Box	None	D Grey/EPA
64276	24 mos.	5 deg. Blk.Box	None	D Clr/EPA
64323	24 mos.	45 deg. S.	None	D Grey/PS
64343	24 mos.	45 deg. S.	None	D Grey/WR
64363	24 mos.	45 deg. S.	None	DS Grey/EPA
64465	24 mos.	45 deg. S.	None	EPA Primer Only

NOTE: EPA=epoxy poly(amide), PS=poly(sulfide), WR=Water reducible
T-328 = Tinuvin 328, T-770 = Tinuvin 770, UV-24 = Uvinol 24

Accelerated Exposure Cycles

The chief accelerated exposure apparatus used for this work is the QUV Weatherometer. The cycle used for most of the tests is 4 hours of U.V. exposure followed by 2 hours of condensation at 50-70°C. The U.V. radiation is at 280 to 320 nm. Test panels were exposed for periods up to 6000 hours.

Exposures were also made in a standard Twin-Arc Weatherometer for periods up to 3000 hours.

The materials, both exposed to natural weathering and to accelerated weathering were the materials examined by the battery of tests. The results and discussion of this testing form the rest of this report.

The QUV weatherometer used was the Q.U.V. Accelerated Weathering Tester manufactured by the Q-Panel Company, Cleveland, Ohio. The apparatus was operated in accordance with ANSI/ASTM G53-77. Previous experience with automotive urethane coatings indicated that this type of weatherometer produced better correlation with actual exterior weathering than do other weatherometer's, e.g. twin-arc types. In addition it was possible to process more samples and to control conditions better than with other apparatus.

SECTION III

RESULTS AND DISCUSSION

Standard Physical Paint Tests

Contact Angle of Water

The contact angle is a measure of the surface energy of a coating [8]. The contact angle should be a useful measure of changes at the surface during weathering. The stationary contact angle of water on all samples, both naturally and artificially weathered were made. Measurements of the contact angle were made by using a clipped mean procedure [9]. For this calculation, nine measurements are made and the highest and lowest are discarded. The remaining values are averaged. An analysis of variance is made to determine if pooling is acceptable. This is followed by a test of significance for the results vs. the control samples. This procedure provides both a measure of the contact angle and a measure of the change which has taken place upon weathering.

In general, the data indicate that the contact angle decreases over time. This is as expected, since degradation should create a rougher or more porous surface which would have higher surface energy. Table 2 contains the contact angle data for QUV exposures up to 6000 hours and Table 3 contains the contact angle results for the exterior exposed coatings described in Table 1.

TABLE 2. CONTACT ANGLE OF WATER

QUV WEATHEROMETER EXPOSURE

Exposure Time (Hrs.)	Contact Angle			
	Grey		Clear	
	Exposed	Unexposed	Exposed	Unexposed
200	41	72	44	66
400	39	72	30	66
600	26	72	33	66
800	26	72	35	66
1000	13	72	30	66
1500	7	72	43	66
2000	21	72	51	66
2500	11	72	45	66
3000	--	--	44	66
3500	3	72	48	66
4000	14	72	48	66
4500	5	72	49	66
5000	6	72	28	66
5500	3	72	--	--
6000	3	72	9	66

TABLE 3. CONTACT ANGLE OF WATER AND PENDULUM HARDNESS

Spl. Code	Contact Angle		Pendulum Hardness	
	Exposed	Unexposed	Exposed	Unexposed
Set 1. Months 1-6				
64201	40	74	115	49
64210	37	74	128	114
64260	51	74	124	49
64270	67	74	139	114
64317	44	69	61	35
64317	50	71	113	54
64357	50	75	78	72
64459	48	84	95	87
Set 2. Months 7-12				
64208	44	74	91	49
64218	44	74	123	114
64268	38	74	96	49
64278	42	74	103	114
64325	43	68	43	35
64345	38	70	87	54
64365	39	75	75	72
64468	45	84	94	87
Set 3. Months 1-12				
64202	46	74	115	49
64212	40	74	134	114
64262	38	74	109	49
64272	41	74	137	114
64319	47	68	57	35
64339	43	71	103	54
64359	47	75	73	72
64461	34	84	124	87
Set 4. Months 1-6 With U.V. Stabilizers				
65108	36	67	125	125
65138	41	67	139	106
65168	43	68	135	111
65198	37	63	136	116
65228	38	72	103	82
65258	37	69	97	72
65288	33	72	105	57
65318	49	69	97	48

Table 3. CONTINUED

Set 5. Months 7-12

65117	54	67	133	125
65147	51	66	132	106
65177	56	68	131	111
65207	50	63	131	116
65237	48	72	94	82
65267	54	69	90	72
65297	55	72	87	57
65327	52	69	83	48

Set 6. Months 1-12

65111	44	67	129	125
65141	40	66	130	106
65171	44	68	112	111
65201	34	63	129	116
65231	46	72	101	82
65261	43	69	96	72
65291	28	72	95	57
65321	49	69	88	48

Set 7 Months 1-18

64205	44	74	124	49
64214	52	74	151	114
64265	34	74	125	49
64275	48	74	140	114
64321	52	69	62	35
64341	35	71	121	54
64361	37	75	86	72
64464	32	84	91	87

The contact angle measurements formed the test case for the development of data analysis techniques. This will be discussed further later. In addition the contact angle was used as one measure of change in several other tests, e.g. salt-spray, this too will be discussed later.

Pendulum Hardness Tester

The test for pendulum hardness was carried out generally according to the German Naional specification, DIN 53 157 (1965) as amended by the International Standards Organization, subcommittee ISO/TC35 upon recommendation of the British Standards Institute subcommittee PVC/10/5.

In the pendulum hardness tester the pendulum rests on two ball bearings and is counterbalanced by means of a weight sliding on a vertical rod attached to the cross bar. A knife edge, the fulcrum of the pendulum, rests on the coating to be tested. The test is made by raising the pendulum to a standard amplitude and counting the swings for a specified time period. The harder the coating the longer it will take for the swings to be damped and therefore the more swings will occur in in the time period [10].

Measurements were made to demonstrate the utility of the pendulum hardness tester, and to provide a more objective measure of hardness than such measures as pencil hardness. Measurements were made of both artificially and naturally weathered coatings. The pendulum hardness for the naturally weathered coatings is given in Table 3. The pendulum hardness vs. hours of QUV exposure is shown in Figure 1 and Figure 2 for clear and pigmented coatings respectively. In both cases the hardness reaches a maximum around 500 hours indicating that the coatings continue to 'cure' for some time after application. Then the hardness slowly declines indicating that the measure of a bulk property is involved

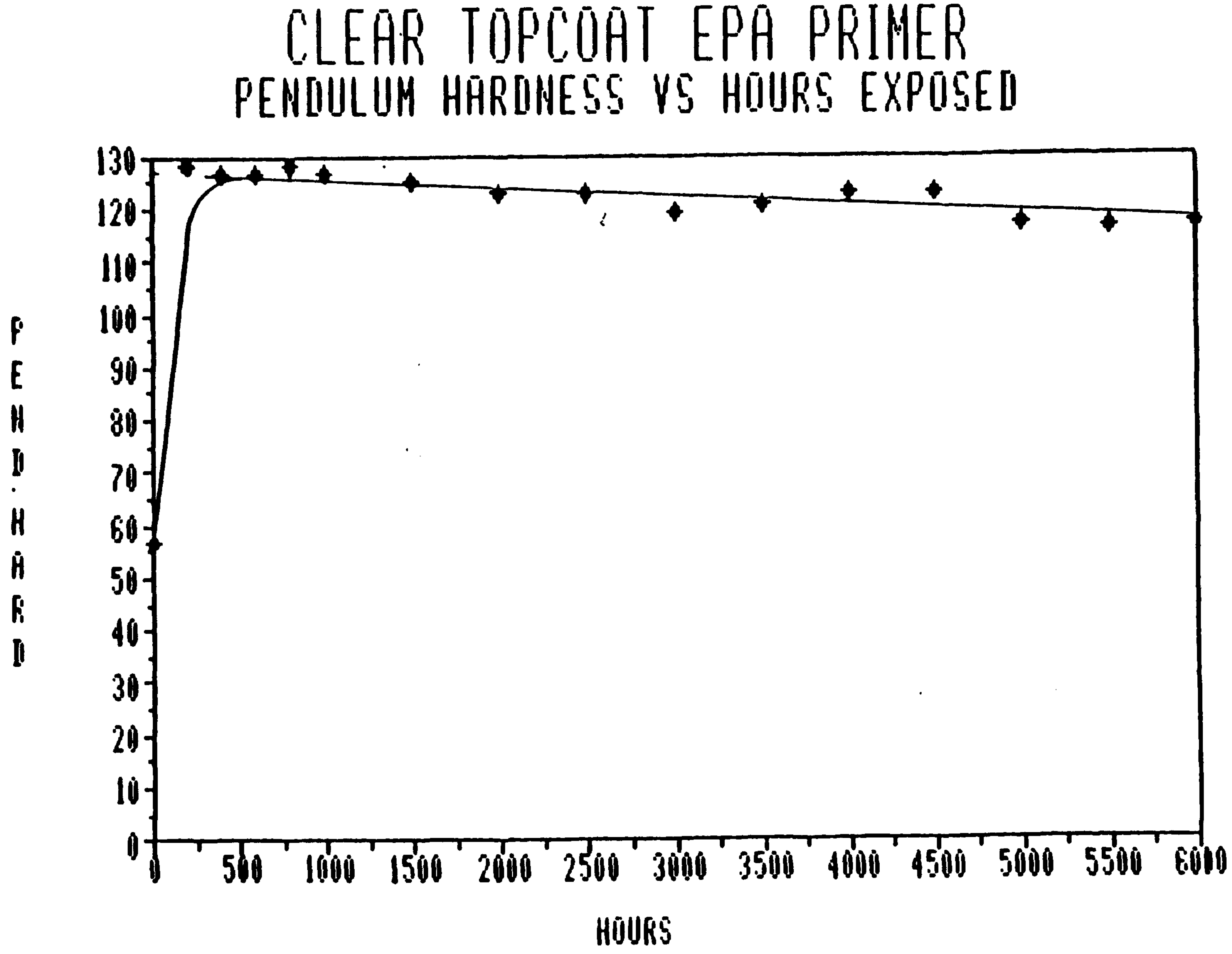


Figure 1. Clear Topcoat EPA Primer Pendulum Hardness vs. Hours Exposed

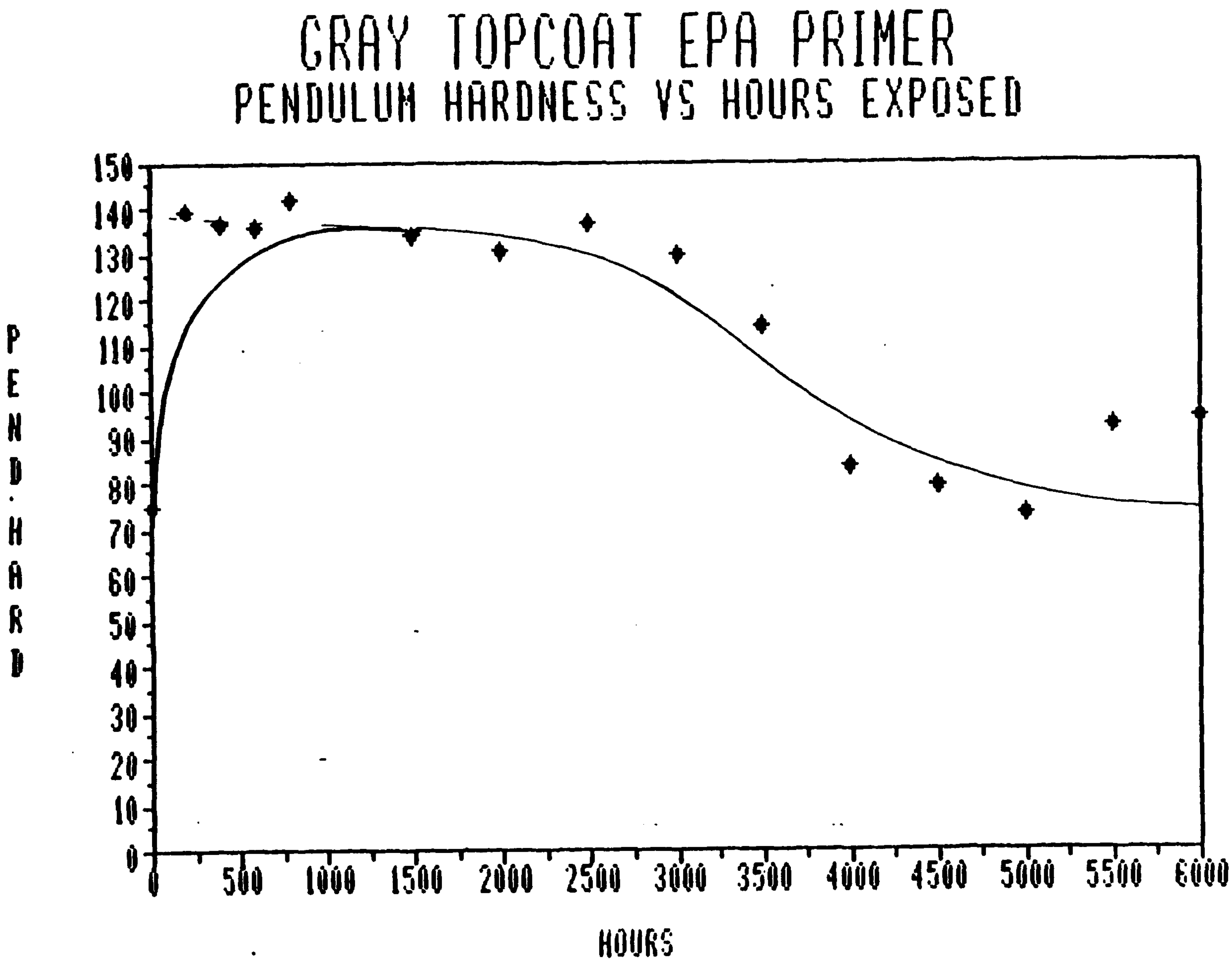


Figure 2. Gray Topcoat EPA Primer Pendulum Hardness vs. Hours Exposed

which may limit the utility of the measure as an indicator of failure. That is, the hardness of the coating does not change much with degradation as long as the adhesion to the substrate is adequate even though the surface may be badly cracked.

The pendulum hardness was also used, as was the contact angle, as an evaluation of salt-spray and other tests.

Cross Hatch Adhesion

The cross hatch adhesion was measured according to ASTM D 3359-78. This test is a combination of crosscut and peel tests. The very simple method consists of making a series of parallel cuts through the coating in one direction and a second series at right angles to the first. The tape is placed over the cuts and rubbed to assure good contact. The tape is quickly peeled away and the number of squares remaining intact is a measure of the adhesion.

The cross hatch adhesion test shows promise as a relatively objective, easy to perform and quantitative test and may prove to be a predictor of coating failure. This test could be performed on any aircraft by an unskilled technician with no significant damage to the aircraft and the measurement could serve as an indicator of the state of the coating. There is signicant scatter in the data and the test seems to be dependent on film thickness thus more data are required before judgement can be made.

Pull Off Adhesion Test

Another adhesion test which was evaluated for this work is the pull off adhesion test in which test dolly is glued to the panel and the force required to pull the dolly off the specimen is measured. For this test cyanoacrylate adhesive or epoxy adhesive may be used to glue the dolly to the test piece. The adhesives are allowed to dry for 24 hours before the test is conducted.

This test was made on several test coatings. All test specimens failed at less than 100 lbs/in^2 of force. Several failure modes were found, viz. primer/substrate, coating/primer, and coating/dolly. The results here were not internally consistent which is probably a result of the added variable of adhesion of the dolly adhesive to the coating. Further the descrimination between samples was not large enough to make strong conclusions. This perhaps could be remedied by a tester with a different range but the adhesive problems would remain.

Salt Spray Fog Test

Salt spray tests were conducted on coatings which had been naturally exposed to see if deterioration of the coatings whould be detected by poorer resistance to salt spray conditions.

The salt spray tests were conducted according to ASTM B117-73 Coatings are subjected to salt spray of a 5% sodium chloride solution atomized at 95°F. The samples were scored down the center with one continous line down to the substrate. These were exposed for 500 hours or more.

The results of 500 hours of salt spray on naturally exposed coatings as measured by cross hatch adhesion, both rating and percent remaining, contact angle of water, and pendulum hardness are given in Tables 4-7 respectively. It is seen that the salt-spray has little affect on the cross hatch adhesion or pendulum hardness. The data is scattered. A rank product correlation analysis is not signicant at the 5% level indicating that there is no difference in the measurements before and after the salt spray. The contact angle of water does go down after exposure to salt spray but this may be due to residual salt on the surface after rinsing. In any event the change is small compared to change due to weathering alone.

TABLE 4.

EFFECT OF SALT SPRAY ON CROSS HATCH ADHESION RATING OF NATURALLY WEATHERED COATINGS

Exposed to 500 Hours of Salt Spray

Spl. Code	Rating			
	500 Hrs Salt Spray		No Salt Spray	
	Exposed	Not Exposed	Exposed	Not Exposed
64210	0B	3B	2B	5B
64337	1B	1B	1B	1B
64357	2B	2B	4B	3B
64325	0B	0B	1B	1B
64202	2B	1B	2B	1B
64212	0B	3B	0B	5B
64272	0B	3B	0B	5B
64359	2B	2B	4B	2B
64205	2B	1B	4B	1B
64214	0B	3B	0B	5B
64361	2B	2B	3B	3B
65108A	1B	5B	1B	4B
65168C	2B	5B	0B	5B
65228E	2B	2B	4B	3B
65297G	1B	2B	3B	2B
65327H	2B	3B	2B	3B
65141B	0B	*	0B	3B
65201D	1B	4B	0B	4B
65261F	2B	2B	2B	3B
65291G	2B	2B	2B	2B

TABLE 5.

EFFECT OF SALT SPRAY ON CROSS HATCH ADHESION PERCENT REMAINING

Spl. Code	Percent Remaining			
	500 Hrs Salt Spray		No Salt Spray	
	Exposed	Not Exposed	Exposed	Not Exposed
64210	7	92	72	100
64337	53	35	49	39
64357	78	69	96	85
64325	5	4	35	49
64202	80	37	69	44
64212	27	92	0	100
64272	16	92	0	100
64359	67	69	97	85
64205	71	37	97	44
64214	0	92	0	100
64361	64	69	86	85
65108A	48	100	63	99
65168C	77	100	31	100
65228E	69	83	96	93
65297G	57	73	93	79
65327H	79	92	83	88
65141B	0	48	0	95
65201D	36	100	12	97
65261F	67	80	77	89
65291G	73	73	80	79

TABLE 6.

EFFECT OF SALT SPRAY ON CONTACT ANGLE OF WATER NATURALLY WEATHERED COATINGS

Spl. Code	Contact Angle of Water			
	500 Hrs Salt Spray		No Salt Spray	
	Exposed	Not Exposed	Exposed	Not Exposed
64210	34	60	37	74
64337	37	52	50	71
64357	37	61	50	75
64325	38	56	43	67
64202	40	59	46	74
64212	40	61	40	74
64272	34	61	41	74
64359	31	61	47	75
64205	32	59	52	74
64214	36	61	52	74
64361	34	61	37	75
65108A	46	57	36	67
65168C	48	62	43	68
65228E	44	56	38	72
65297G	38	61	55	72
65327H	37	62	52	69
65141B	48	63	40	66
65201D	34	62	34	63
65261F	37	49	43	69
65291G	42	61	44	72

TABLE 7.

EFFECT OF SALT SPRAY ON PENDULUM HARDNESS OF NATURALLY EXPOSED COATINGS

Spl. Code	Pendulum Hardness			
	500 Hrs Salt Spray		No Salt Spray	
	Exposed	Not Exposed	Exposed	Not Exposed
64201	127	121	129	60
64205	128	121	124	60
64208	129	121	91	60
64214	138	134	151	90
64265	124	121	125	60
64268	129	121	96	60
64341	127	119	121	60
64345	122	119	87	60
64365	82	69	75	75
64459	86	76	95	90
64464	85	76	91	90
65111A	135	128	129	135
65117A	136	128	133	135
65171C	137	119	112	121
65138B	138	131	139	118
65318H	108	87	97	67
65231E	117	79	101	90
65258F	106	89	97	76

Physical Property Measurements

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis deals with the ability of materials to store and dissipate mechanical energy on deformation. The natural resonance frequency and the energy dissipation are the two properties of interest. This resonance frequency is related to the modulus or stiffness by sample geometry. The energy dissipation relates to properties such as impact resistance and brittleness.

When a viscoelastic material is deformed and then released, a portion of the stored deformation energy will be released at a rate which is a fundamental property of the material. This causes the sample to go into damped oscillation at its resonance frequency. A portion of the energy is dissipated through other routes; the more dissipation, the faster the oscillations decrease.

For this work the DuPont Instrument Co. Model 982 Dynamic Mechanical Analyzer was used. In this instrument the sample of known dimensions is clamped between two arms, one forming the compliant axis and the other counterweighted arm is the axis of physical support. During a measurement the sample is deformed to a known amplitude and constant oscillatory amplitude is maintained by an electro-mechanical transducer. The power added to maintain the constant amplitude is measured and is a direct measure of the damping caused by the sample. The various moduli and other properties are calculated from this measurement [11,12], and the accompanying time based differential scans.

The damping is the measure the energy dissipated in the material as heat.

The storage modulus, E' is a measure of the elastic properties defined as the ratio of the stress in phase with the strain to the magnitude of the strain. The loss modulus, E'', is a measure of the energy dissipation properties, defined as the ratio of the stress 90 deg. out of phase with the strain to the magnitude of the strain.

Tan delta is the ratio of the loss modulus to storage modulus. The complex modulus, E*, is the ratio of the maximum linear stress to the maximum linear strain.

Dynamic mechanical thermal analysis (DMA) measurements were made of both clear and pigmented coatings which had been exposed in the QUV weatherometer for up to 6000 hours. The data obtained are given in Table 8. Figure 3 shows plots of the glass transition temperature versus time in the weatherometer for both the clear and pigmented coatings. The least squares regression line is indicated in both cases. For the clear coating the glass transition temperature increases with increasing time. The regression equation for the clear coatings has an intercept of 79°C, and slope of 0.008 degrees/hour. The T-ratios are 50 and 16 respectively and the adjusted R-squared is 95%. These data and the other statistical diagnostics such as randomness of residuals and the analysis of variance indicate that the fit of the linear relationship is good for this set of data.

The DMA response curves for the pigmented coatings is rather broader than the response curves for the clear coatings. Because of this the calculation of glass transition temperature is somewhat ambiguous in several cases. The two lines given in Figure 3 represent the two extremes of glass transition temperature for these coatings. The main point here is that the slope of the regression line in either case is not significantly different from zero at the 5% level. Thus, in the first analysis the glass transition temperature of the pigmented coatings does not seem to have predictive value.

Figure 4 shows the same plots for storage modulus as those described above for glass transition and similar conclusions hold. The DMA thermograms for the clear coatings are shown in Appendix D.

DMA measurements were also made on the naturally weathered coatings from the Florida exposure station. These data are given in Table 11. Very little change occurs in the data obtained from DMA over 24 months of Florida exposure.

The DMA is a measure of a bulk property, as is e.g. the pendulum hardness discussed above. The interpretation is that degradation does not affect the bulk properties of the materials until very late or until failure is imminent. This is another indication that surface characterization is a more fruitful investigation.

TABLE 8.

DYNAMIC MECHANICAL ANALYSIS OF QUV EXPOSED COATINGS

Sample	QUV Hrs.	Glass Transition		Damping Peak		Tan Delta
		Temp.	Stor.Modulus	Width	Height	
Clear	0	73	515	85	5.3	0.005
	200	84	50	80	4.5	0.005
	480	83	24	82	4.5	0.004
	600	82	22	58	2.9	0.005
	1000	89	26	75	3.5	0.006
	1500	86	20	63	3.3	0.004
	2000	97	32	80	4.7	0.007
	2500	98	41	76	4.0	0.006
	3000	101	55	87	2.9	0.003
	3500	112	67	55	2.4	0.006
	4000	110	91	59	3.2	0.005
	4500	116	95	60	2.7	0.006
	5000	118	129	68	3.5	0.004
	5500	124	129	68	3.6	0.005
	6000	119	525	82	3.6	0.008
Grey	0	65	22	68	2.8	0.002
	200	71	20	73	3.6	0.003
	1000	81	24	62	2.2	0.028
	1500	79	18	54	4.6	0.000
	2000	84	21	80	4.5	0.004
	2500	82	17	70	2.8	0.001
	3000	78	21	88	2.9	0.001
	3500	70	21	76	2.2	0.003
	4000	75	20	82	4.5	0.002
	4500	70	20	85	5.1	0.004
	5000	78	21	87	3.8	0.003
	5500	76	18	85	3.3	0.000
	6000	73	24	70	2.5	0.008

Temp. is in °C.
Stor. Modulus is in GPa.
Damping Peak Width is in °C.
Damping Peak Height is in mV.

TABLE 9.

DYNAMIC MECHANICAL ANALYSIS OF NATURALLY EXPOSED COATINGS

Sample Code	Months Exp.	T_g	Peak Width (cm)
D Grey/EPA Primer			
64201	6	82	3.0
64202	12	--	--
64205	18	87	3.8
64206	24	87	3.9
64208	6(2nd)	82	3.7
D Clear/EPA Primer			
64210	6	88	3.0
64212	12	--	--
64214	18	81	3.0
64216	24	87	3.0
64218	2(2nd)	82	3.3
D Grey/PS Primer			
64317	6	77	4.4
64319	12	--	---
64321	18	75	3.5
64323	24	80	3.6
64325	6	72	3.4
D Grey/WR Primer			
64337	6	85	3.7
64339	12	--	---
64341	24	79	4.0
64343	24	81	4.3
64345	6	80	2.1
D Grey/EPA Primer Black Box			
64260	6	86	4.9
64262	12	--	--
64265	18	85	4.4
64266	24	88	4.1
64268	6	78	4.0
D Clear/EPA Primer Black Box			
64270	6	100	5.2
64272	12	---	---
64275	18	113	5.8
64276	24	117	3.4
64278	6	81	3.9

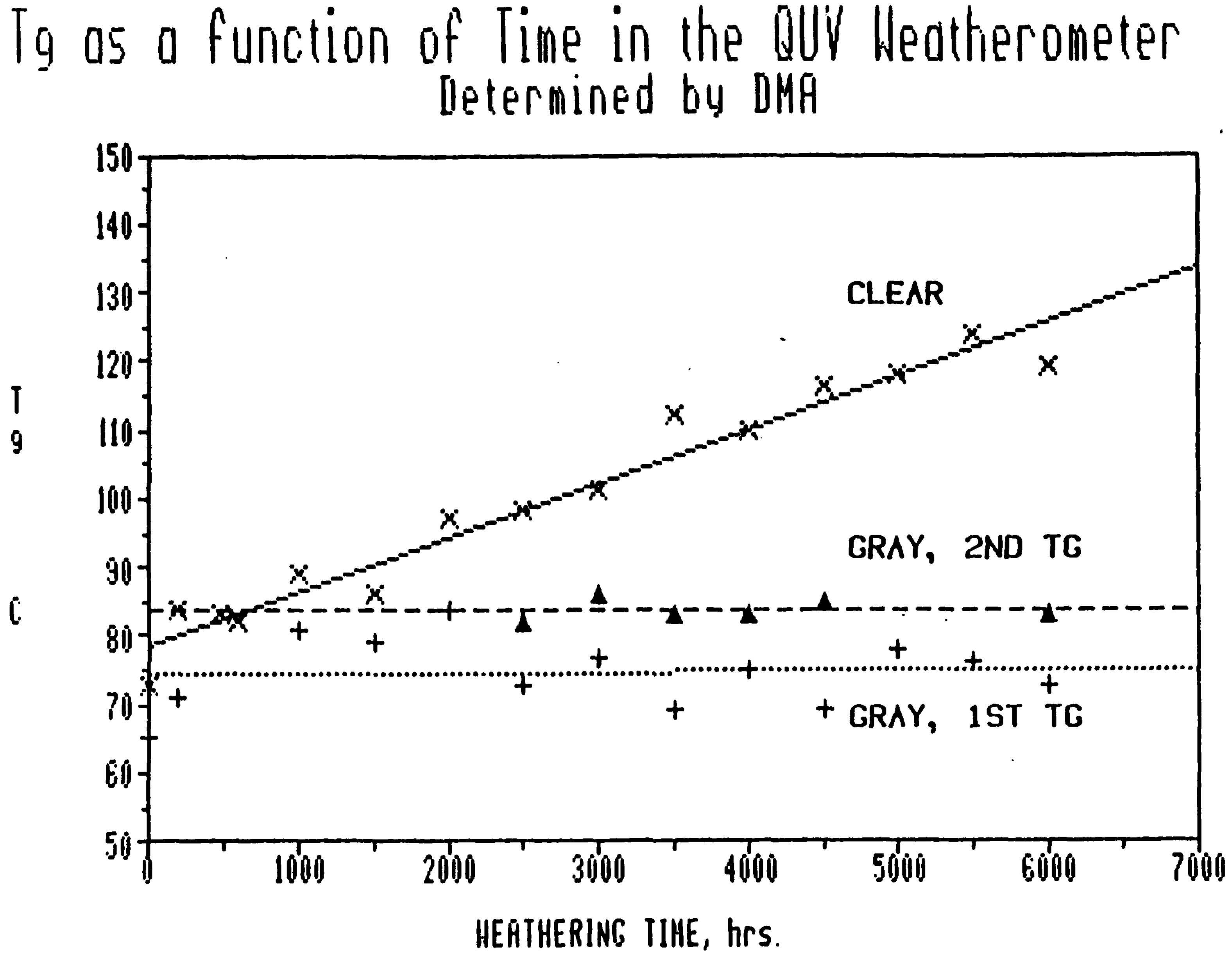


Figure 3. Tg as a Function of Time in tne QUV Weatherometer

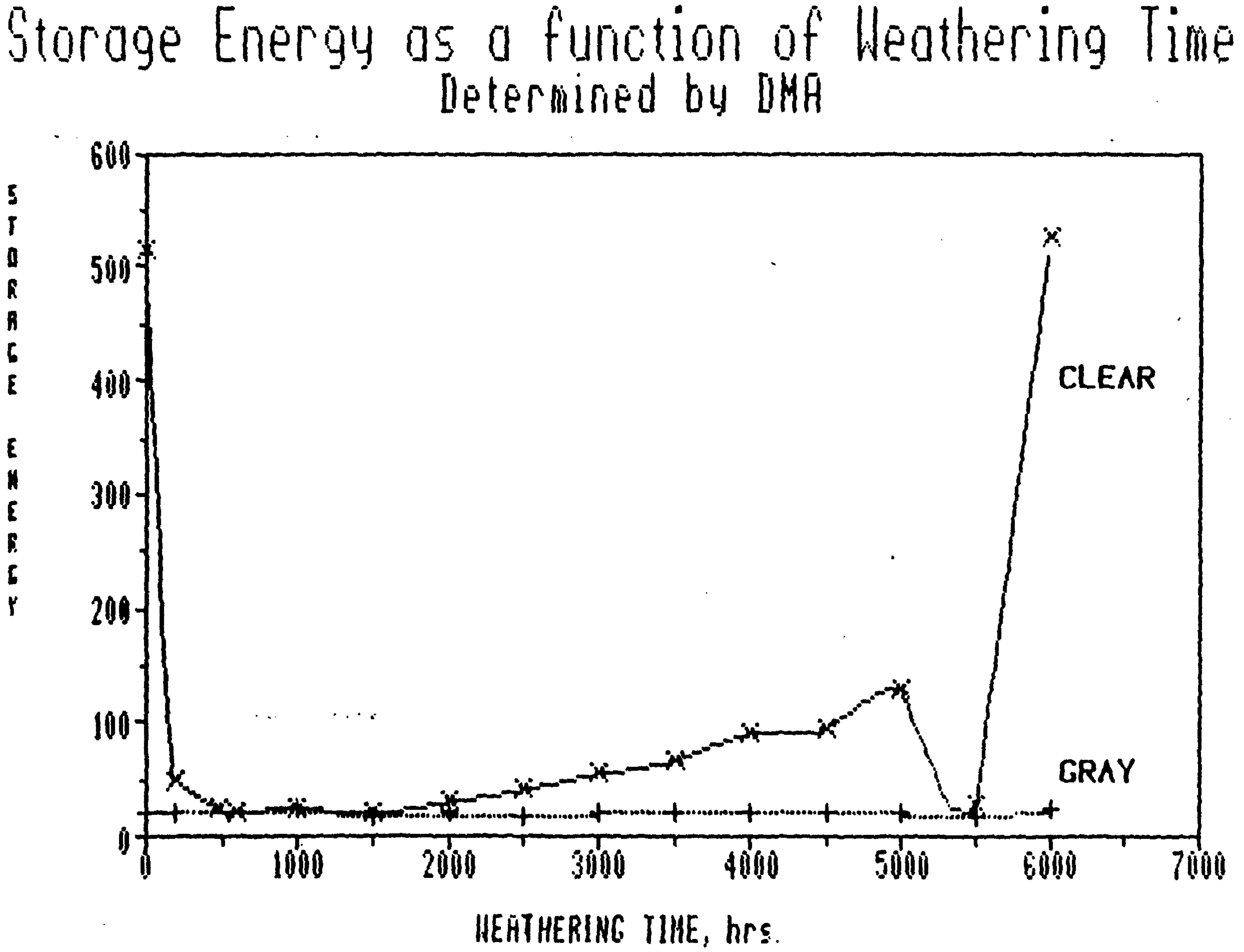


Figure 4. Storage Energy as a Function of Weatnering Time

Scanning Laser Acoustic Microscopy (SLAM)

An acoustic microscope imaging system applies ultrasonic energy to an object. The waves scattered by and through the object fall upon a detector plane where the sonic energy is measured and converted to a visual display. The dried latex films were examined by the SONOMICROSCOPE 100 [13] operated at a frequency of 100 MHz. The SLAM instrument consists of a laser system which can scan in two dimensions and which is synchronous with television monitors. The sample is placed on a stage where it is insonified with plane acoustic waves and illuminated with laser light.

There are three operating modes of SLAM which were all investigated for this work.

Normal Amplitude Mode

In this mode the acoustic transmission microscope operates at a single acoustic frequency. Variations in the acoustic transmission cause variations in the micrographs; bright regions correspond to good acoustic transmission and dark regions correspond to poor acoustic transmission.

Interferometric mode

In this mode the acoustic phase is measured on the screen as the wave is propagated through various structures within the field of view. Localized variations in the velocity of sound can be measured. The technique is more sensitive to density and elasticity than the other modes.

Optical Mode

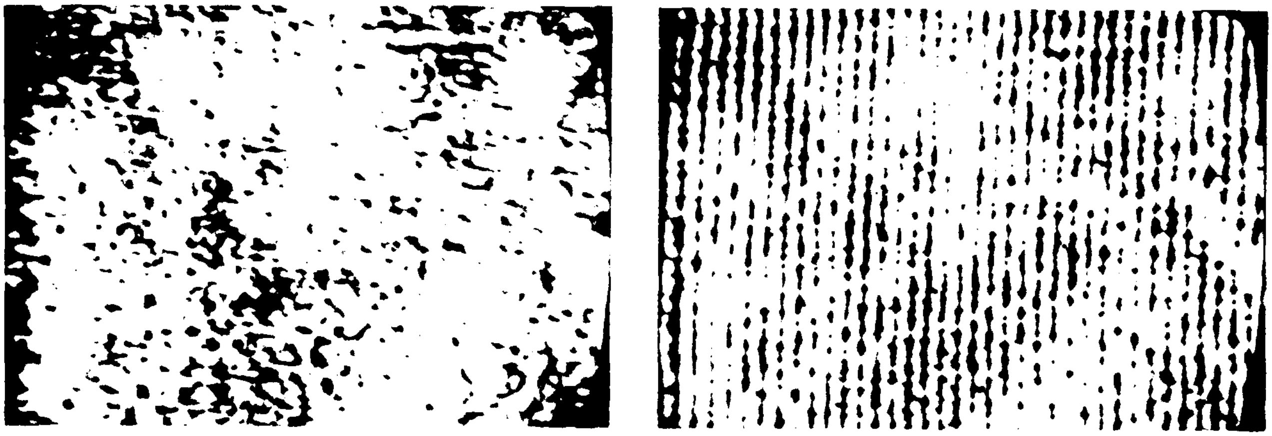
As a by-product of the laser scanning technique, a corresponding optical image of the sample is obtained. The optical image clearly shows the region over which the acoustic image is made.

SLAM micrographs in both the normal amplitude and interferometric modes for unexposed coatings are shown in Figure 5. Micrographs of coatings exposed in the QUV weatherometer are shown in Figure 6. Light areas indicate high acoustic transmission and dark areas indicate areas of low transmission such as voids or cracks.

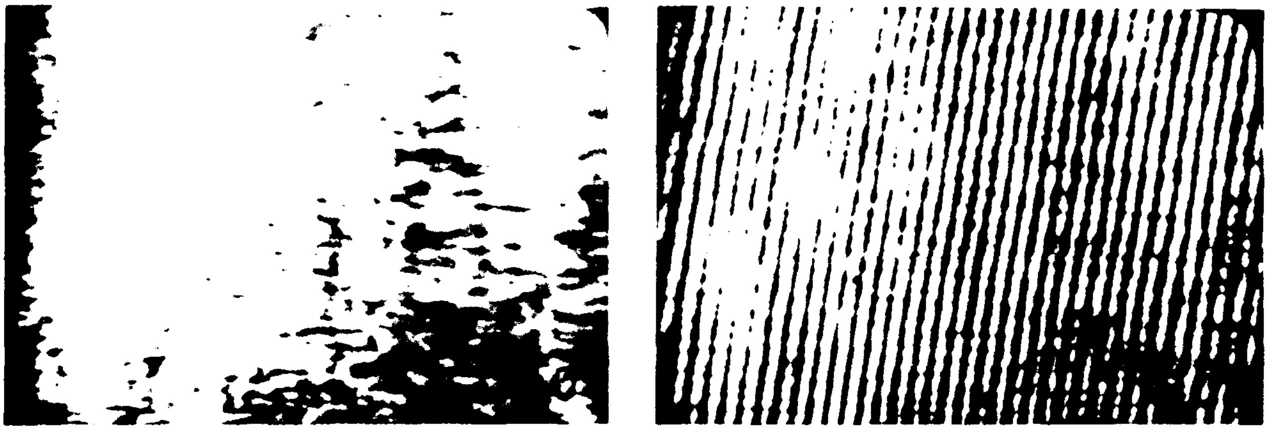
The application of this technique coatings is limited by the thickness of the coatings which is near the limit of resolution of the instrument used for this test. Some defects were detected but these were gross and would have been indicative of imminent failure. The technique would be extremely useful for thicker materials [14]. Newer instruments have higher resolution which would be much more effective for coating measurements, however, the problems concerning measurements of bulk properties remain, i.e. by the time defects are found in a bulk property then coating failure is imminent.

Water Vapor Transmission

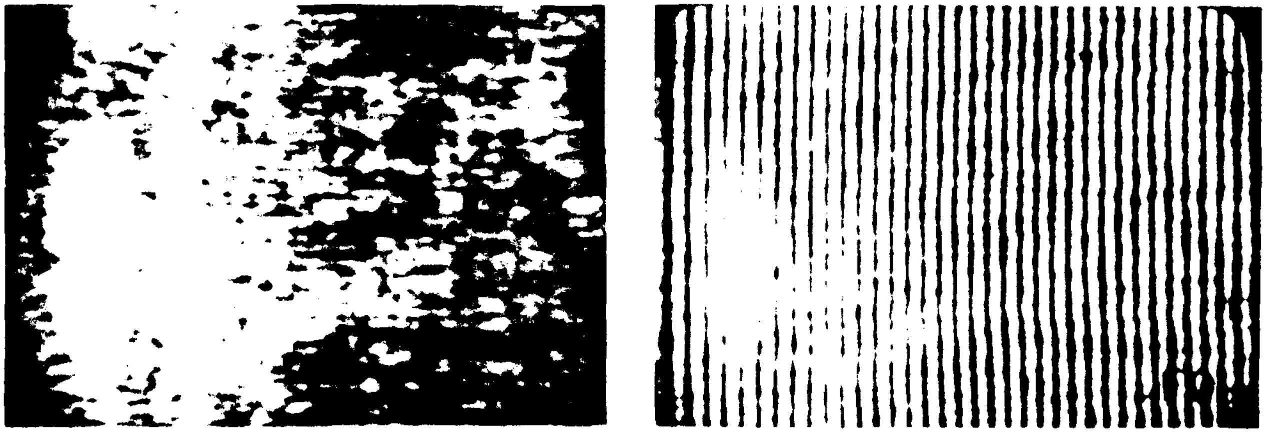
Free coating films were sent to Modern Controls, Inc. for measurement of the water vapor transmission [15]. Measurements of the water vapor tranmission rates were made on a Permatran-W instrument. This instrument employs an infrared sensor to measure the amount of water vapor diffusing through a test film. The sensor measures radiation at a wavelength absorbed by water vapor. The sample is never exposed to an unnatural pressure conditon. All testing and conditioning is performed at atmospheric pressure, and is much faster than traditional weight-gain techniques. A built-in desiccant system dries the air stream to a very low vapor density. This dry air stream enters the test chamber cavity at a constant rate and picks up water vapor permeating through the sample



DO, Primer on treated panel.

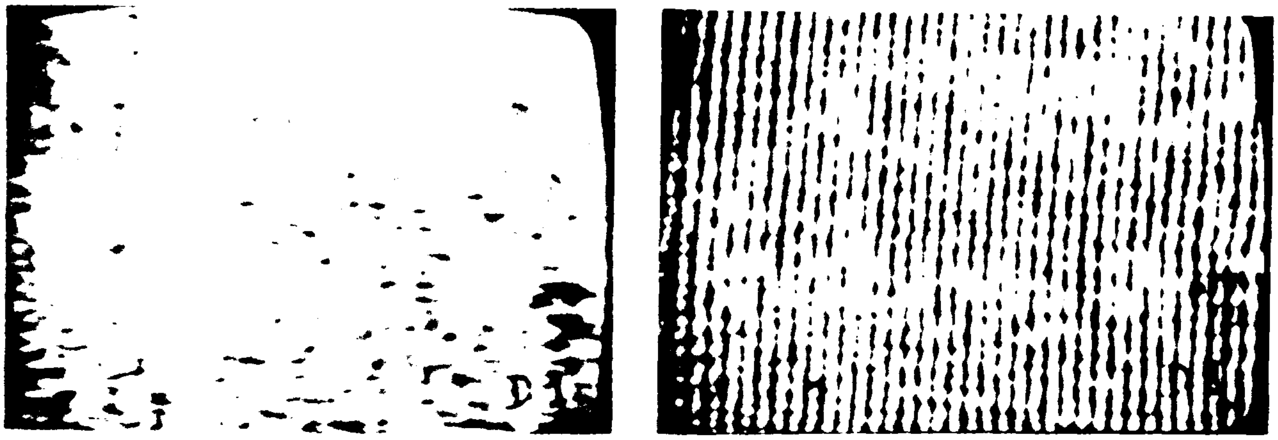


EO, Topcoat on treated panel.

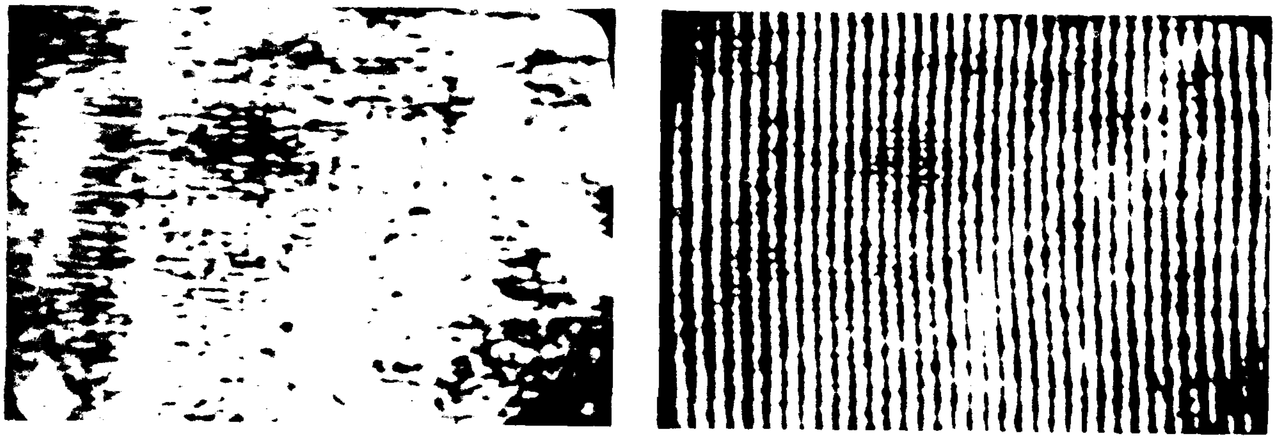


EO, Topcoat and primer on treated panel.

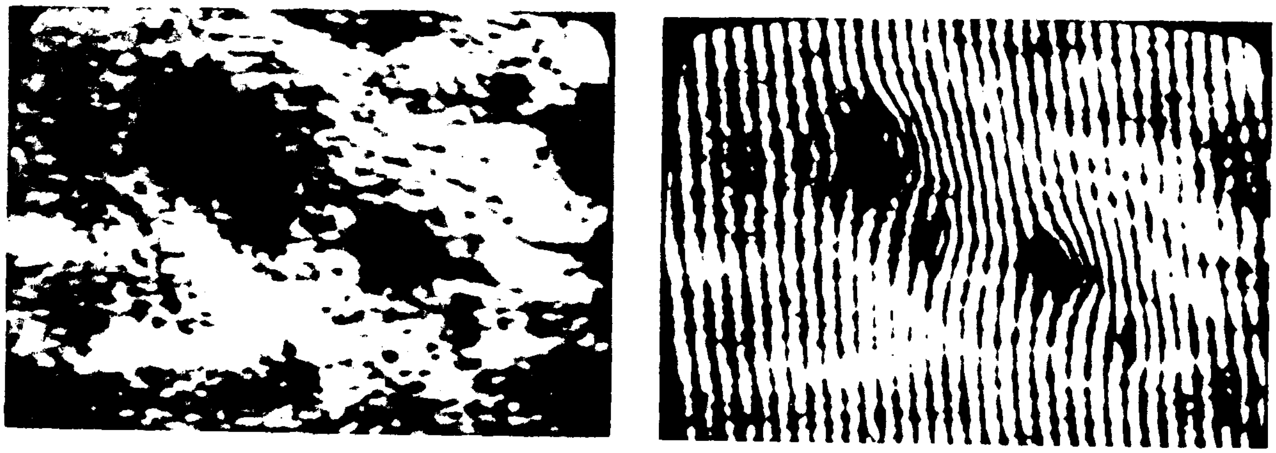
Figure 5: Normal (left) and Interferogram (right) micrographs of the Scanning Laser Acoustic Microscope of unexposed samples on treated aluminum.



D1, 139 hours exposure.



E1, 139 hours exposure.



F1, 139 hours exposure.

Figure 6 : Normal (left) and Interferogram (right) micrographs of the Scanning Laser Acoustic Microscope of coatings after 139 hours Weather-Ometer exposure.

The gas leaving the cavity consists of a mixture of air and water vapor in a ratio determined by the dry air purge rate, and the rate of water vapor transmission through the film. The water vapor density measured by the sensor is then proportional to the water vapor transmission rate of the test sample if the dry air flow rate is maintained at a constant value.

The water vapor transmission rates of coatings artificially exposed in the QUV weatherometer are given in Table 10. Water vapor transmission rates for coatings containg U. V. stabilizers is given in Table 11. Results for naturally exposed coatings is given in Table 12.

TABLE 10.

WATER VAPOR TRANSMISSION RATES OF QUV EXPOSED COATINGS

Coating	QUV Exposure (Hours)	Water Vapor Transmission Rates	
		(g/M^2 2* /day)	Metric Perms
System D Gray	0	15	0.86
System D Gray	800	16	0.90
System D Gray	1500	15	0.90
System D Clear	0	12	0.69
System D Clear	800	13	0.76
System D Clear	850	15	0.85
System D Clear	900	57	3.2
System D Clear	950	92	5.0
System D Clear	1000	650	57.0

Test Conditions: Area = 5 cm^2

Temp = 70°F

Gradient Established by 90% Relative Humidity

TABLE 11.

WATER VAPOR TRANSMISSION RATES (1000 HRS. QUV) COATINGS WITH U. V. STABILIZERS

Coatings	Stabilizer	Water Vapor Transmission Rates (g/sq.m/day) No Exposure	 1000 hrs. QUV
Clear	1% T-328	11	---
Clear	1% T-770	11	---
Clear	1% UV-24	11	14
Clear	T-328/T-770	12	12
Grey	1% T-328	16	17
Grey	1% T-770	17	20
Grey	1% UV-24	14	15
Grey	T-328/T-770	14	14

TABLE 12.

WATER VAPOR TRANSMISSION RATE 12 MONTH FLORIDA EXPOSED COATINGS

Coating/Stabilizer	Water Vapor Transmission Rate (Grams/Sq. Meter/Day	
	Test Coating	Control Coating
Clear/Tinuvin 328	11	11
Clear/Tinuvin 770	9	11
Clear/UV-24	10	11
Clear/Tin 328+Tin 770	11	12
Grey/Tinuvin 328	17	15
Grey/Tinuvin 770	17	17
Grey/UV-24	13	14
Grey/Tin 328+Tin 770	12	14
Clear/None	10	12
Grey/None	13	14

The coatings were prepared on tin foil and the free films were obtained by amalgamation of the tin.

The water vapor transmission of the pigmented films show no significant change after 1500 hrs in the QUV weatherometer under the standard cycle. The clear films showed a dramatic increase in water vapor transmission between 800 and 1000 hours. The increase may simply be due to development of tiny holes in the film and not to an increase in the transmission rate of the bulk material. However this would be indicative of coating failure. Further, the pigmented film did not show the dramatic increase in permeation up to 1500 hours. Thus, the pigment may play a large role in stabilizing the polymer towards ultra-violet radiation induced degradation [16].

For naturally weathered samples, there is essentially no difference in water vapor transmission, after twelve months exposures, between controls and exposed coatings. Nor is there any apparent variation between the pigmented and clear coatings nor the various stabilizers.

The data in Table 11 was obtained in order to gain some information on the relative value of various U.V. stabilizers. Very little variation was observed. There has been essentially no change in the water vapor transmission rates at 1000 hrs. and therefore no conclusions about the effectiveness of the various stabilizers can be made.

Scanning Electron Microscopy (SEM)

Scanning electron microscopic examination was used to examine the surface morphology of coating surfaces as a means to detect small defects in the coatings. Both artificially and naturally weathered coatings were examined.

Appendix A, pages A1-A7, show electron photomicrographs of clear and grey coatings artificially weathered in the QUV weatherometer up to 5000 hrs. Examination of the photomicrographs of the clear coatings reveal cracks appear after 1000 hrs. These cracks become more numerous and larger with increasing exposure. Examination of the same exposure conditions of pigmented, i.e. grey coatings indicate some surface erosion at 1000 hrs. which continues at increasing exposures. However, the pigment seems to moderate the degradation so that the coatings maintain, to a large extent, the film integrity.

Appendices B and C, pages B1-B9d and pages C1-C5, show electron photomicrographs of naturally weathered coatings. The code numbers on these photomicrographs refer to the test coatings previously described.

Except for the case of the primer only, which is expected to fail rapidly when exposed, there is very little change apparent in the coatings after 18 mos. of south Florida exposure. This is true of 45 degree south and black box exposure. Since very little change is seen for standard coatings it is not surprising that no change was seen in coatings which contain U.V. stabilizers. Exposure for longer than 24 mos. is required to find morphological changes in these coatings.

The SEM may be useful for detecting degradation, however, the degradation visible after 24 months of natural exposure is very slight. It remains to be seen how far in advance of ultimate failure the degradation can be seen by SEM techniques.

Chemical Property Testing

X-Ray Photoelectron Spectroscopy (XPS)

Information obtained from this work points to the need for measurements of changes in the coatings at or near the surface since very little change is seen in any of the bulk property measurements. One measurement designed for surface analysis is X-ray photoelectron spectroscopy (XPS or ESCA). This technique determines elemental concentrations by examination of the X-ray produced by electron bombardment.

Five samples containing naturally and artificially exposed coatings were analyzed with XPS. The instrument used is that at the University of Wisconsin-Milwaukee. It employs a Varian vacuum system and X-ray source with a Physical Electronics cylindrical mirror analyzer (CMA). Both overall spectra as well as high resolution scans in the region of the carbon peak were obtained. Overall spectra scans are shown in Figures 7 and 8 and a high resolution scan is shown in Figure 9. The results shown in Table 13 are the atomic surface composition determined from peak height data by applying the sensitivity factors of Wagner [17]. A method described by Dilks and Clark [18] has been applied to the high resolution carbon data. Very little difference is seen in the high resolution data problably due to the fact that the reacted species have left the surface through natural erosion processes.

The XPS shows definite promise as a tool to monitor coating degradation. A comprehensive program could be designed to obtain data from naturally and artificially weathered coating surfaces to examine the mechanisms of coating degradation. The data from this work lend credence to the proposed photo-oxidation mechanism discussed earlier in that the increase in oxygen is consistent with the mechanism, which presumes attack by oxygen between the urethane nitrogen and the carbonyl carbon. This would require an increase of oxygen at the surface for further reaction to take place.

TABLE 13.

ELEMENTAL SURFACE COMPOSITION (ATOMIC %)

Coating	Hours of QUV Exposure		Mths. Natural Exp.
Clear	0 Hrs.	3000 Hrs.	18 Months
Element			
C	59	44	
N	7	6	
O	41	57	
Grey			
Element			
C	47	43	39
N	9	3	2
O	45	48	50
Si		6	9

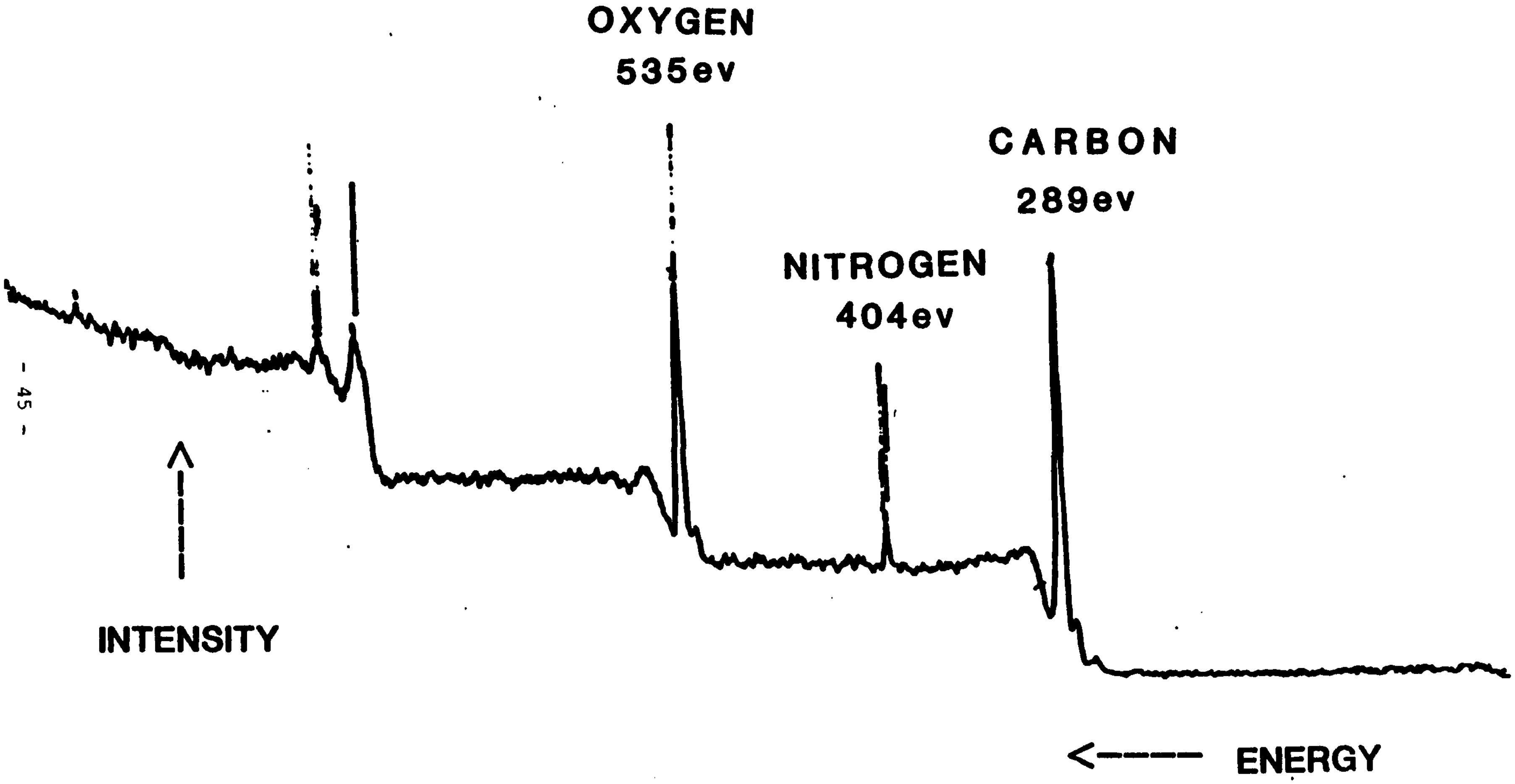


Figure 7 - XPS Spectrum of Clear Coating, 0 Hrs. Exposure

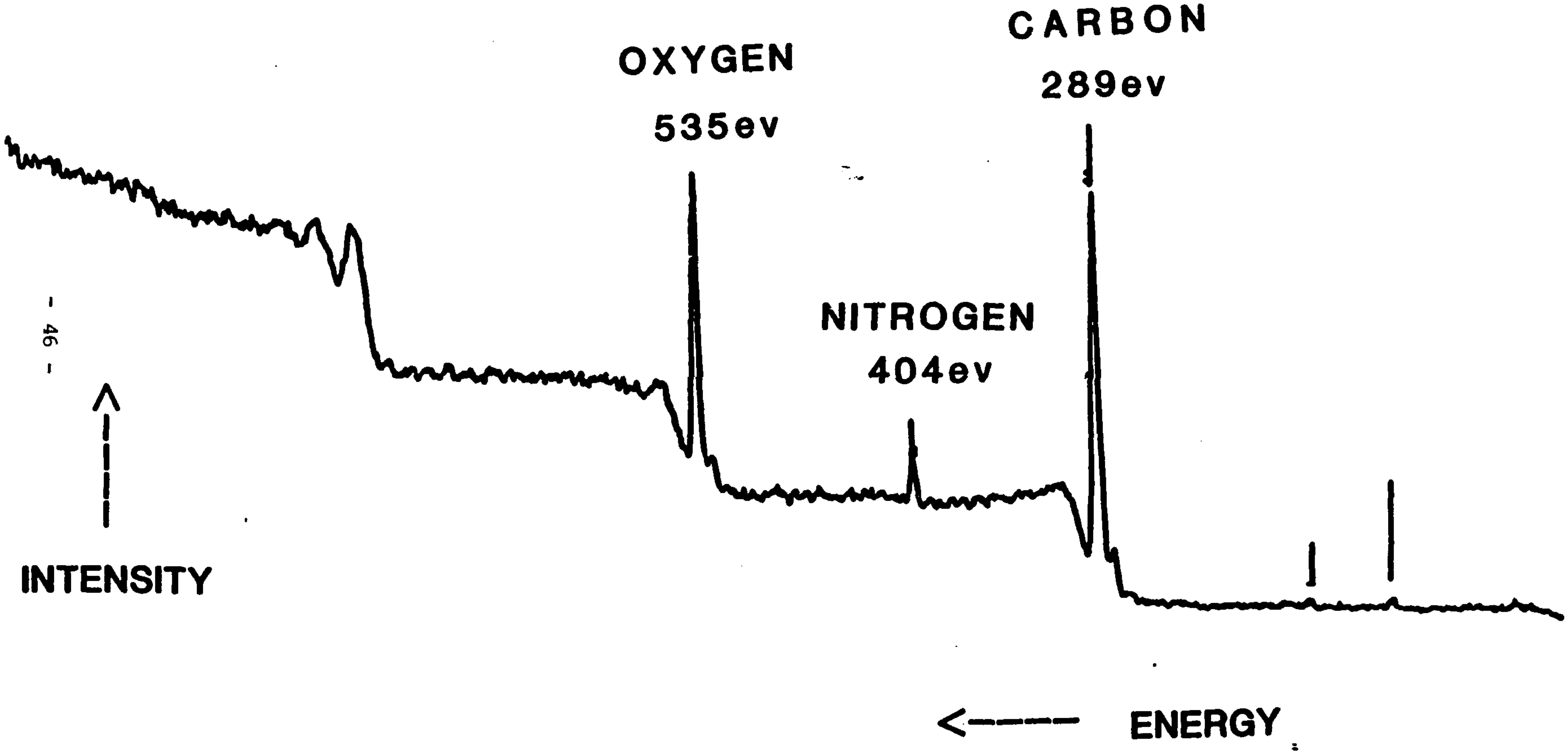


Figure 8 - XPS Spectrum of Clear Coating, 300 Hrs. Exposure

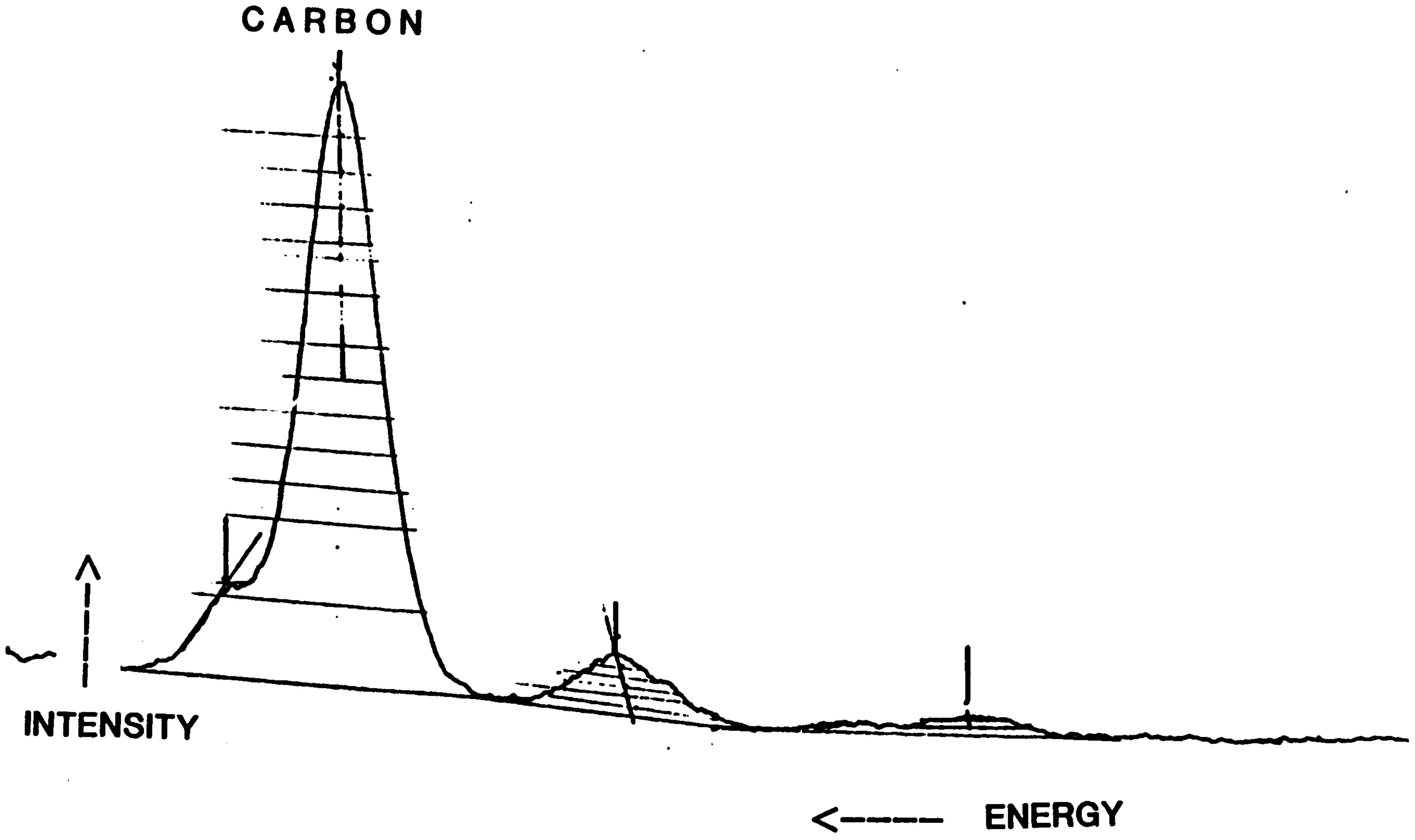


Figure 9 - High Resolution XPS Spectrum of Clear Coating, 0 Hrs. Exposure

Electron Spin Resonance Spectrometry (ESR)

Electron spin resonance has been used for analysis of degradation of polymers [19] but in general the techniques were not quantitative. The electron spin resonance technique developed by J. Gerlock of Ford Motor Co. is quantitative [20,21,22] and is extremely promising for both early determination of the photooxidative stability of coatings and investigation of the mechanism of polymeric degradation. Steps have been taken to expand the technique to other operators and coating systems under the aegis of the Sherwin-Williams Co. for the purposes of this contract and any future work.

The method involves addition of a known amount of a free radical source to the coating in question. The coating is exposed to U. V. light and the ESR measurement is used to determine the amount of free radical source in the coating. This is done several times and the decay of the free radical source is used to calculate the photo-initiation rates within the coating. A low photo-initiation rate is indicative of a stable coating.

This ESR spectroscopic technique was used to measure the photoinitiation rates of a free radical marker in three urethane coatings, designated as System DS, the standard D and a high solids coating, HS76. The photoinitiation rates for these three coatings is listed below:

System DS	1.8×10^{-8} mol/g/min
System D	0.6×10^{-8} mol/g/min
HS76	0.4×10^{-8} mol/g/min

If current suppositions about the ESR data are correct then, system DS should be degraded most rapidly and the HS76 should be degraded least rapidly. Direct comparisons of the three items are not available.

However, based upon physical properties determined before and after twin arc weatherometer exposure for System DS, which was reported in AFWAL-TR-80-4148 Part III, and QUV exposure of the System D would be ranked as more stable than the System DS. No direct exposure data is yet available for HS76 but it is expected that this will be a stable coating based upon formulation parameters.

The measurements were made by Dr. J. Gerlock.

Scanning Auger Microprobe (SAM)

Another technique designed for surface analysis is scanning Auger microprobe (SAM). An electron microscope is used to examine and aim the electron beam and elemental analysis is obtained by examination of secondary emmissions from the surface. This is a complimentary technique to XPS. The measurements reported here were made at Northwestern University.

A series of samples were examined by SAM to verify the conclusions that the oxygen concentration and the nitrogen concentration at the coating surfaces increases upon weathering. The SAM measurements were made on a PHI Model 590A Scanning Auger Microprobe. The area examined in each case was ~0.2 millimeters. The energy beam was at 2000 ev with 6 ev modulation and the beam current was 6 x 10 E^{-8} amp. Normalized intensities were used for all calculations. Peak heights were divided by the normalizing factors and these results were used in subsequent calculations. The carbon response was chosen as the reference peak and the ratios of the normalized intensities for oxygen and nitrogen to that of carbon was used to determine the relative atomic concentrations of oxygen and nitrogen.

The normalized concentrations which were measured are given in Table 14. The data for nitrogen content vs. hours of exposure is shown in Figure 10 and is random i.e., a correlation coefficient not significantly different from zero.

The data for oxygen, while not compelling, does show a trend to higher surface oxygen concentrations at longer exposures. The scatter plot of this data is shown in Figure 11. In this case the correlation coefficient is 0.70 (omission, which is not statistically legitimate, of the point at 1010 hours, would bring the correlation coefficient to 0.98). Thus, considering the times involved the trend seems confirmed and more importantly, the measurement shows enough promise for future investigation.

Fourier Transform Infra Red Spectroscopy (FT-IR)

For initial evaluation and investigation of FT-IR techniques for the measurement of polymeric degradation, photoacoustic (PAS), diffuse reflectance (DR) and attenuated total reflectance (ATR) infrared spectra were obtained of several naturally and artificially weathered coatings. These techniques allow examination of changes in the chemical structure within the first 25-50 μm of the coatings.

TABLE 14.

NORMALIZED ATOMIC SURFACE CONCENTRATIONS RELATIVE TO CARBON MEASURED BY SCANNING AUGER MICROPROBE

Hours	Nitrogen	Oxygen
0	0.03	0.08
0	0.03	0.06
645	0.02	0.09
1010	0.04	0.15
3000	0.04	0.12
6000	0.03	0.18

```
Nitrogen
   .05+
       -
       -
       -        *            *
       -
   .04+
       -
       -
       - 2                                      *
       -
   .03+
       -
       -
       -
       -     *
   .02+
         +---------+---------+---------+---------+---------+Hours
        .00  1500.00   3000.00   4500.00   6000.00   7500.00
```

FIGURE 10. Scatter Plot of Relative Nitrogen Surface Concentration vs Hours QUV

```
   Oxygen
     .20+
        -
        -                                         *
        -
        -
     .15+        *
        -
        -
        -                     *
        -
     .10+
        -     *
        - *
        -
        - *
     .05+
          +---------+---------+---------+---------+---------+Hours
         .00   1500.00   3000.00   4500.00   6000.00   7500.00
```

FIGURE 11. Scatter Plot of Relative Oxygen Surface Concentration vs Hours QUV

Initial Investigations

The PAS spectra of the unexposed clear coating is characteristic of an aliphatic urethane with absorbances due to residual OH (3365 cm^{-1}), ester C=O (triplet with major absorbance at 1736cm^{-1} followed by lesser absorbances at 1690 and 1643 cm^{-1}) and urethane (1530 cm^{-1}).

Comparison of the unexposed coating spectrum to those obtained from 2500, 3000, 3500, 4000 and 5000 hours QUV exposures indicates reduction of the urethane peak at 1530 cm-1*as well as other major changes in the spectrum.

Florida exposure panels were analyzed after 6, 12 and 18 month intervals. Comparison of the series with the QUV exposure series indicates that 5000 hours QUV exposure is nearly equivalent to 18 months Florida exposure.

The diffuse reflectance spectrum of the Clear/Primer control differs from the PAS spectrum in the aliphatic CH region and in the C=O region. Also the urethane absorbance at 1558 cm^{-1} is weaker relative to the single ester C=O at 1748 cm^{-1}. This indicates that the polyester portion of the systems may be more concentrated on the surface of the coating since the depth of penetration by diffuse reflectance is very low.

The QUV exposure series was then analyzed by the diffuse reflectance mode. The first QUV exposure measured was at 2500 hours and this spectrum indicated an almost complete loss of the urethane absorbance at 1559 cm^{-1}. The PAS spectrum of this same specimen indicates some loss of the urethane but not as much as in the DR spectrum. This indicates the loss is most prevalent on the surface of the coating. Analysis of the other sample in this series (3000, 3500, 4000 and 5000 hrs. QUV exposure) showed that the urethane peak at 1559 cm^{-1} did not decrease further. Other changes are also apparent in the QUV exposure. A new OH or NH peak appears at 3500 cm^{-1} and the C=O peak which was a single peak at 1748 cm^{-1} has split into two peaks at 1790 and 1770 cm^{-1}. This change in C=O absorbance was not apparent in the PAS spectra.

The general conclusion here is that QUV exposure causes a drastic change in the surface chemistry of the clear coating as shown by the new OH and C=O absorbances and the loss of methane absorbance.

The DR spectra obtained for 6, 12 and 18 months Florida exposure indicated a moderate decrease in urethane absorbance at 1558 cm^{-1}. However, even after 18 months exposure this absorbance was still easily detectable indicating some degradation but nothing as severe as the 2500 hours QUV exposure produced. There was no detectable change in the ester C=O absorbance for the first twelve months although the absorbance did decrease after 18 months. No additional ester C=O peaks were observed. The OH absorbance found in the QUV exposures also occurs in the Florida exposures but is not nearly as prominent.

The conclusion here is that much less surface degradation takes place in the clear coating during 18 months Florida exposure versus 2500 hrs. QUV exposure. But there is no qualitative difference between this accelerated weathering and the natural weathering.

Photoacoustic Spectroscopy Evaluation (PAS)

Photoacoustic Fourier transform infra red [23] spectra were obtained of the System D grey and System D clear controls, i.e. unexposed. Spectra were also obtained of the same coatings after 4000 hrs. and 5000 hrs. of QUV exposure. For reference a spectrum of the unexposed primer was also obtained. The primer was the standard epoxy poly(amide) in all cases.

The PAS technique can produce good infra red spectra of the all films analyzed. The anticipated depth of penetration into the coating is 20 to 100 micrometers depending upon the composition of the material being analyzed. In the experiments reported here the depth of penetration is ~25 micrometers. Observation on each coating follow.

System D Clear

Figure 12 is the spectrum of the epoxy poly(amide) primer for reference. Some absorbances due to the pigment are present in addition to the basic polymer absobances.

1. The spectrum of the clear, unexposed top coat is shown in Figure 13. There is no evidence of absorbances due to the primer which indicates that the depth of penetration is no greater than the top coat film thickness.
2. The spectrum of the clear coating after 4000 hrs. QUV exposure is shown in Figure 14. Note that the absorbance in the 1600 wavenumber region has decreased and the peaks have broadened indicating a possible change in the chemical composition. There is also some evidence of absorbances due to the primer pigment indicating erosion of the top coat.
3. The spectrum of the clear coating after 5000 hrs. QUV exposure is shown in Figure 15. Further degradation of the urethane absorbance is noted. The difference between 4000 and 5000 hrs. is minor.
4. Figure 16 shows the difference spectrum obtained by subtracting the 5000 hrs. spectrum from the control spectrum. The resultant spectrum indicates that there is no interference from the primer.

System D Grey

1. The spectrum of the grey topcoat over the primer is shown in Figure 17. The spectrum is very similar to that of Fig. 13 although there is evidence of absorbances due to the pigment of the top coat.
2. Figure 18 is the spectrum of the grey coating after 4000 hrs. of QUV exposure. The spectrum is not very different from that of the unexposed grey coating. There is a slight decrease in the urethane absorbance at 1600 wavenumbers.

3. The spectrum of grey coating after 5000 hrs. QUV is shown in Figure 19. The spectrum is very similar to the 4000 hrs. spectrum.

4. Figure 20 shows the difference spectrum of the control, Fig. 17 minus the 5000 hrs exposure spectrum. This spectrum indicates that the unexposed coating has a higher urethane absorbance and hence higher urethane content than the exposed coating. The observed difference is small in this case.

5. A difference spectrum of the 4000 hrs. spectrum minus the 5000 hrs. spectrum, Fig. 18 minus Fig. 19, was also obtained and is shown in Figure 21. This difference spectrum indicates a further slight decrease in the urethane absorbance from 4000 to 5000 hrs. QUV.

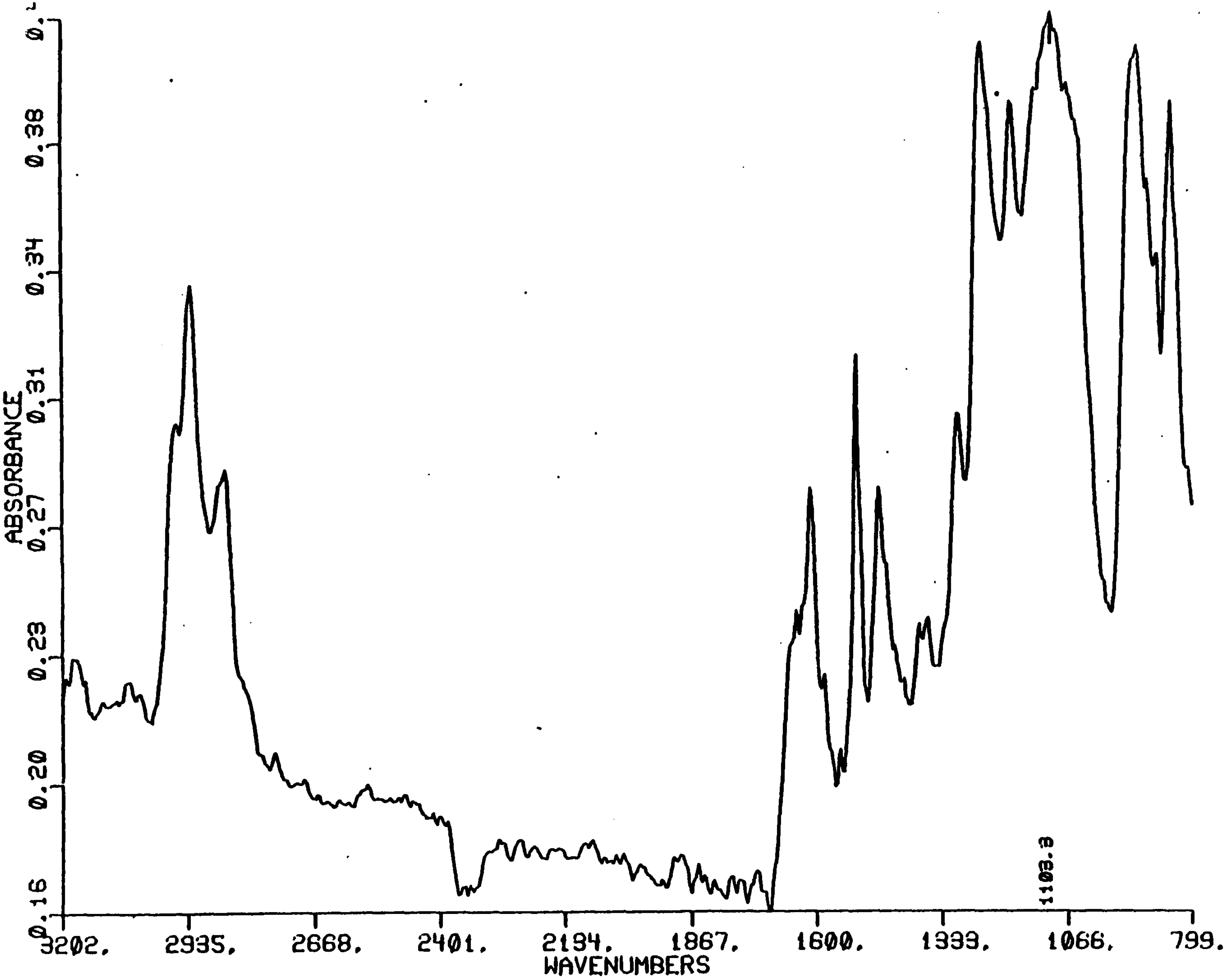


Figure 12 - Photoacoustic Spectra of Unexposed Primer

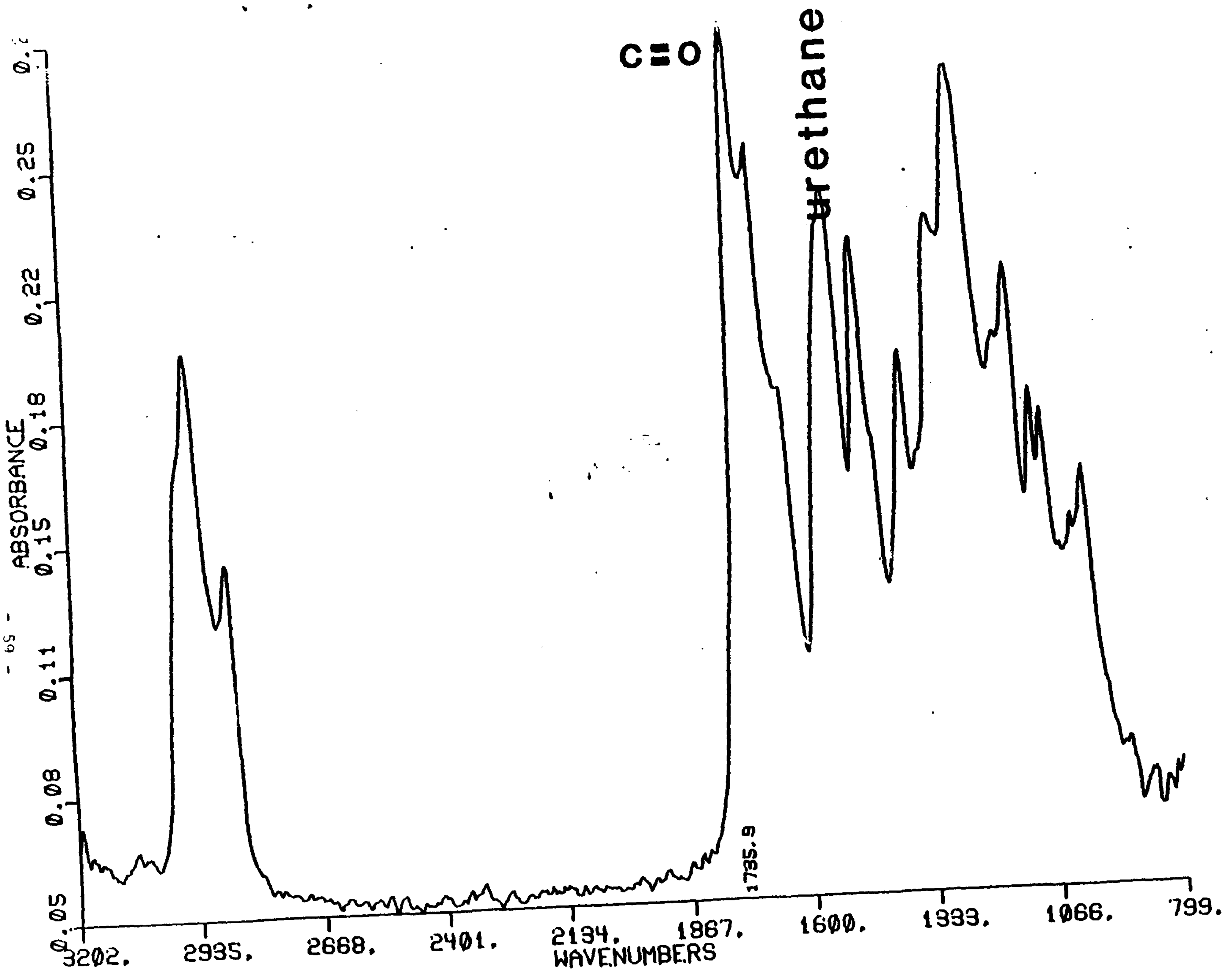


Figure 13 - Photoacoustic Spectra of Clear Coating, 0 Hrs. Exposure

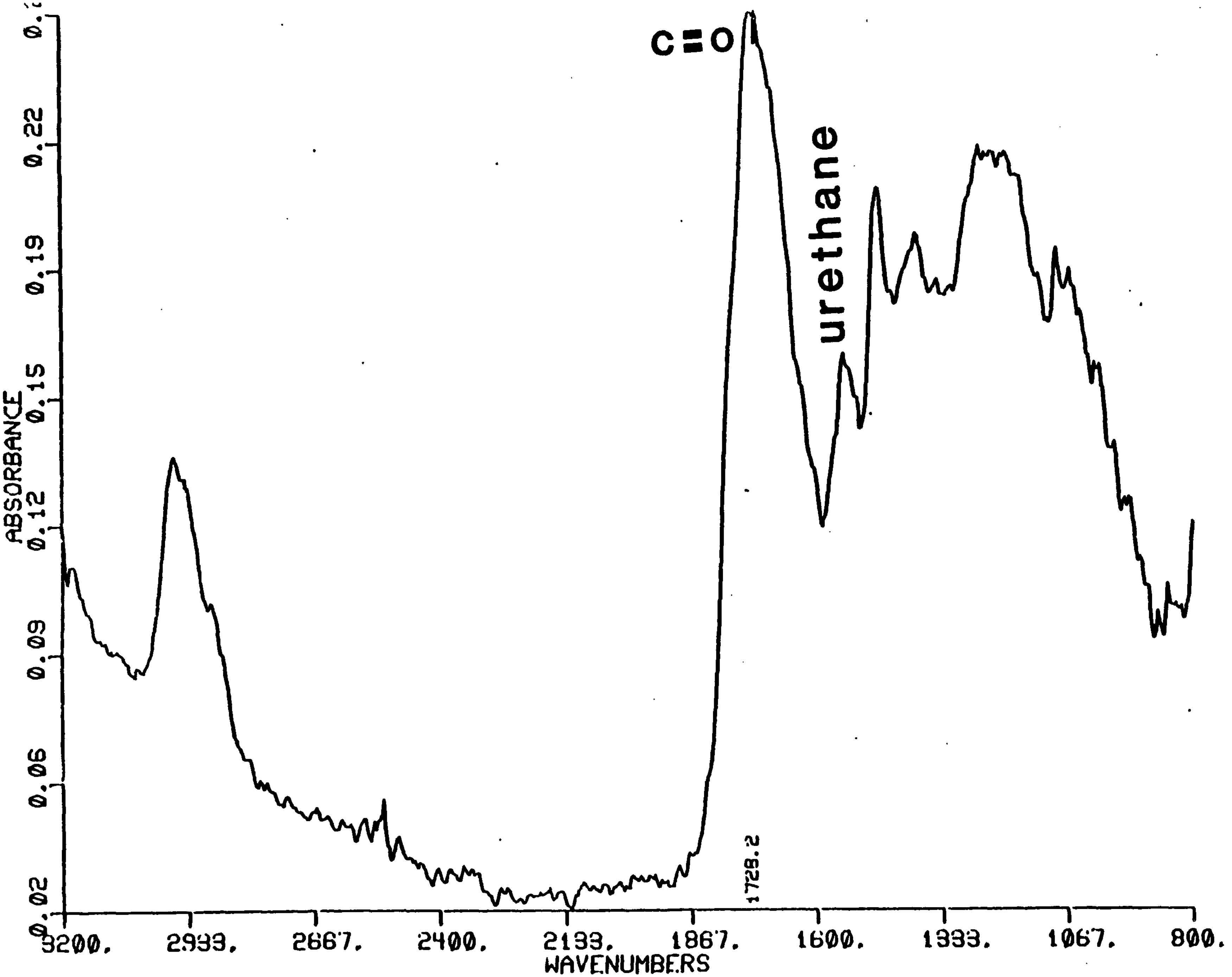


Figure 14 - Photoacoustic Spectra of Clear Coating, 4000 Hrs. QUV

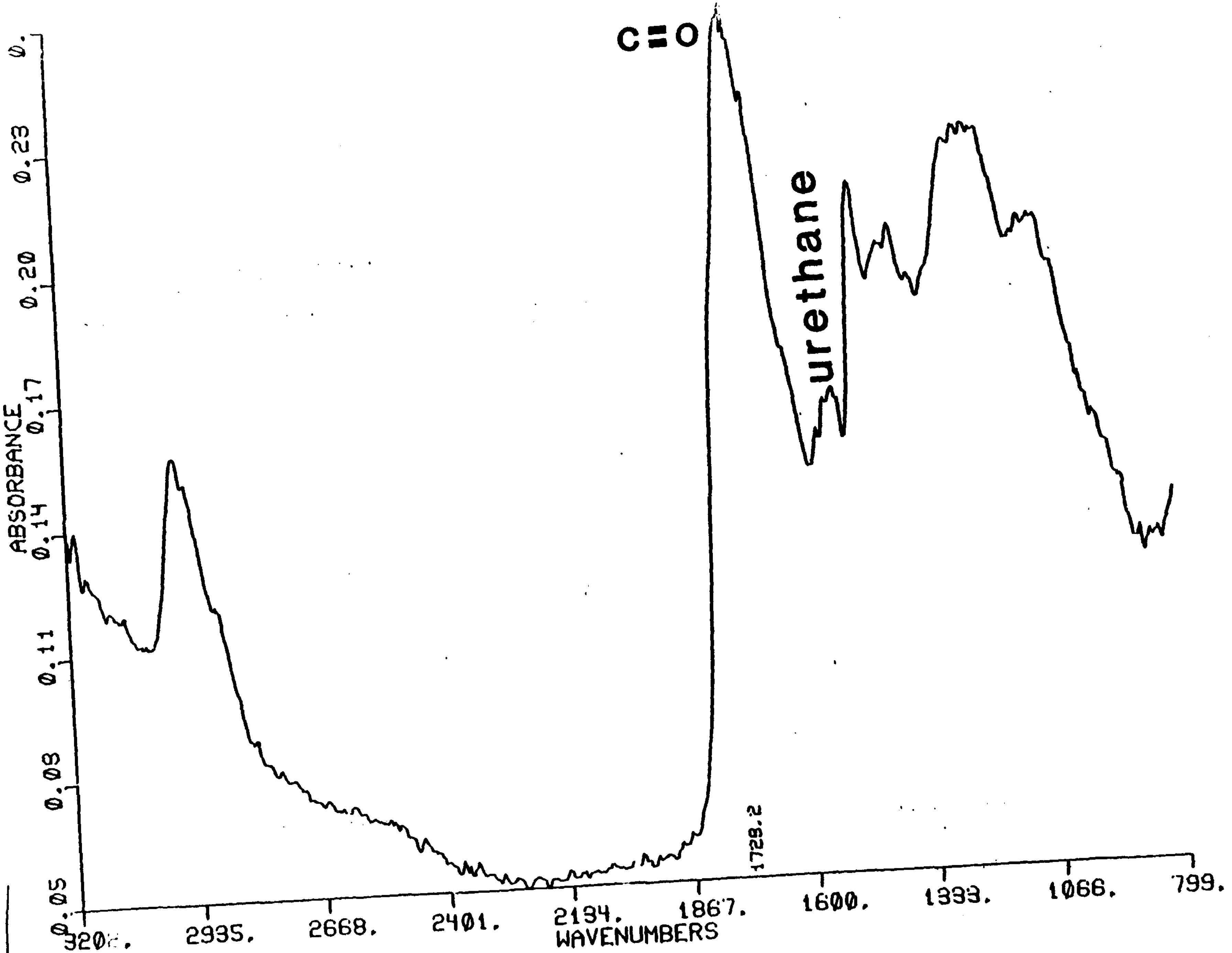


Figure 15 - Photoacoustic Spectra of Clear Coating; 5000 Hrs. QUV

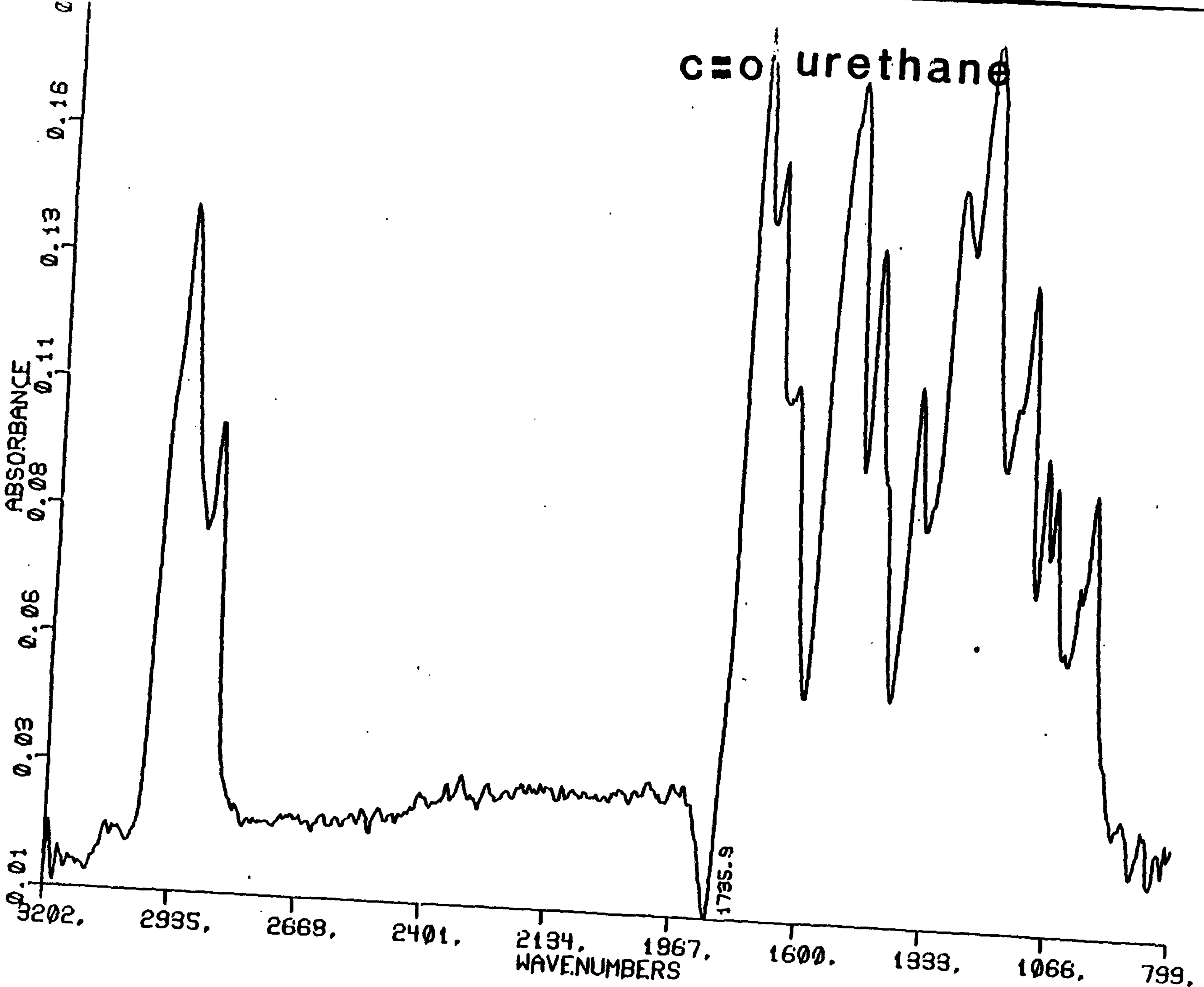


Figure 16 - Photoacoustic Difference Spectra of Clear Coating, 0 Hrs. - 5000 Hrs. QUV

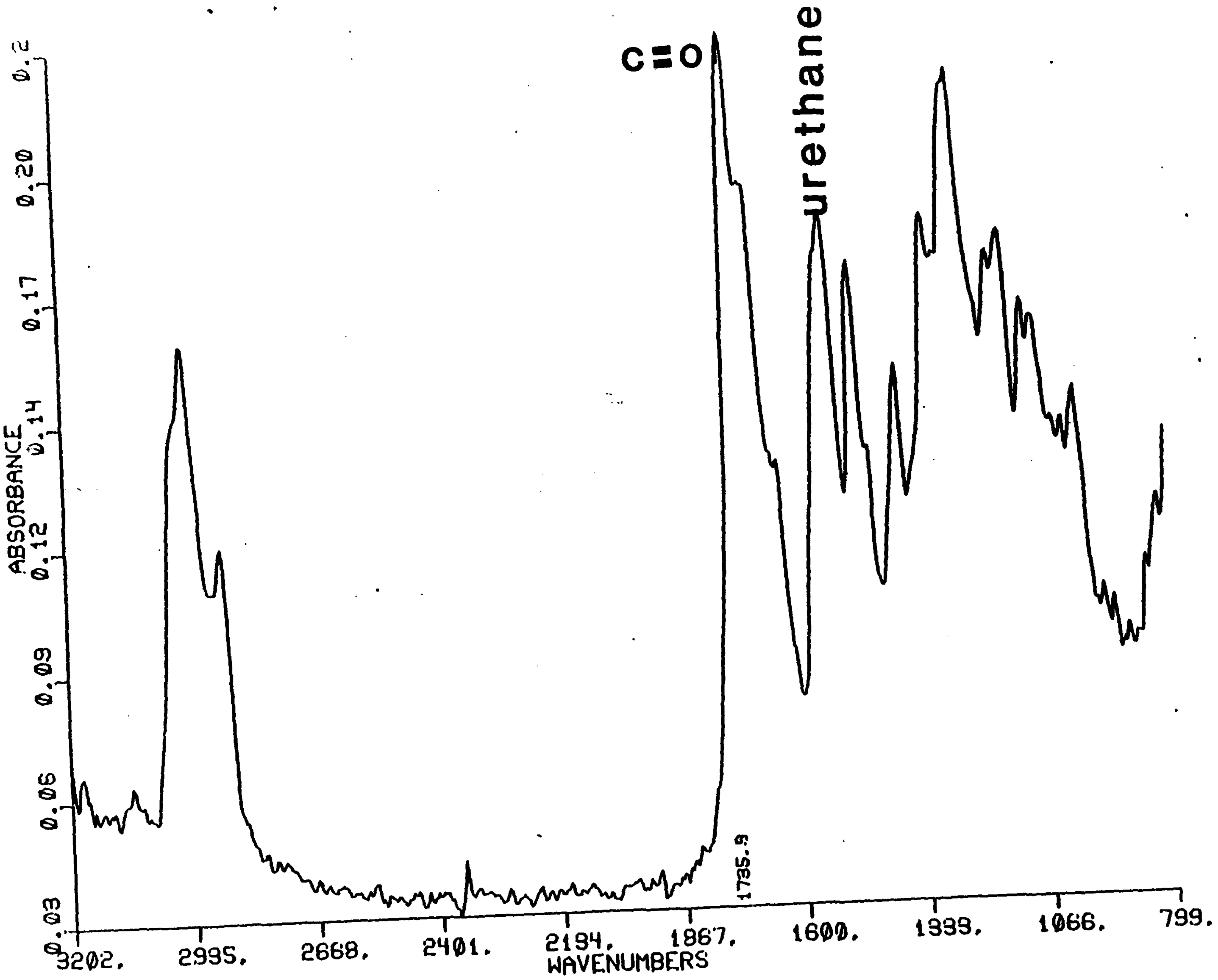


Figure 17 - Photoacoustic Spectra of Grey Coating. 0 Hrs. Exposure

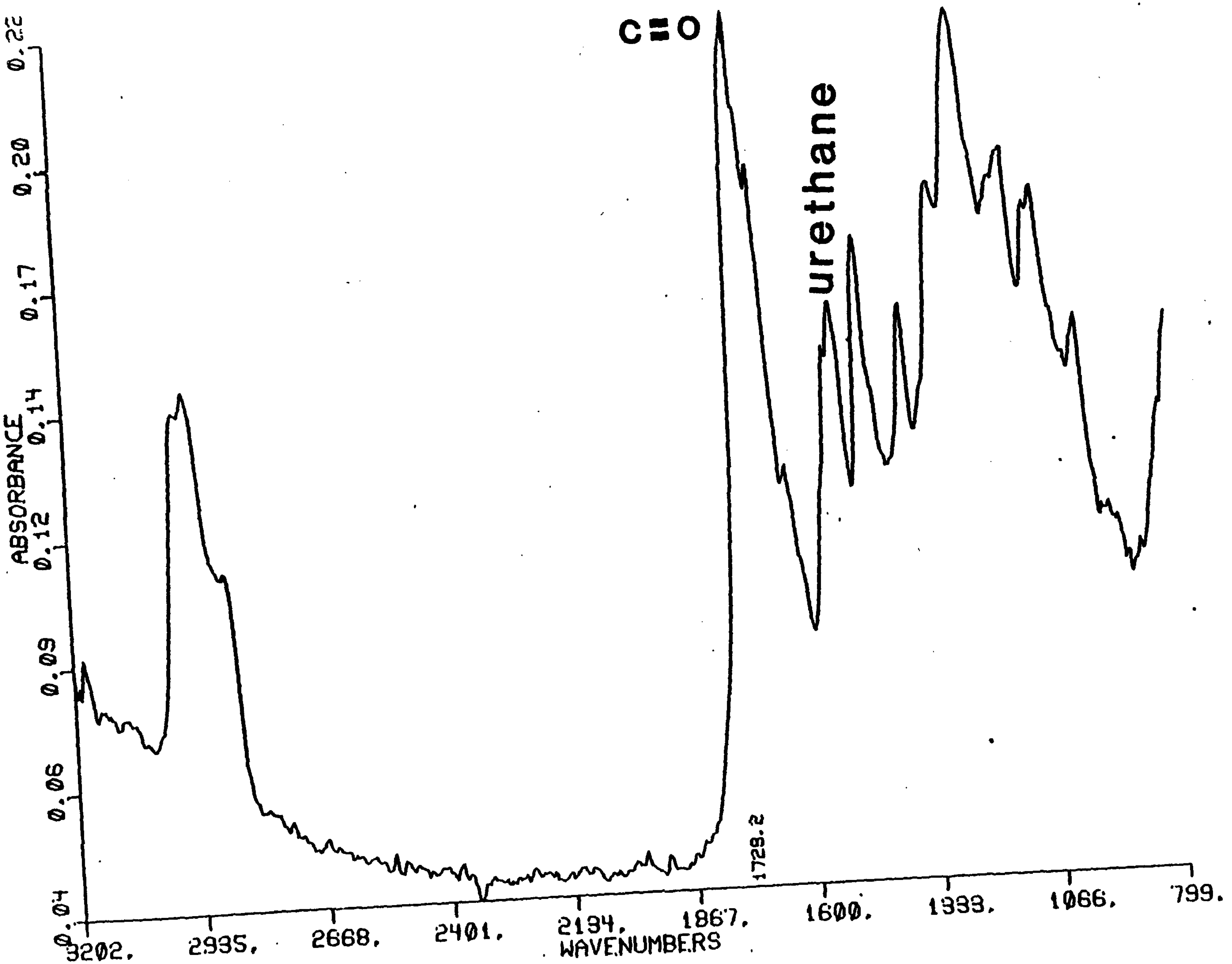


Figure 18 - Photoacoustic Spectra of Grey Coating, 4000 Hrs. QUV

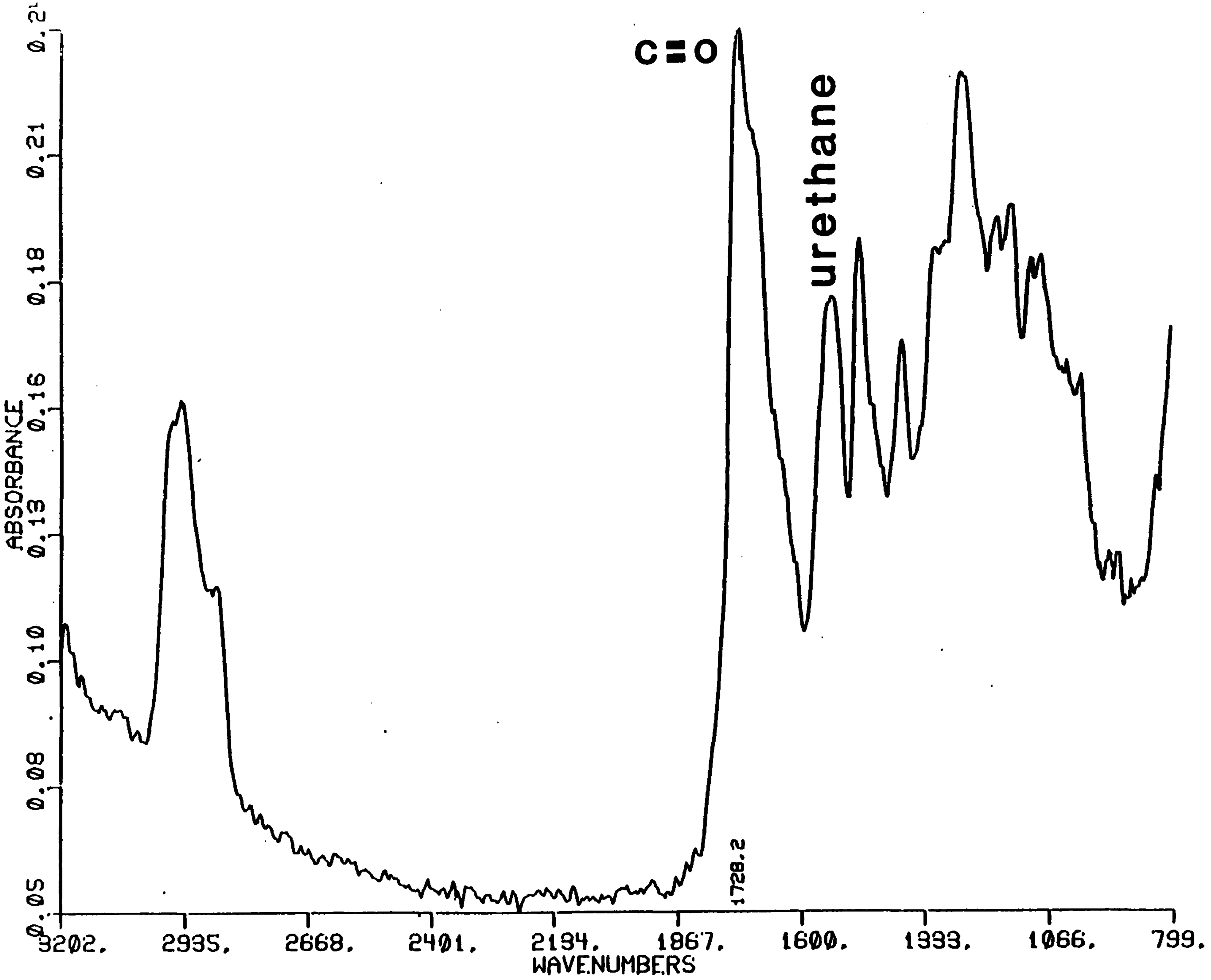


Figure 19 - Photoacoustic Spectra of Grey Coating, 5000 Hrs. QUV

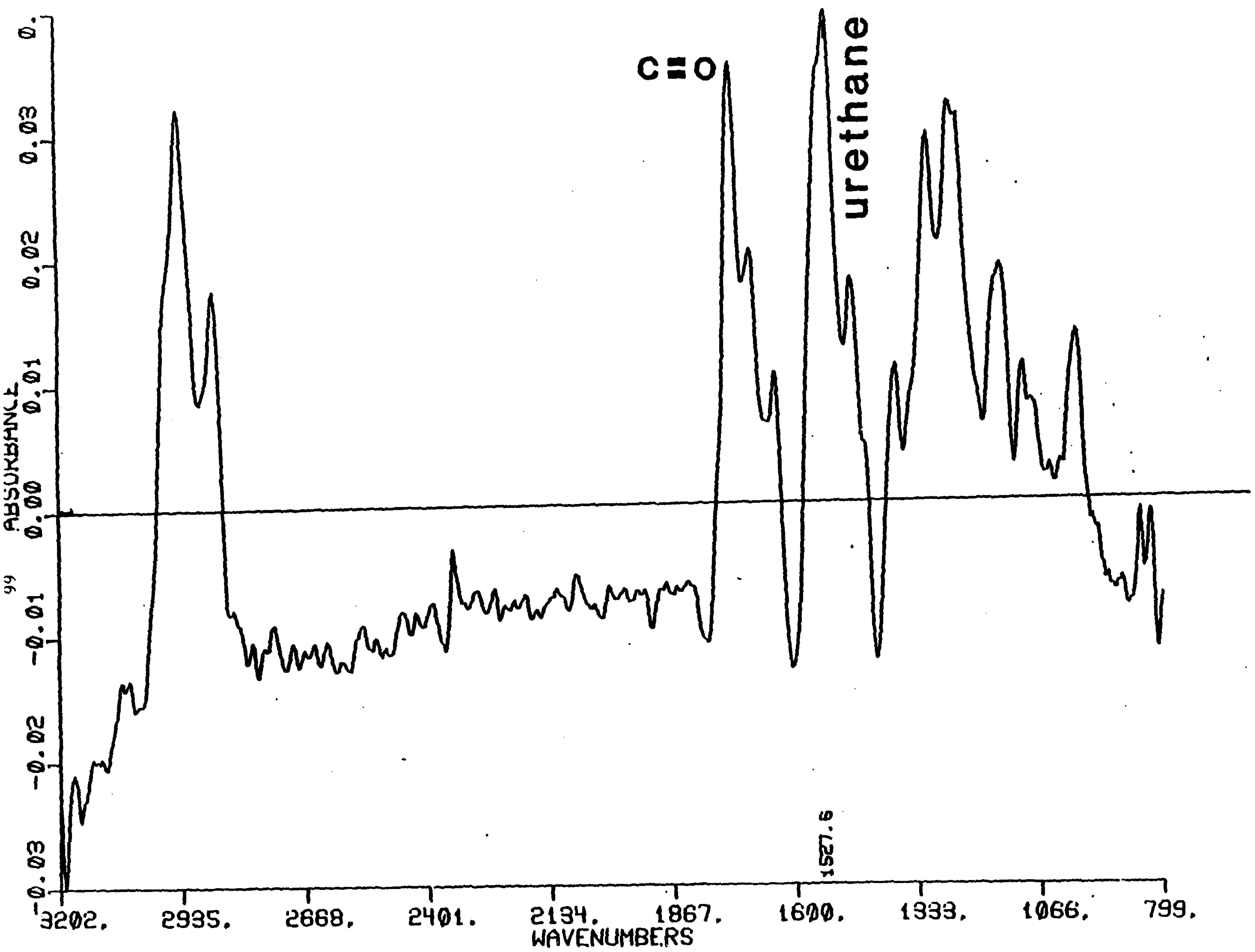


Figure 20. Photoacoustic Difference Spectra of Grey Coating, 0 Hrs. - 5000 Hrs. QUV

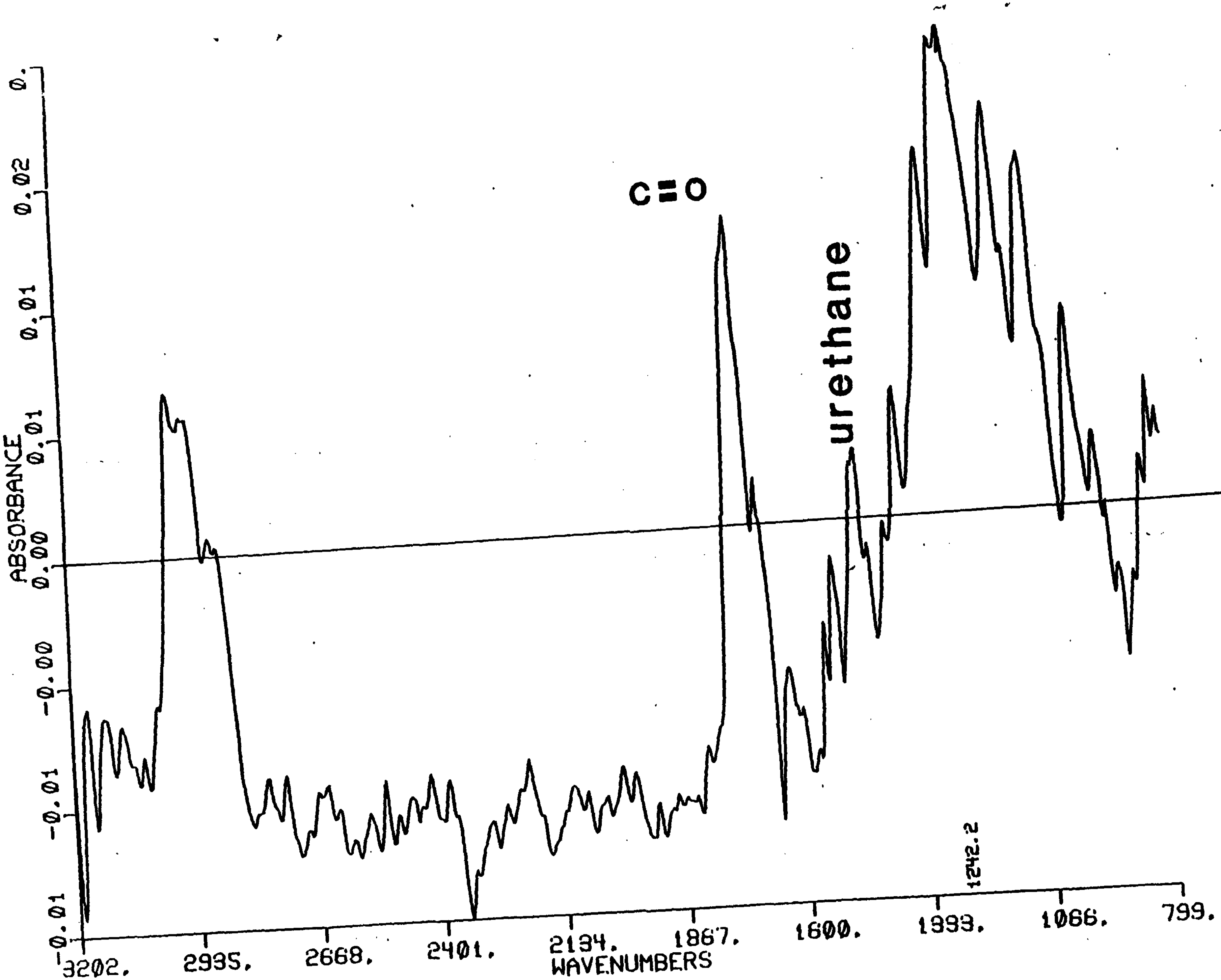


Figure 21 - Photoacoustic Difference Spectra of Grey Coating, 4000 Hrs. - 5000 Hrs. QUV

Photoacoustic Spectroscopy Conclusions

Following preliminary FT-IR spectroscopic investigations of the the aliphatic poly(urethane) system it was decided that the most useful technique was the PAS. A more careful examination of artificially and naturally exposed coatings was undertaken.

Careful interpretation of the PAS spectra indicated that a marked change took place in the absorbance at 1528 cm^{-1} as a function exposure time. This peak is due to the C-N group in the urethane molecule. The absorbances due to the $-CH_2-$ group remained relatively constant in all the spectra and was thus chosen as an internal standard. The ratio of the urethane group peak to the $-CH_2-$ peak was calculated as a measure of the relative measure of the C-N group. This ratio was plotted vs. exposure time and this plot is shown in Figure 22 for the standard clear coating system. A rapid change in C-N linkage during the first 2500 hours of QUV exposure which then continues at a slower rate is evident. Examination of the spectra of Figure 23 confirms that most of the C-N absorbance is gone after the first 2500 hours of QUV exposure.

It is interesting to note that exposure of the same clear coating in Florida at 45 deg. south takes 24 months to achieve the same degree of degradation as the 2500 hour QUV exposure. This is also seen in Figure 22. This conclusions is confirmed by comparison of the spectra of the two different exposure panels which are shown in Figure 24 and 25.

When the system is pigmented the degree of degradation is markedly different as shown again on Figure 22. In this situation it appears that the Florida 45 deg. south exposure may produce a slightly greater degradation than the QUV weatherometer. As shown by the spectra in Figures 22 and 23, the overall absorbance of the urethane C-N has not decreased as significantly as it has in the clear coating.

The clear coating when exposed in the Black Box 5 deg. Florida for 24 months undergoes complete destruction. This is shown in Figure 26 where the spectrum of the Florida 45 deg. south exposure still indicates the presence of an ester component and some urethane while the Black Box exposure only shows the epoxide due to the primer. This epoxide primer was not seen in any of the other systems discussed in this report.

In Black Box exposure, the panel is placed inside of a black box, open at the top and exposed at a slight angle (5°). The purpose of this arrangement is to allow direct sunlight at midday and, primarily to increase the heat around the test panel by absorbtion of the black walls of the box.

A similar comparison of the grey pigmented system indicates relatively little difference between black box and 45 deg. south exposure this is seen in Figure 27.

PAS-FT-IR analysis can be used to monitor the rate of degradation in pigmented or unpigmented coatings. With further experimentation a more direct correlation may be made between actual long term weathering and short term accelerated testing. Once this correlation is made some long term weathering tests may be eliminated.

The change in absorbance or the urethane C-N peak indicates either a change in the molecule or a loss of that component. Since the aliphatic $-CH_2-$ absorbance remains relatively constant it seems more likily that a change in the molecule has taken place.

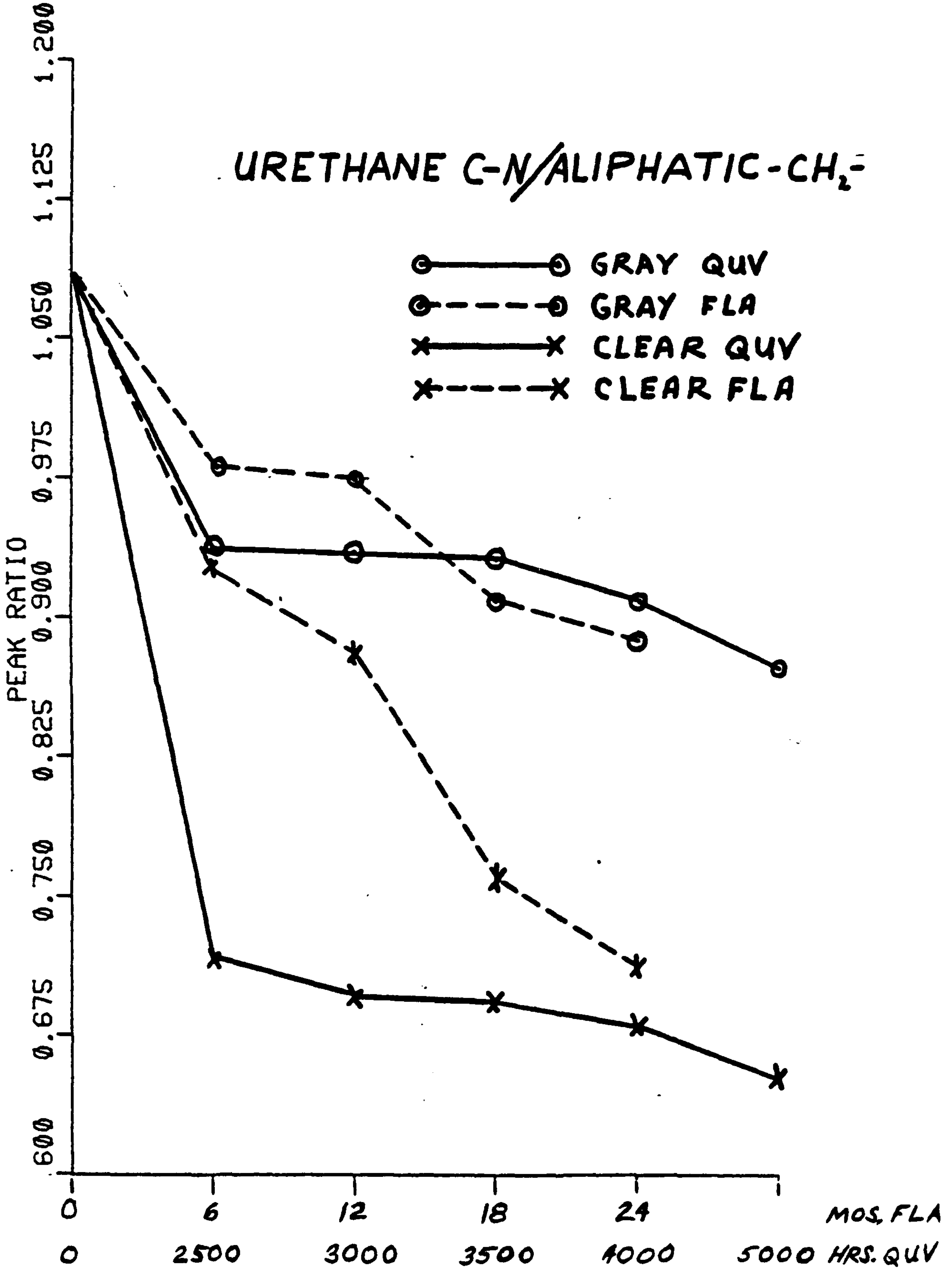


Figure 22 - Urethane Functional Group Vs. Exposure Time

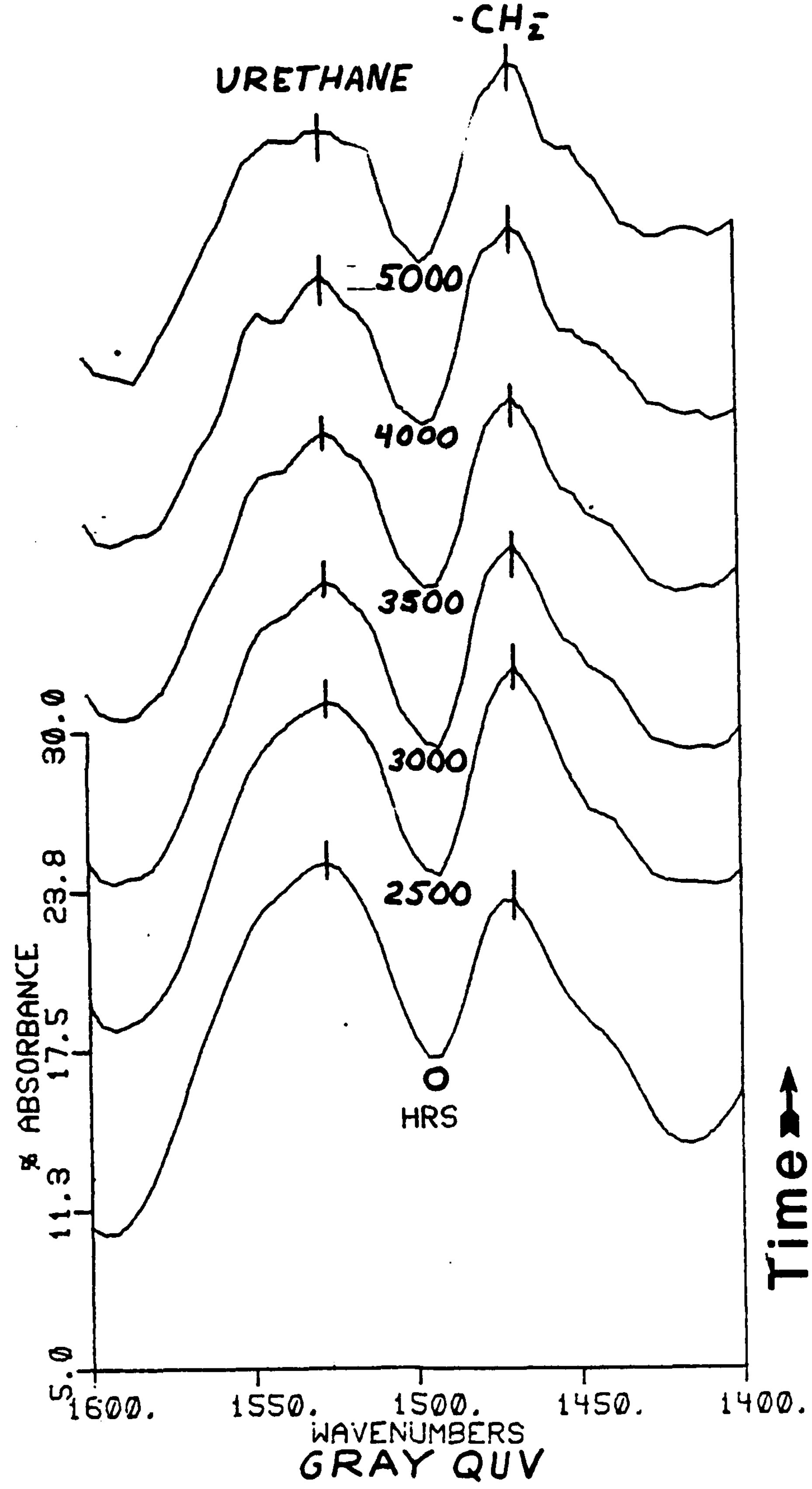


Figure 23 - Photoacoustic Spectra of Urethane Functional Absorbance vs. Exposure Time QUV, Grey Coating

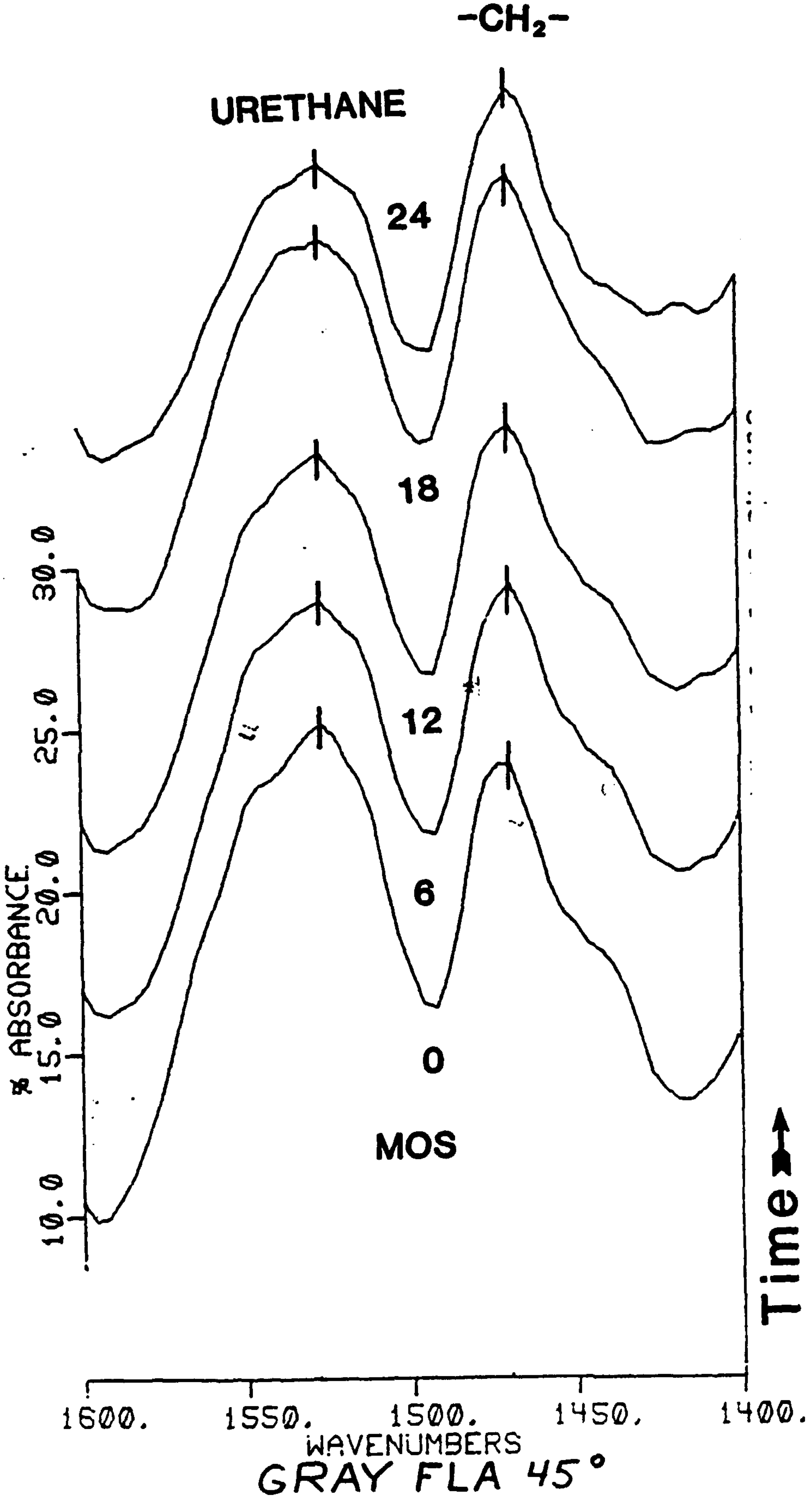


Figure 24 - Photoacoustic Spectra of Urethane Functional Absorbance vs. Exposure Time Natural Exposure, Grey Coating

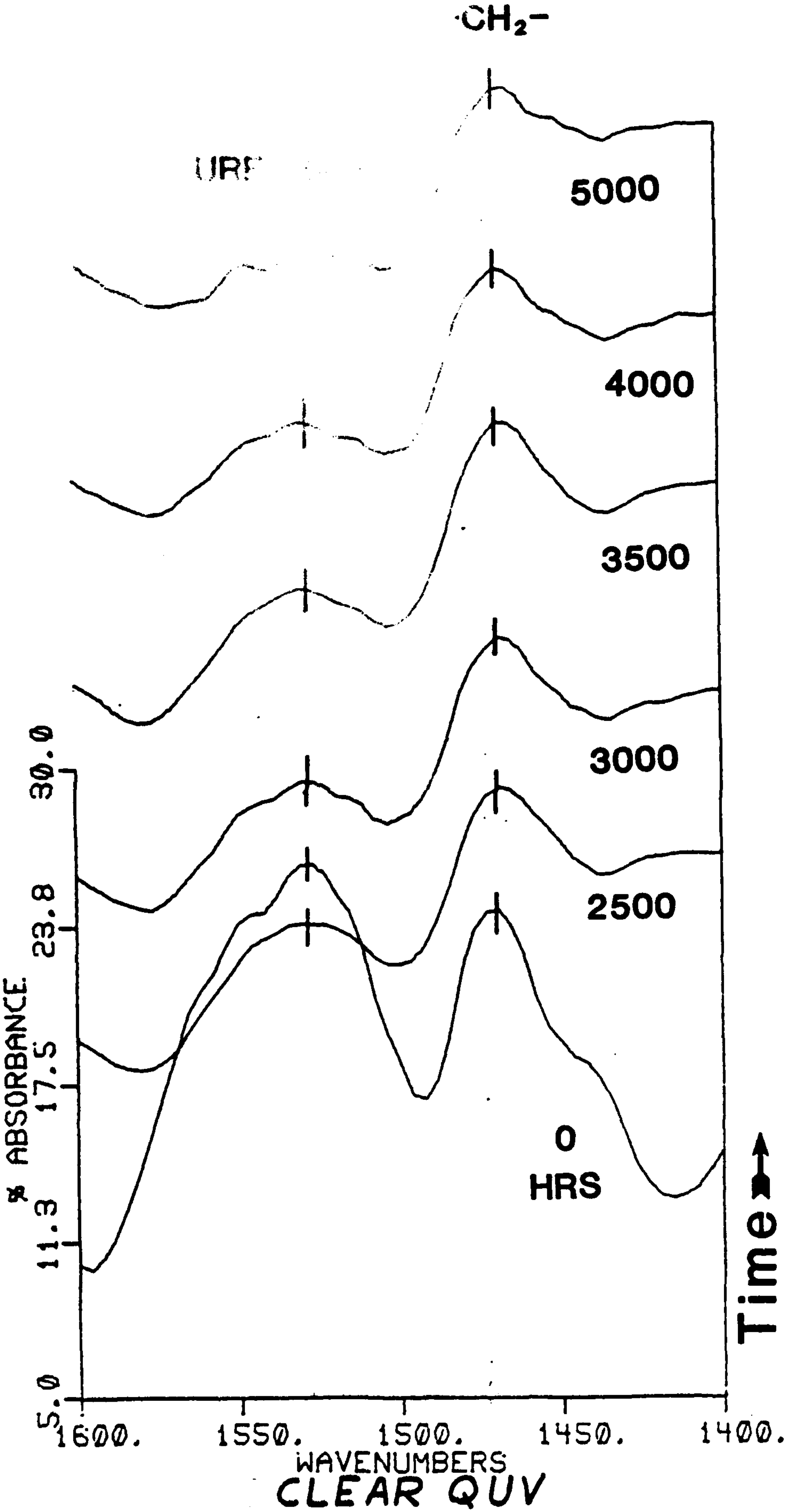


Figure 25 - Photoacoustic Spectra of Urethane Functional Absorbance vs. Exposure Time QUV, Clear Coating

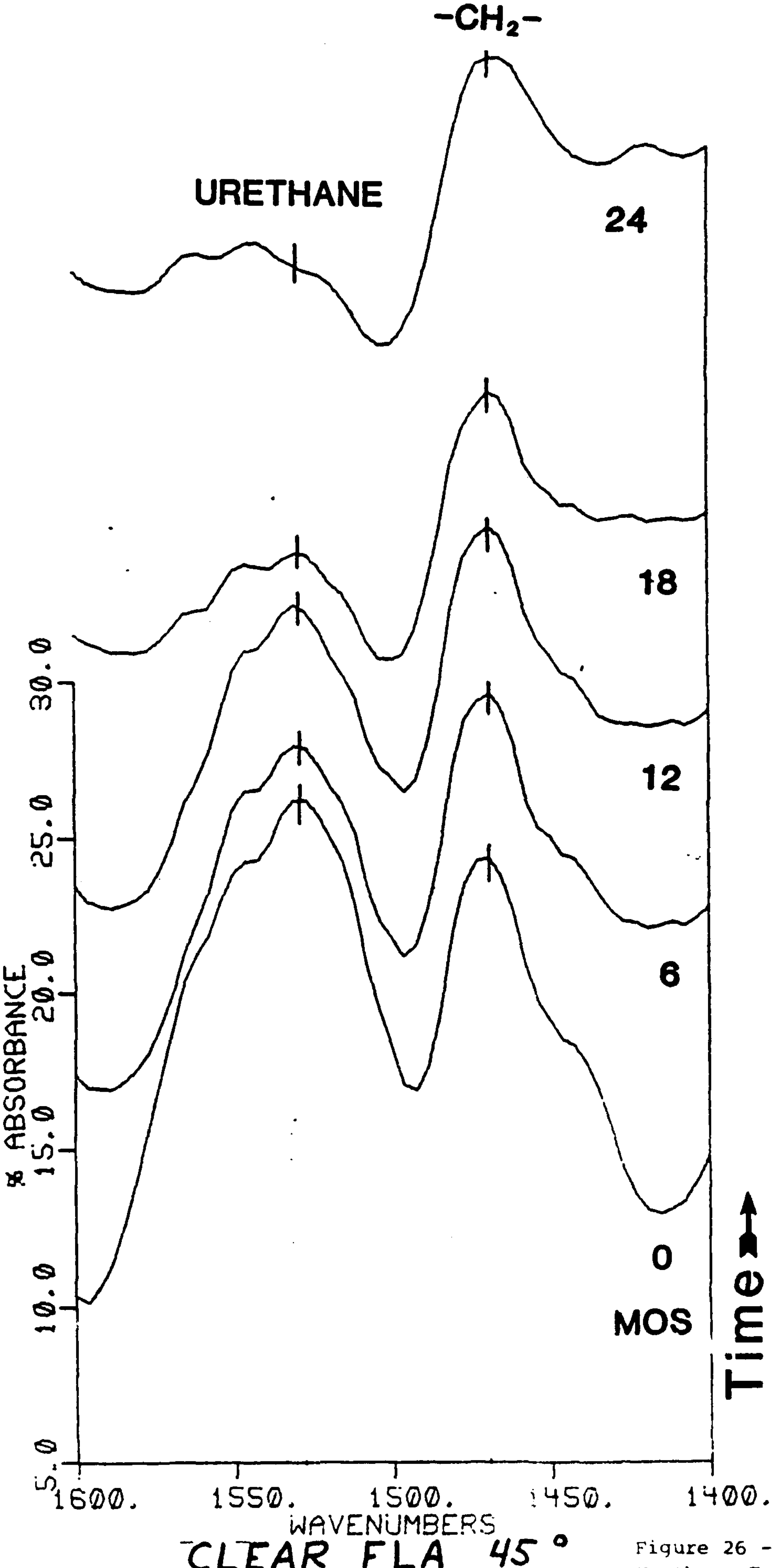


Figure 26 - Photoacoustic Spectra of Urethane Functional Absorbance vs. Exposure Time Natural Exposure.

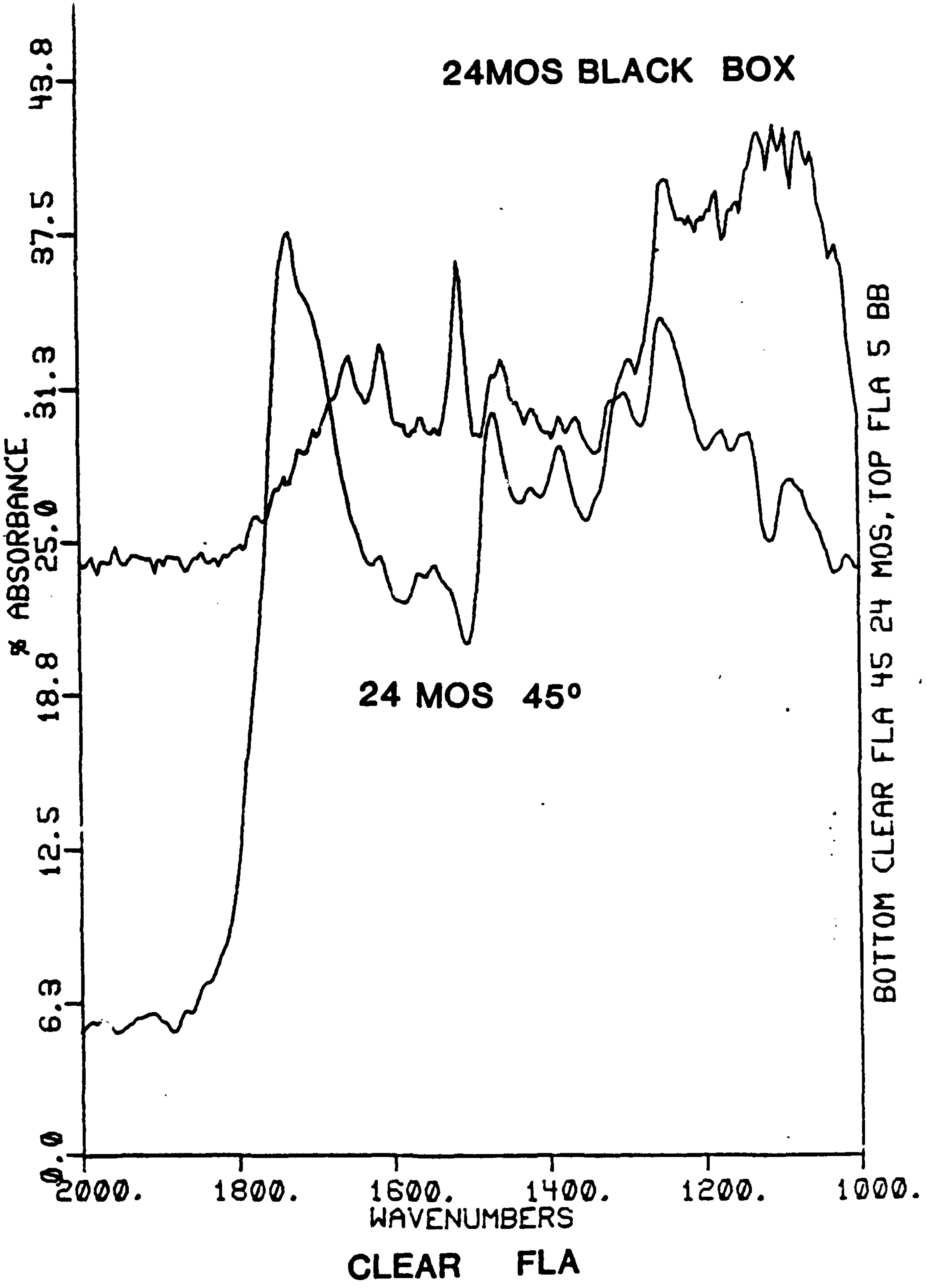


Figure 27 - Photoacoustic Spectra of Clear Coating, 24 Months Natural Exposure vs. 24 Months Black Box Exposure

Data Analysis and Interpretation

Predictors Discarded

Early in this work gloss retention data for all sample coatings was collected. Examination of this data revealed an obvious decrease in gloss with exposure time. This result was expected and may prove predictive of failure to some extent. However, the data is of questionable use in a pragmatic sense since ultimately the concern is with camouflage coatings which initially have very low gloss. Thus any decrease in gloss would be insignificant as a predictor of degradation. Therefore, gloss measurements were eliminated as useful to this program.

Similarly, it has been determined that the pencil hardness test is of little real value. In our attempts to use measurements of pencil hardness we found it obvious that the variation of pencil hardness between two or more operators and ,indeed, for the same operator at widely different times is at least as great as the variation due to degradation of the coatings. This data is not reported here. Thus, pencil hardness was eliminated from consideration in this program.

The pendulum hardness versus QUV exposure time for clear and pigmented coatings respectively are plotted in Figure 1 and Figure 2. The pendulum hardness decreases only slightly for the clear coating over 6000 hours after an initial large increase. After the initial large increase the pendulum hardness remains high and relatively constant for about 3000 hours and then decreases gradually to a somewhat lower level. The small change in pendulum hardness relative to the scatter in the data indicates that this measurement may have limited value for early prediction of failure.

Reverse impact measurements have a large amount of scatter and are of limited value.

The more sophisticated technique, SLAM, showed some promise for detection of coating flaws but does not have enough resolution to make measurements on the thin films of typical aircraft coatings.

Water vapor transmission measurements do appear to reflect basic changes in the film structure but are of little value as a field test.

Predictors Retained

Physical Properties

The cross hatch adhesion test shows promise as a relatively objective, easy to perform and quantitative test which may prove to be a predictor of coating failure. This test could be performed on any aircraft by an unskilled technician with no significant damage to the aircraft and the measurement could serve as an indicator of the state of the coating. This test may be thickness dependent but is relativly precise compared to such tests as pencil hardness. This test has also shown variation with weathering of the test coatings. Information is inconclusive but this should be included in future work on predictve or descriptive methods.

The contact angle, as described below, does show usefulness as a predictor of coating degradation when the data are properly analyzed. This test should also be included in future monitoring and development work.

Chemical Properties Measurements

The electron spin resonance technique shows great promise as a very early predictor of coating failure and, in fact, may be a useful screening technique. The technique promises to produce not only an early predictor but a means to investigate the mechanism of coating degradation.

Scanning Auger spectroscopy and or x-ray photo-electron spectroscopy can be used to measure the increase of oxygen at the coating surface. This is a very sensitive measurement and can detect early changes which will ultimately lead to coating failure.

The oxygen and nitrogen content at the surface are factors in the proposed degradation mechanism described above. The data obtained from SAM and XPS in this work is consistent with this mechanism. Thus, we can both predict, with proper data analysis techniques, the condition of the coating surface and also examine the effects of accelerated degradation techniques or conduct other mechanistic experiments.

The data obtained by infra red PAS is also consistent with the probable degradation mechanism, i.e. disappearance of the urethane linkages. This is another sensitive technique which lends itself both to the measurement of the state of coating degradation and also mechanistic studies, e.g. as the detection method for accelerated techniques.

Box-Jenkins Time Series Analysis

Analysis of data for contact angle of water on samples exposed to artificial weathering in the QUV was undertaken. Data for both clear and grey coatings from the QUV were analysed for time series trends by using Box-Jenkins techniques. The data were first analyzed by using standard linear regresion technique and it was found that the data were poorly described by either logarithmic or polynomial functions of exposure time. However, the statistical diagnostics indicated a possible cyclic nature to the data, thus, a Box-Jenkins analysis was undertaken [24].

The Box-Jenkins approach first evaluates the partial auto-correlation function and determines the order of the moving average memory function.

Tables 15 and 16 show the results from the partial auto correlation plots. Second order moving averages with the appropriate lags were calculated by using a ARIMA algorithm written by W. Q. Meeker of Iowa State University [25]. The fits and residual analyses are shown in Figures 28-37 which are plots generated by our Box-Jenkins computer program. Figures 28 and 33 display the scatter plot of contact angle vs. hours of exposure for the grey and clear coatings respectively. Figures 29 and 34 illustrate the partial autocorrelations functions for the grey and clear coatings respectively and demonstrate the lags. Figure 30 and 35 are scatter plots of the residuals from the Box-Jenkins analysis, i.e. the difference between the predicted and actual measurements, vs. the actual measurement. The plots indicate random behavior about zero as they should for a good model. Figures 31 and 36 are plots of the residuals in sequence for the grey and clear coatings and indicate random behavior about zero, i.e. the residuals are not dependent upon the order of the data. Figures 32 and 37 show plots of the predicted vs. actual values for the grey and clear coatings. In this case there is a definite linear trend showing that the predicted values are close to the actual values as is necessary for a good model.

The ARIMA model will allow forecasts of future contact angles, and therefore, the condition of the coating with respect to degradation.

TABLE 15.

BOX-JENKINS ANALYSIS AND MODEL FOR GREY COATING

```
Estimates at Each Iteraton
Iteration          SSE        PARAMETERS

   0            65124.6    0.100     0.100     0.100      0.100
   1            44647.4   -0.050     0.066     0.248      0.133
   2            41895.2    0.052     0.132     0.398      0.190
   3            38394.4    0.132     0.197     0.548      0.250
   4            32804.5    0.057     0.290     0.590      0.400
   5            30017.8   -0.093     0.309     0.518      0.505
   6            26726.4   -0.243     0.283     0.461      0.566
   7            21629.5   -0.393     0.185     0.496      0.534
   8            18510.8   -0.543     0.124     0.478      0.554
   9            15915.5   -0.693     0.031     0.533      0.504
  10            15392.1   -0.843    -0.032     0.480      0.568
  11            14942.3   -0.912    -0.072     0.508      0.542
  12            14934.9   -0.960    -0.090     0.451      0.601
  13            14862.7   -0.970    -0.103     0.457      0.598
  14            14861.9   -0.969    -0.103     0.457      0.597

Relative change is each estimate less than .0010


Final Estimates of Parameters

Number        Type       Estimate        St. Dev.      T-Ratio

  1           AR 1       -.9694          .1549          -6.26
  2           AR 2       -.1033          .1284           -.80
  3           MA 1        .4572          .1160           3.94
  4           MA 2        .5974          .1012           5.90

Differencing    2 Regular
Residuals       SS =     14860.2 (Backforecasts excluded)
                DF =  86       MS =    172.8

No. of Obs.     Original Series    92      After Differencing    90

Correlation Matrix of the Estimated Parameters

            1           2           3

2        .905
3        .720        .547
4       -.720       -.547        -.999
```

TABLE 16.

BOX-JENKINS ANALYSIS AND MODEL FOR CLEAR COATING

```
Estimates at Each Iteraton
Iteration          SSE        PARAMETERS

    0            5947.12    0.100      0.100      0.100      0.100
    1            5476.63   -0.038      0.019      0.229      0.119
    2            5469.19    0.109      0.002      0.379      0.061
    3            5466.04    0.259     -0.037      0.529     -0.019
    4            5462.99    0.409     -0.078      0.679     -0.101
    5            5459.79    0.558     -0.119      0.829     -0.183
    6            5456.17    0.708     -0.161      0.979     -0.266
    7            5451.84    0.857     -0.203      1.129     -0.349
    8            5446.30    1.007     -0.247      1.279     -0.434
    9            5441.06    1.155     -0.292      1.429     -0.520
   10            5437.55    1.299     -0.352      1.579     -0.619

Unable to reduce sum of squares any further.


Final Estimates of Parameters

Number          Type         Estimate          St. Dev.     T-Ratio

  1             AR 1          1.2992            .1053         12.34
  2             AR 2          -.3516            .1485         -2.37
  3             MA 1          1.5787            .0000      87726.19
  4             MA 2          -.6194            .0604        -10.25

Differencing     1 Regular
Residuals        SS =    5431.55 (Backforecasts excluded)
                 DF =  86       MS =    63.16

No. of Obs.      Original Series    91      After Differencing    90


Correlation Matrix of the Estimated Parameters

           1           2           3

2       -.775
3        .206       -.140
4       -.179        .717       -.196
```

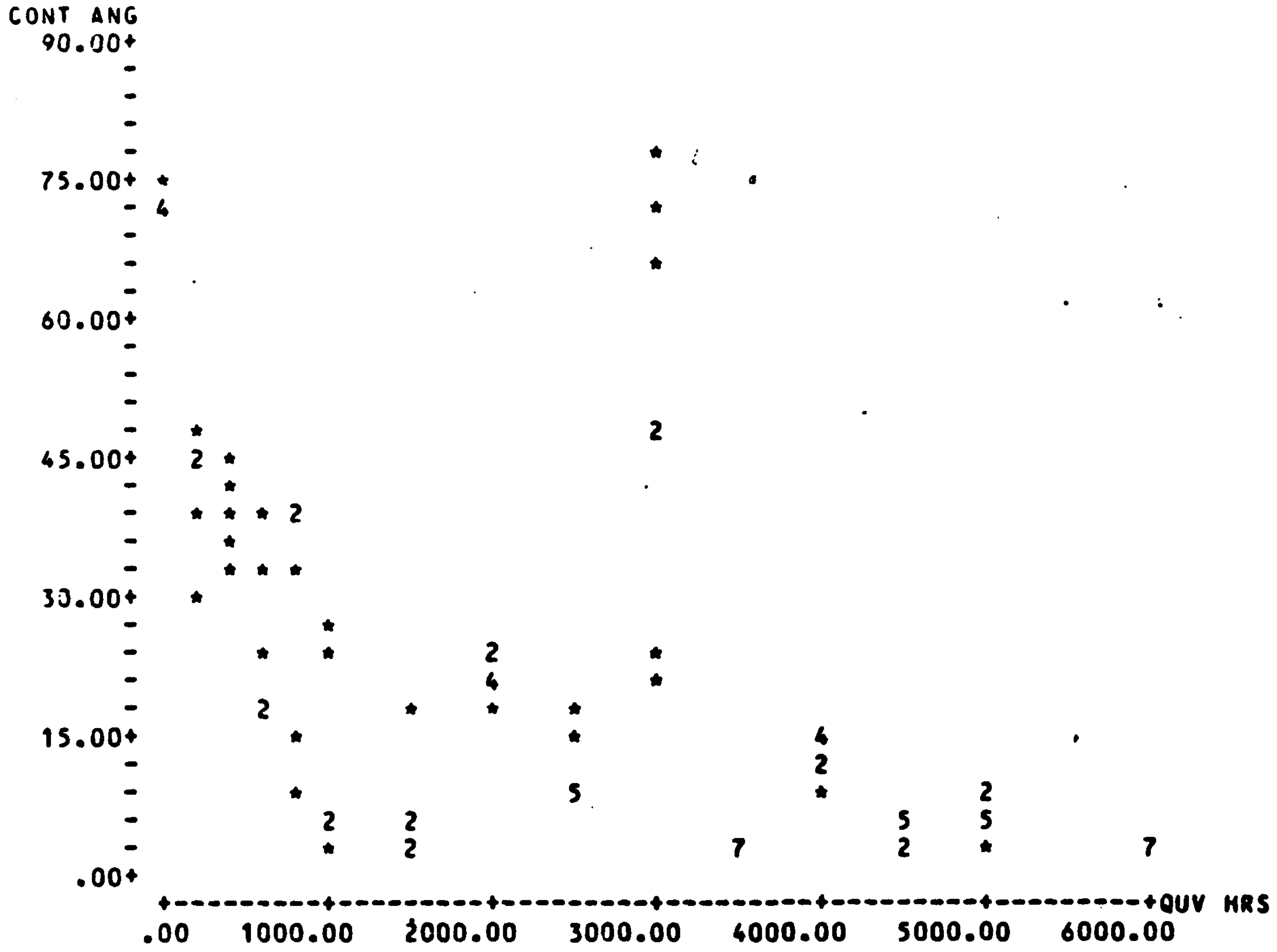
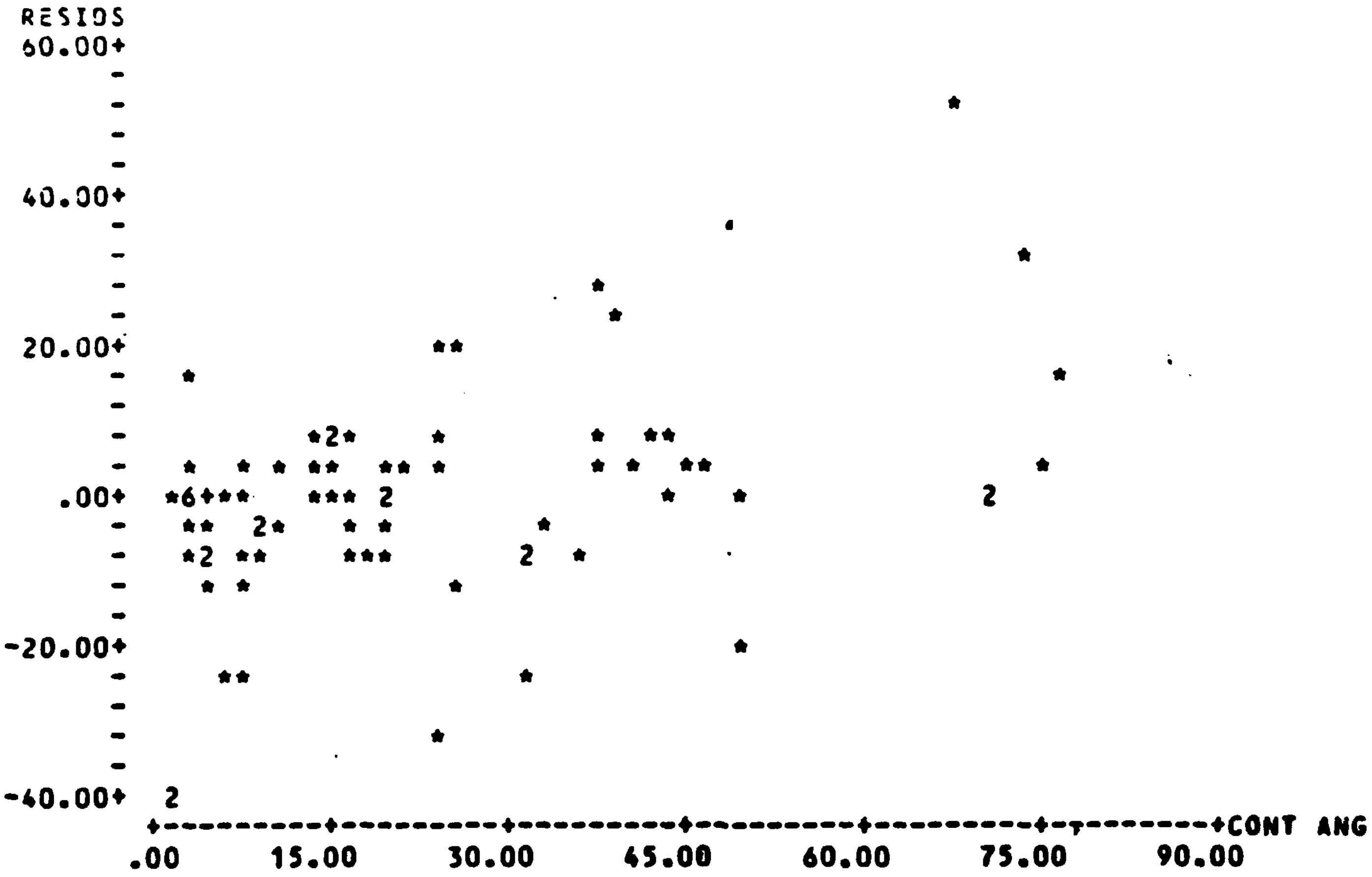


FIGURE 28 Scatter Plot of Contact Angle vs. Hrs. of Exposure (QUV) for Grey Coating

```
PACF OF GREY

           -1.0 -.8  -.6  -.4  -.2   .0   .2   .4   .6   .8  1.0
             +----+----+----+----+----+----+----+----+----+----+
  1    .695                           XXXXXXXXXXXXXXXXXX
  2    .332                           XXXXXXXXX
  3   -.201                        XXXXXX
  4    .254                           XXXXXXX
  5   -.101                          XXXX
  6   -.106                          XXXX
  7    .016                           X
  8    .035                           XX
  9    .167                           XXXXX
 10    .024                           XX
 11   -.041                          XX
 12    .015                           X
 13   -.042                          XX
 14    .062                           XXX
 15   -.051                          XX
 16   -.010                           X
 17   -.032                          XX
 18   -.108                        XXXX
 19    .084                           XXX
```

FIGURE 29 Partial Autocorrelation Function for Grey Coating



2 MISSING OBSERVATIONS

FIGURE 30 Scatter Plot of Box-Jenkins Residuals vs. Measured Contact Angle for Grey Coating

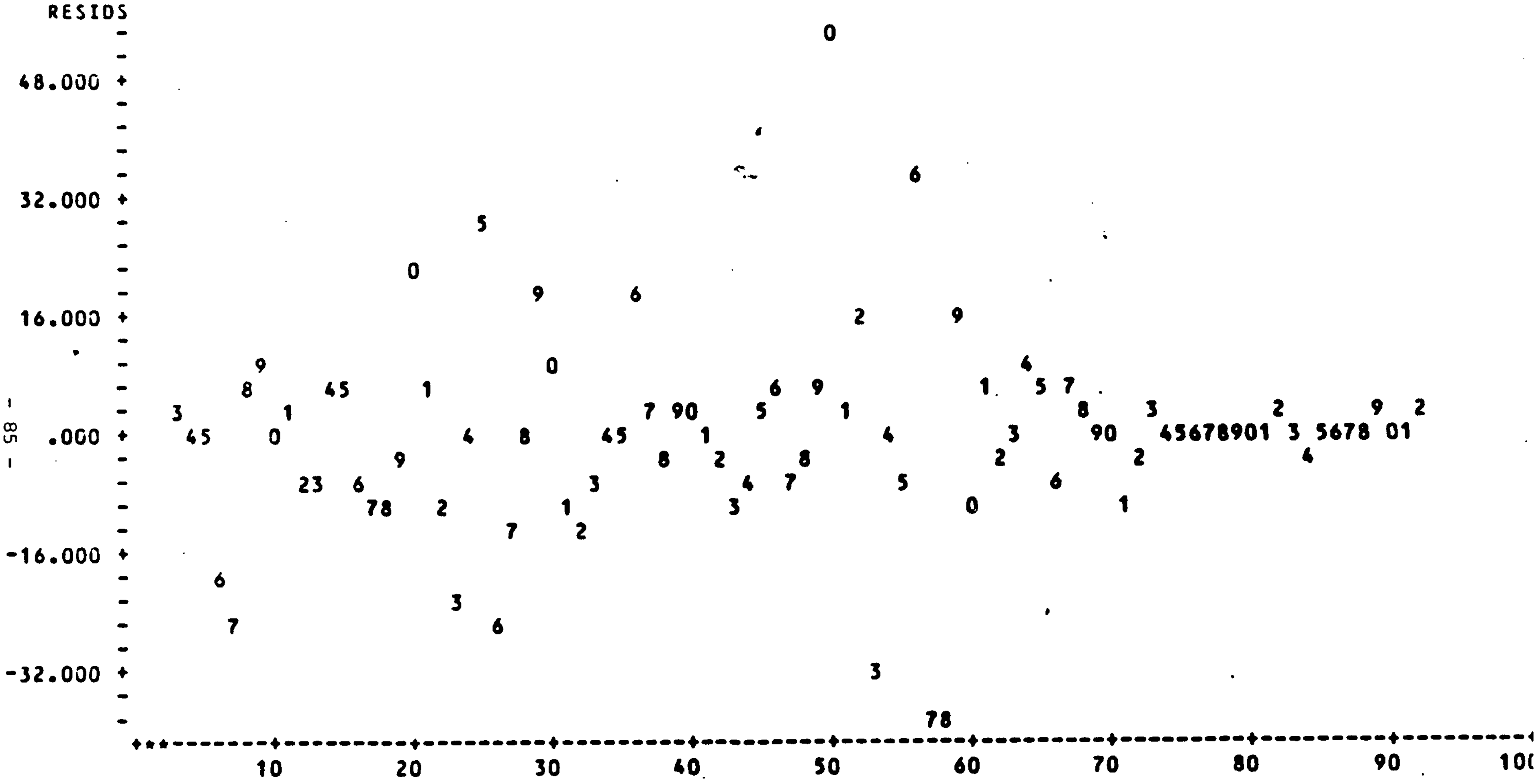
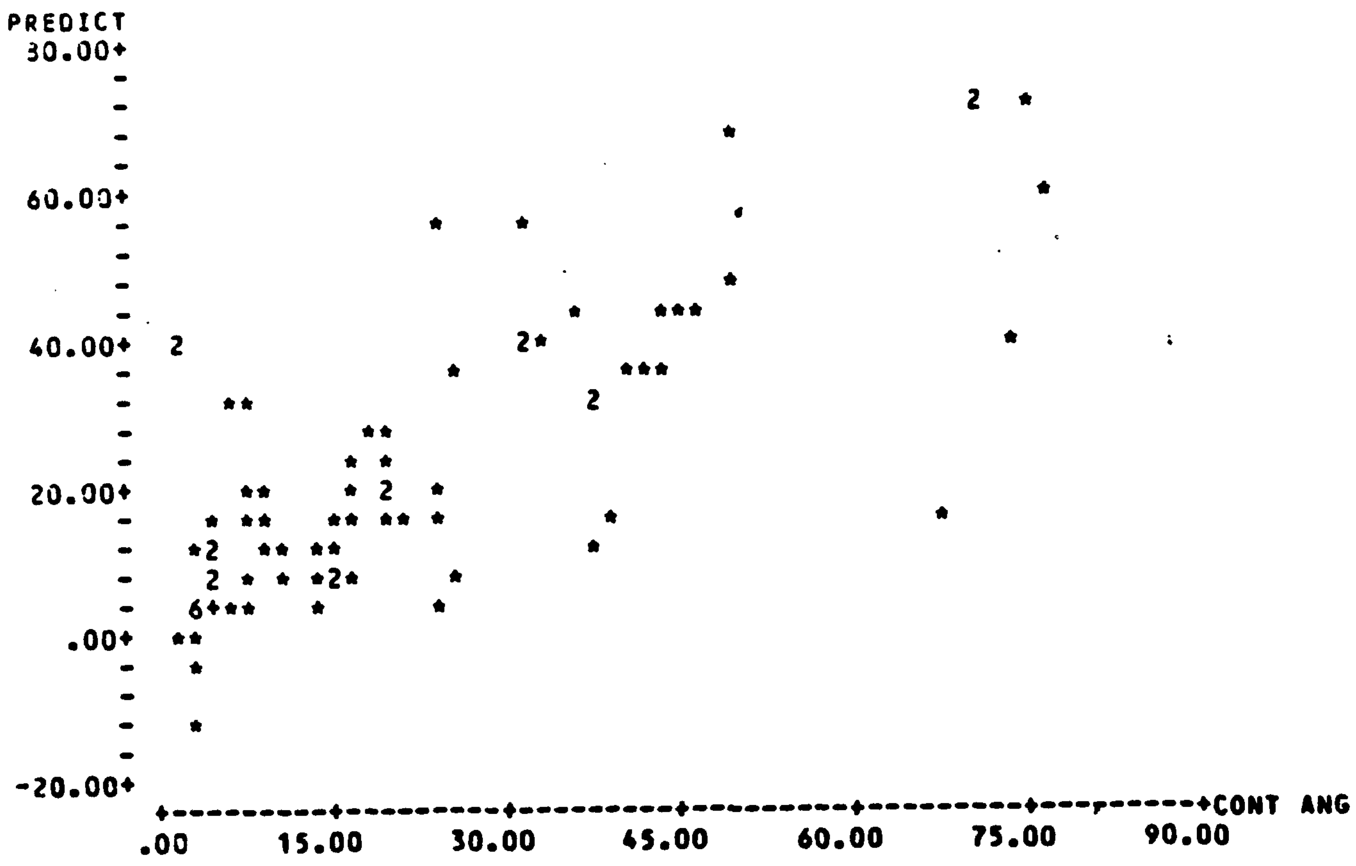


FIGURE 31 Scatter Plot of Residuals vs. Sample for Grey Coating



2 MISSING OBSERVATIONS

FIGURE 32 SCATTER PLOT OF PREDICTED VS. ACTUAL CONTACT ANGLE FOR GREY COATING

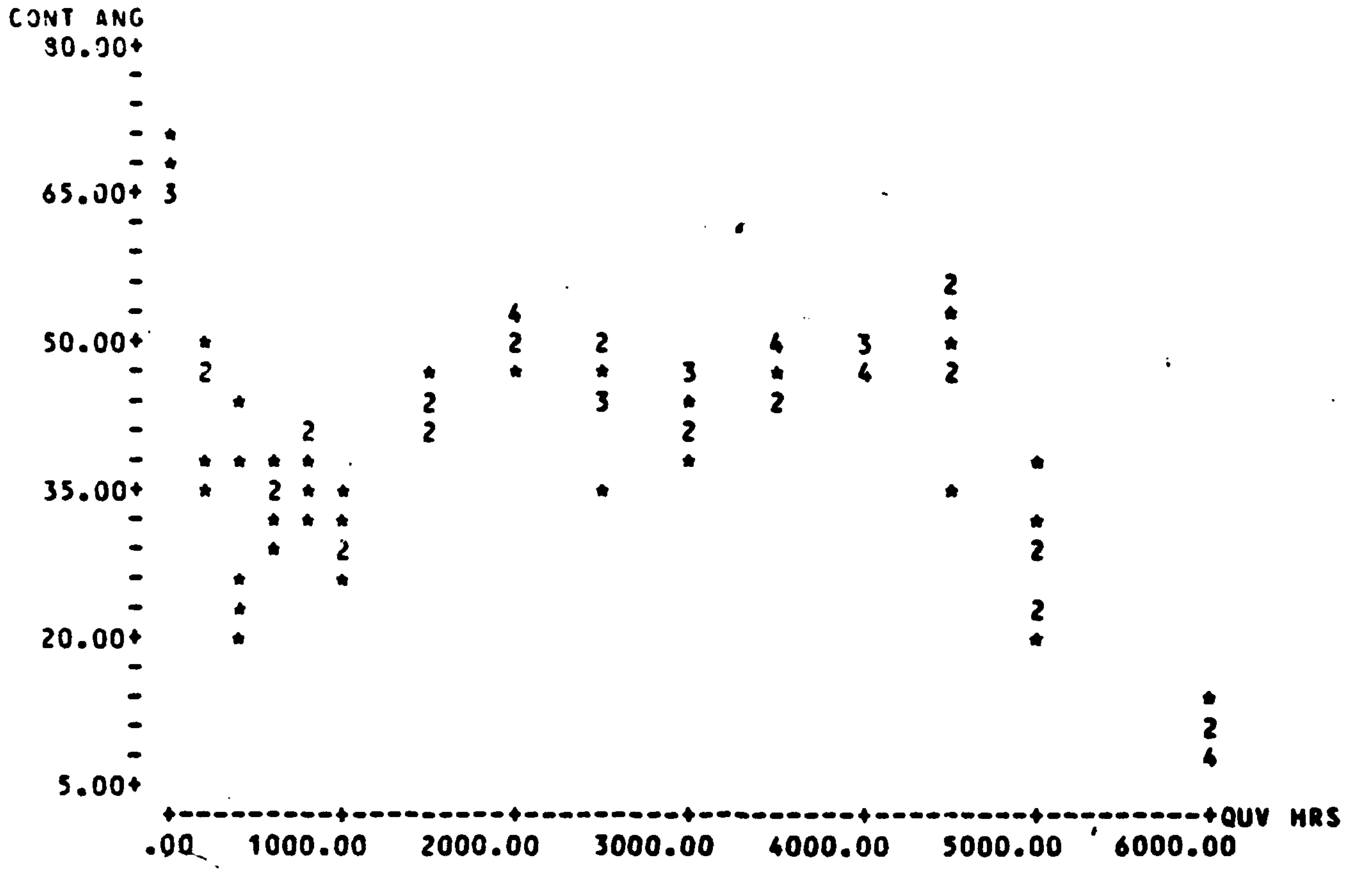
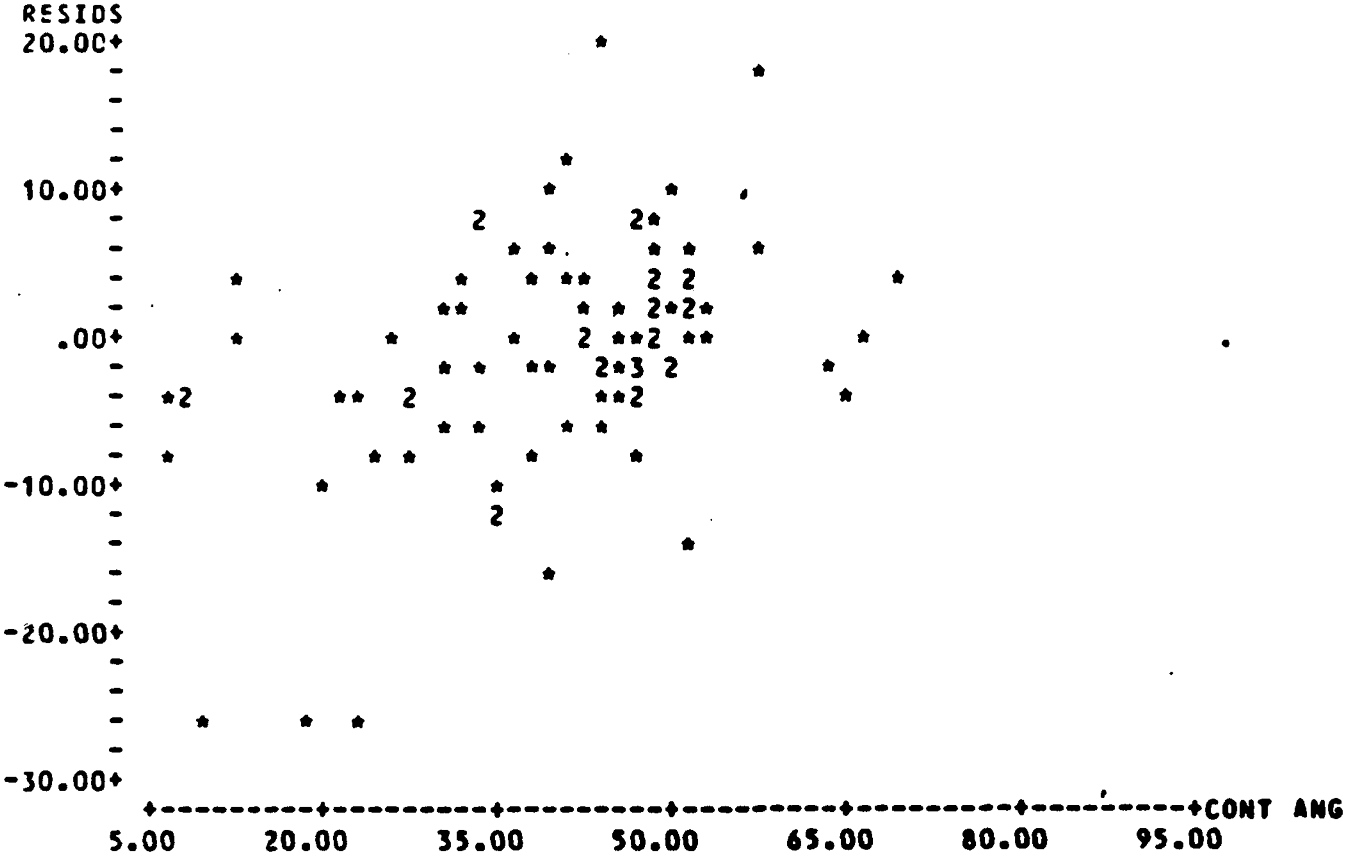


FIGURE 33. Scatter Plot of Contact Angle vs. Hours of Exposure (QUV) for Clear Coating

```
 PACF OF CLEAR

          -1.0  -.8  -.6  -.4  -.2   .0   .2   .4   .6   .8  1.0
            +----+----+----+----+----+----+----+----+----+----+
  1    .772                          XXXXXXXXXXXXXXXXXXXX
  2    .100                          XXXX
  3   -.021                         XX
  4    .014                          X
  5   -.016                          X
  6   -.122                       XXXX
  7    .087                          XXX
  8    .019                          X
  9   -.076                        XXX
 10   -.089                        XXX
 11    .055                          XX
 12   -.087                        XXX
 13   -.110                       XXXX
 14   -.020                          X
 15    .159                          XXXXX
 16   -.125                       XXXX
 17    .124                          XXXX
 18   -.039                         XX
 19   -.147                      XXXXX
```

FIGURE 34 Partial Autocorrelation Function for Clear Coating



1 MISSING OBSERVATIONS

FIGURE 35 Scatter Plot of Residuals vs. Contact Angle for Clear Coating

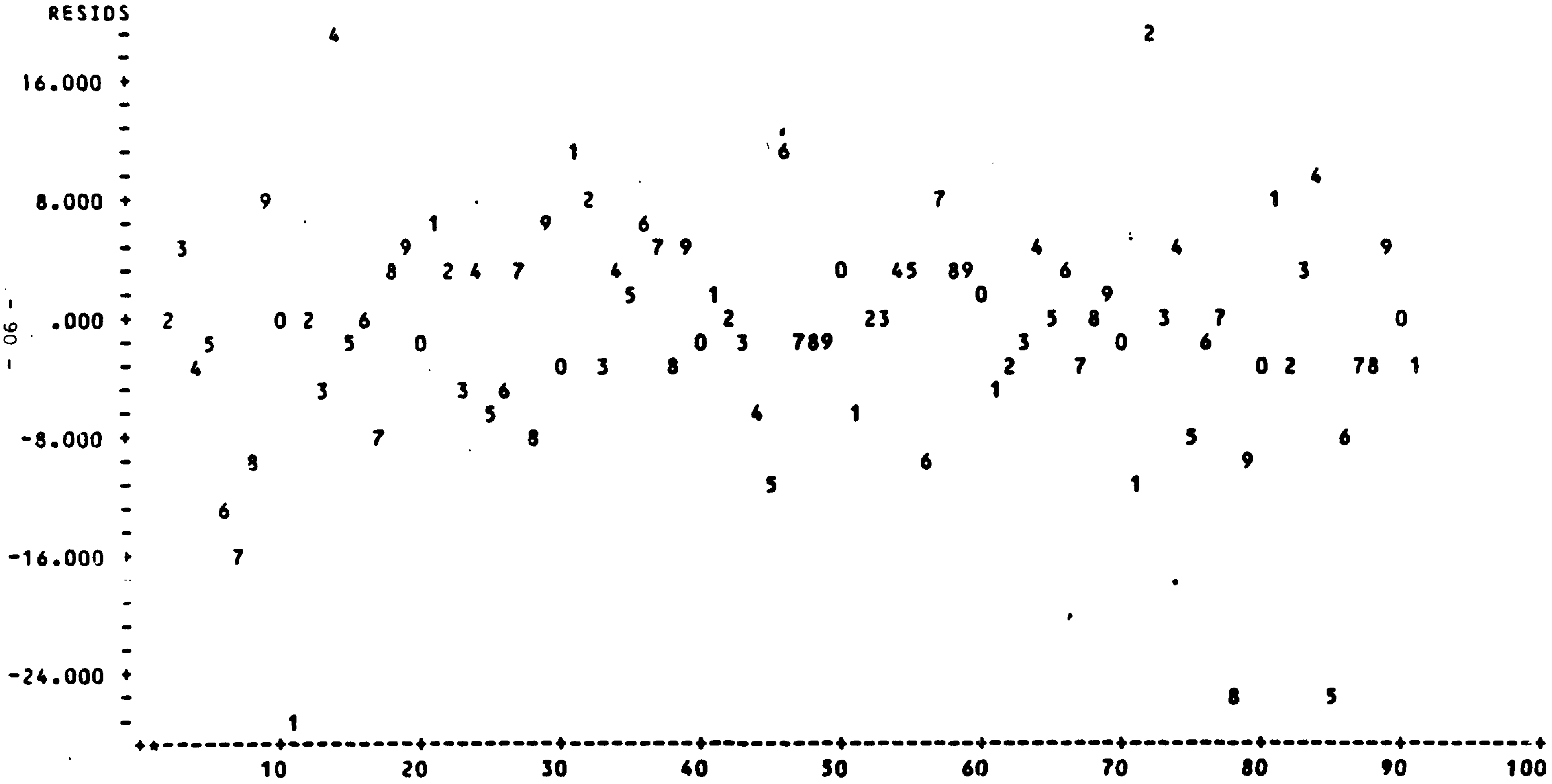
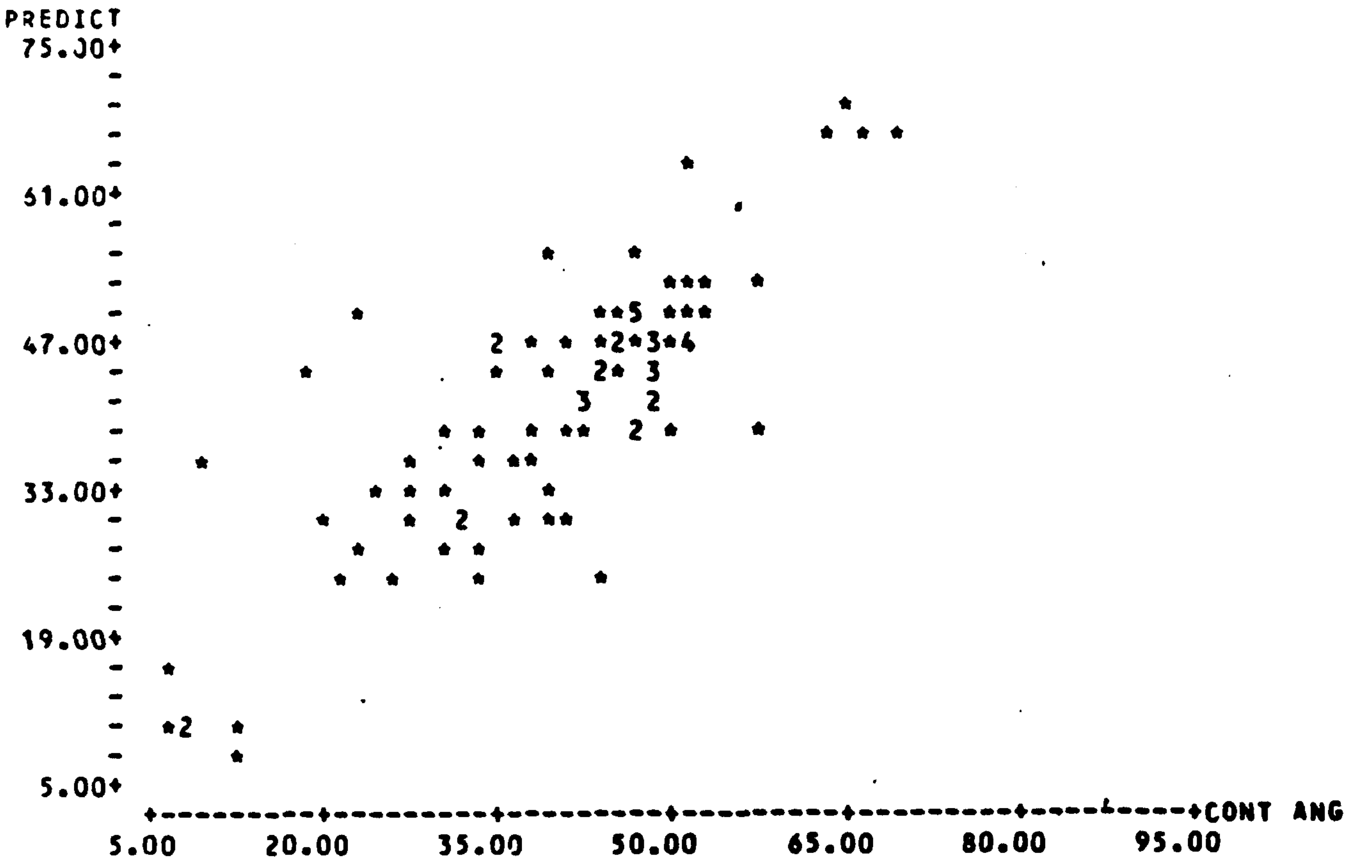


FIGURE 36 Scatter Plot of Residuals vs. Sample for Clear Coating



1 MISSING OBSERVATIONS

FIGURE 37 Scatter Plot of Predicted vs. Actual Contact Angle for Clear Coating

The Box-Jenkins Time Series analysis provides a very good fit of the contact angle of water as a function of exposure time in the QUV weatherometer. This statistical technique was developed (4) as a special case of more standard statistical techniques for the determination of the relationships between two or more variables, e.g. regression analysis. Standard regression analysis techniques are less effective when one of the variables is time or when the analysis involves the same phenomena measured at different times. This is so because in the case of time series the individual measurements are not usually independent of one another as required under the assumptions of regression. The first applications of time series analysis were for industrial control and socioeconomic data [26]. The chief interest is to describe the factors which produce the patterns in a time series and thus to obtain a forecast of the condition at some future time. In the usual time series analysis technique the components are the overall trend in the data, seasonal variation, cyclical variation, and the always present random noise. These variations are easily seen for control or business cycles.

But let us consider the degradation of coatings in this light. The trend is toward ultimate failure of the coating is obvious. But there are also seasonal variations as well as geographical ones. In the analysis at hand the weatherometer exposures are cyclical by design. Thus the analysis does fit our problem. Indeed the diagnostic tests of the regression analyses which were initially conducted indicated that individual contact angle measurements were not independent and that there was a very strong cyclical component in the data as indicated by a high Durbin-Watson [27] statistic and examination of the residuals. This led to a time series analysis of the data.

General Techniques for Data Analysis

For screening, the standard statistical techniques [28,29,30] are valuable. For example, a standard regression analysis was used to determine that there is neither trend nor correlation nor suitable non-random behavior in such tests as pencil hardness and reverse impact. However, these are not adequate for predictive purposes and cannot determine the nature of trends over time. Thus, the Box-Jenkins approach was used. This technique is particularly powerful for analysis of data taken over long time periods or when the same measurements are made at different times. This is not the only technique available for these analyses and at times the assumptions necessary for Box-Jenkins analysis may not be true. In addition and of necessity a relatively long time is involved to obtain enough data for an adequate analysis.

Two other techniques which may prove useful for analysis of the kinds of data reported here are those which involve Weibull [31] distribution analysis and those which involve Bayesian [32] analysis. The Weibull analysis has been developed primarily for analysis of expected lifetime of industrial products for purposes of quality control and to provide a measure of the reliability of components. This type of analysis gives greater weight to early events, since in failure analysis an early failure is more notable. Thus, it is often possible to do an adequate analysis earlier than is possible with other techniques. However, a proper analysis usually requires some reasonable knowledge of failure rates which may limit the application in the case of high performance coatings. The technique is powerful and worthy of investigation particularly as we learn more about the actual rate of failure.

The Bayesian technique does not require prior knowledge of the failure rates or sampling distributions of the data. Estimates of the needed parameters are estimated by whatever means available, e.g. from a similar but known system. Built into the analysis are continuing checks on the appropriateness of the estimated parameters and the proper adjustment during the course of the experiments. Thus, inferences may be made quickly during the course of the study. As we progress with longer term weathering both of these techniques should be added to the arsenal of data analysis techniques and the inferences will become better as more data is added on a series of coatings.

Models of Degradation Behavior

It was thought that a deterministic model of coating degradation could be developed from the data obtained in this work. The model must include long term cycles, e.g. annual and seasonal and short term cycles e.g. morning dew and afternoon sun. Other short term cycles should include operational cycles such as the mechanical stress of take-off and landings. Both weathering and mechanical cycles must be consistent with standard reliability analysis.

The aim should be to develop a model such that the ratio of the rate of change of the test parameters to the actual rate of degradation is constant, i.e.

$$dpi/dt:dP^*/dt=k \qquad (1)$$

where P^* is the ultimate failure of a property, pi is the test property i, t is the time and k is a constant which is much less than 1.

Such models have been attempted with some success [33,34]. However, the extremly large set of physical and environmental variables which must be considered for an aircraft coating make the task of model construction formidable in practice no matter how useful the concept may be in approaching the problem.

The results from the statistical analysis indicated that stochastic models may be quite appropriate and very useful for predictive and reliability purposes. The Box-Jenkins approach was designed to be predictive and data to date indicate that the ARIMA model underlying Box-Jenkins will provide the same utility in practical application as would a deterministic model and will be much easier to use.

Both of the other techniques, Weibull and Bayesian analysis also produce predictive results with a well known underlying model once the analysis is completed for sufficient number of samples over a suitable time period. The number and time needed will be different for each type of analysis.

Proposed Work in Continuation

During the course of the work on this project some techniques were discussed which may be useful but which we could not fully investigate. One of these was the use a bonded fluoresence (or ultra violet absorbance). One would apply a fluorescent or ultra violet reagent which would react with the degradation products, then the fluoresence spectra would be a measure of the amount of degradation product and hence the amount of degradation. For example, one of the proposed degradation products and one which is consistent with the proposed mechanism of degradation, is an aldehyde. There are known fluoresence reagents for aldehydes [35, 36] which could be used. This would be a very sensitive technique and would capable of detecting at least picomoles of materials.

Oxygen is implicated strongly in the proposed photo-oxidation mechanism, so a proposed accelerated technique for degradation would oxygen ion bombardment. An ion gun would be constructed which would direct a stream of highly reactive oxygen ions to the coating surface under controlled conditions. This would be followed by techniques discussed above such a SAM or XPS. The reactions should be much faster than current techniques allow and thus would improve the efficiency of mechanistic studies [37].

SECTION IV

CONCLUSIONS

Necessary Measurement Techniques

The measurements necessary for predictive characterization of degradation of aircraft coatings are those which measure surface chemistry or physics [38,39]. This work shows that by the time the bulk properties have changed measureably coating failure is imminent, therefore, they are of no predictive use.

Degradation starts at the surface and proceeds into the coating, therefore measurements of chemical and physical changes occuring at or near the surface provide information on the state of the coating and on the likelihood of failure within a specified time period.

Conventional, standard techniques of data analysis are not sufficient in themselves to allow reasonable inferences to be made from the data about the condition of the coating. Standard regression and normal statistical calculation can be used to eliminate totally random data but for inferences more sophisticated techniques such as Box-Jenkins Time Series analysis must be used.

Techniques such as Fourier transform infra red spectroscopy in the photoacoustic mode, contact angle, electron spin resonance, scanning Auger microprobe, and x-ray photo-electron spectroscopy are most suitable for the required analysis of the coating surfaces.

Hardness, impact resistance, dynamic mechanical analysis, and other bulk property measurements do not provide useful information about the state of coating degradation unless near failure.

Deterministic models of coating degradation may be too complex to be used for other than conceptual analysis; but the inference of stochastic models provide the necessary predictive capability.

During the times investigated, viz. 24 months of natural exposure, very little difference was detected between coatings which had ultra violet radiation stabilizers and those which did not. Therefore, no conclusions can be drawn concerning the efficacy of these additives until samples which have been exposed substantially longer can be examined.

Further investigation should be made of the electron spin resonance technique, the grafted fluoresence technique, and the ion bombardment degradation technique. The Bayesian, Weibull, and Box-Jenkins techniques of data analysis should be advanced.

SECTION V

SUMMARY

General Summary

A large number of aircraft coating samples have been investigated by using a wide variety of physical and chemical test methods. A range of artificial and natural weathering conditions were imposed upon the test coatings.

The work has shown that sophisticated statistical techniques are necessary to make valid inferences from degradation data but that these techniques may be used in a predictive manner.

All data is consistent with a proposed mechanism for degradation of poly(urethane) coatings.

It has been shown that surface chemistry is more significant than bulk properties for interpretations about the conditions of a weathered coating.

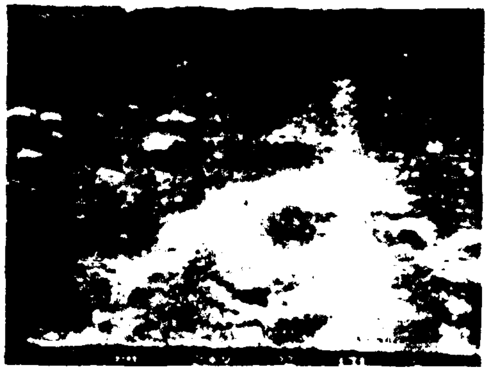
Continuation of Monitoring Programs

We propose to continue monitoring test coatings which are currently on exterior exposure until degradation significant enough to test the conclusions of the stochastic analysis have been achieved. The statistical techniques discussed will be applied to the materials over a longer time period in order to verify these models.

In addition, more basic information about the reliability of poly (urethane) coatings will be obtained. This will include further evaluation of ultra violet stabilizers and higher solids coatings.

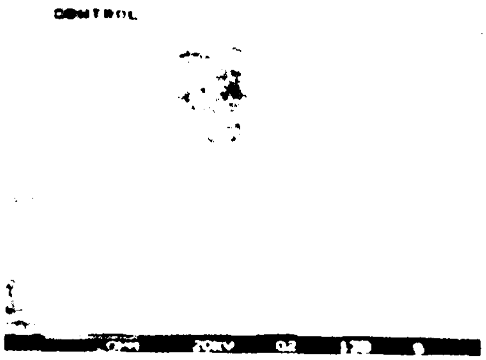
APPENDIX A

Scanning Electron Photomicrographs of Artificially Weathered Coatings

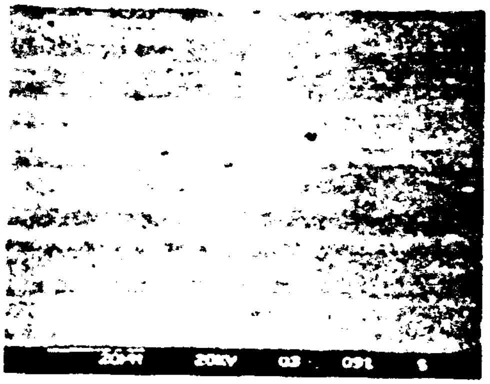


CLEAR/EPA 0 HRS. 10K X

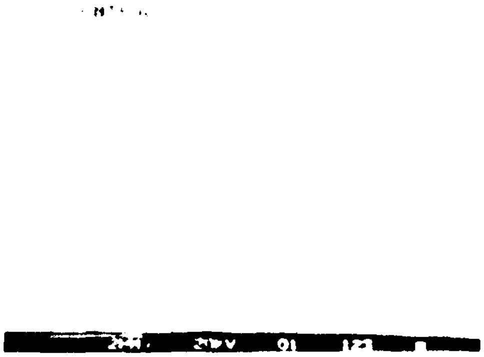
QUV CLEAR/EPA 200 HRS. 10K X



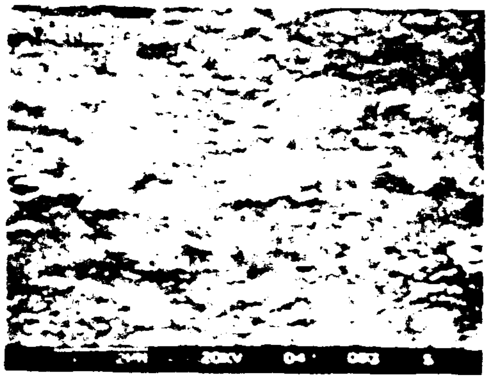
CLEAR/EPA 0 HRS. 1K X



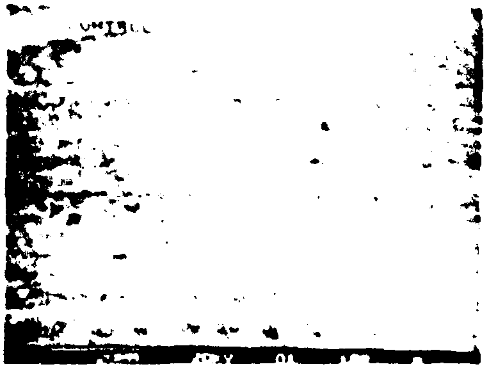
QUV CLEAR/EPA 200 HRS. 1K X



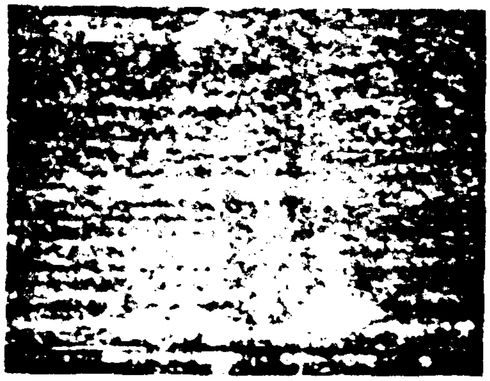
GRAY/EPA 0 HRS. 10K X



QUV GRAY/EPA 200 HRS. 10K X

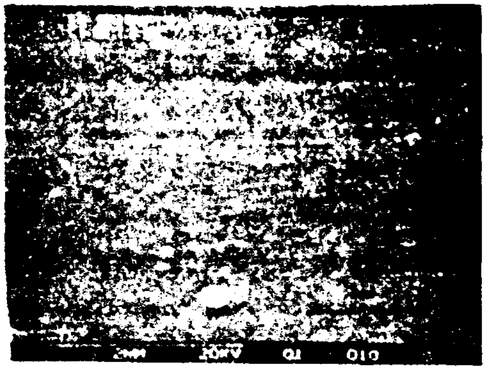


GRAY/EPA 0 HRS. 1K X

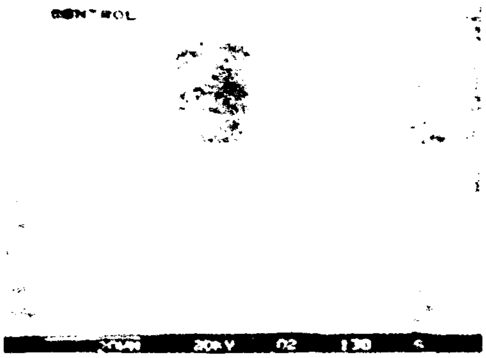


QUV GRAY/EPA 200 HRS. 1K X

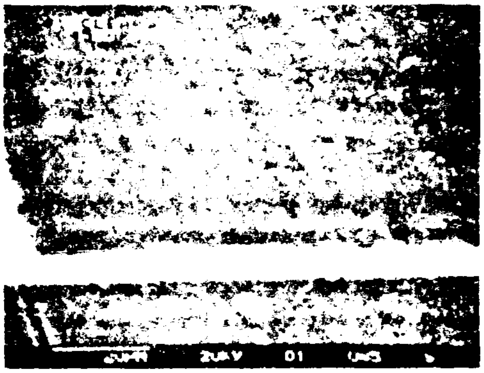
CLEAR/EPA 0 HRS. 10K X



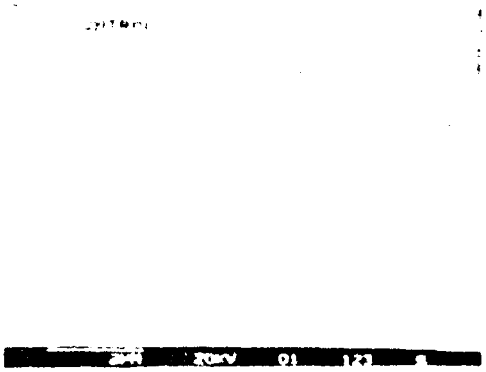
QUV CLEAR/EPA 645 HRS. 10K X



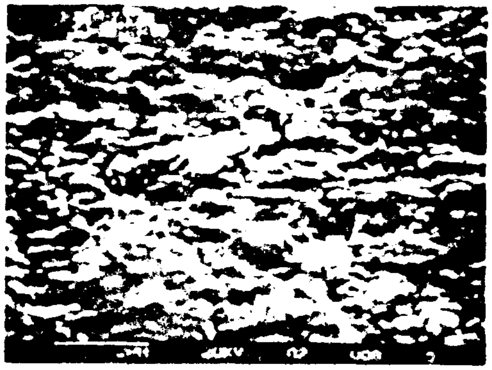
CLEAR/EPA 0 HRS. 1K X



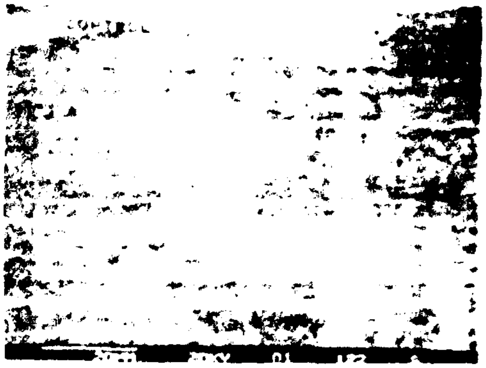
QUV CLEAR/EPA 645 HRS. 1K X



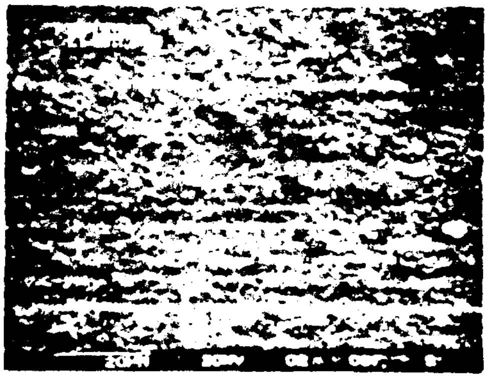
GRAY/EPA 0 HRS. 10K X



QUV GRAY/EPA 645 HRS. 10K X



GRAY/EPA 0 HRS. 1K X

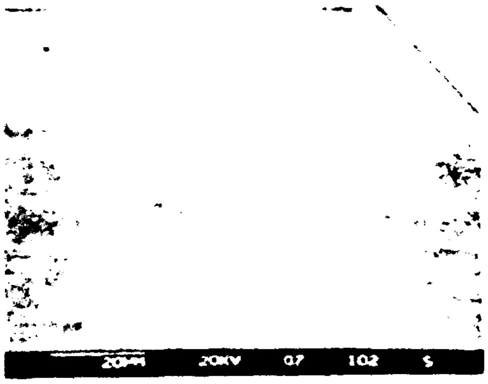


QUV GRAY/EPA 645 HRS. 1K X

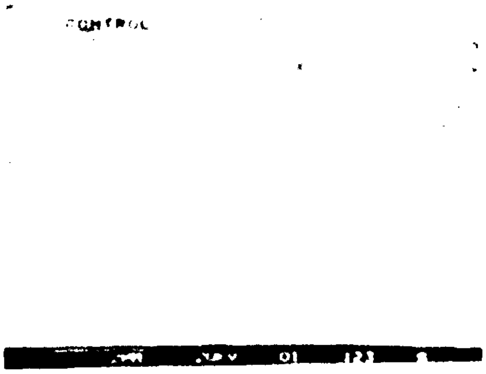
CLEAR/EPA 0 HRS. 10K X

QUV CLEAR/EPA 1000 HRS. 10K X

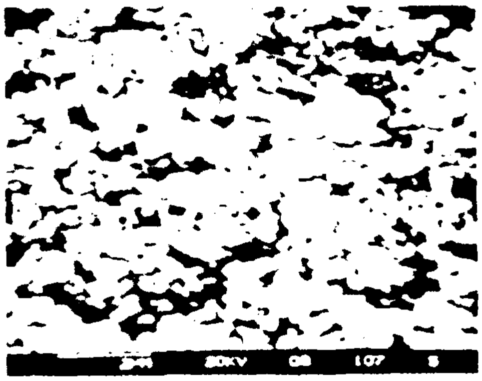
CLEAR/EPA 0 HRS. 1K X



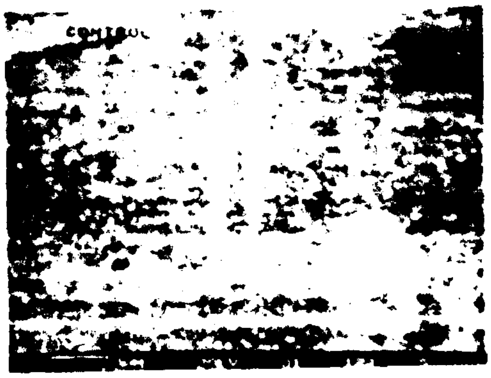
QUV CLEAR/EPA 1000 HRS. 1K X



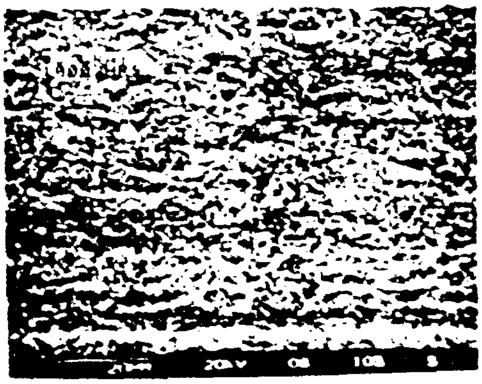
GRAY/EPA 0 HRS. 10K X



QUV GRAY/EPA 1000 HRS. 10K X

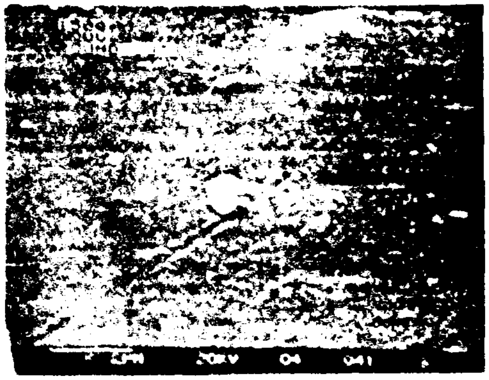


GRAY/EPA 0 HRS. 1K X

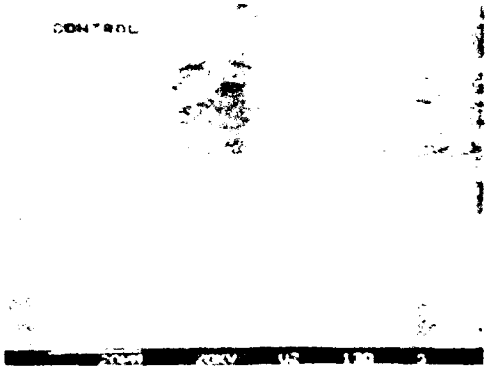


QUV GRAY/EPA 1000 HRS. 1K X

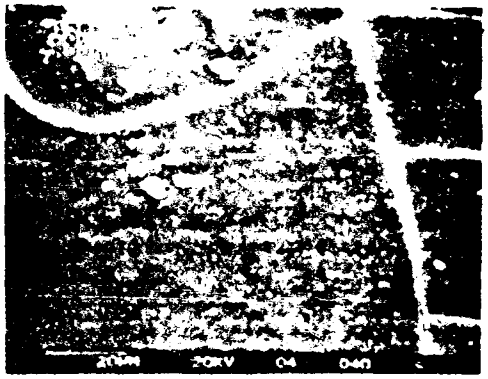
CLEAR/EPA 0 HRS. 10K X



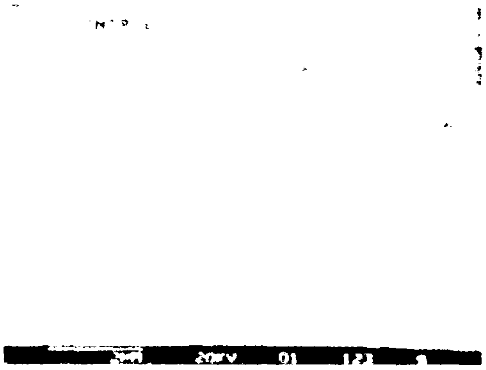
QUV CLEAR/EPA 1500 HRS. 10K X



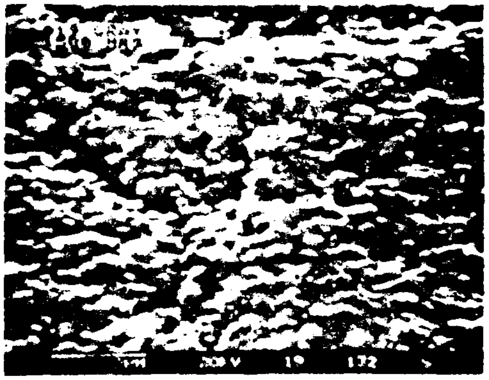
CLEAR/EPA 0 HRS. 1K X



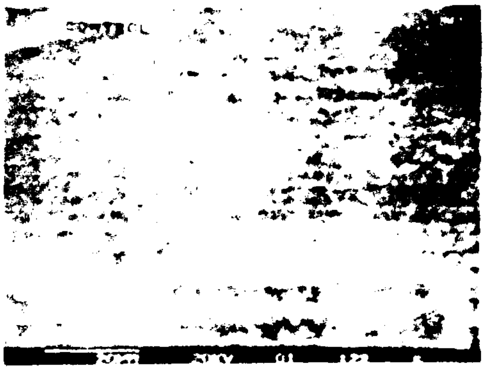
QUV CLEAR/EPA 1500 HRS. 1K X



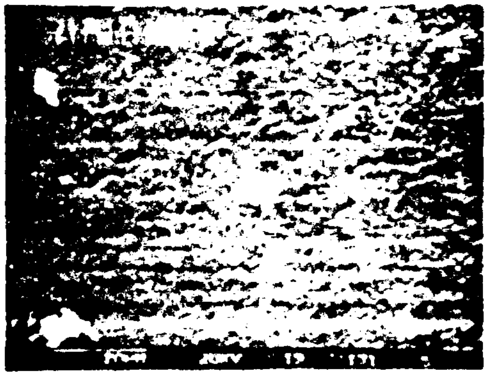
GRAY/EPA 0 HRS. 10K X



QUV GRAY/EPA 1500 HRS. 10K X

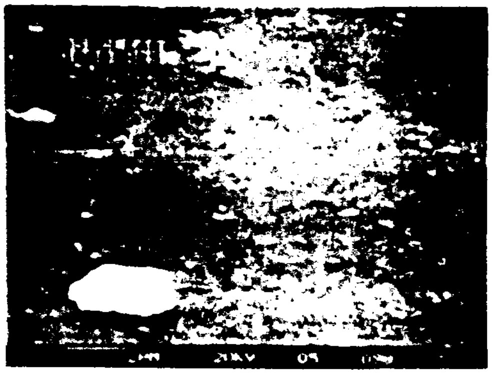


GRAY/EPA 0 HRS. 1K X

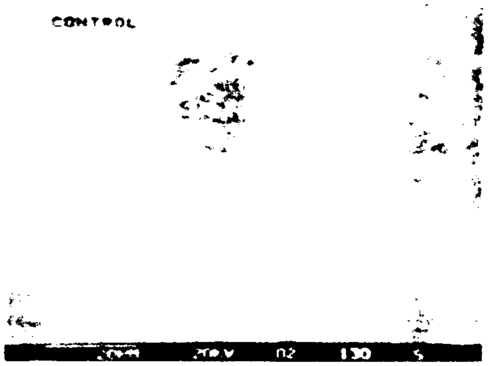


QUV GRAY/EPA 1500 HRS. 1K X

CLEAR/EPA 0 HRS. 10K X

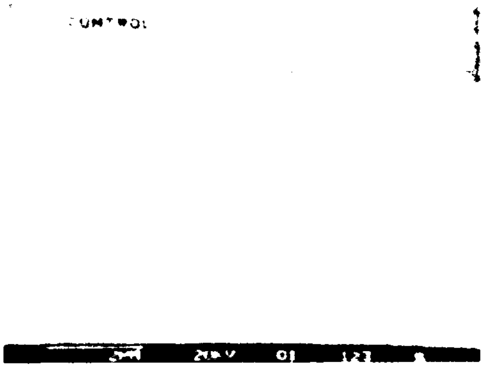


QUV CLEAR/EPA 3000 HRS. 10K X

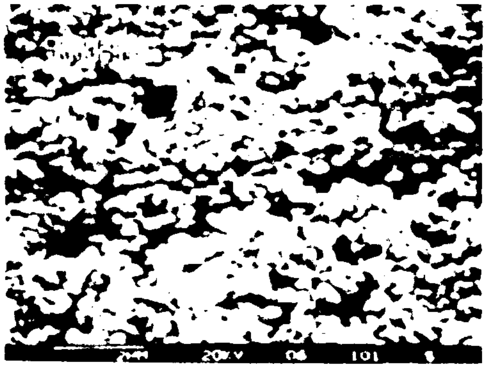


CLEAR/EPA 0 HRS. 1K X

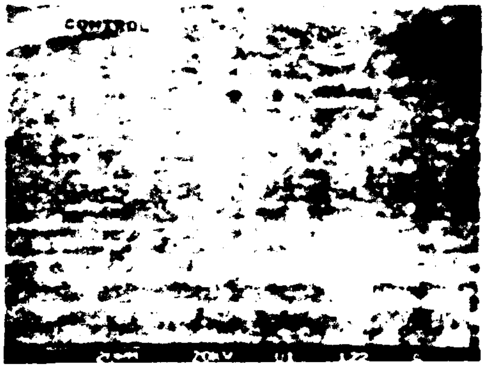
QUV CLEAR/EPA 3000 HRS. 1K X



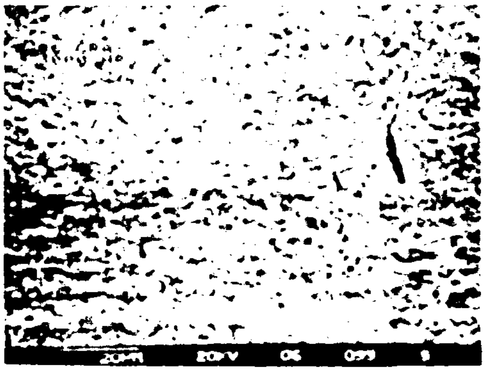
GRAY/EPA 0 HRS. 10K X



QUV GRAY/EPA 3000 HRS. 10K X

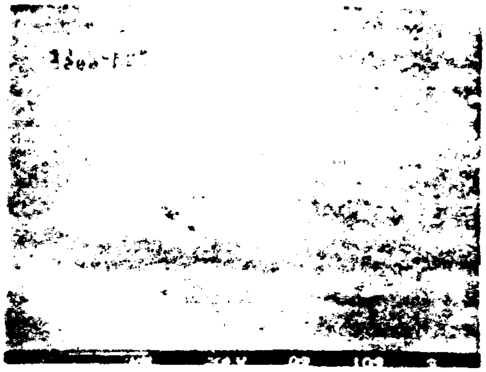


GRAY/EPA 0 HRS. 1K X

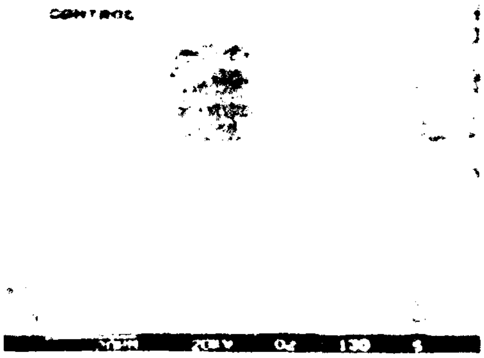


QUV GRAY/EPA 3000 HRS. 1K X

CLEAR/EPA 0 HRS. 10K X

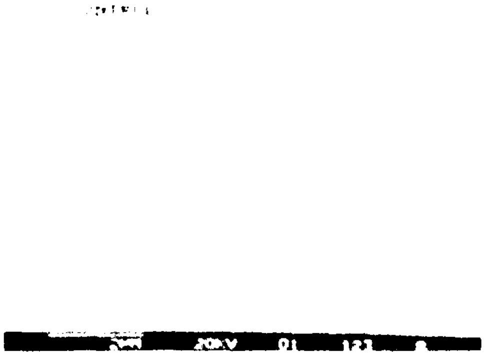


QUV CLEAR/EPA 5000 HRS. 10K X

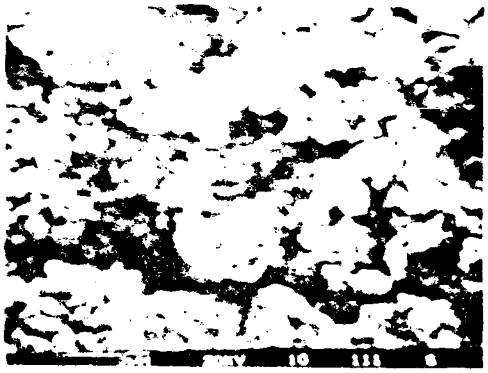


CLEAR/EPA 0 HRS. 1K X

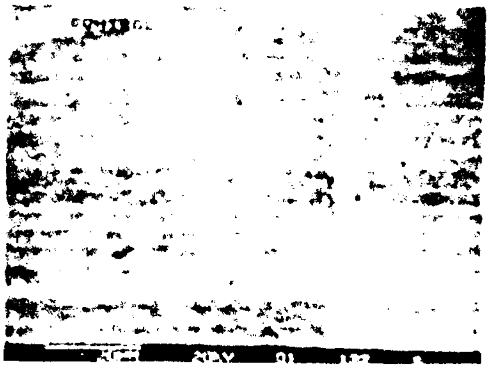
QUV CLEAR/EPA 5000 HRS. 1K X



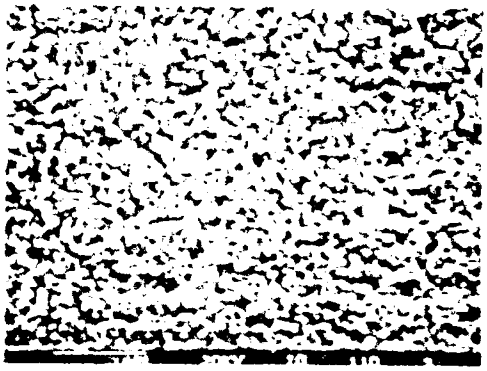
GRAY/EPA 0 HRS. 10K X



QUV GRAY/EPA 5000 HRS. 10K X



GRAY/EPA 0 HRS. 1K X



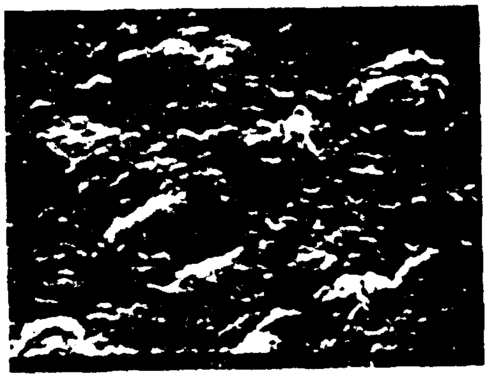
QUV GRAY/EPA 5000 HRS. 1K X

APPENDIX B

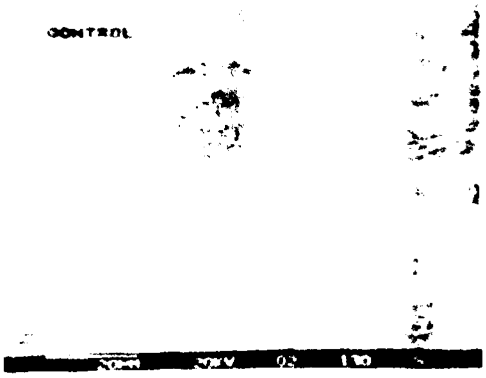
Scanning Electron Photomicrographs of Naturally Weathered Coatings

Coatings Without Ultra Violet Stabilizers

CLEAR/EPA 0 HRS. 10K X

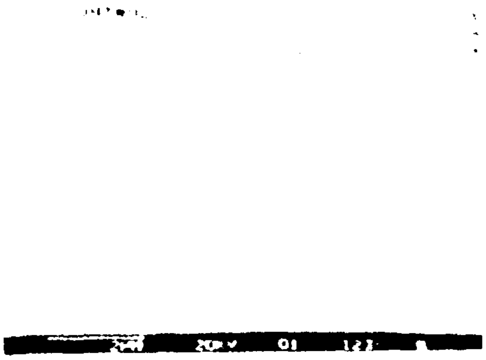


64212 CLEAR/EPA 12 MOS. 10K X

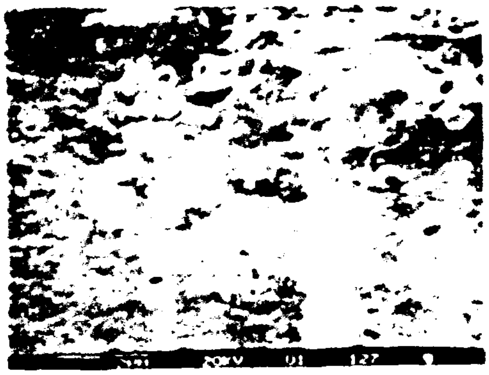


CLEAR/EPA 0 HRS. 1K X

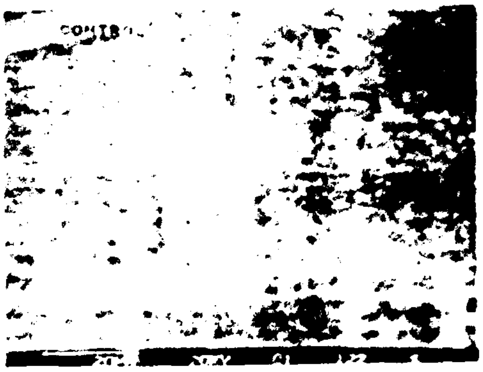
64212 CLEAR/EPA 12 MOS. 1K X



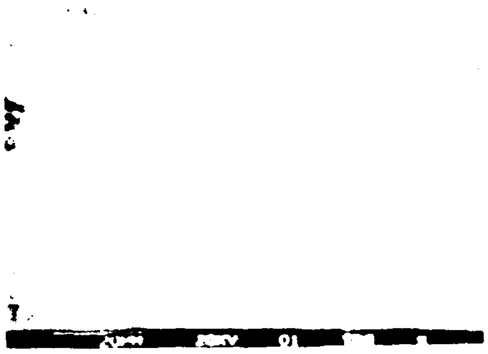
GRAY/EPA 0 HRS. 10K X



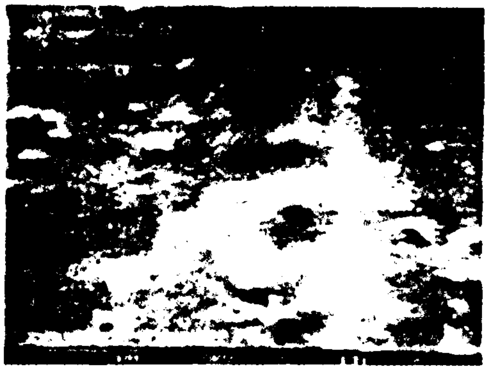
64202 GRAY/EPA 12 MOS. 10K X



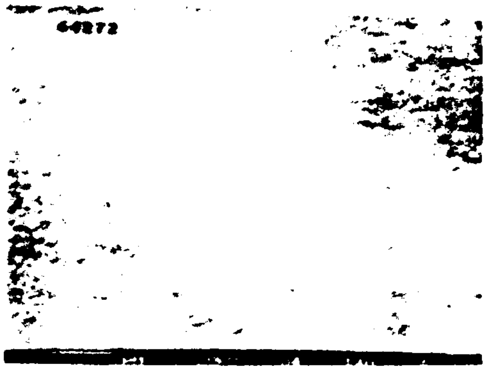
GRAY/EPA 0 HRS. 1K X



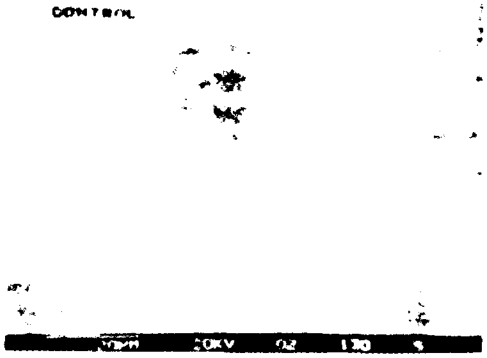
64202 GRAY/EPA 12 MOS. 1K X



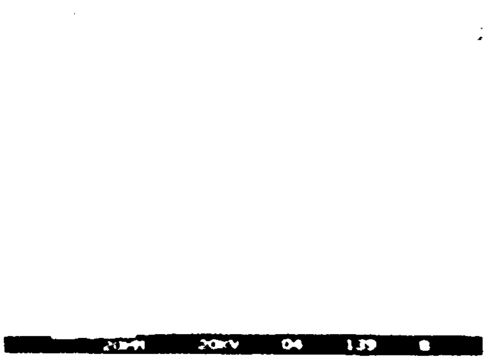
CLEAR/EPA 0 HRS. 10K X



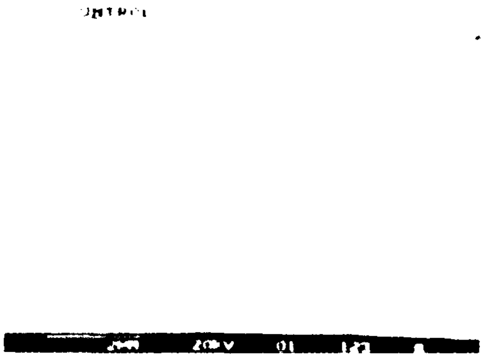
64272 CLEAR/EPA 12 MOS. BB 10K X



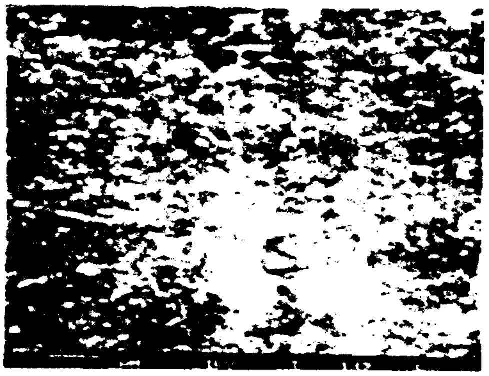
CLEAR/EPA 0 HRS. 1K X



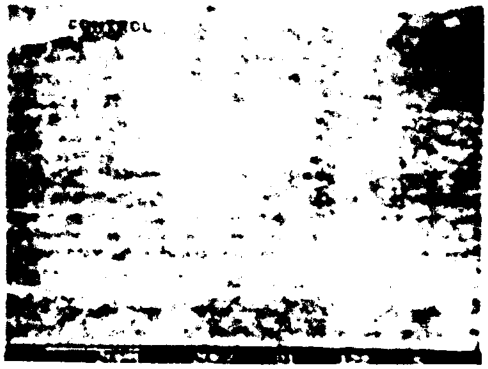
64272 CLEAR/EPA 12 MOS. BB 1K X



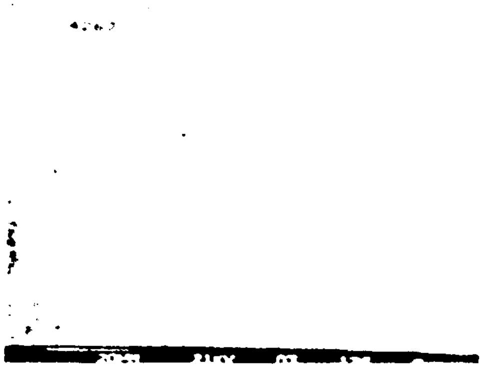
GRAY/EPA 0 HRS. 10K X



64262 GRAY/EPA 12 MOS. BB 10K X

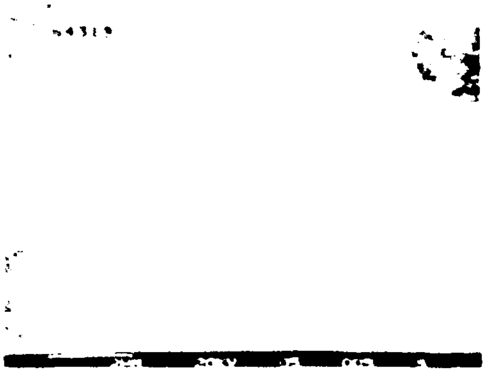


GRAY/EPA 0 HRS. 1K X

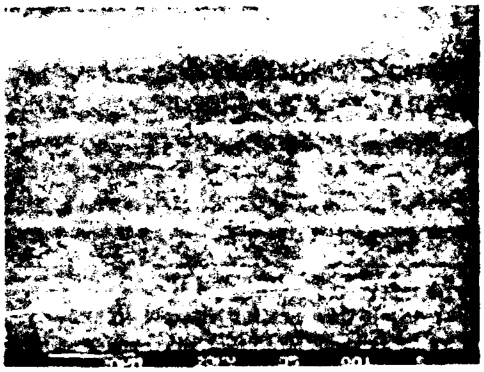


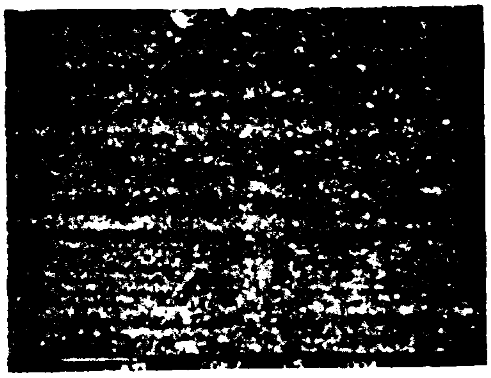
64262 GRAY/EPA 12 MOS. BB 1K X

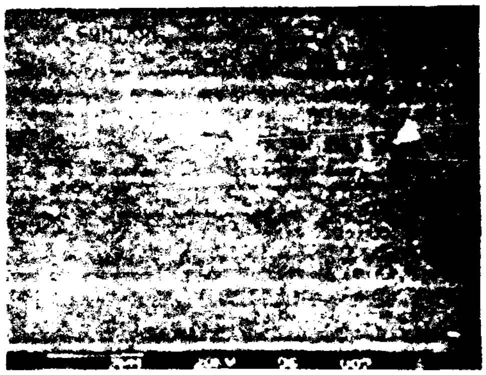

GRAY/PS 0 HRS. 10K X



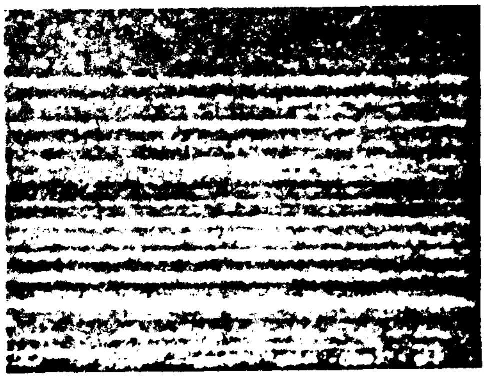
64319 GRAY/PS 12 MOS. 10K X

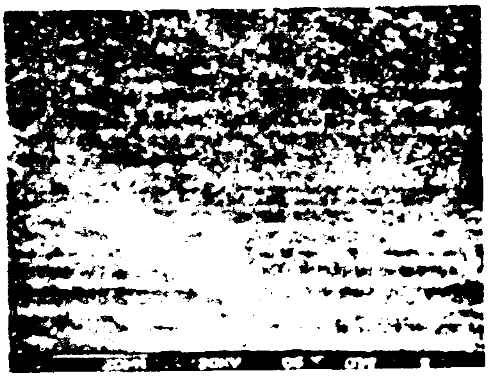

GRAY/PS 0 HRS. 1K X


64319 GRAY/PS 12 MOS. 1K X

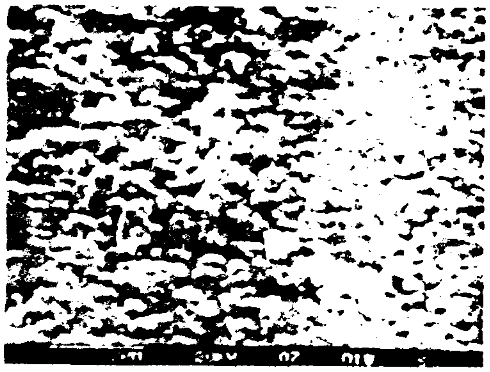

GRAY/WR 0 HRS. 10K X


64339 GRAY/WR 12 MOS. 10K X

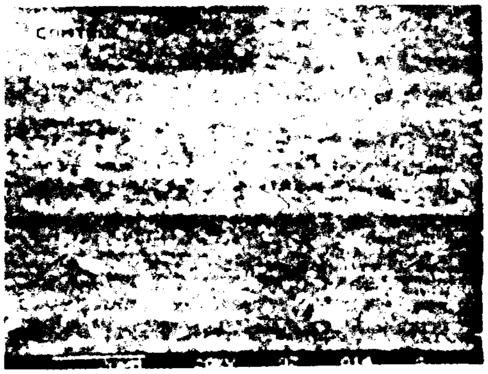

GRAY/WR 0 HRS. 1K X


64339 GRAY/WR 12 MOS. 1K X

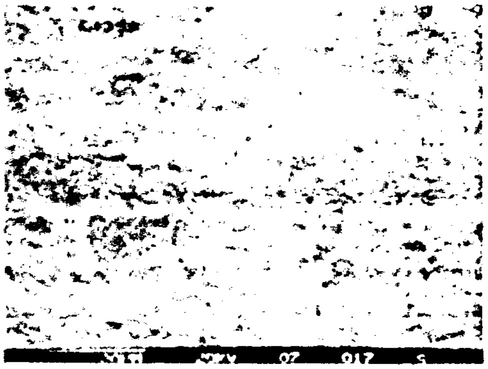
DS GRAY/EPA 0 HRS. 10K X



64359 DS GRAY/EPA 12 MOS. 10K X

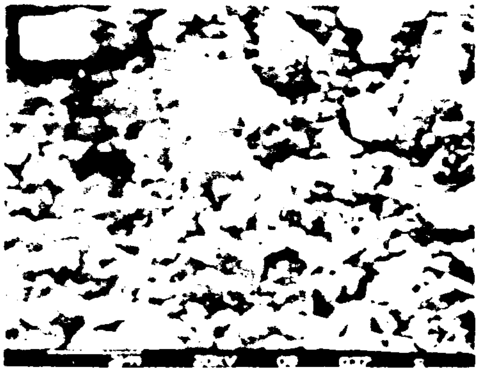


DS GRAY/EPA 0 HRS. 1K X

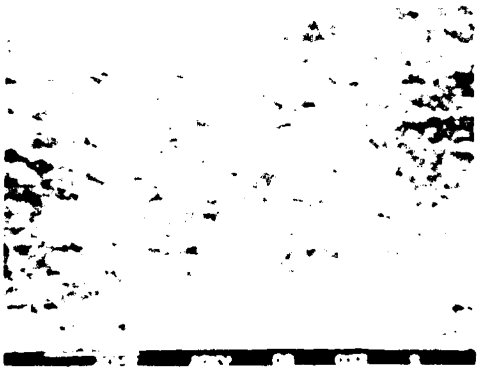


64359 DS GRAY/EPA 12 MOS. 1K X

PRIMER ONLY 0 HRS. 10K X

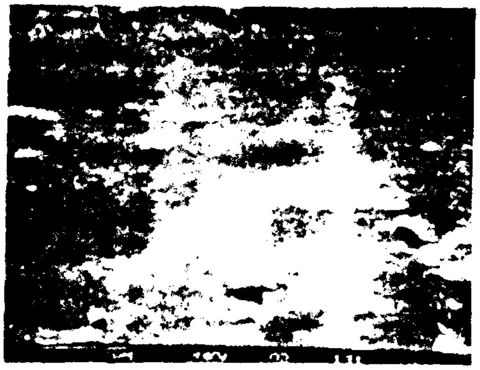


64461 PRIMER ONLY 12 MOS. 10K X

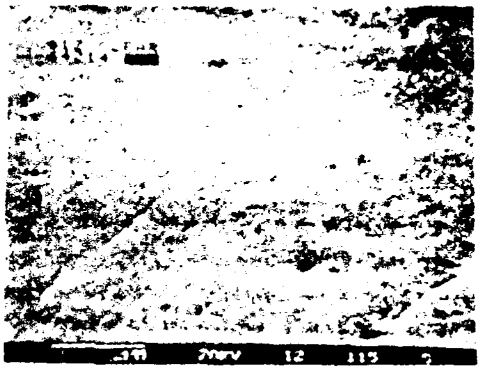


PRIMER ONLY 0 HRS. 1K X

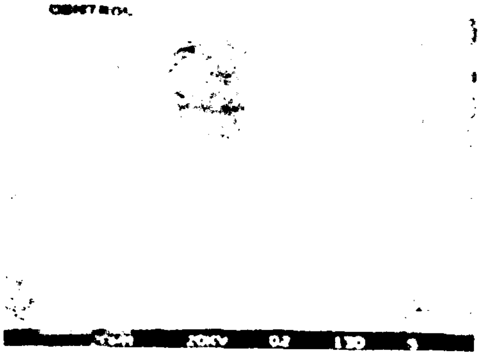
64461 PRIMER ONLY 12 MOS. 1K X



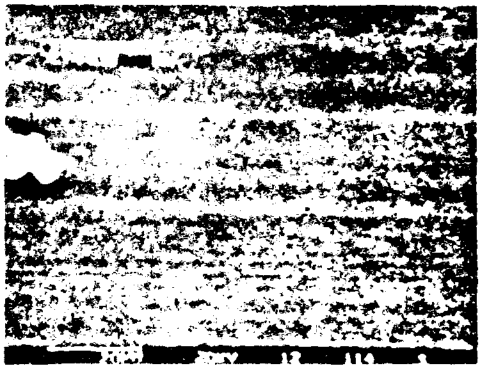
CLEAR/EPA 0 HRS. 10K X



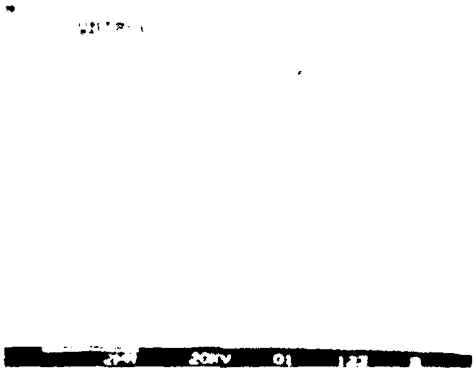
64214 CLEAR/EPA 18 MOS. 10K X



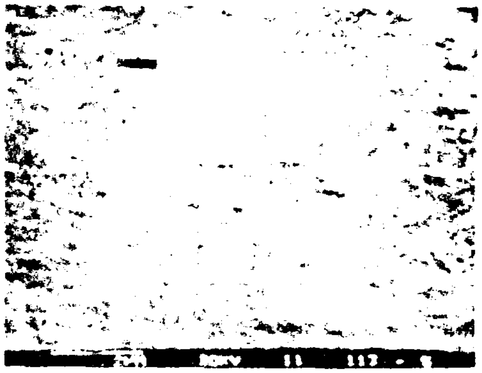
CLEAR/EPA 0 HRS. 1 K X



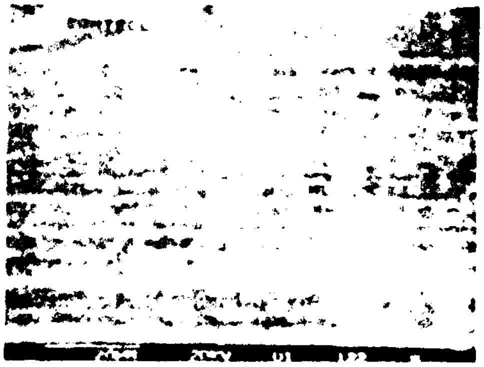
64214 CLEAR/EPA 18 MOS. 1K X



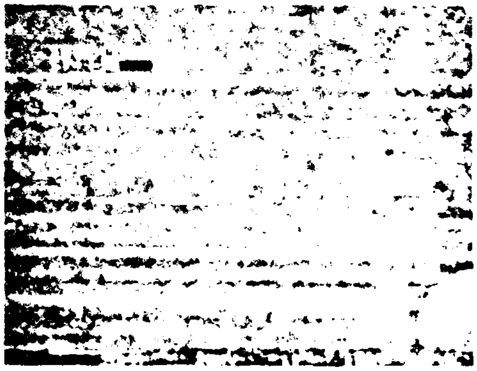
GRAY/EPA 0 HRS. 10K X



64205 GRAY/EPA 18 MOS. 10K X



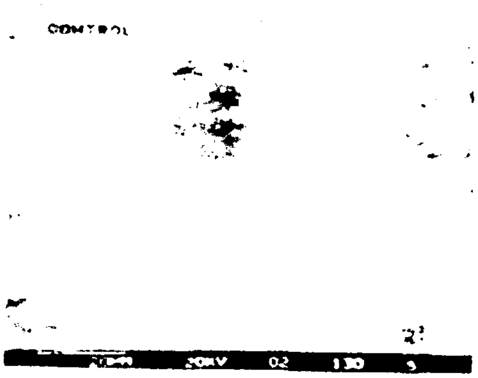
GRAY/EPA 0 HRS. 1K X



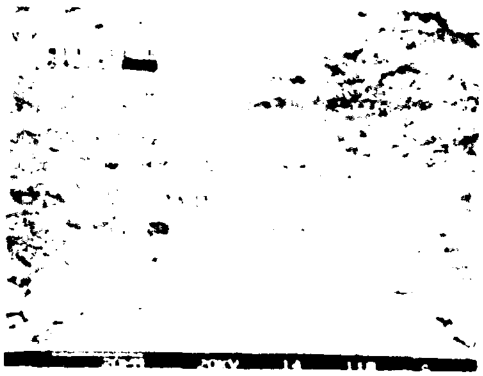
64205 GRAY/EPA 18 MOS. 1K X

CLEAR/EPA 0 HRS. 10K X

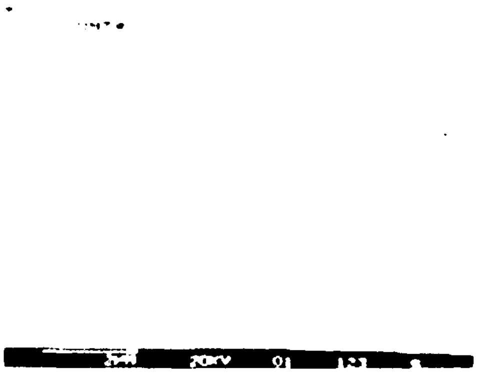
64275 CLEAR/EPA 18 MOS. BB 18K X



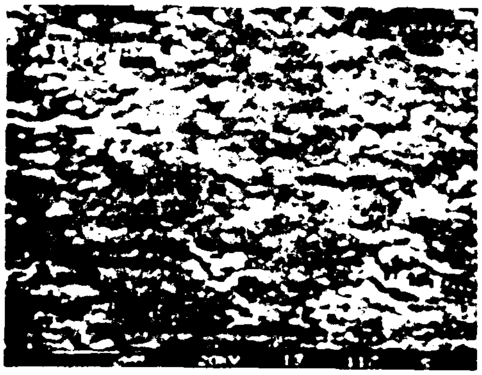
CLEAR/EPA 0 HRS. 1K X



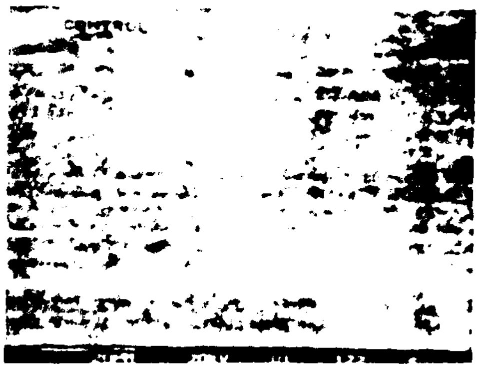
64275 CLEAR/EPA 18 MOS. BB 1K X



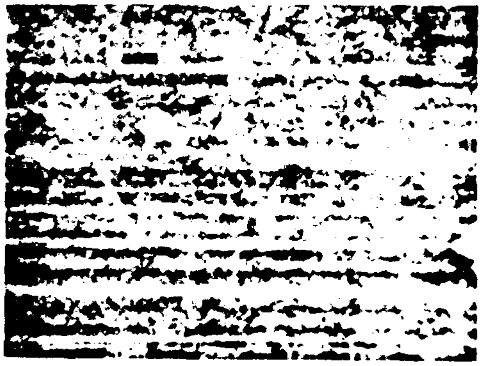
GRAY/EPA 0 HRS. 10K X



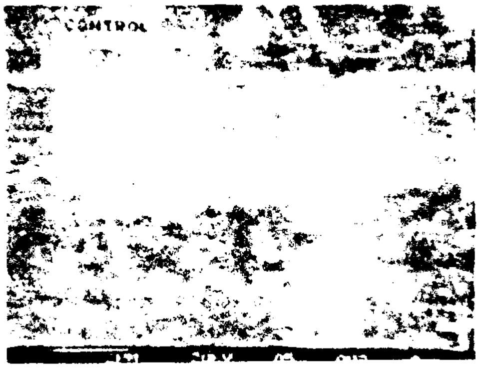
64265 GRAY/EPA 18 MOS. BB 10K X



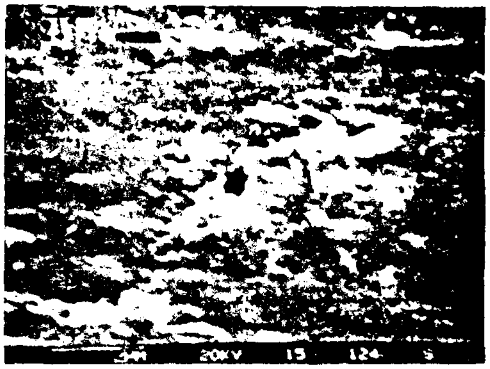
GRAY/EPA 0 HRS. 1K X



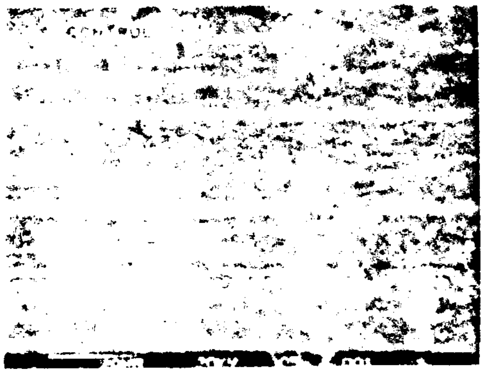
64265 GRAY/EPA 18 MOS. BB 1K X



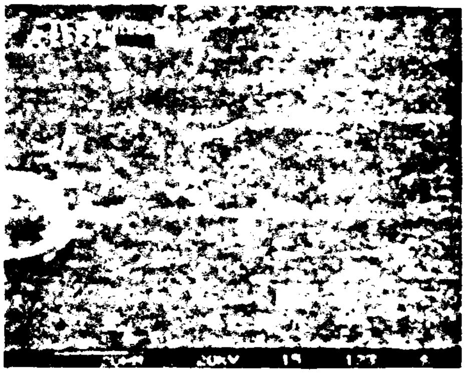
GRAY/PS 0 HRS. 10K X



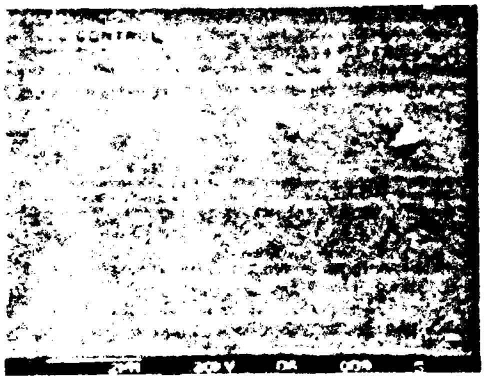
64321 GRAY/PS 18 MOS. 10K X



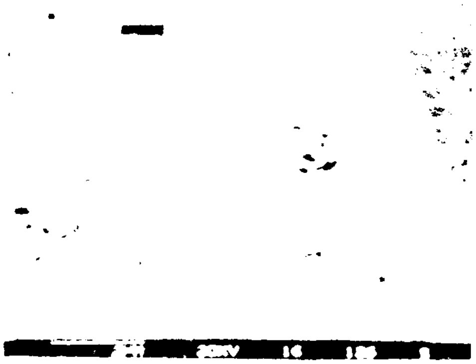
GRAY/PS 0 HRS. 1K X



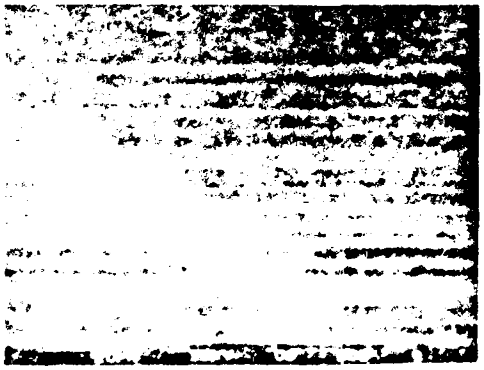
64321 GRAY/PS 18 MOS. 1K X



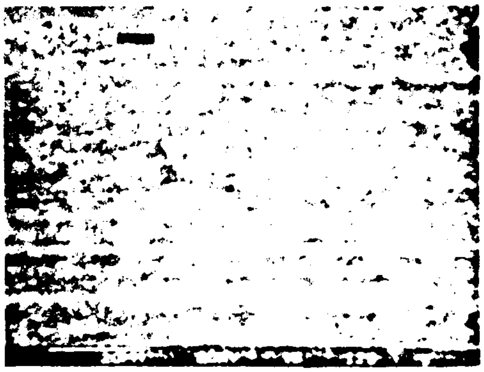
GRAY/WR 0 HRS. 10K X



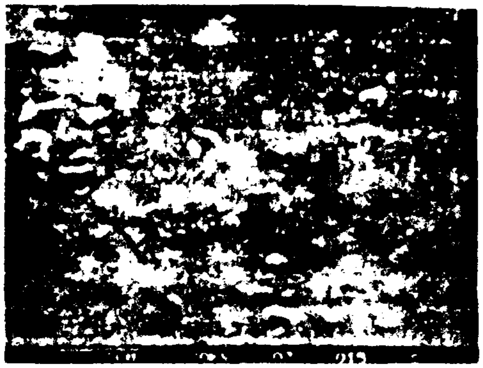
64341 GRAY/WR 18 MOS. 10K X

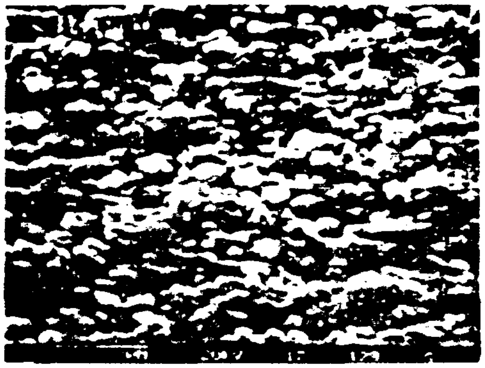


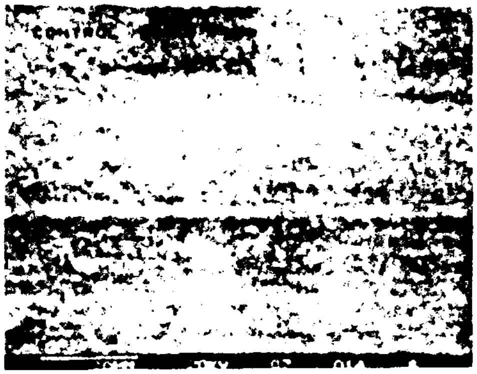
GRAY/WR 0 HRS. 1K X

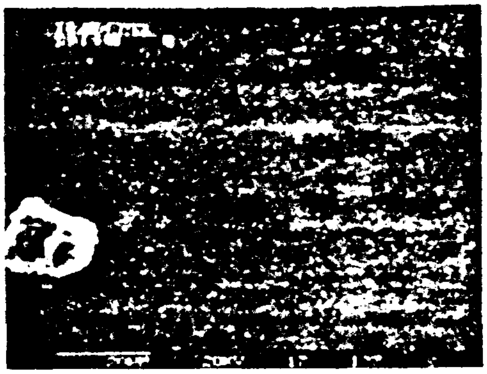


64341 GRAY/WR 18 MOS. 1K X

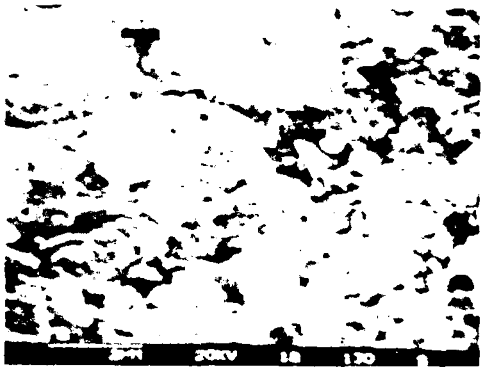

DS GRAY/EPA 0 HRS. 10K X

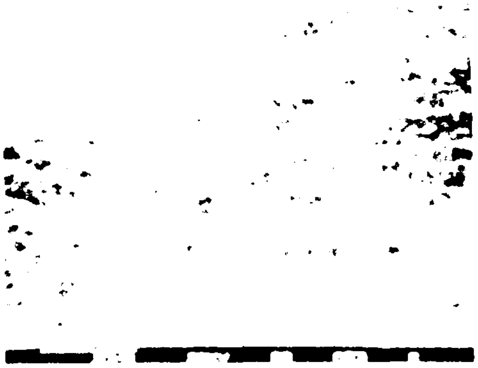

64361 DS GRAY/EPA 18 MOS. 10K X

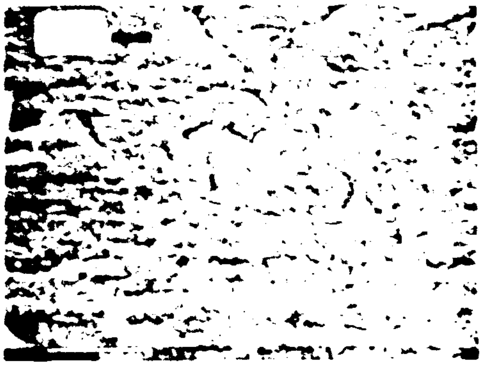

DS GRAY/EPA 0 HRS. 1K X


64361 DS GRAY/EPA 18 MOS. 1K X


PRIMER ONLY 0 HRS. 10K X


64464 PRIMER ONLY 18 MOS. 10K X

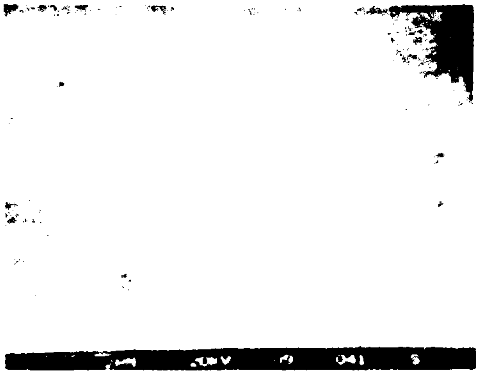

PRIMER ONLY 0 HRS. 1K X


64464 PRIMER ONLY 18 MOS. 1K X

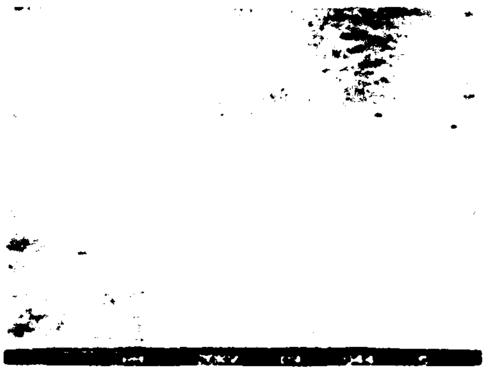
APPENDIX C

Scanning Electron Photomicrographs of Naturally Weathered Coatings

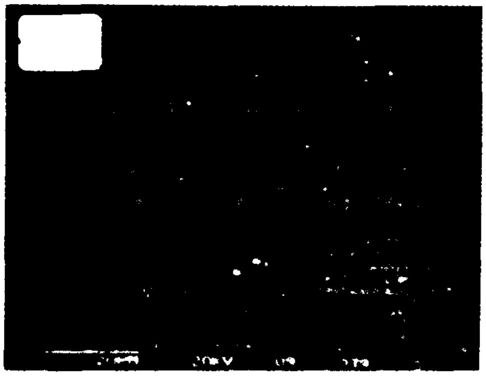
Coatings With Ultra Violet Stabilizers



A T-328 CLEAR/EPA 0 HRS. 10K X

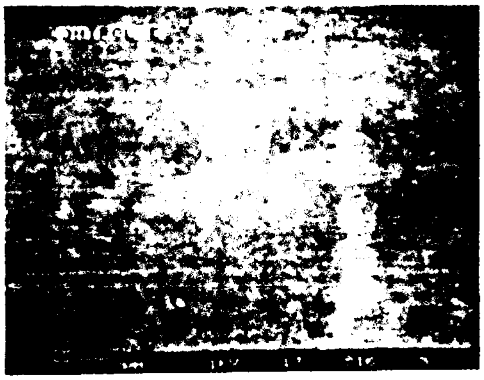


65111A T-328 CLEAR/EPA 12 MOS. 10K X

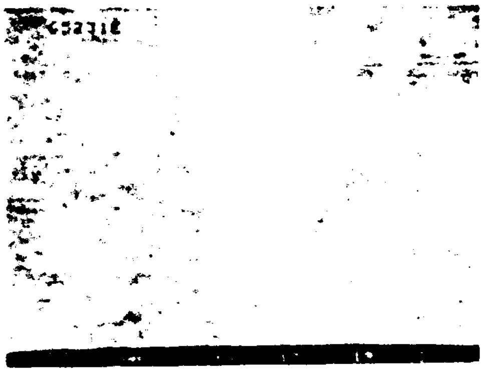


A T-328 CLEAR/EPA 0 HRS. 1K X

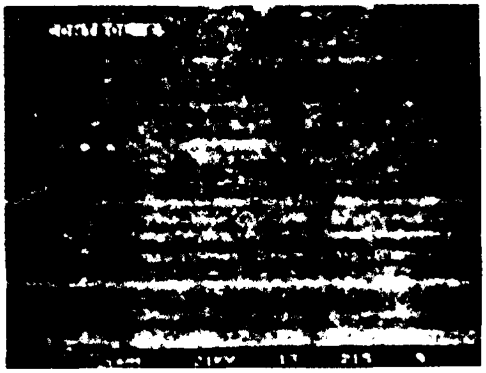
65111A T-328 CLEAR/EPA 12 MOS. 1K X



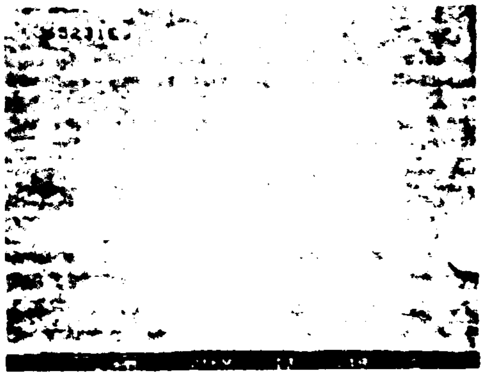
E T-328 GRAY/EPA 0 HRS. 10K X



65231E T-328 GRAY/EPA 12 MOS. 10K X



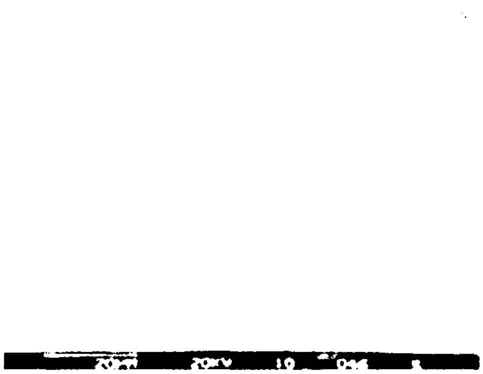
E T-328 GRAY/EPA 0 HRS. 1K X



65231E T-328 GRAY/EPA 12 MOS. 1K X

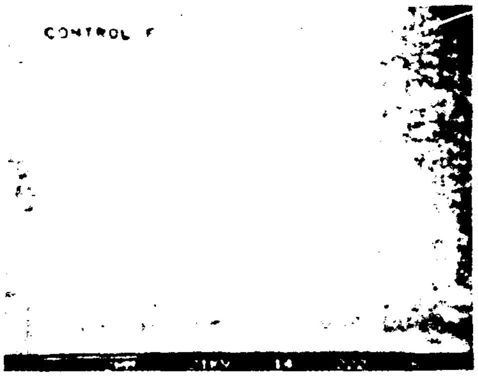
B T-770 CLEAR/EPA 0 HRS. 10K X

65141B T-770 CLEAR/EPA 12 MOS. 10K X

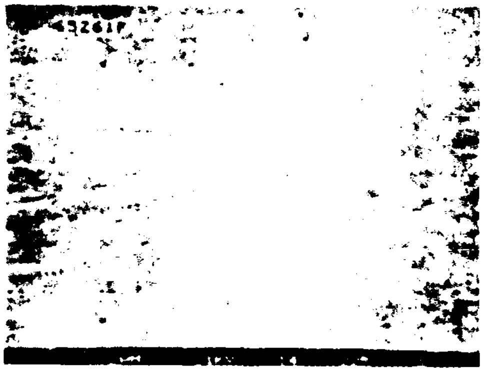


B T-770 CLEAR/EPA 0 HRS. 1K X

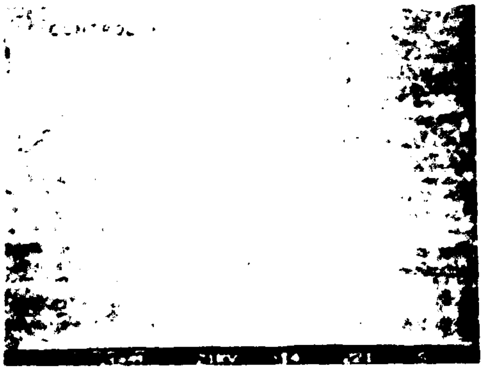
65141B T-770 CLEAR/EPA 12 MOS. 1K X



F T-770 GRAY/EPA 0 HRS. 10K X

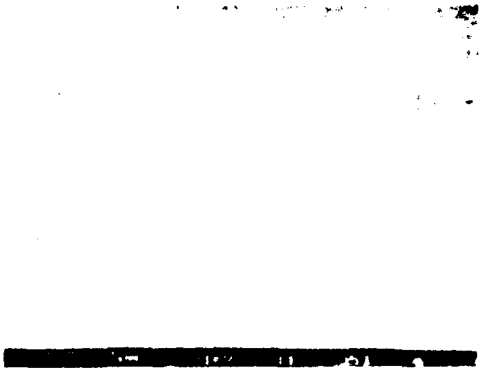


65261F T-770 GRAY/EPA 12 MOS. 10K X

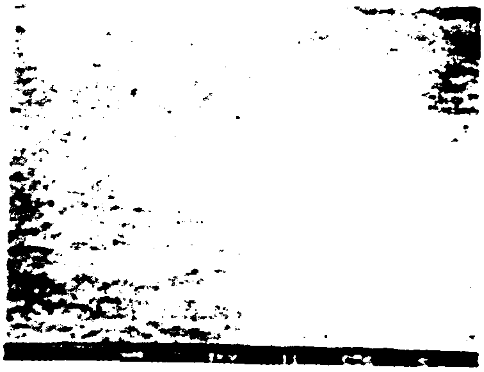


F T-770 GRAY/EPA 0 HRS. 1K X

65261F T-770 GRAY/EPA 12 MOS. 1K X



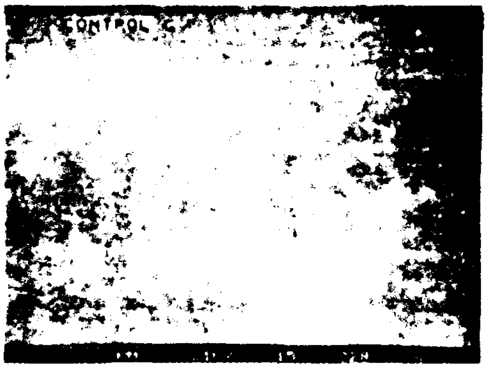
C UV-24 CLEAR/EPA 0 HRS. 10K X



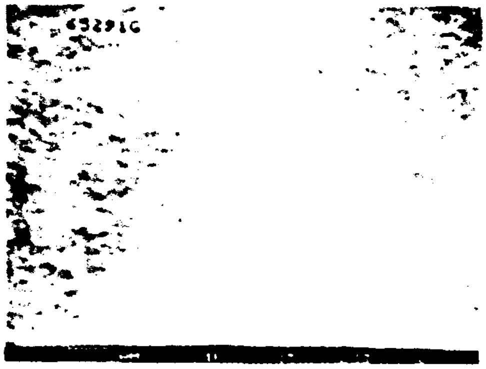
65171C UV-24 CLEAR/EPA 12 MOS. 10K X

C UV-24 CLEAR/EPA 0 HRS. 1K X

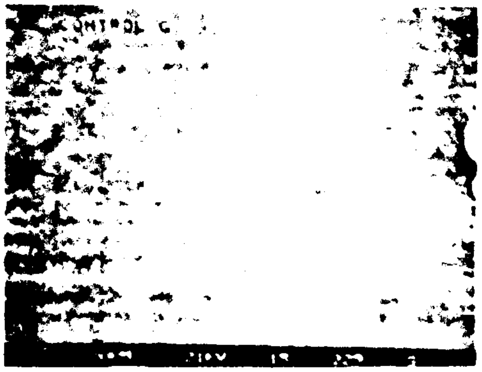
65171C UV-24 CLEAR/EPA 12 MOS. 1K X



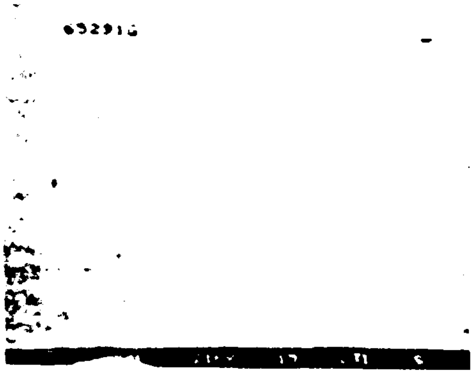
G UV-24 GRAY/EPA 0 HRS. 10K X



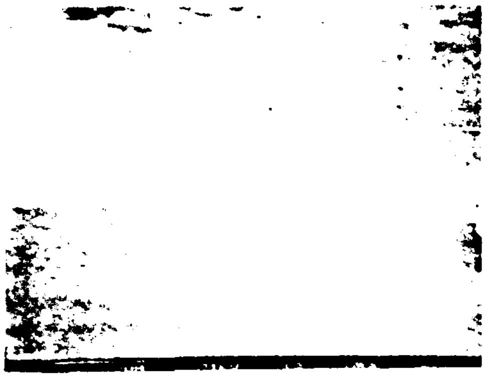
65291G UV-24 GRAY/EPA 12 MOS. 10K X



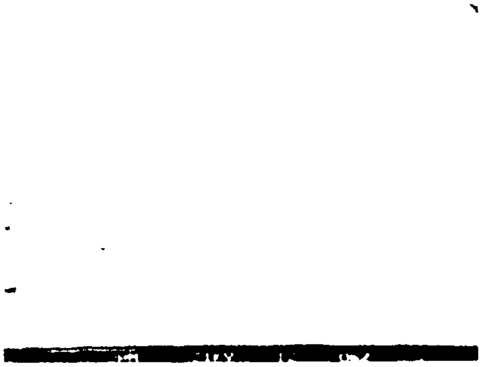
G UV-24 GRAY/EPA 0 HRS. 1K X



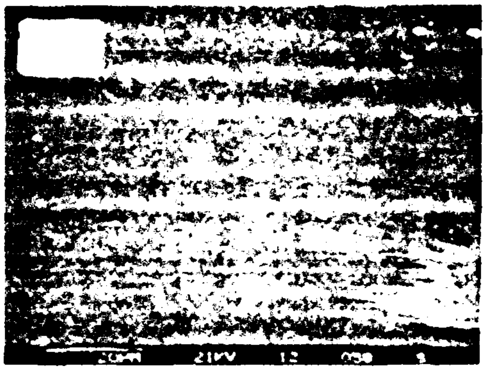
65291G UV-24 GRAY/EPA 12 MOS. 1K X



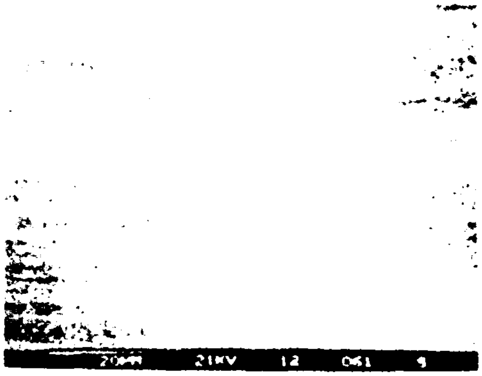
D T-328/770 CLEAR/EPA 0 HRS. 10K X



65201D T-328/770 CLEAR/EPA 12 MOS. 10K X

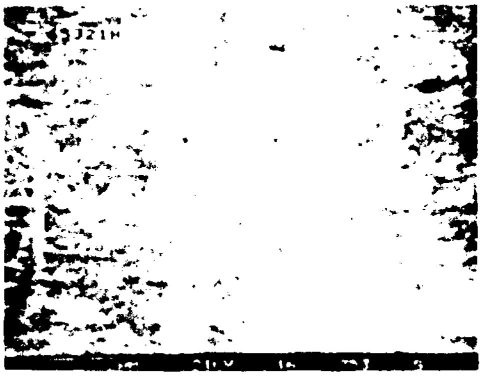


D T-328/770 CLEAR/EPA 0 HRS. 1K X

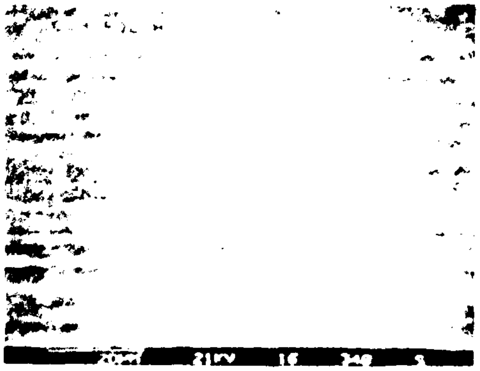


65201D T-328/770 CLEAR/EPA 12 MOS. 1K X

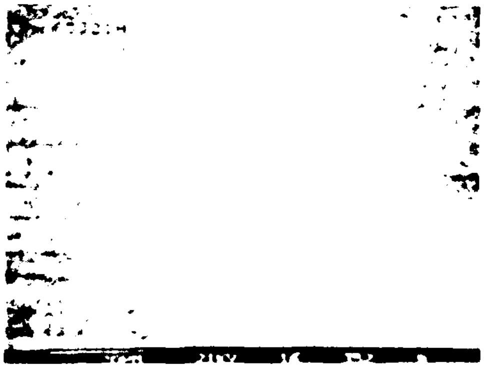
H T-328/770 GRAY/EPA 0 HRS. 10K X



65321H T-328/770 GRAY/EPA 12 MOS. 10K X



H T-328/770 GRAY/EPA 0 HRS. 1K X



65321H T-328/770 GRAY/EPA 12 MOS. 1K X

APPENDIX D

Dynamic Mechanical Analysis Thermograms

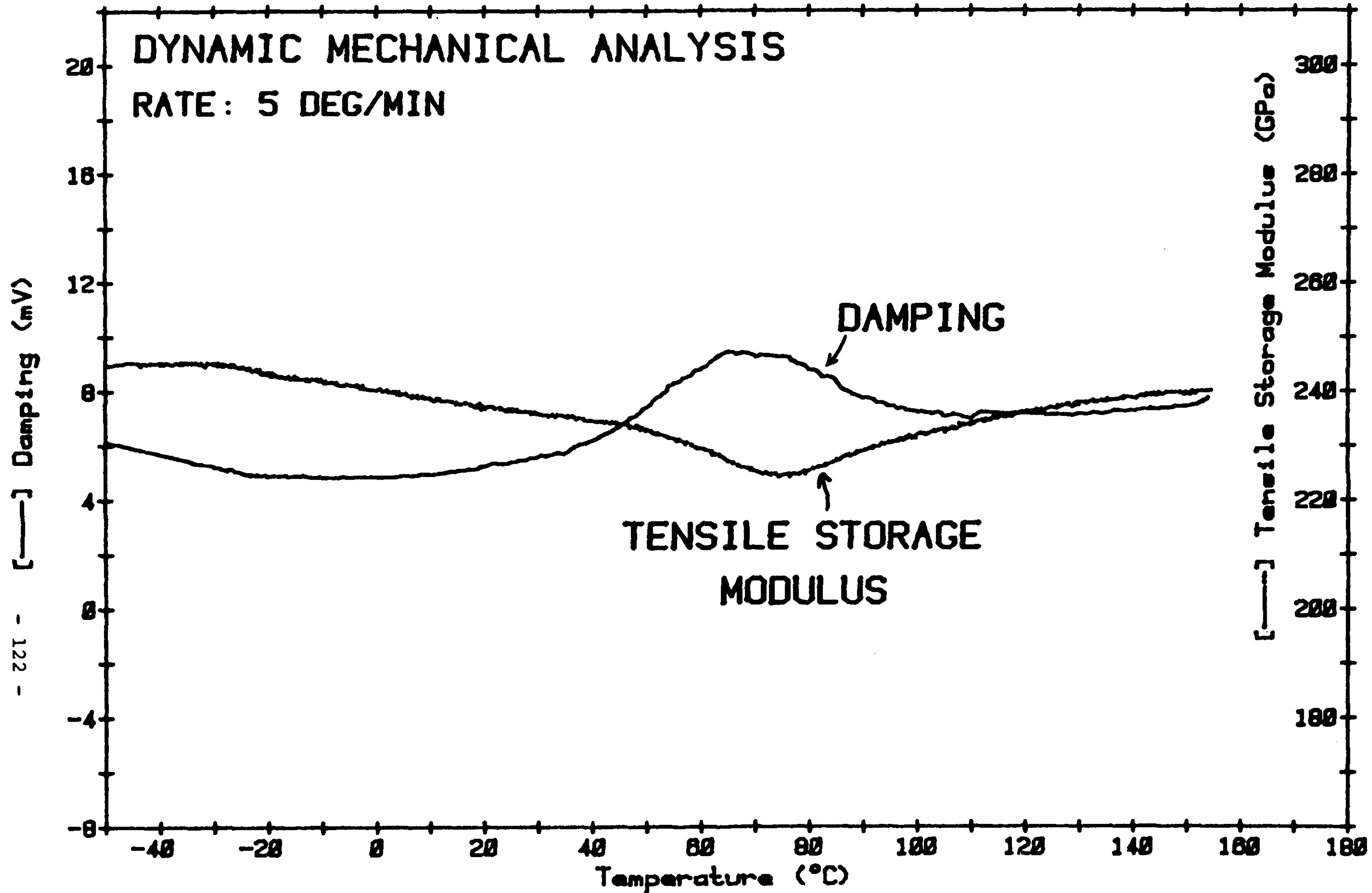


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 0 HOURS

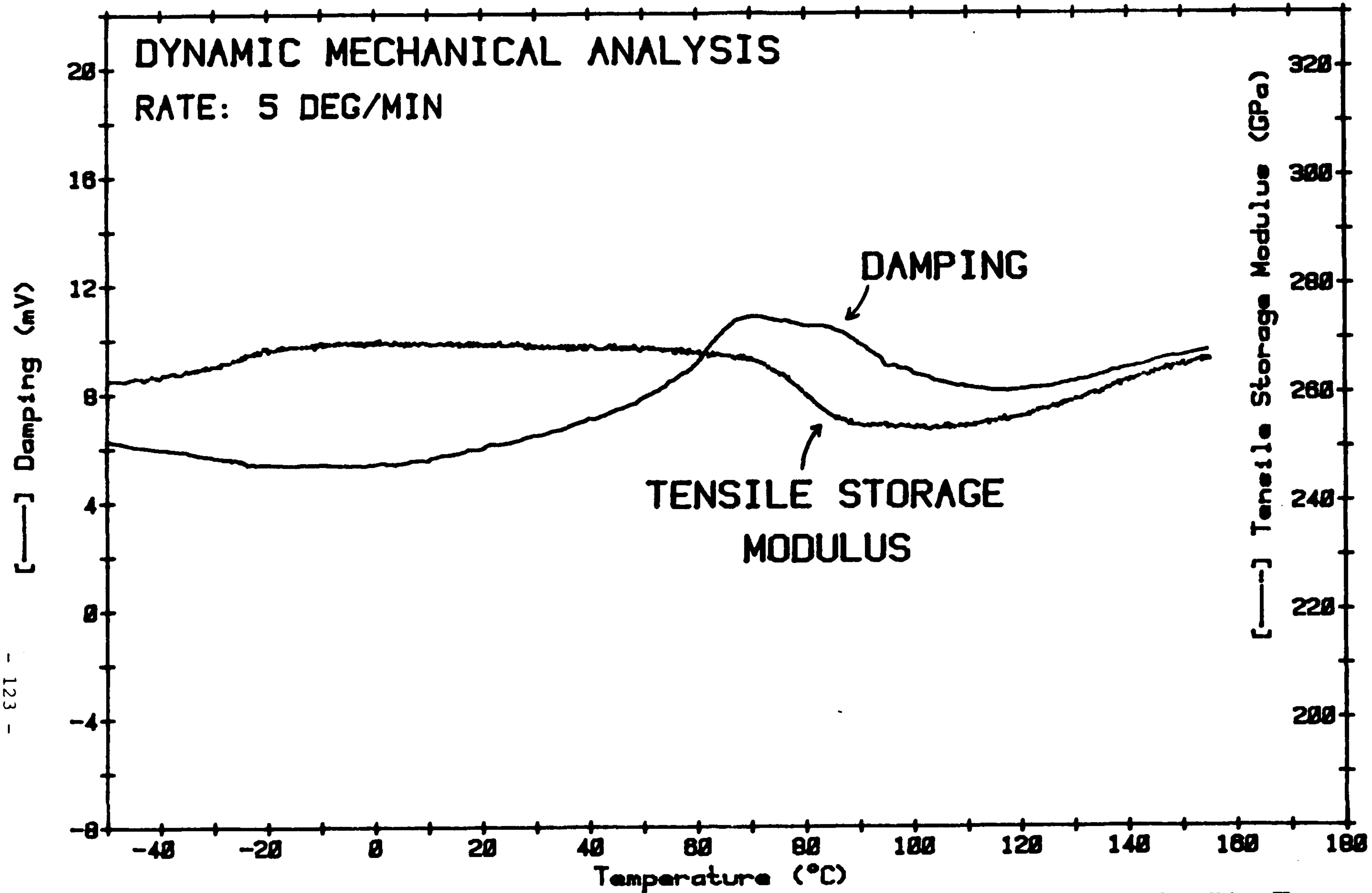


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT – QUV 200 HOURS

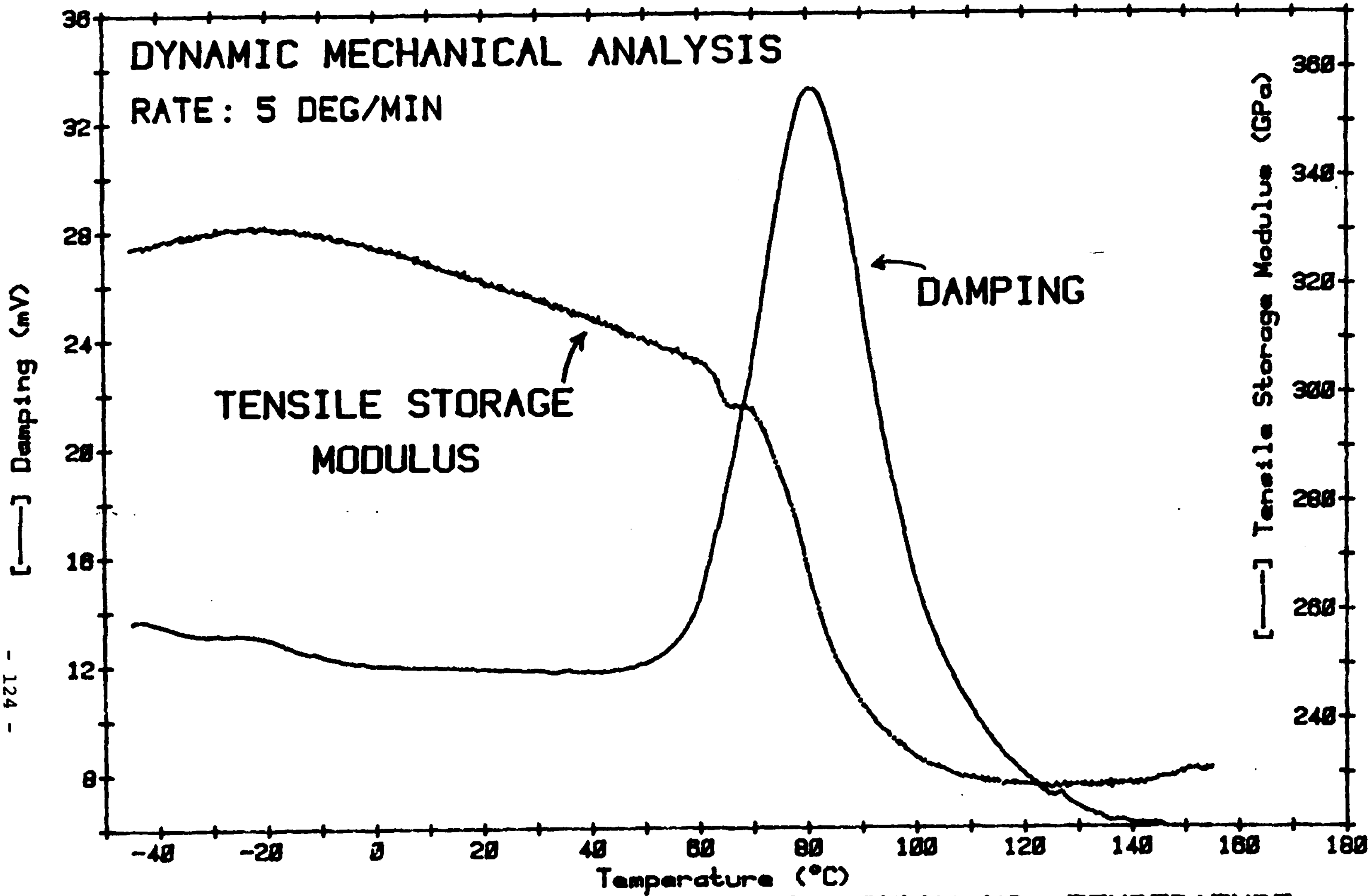


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT – QUV 1000 HOURS

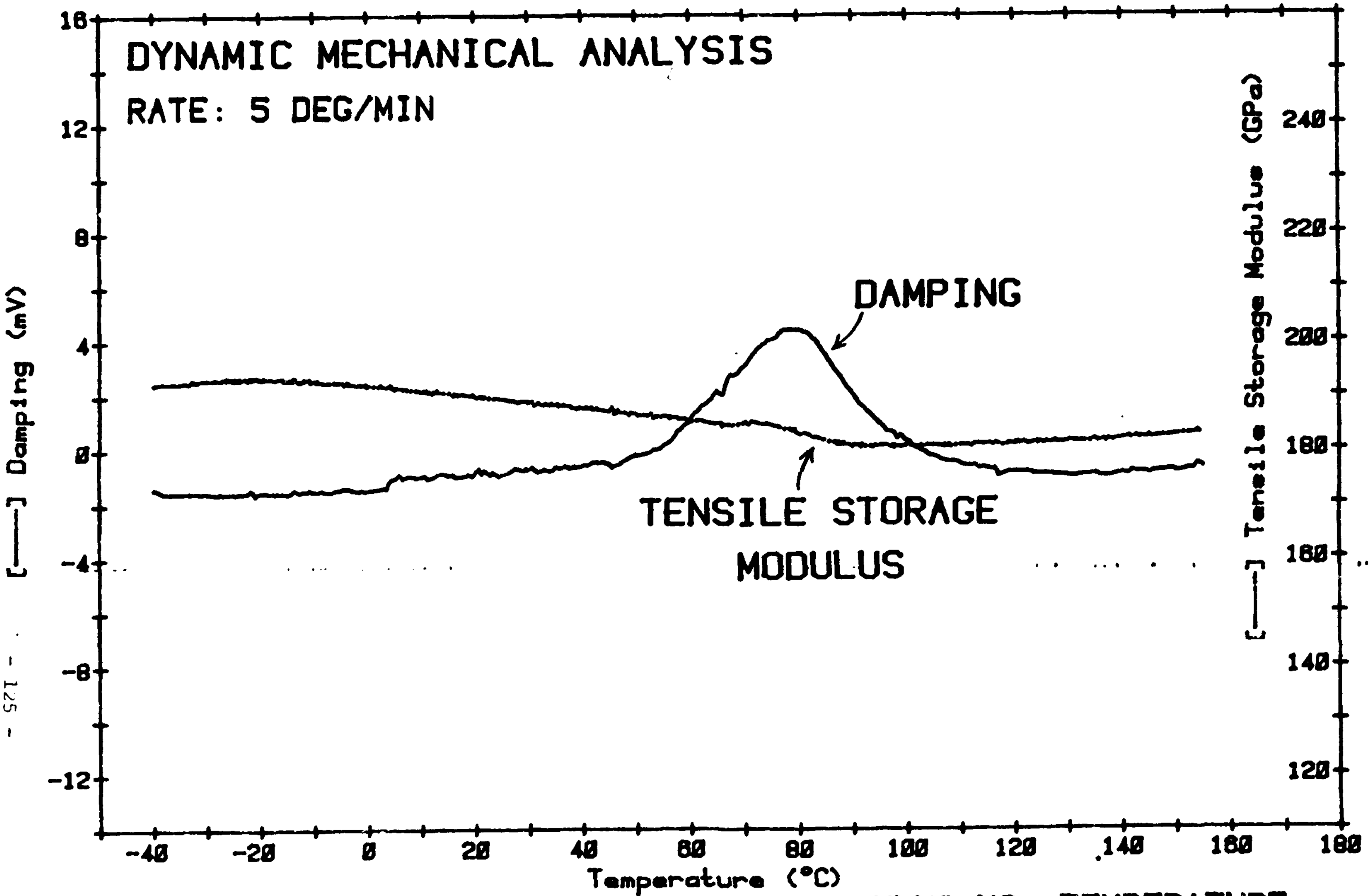


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT – QUV 1500 HOURS

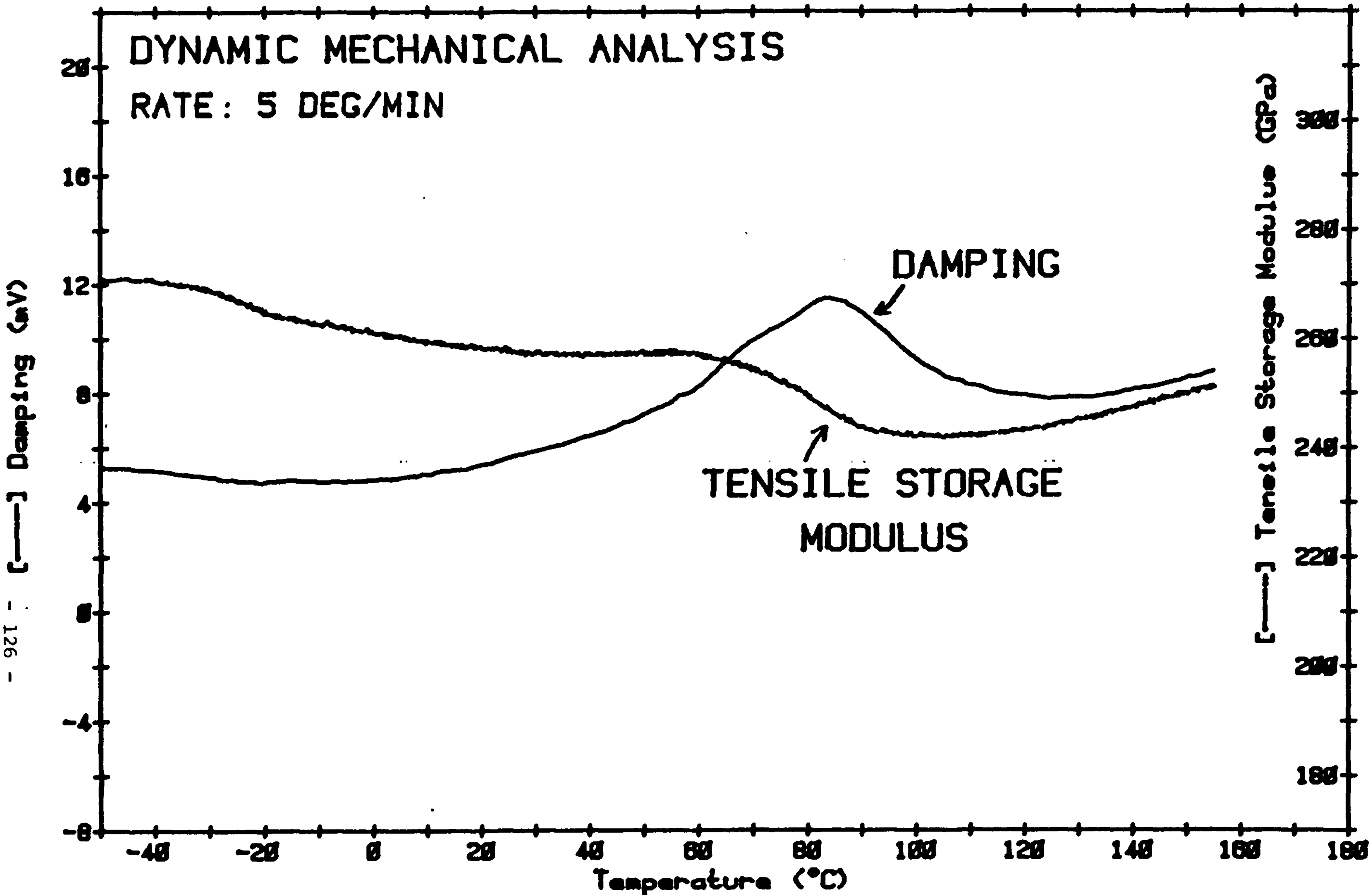


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 2000 HOURS

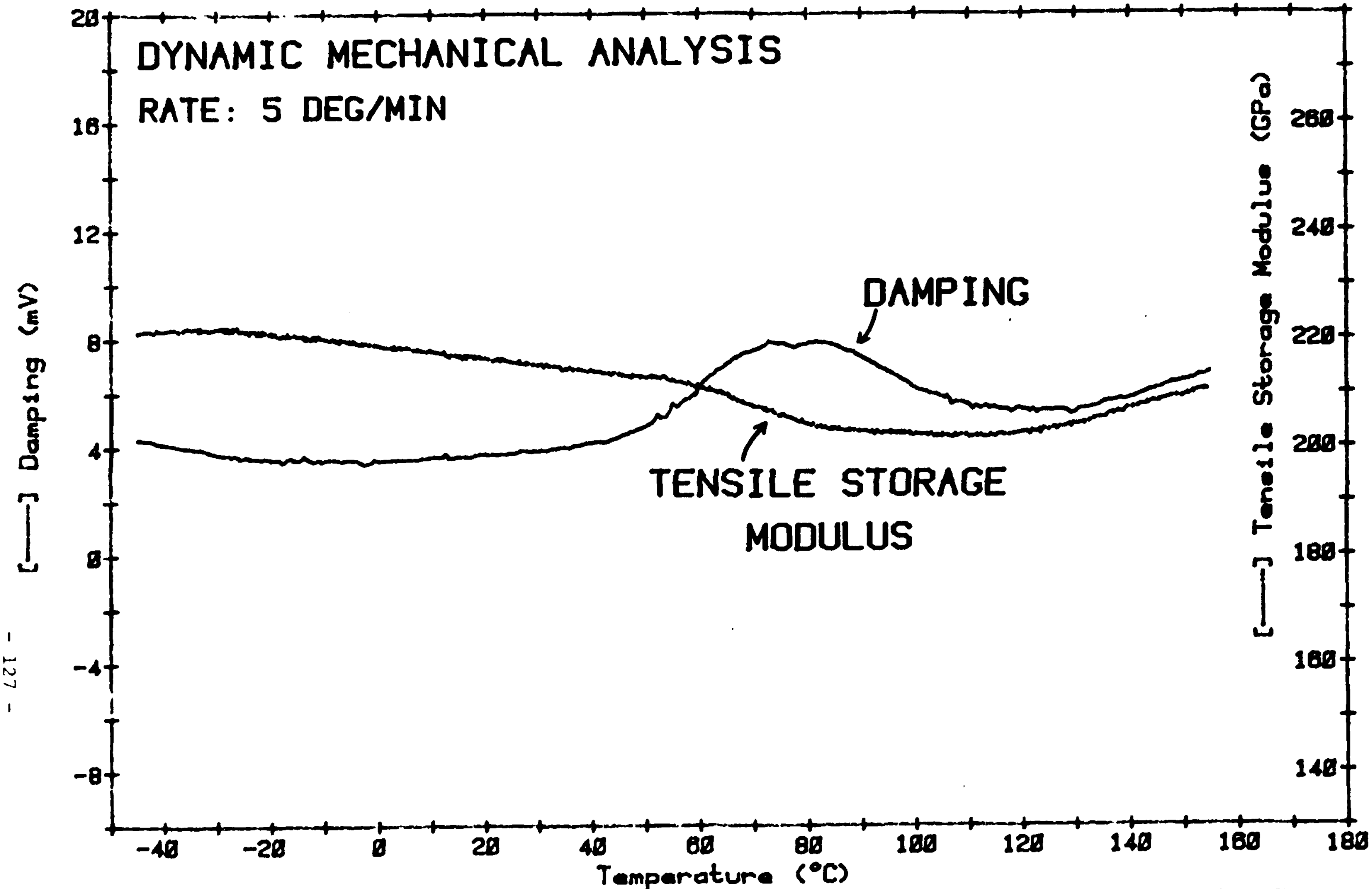


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE GRAY TOPCOAT - QUV 2500 HOURS

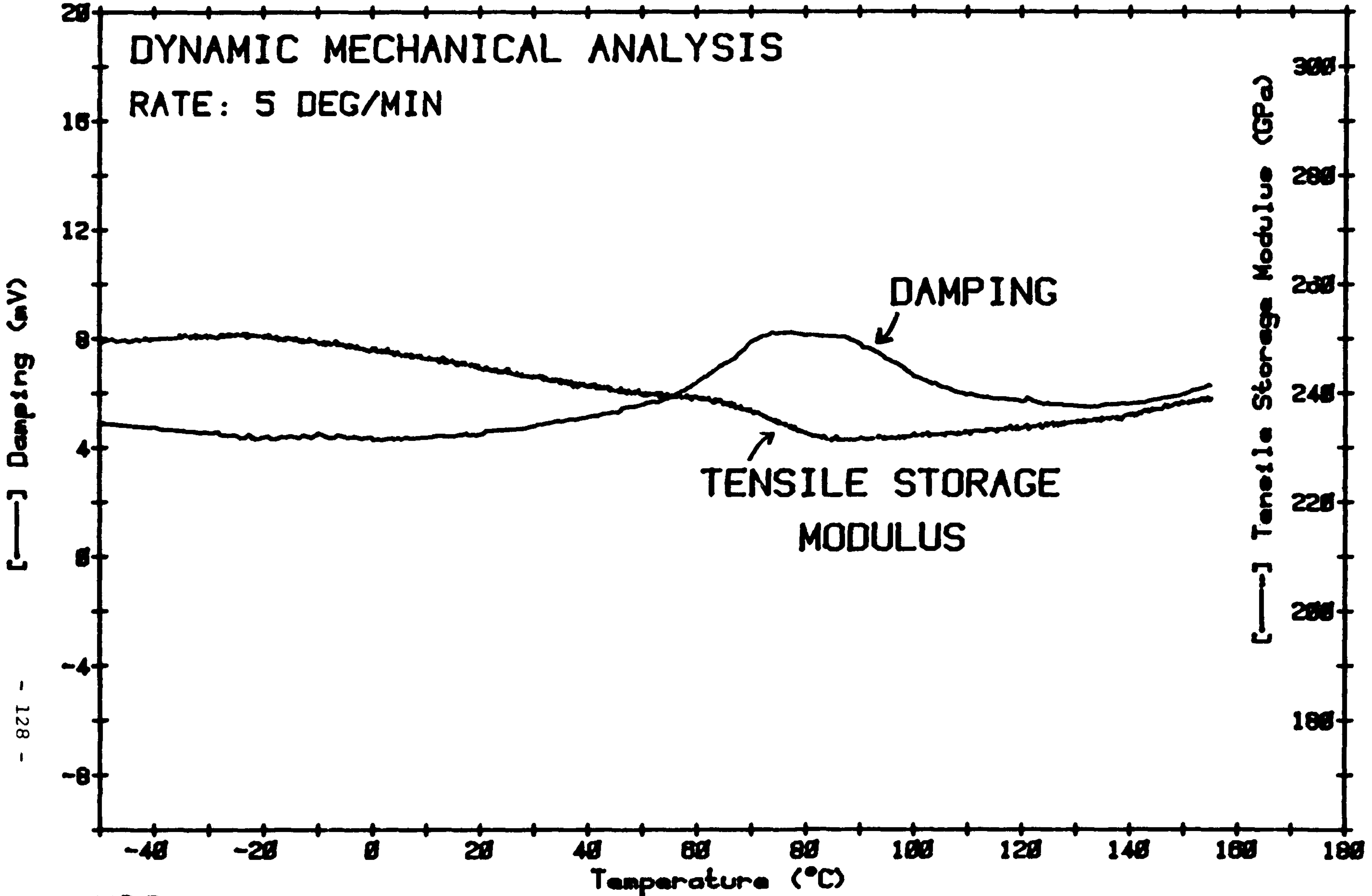


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 3000 HOURS

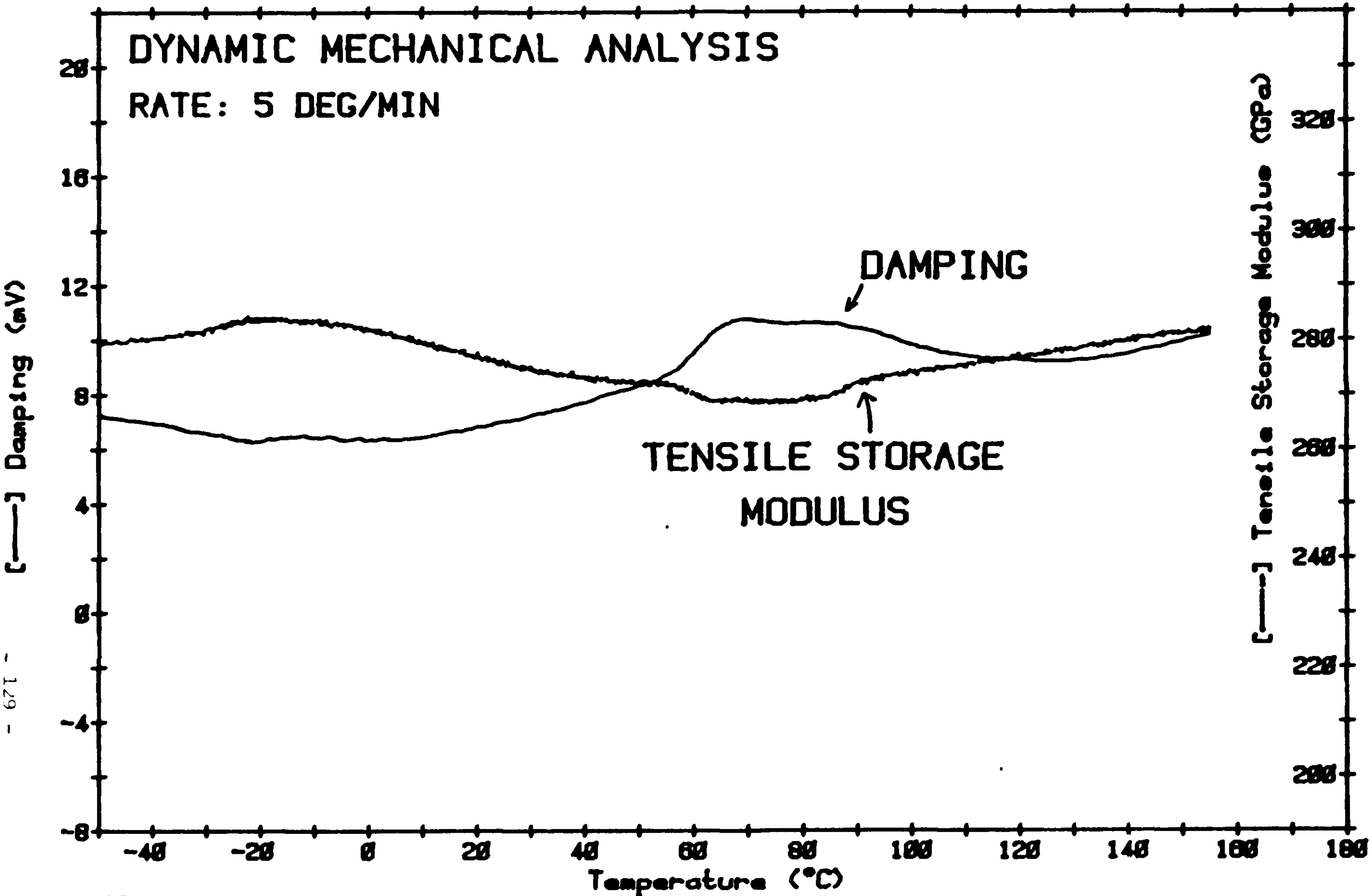


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 3500 HOURS

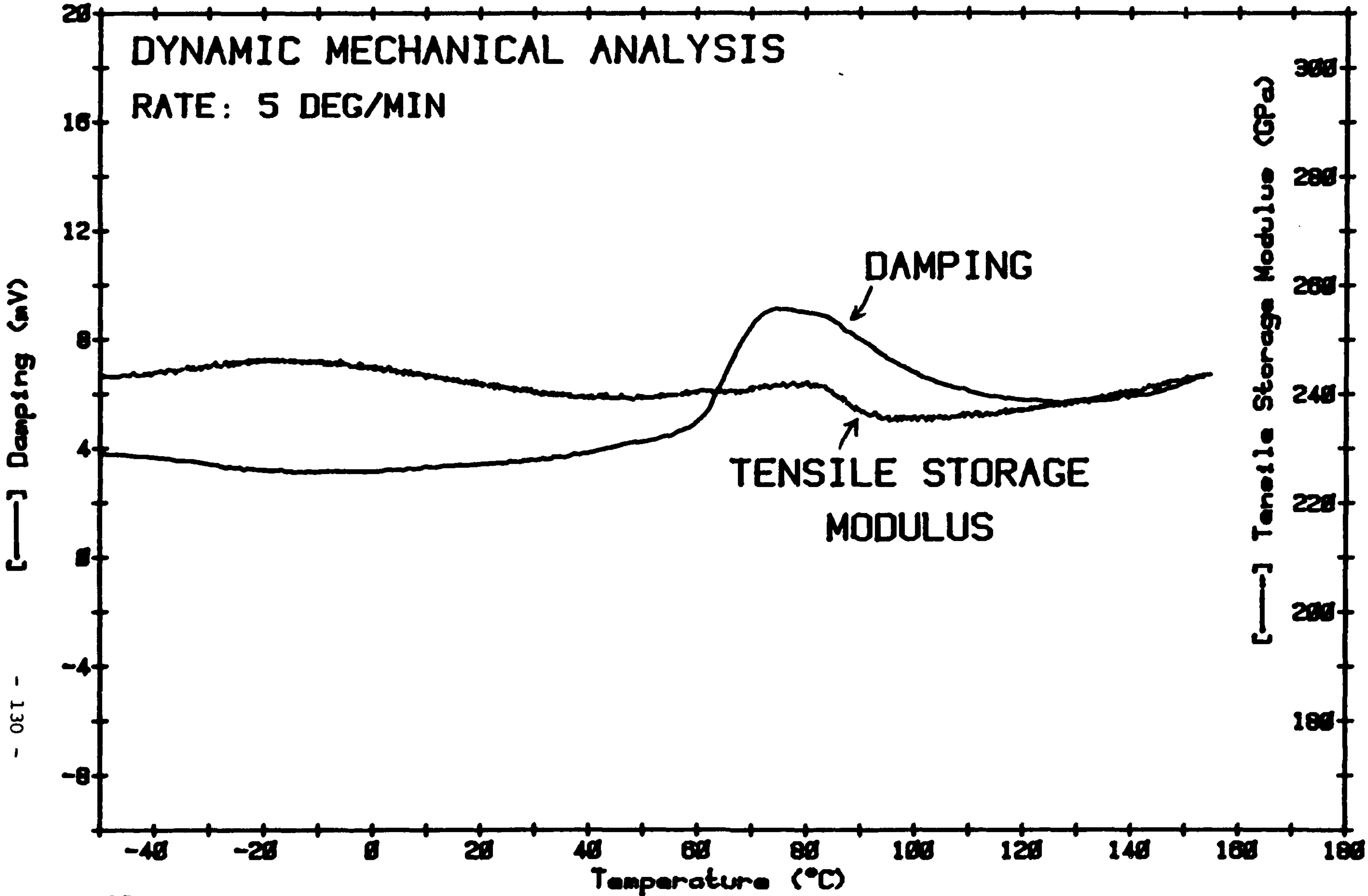


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 4000 HOURS

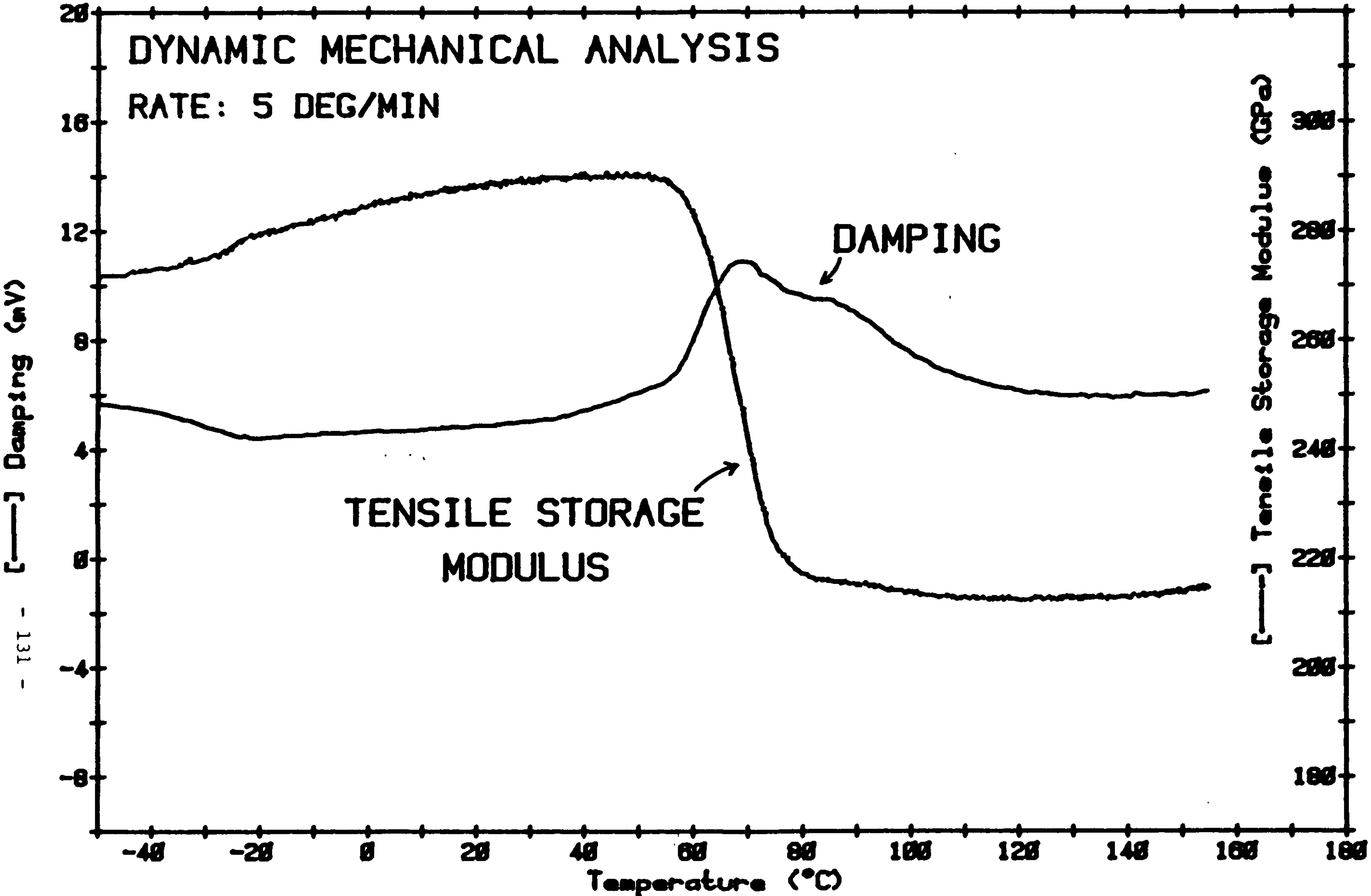


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 4500 HOURS

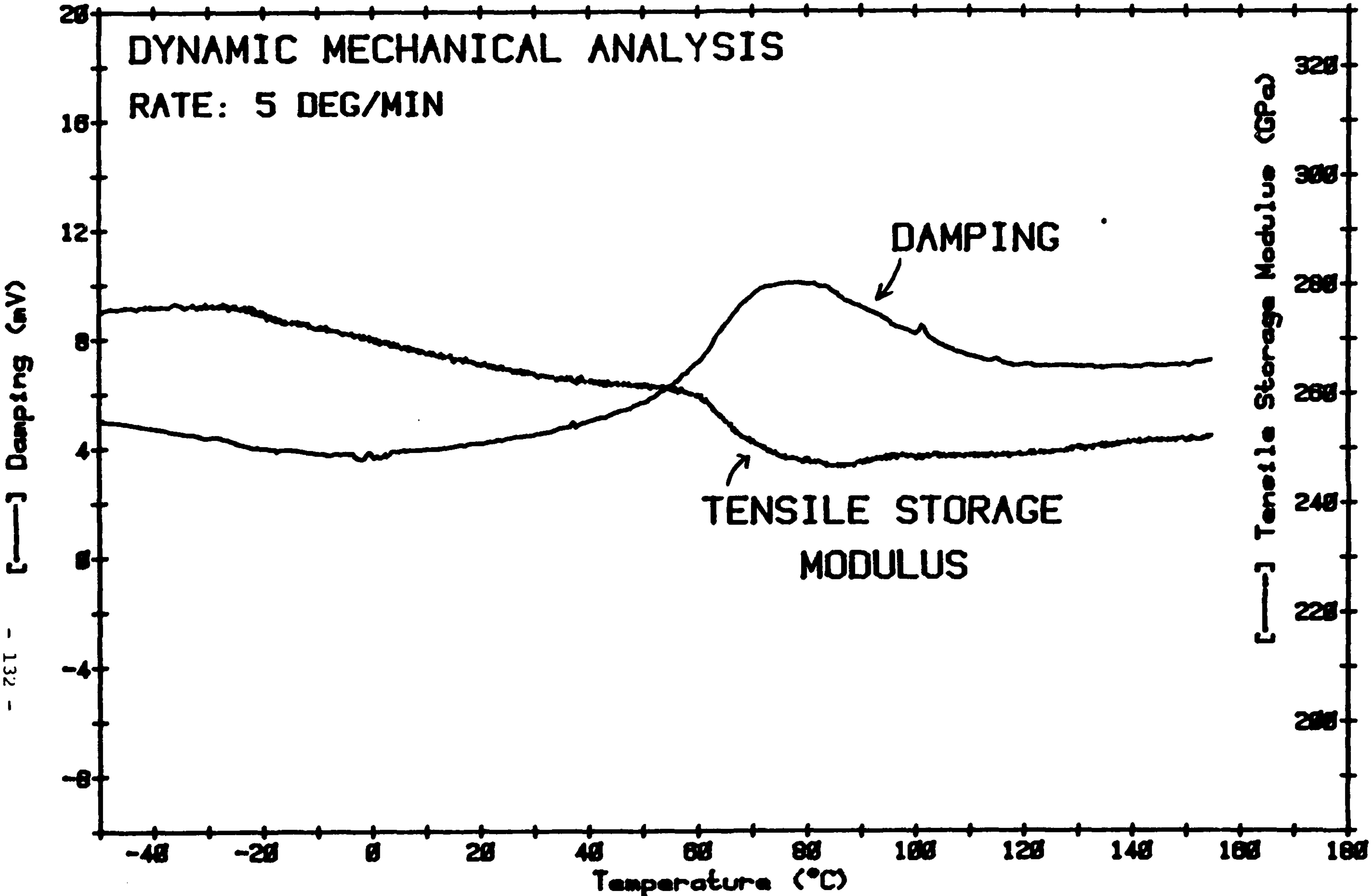


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 5000 HOURS

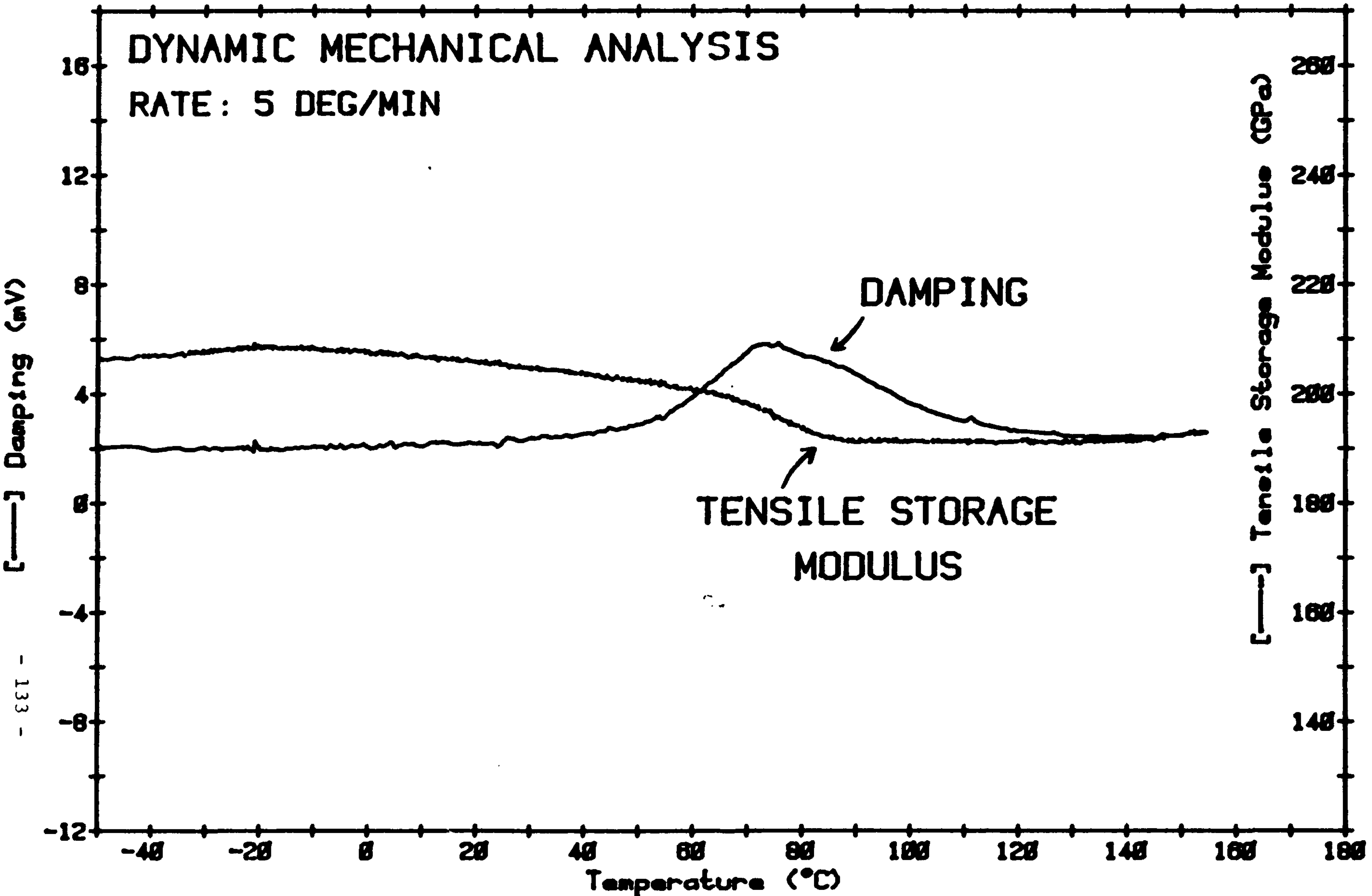


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT - QUV 5500 HOURS

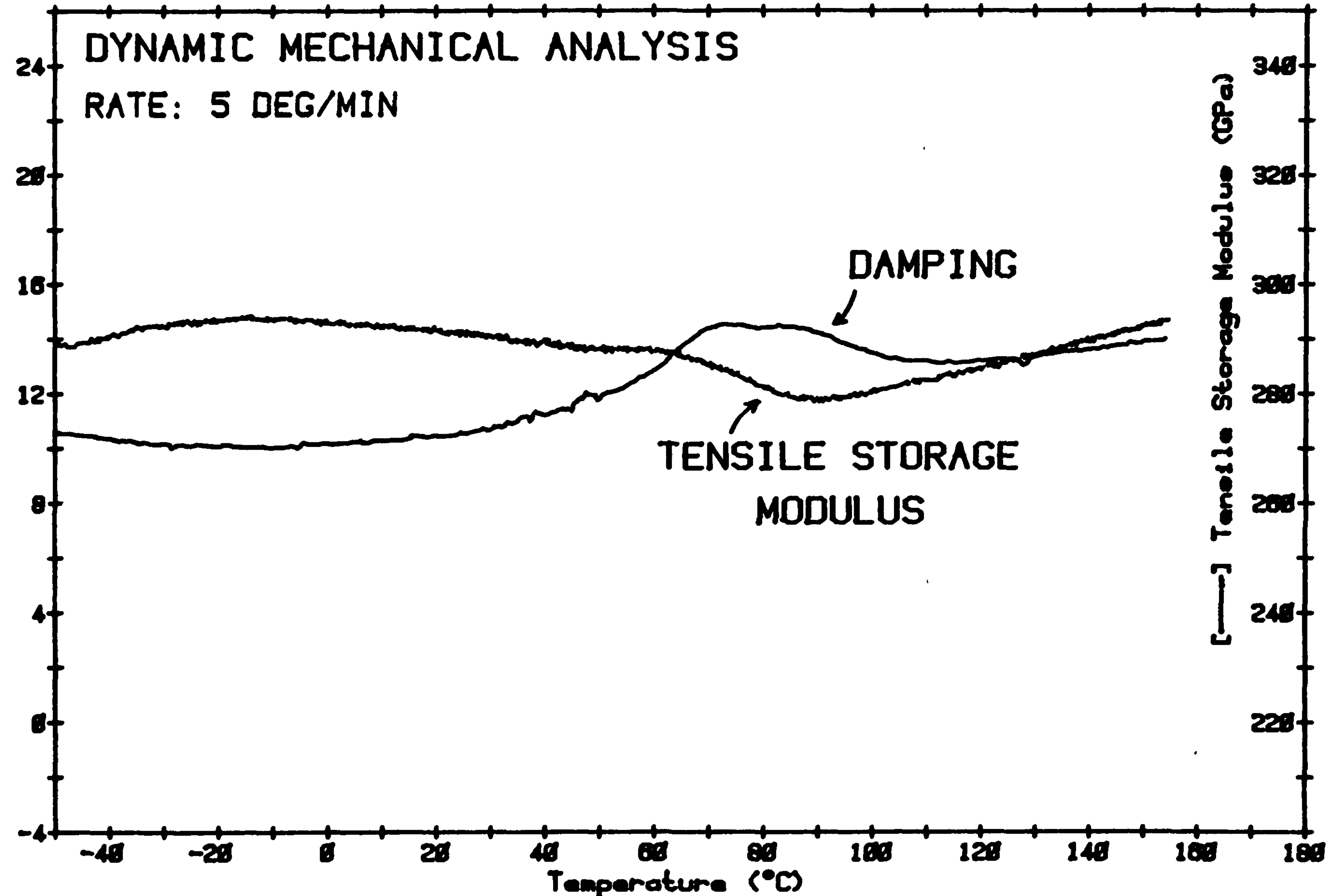


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
GRAY TOPCOAT – QUV 5000 HOURS

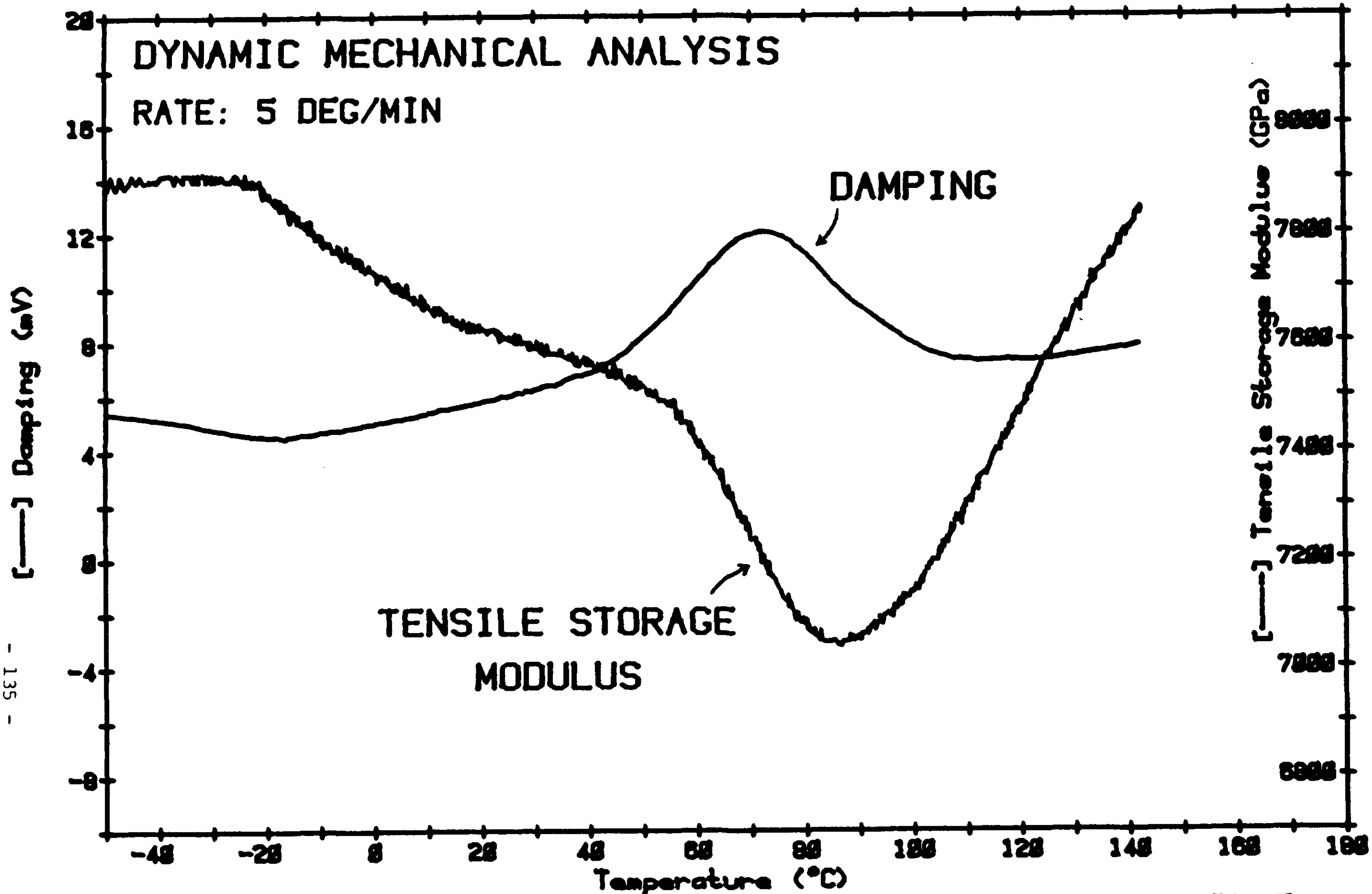


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 0 HOURS

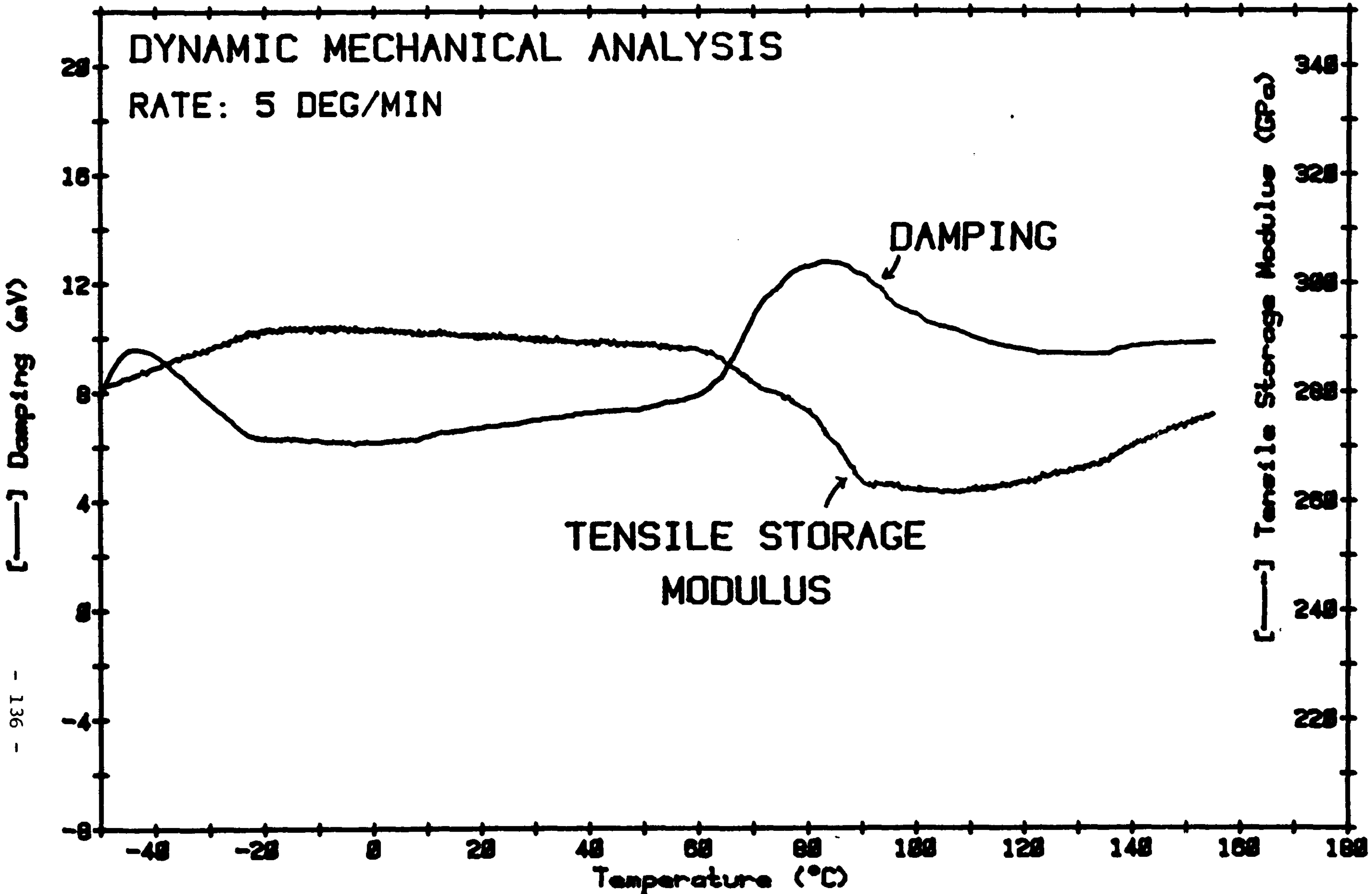


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 200 HOURS

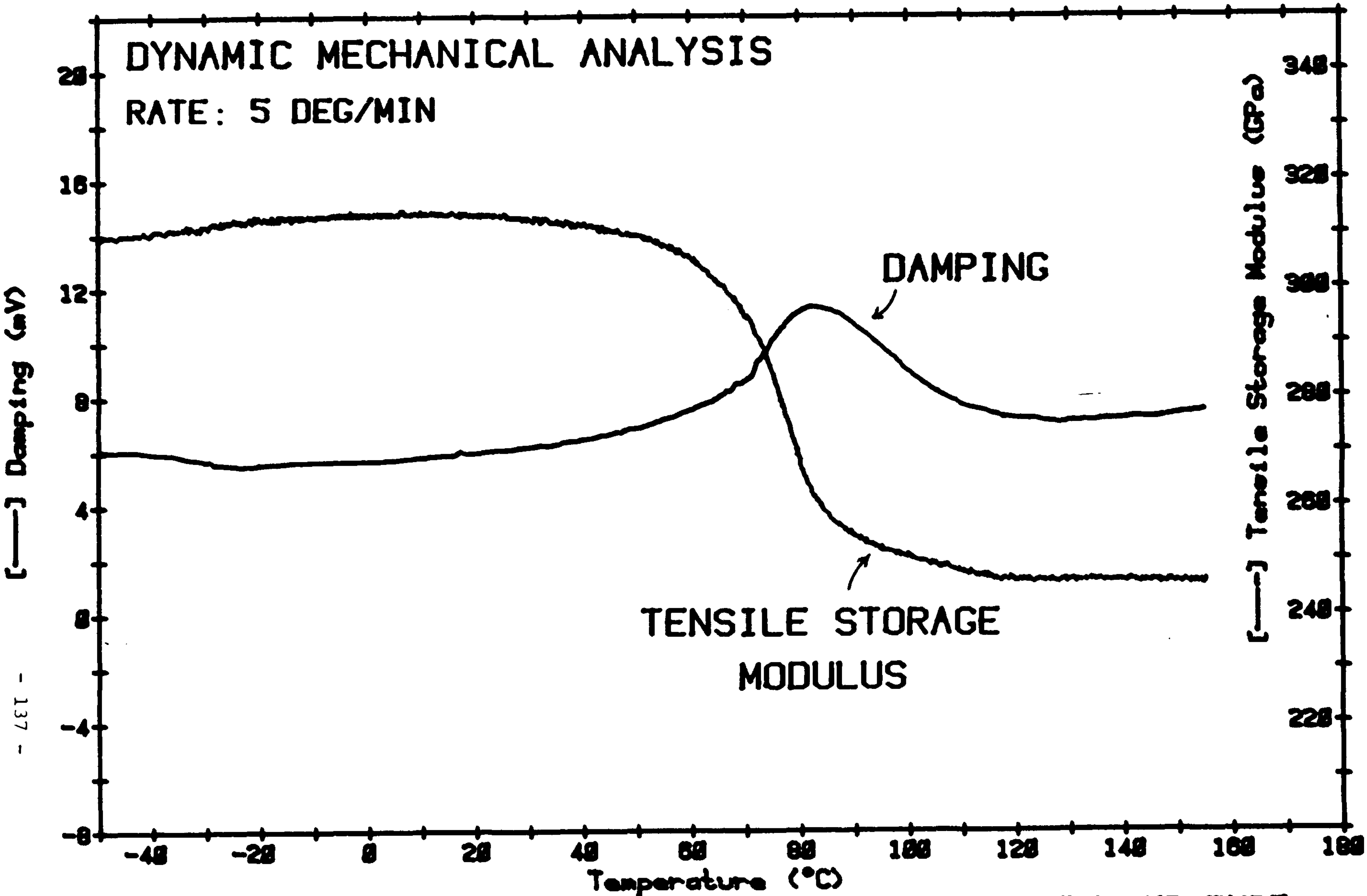


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 480 HOURS

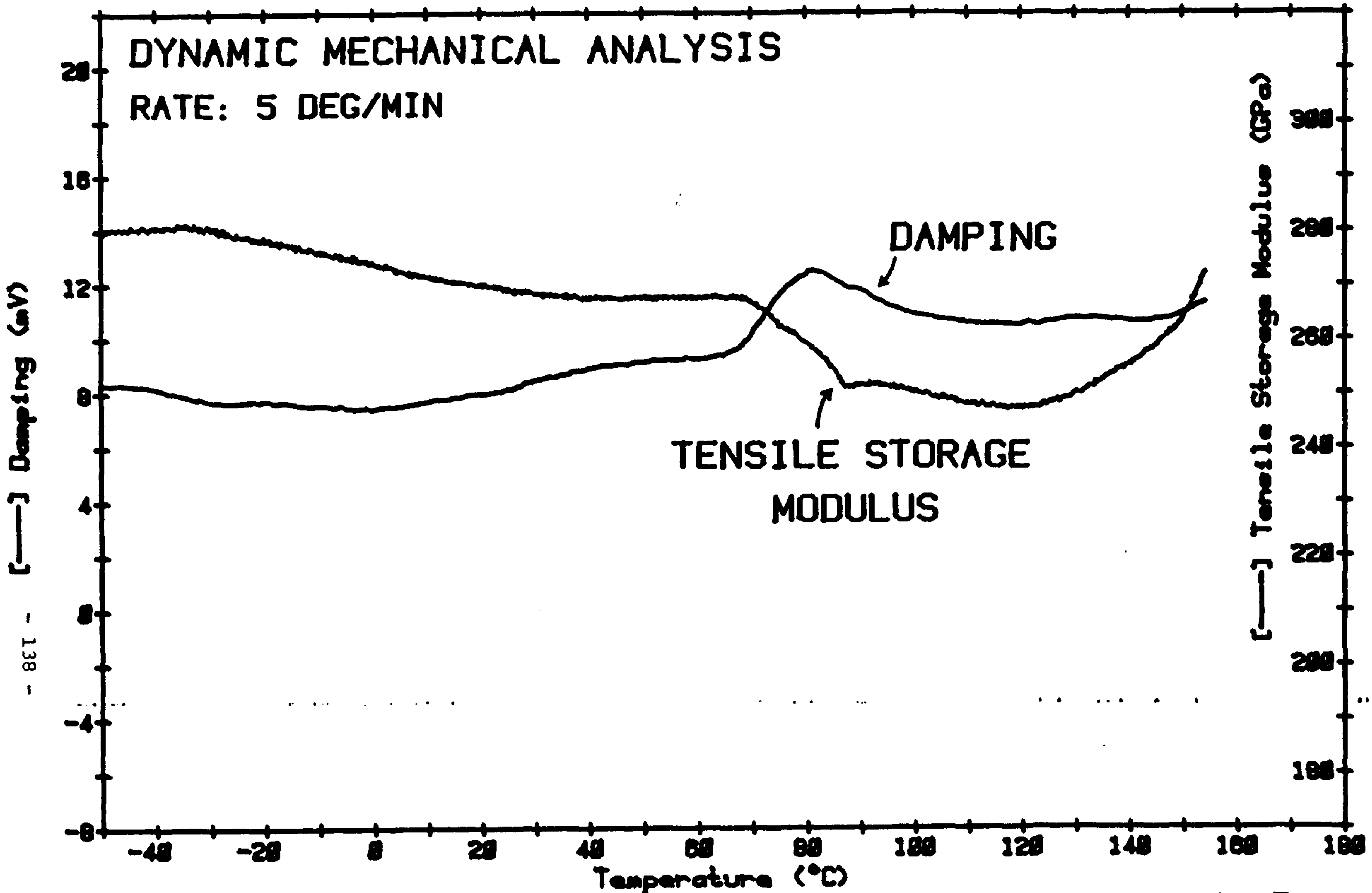


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 500 HOURS

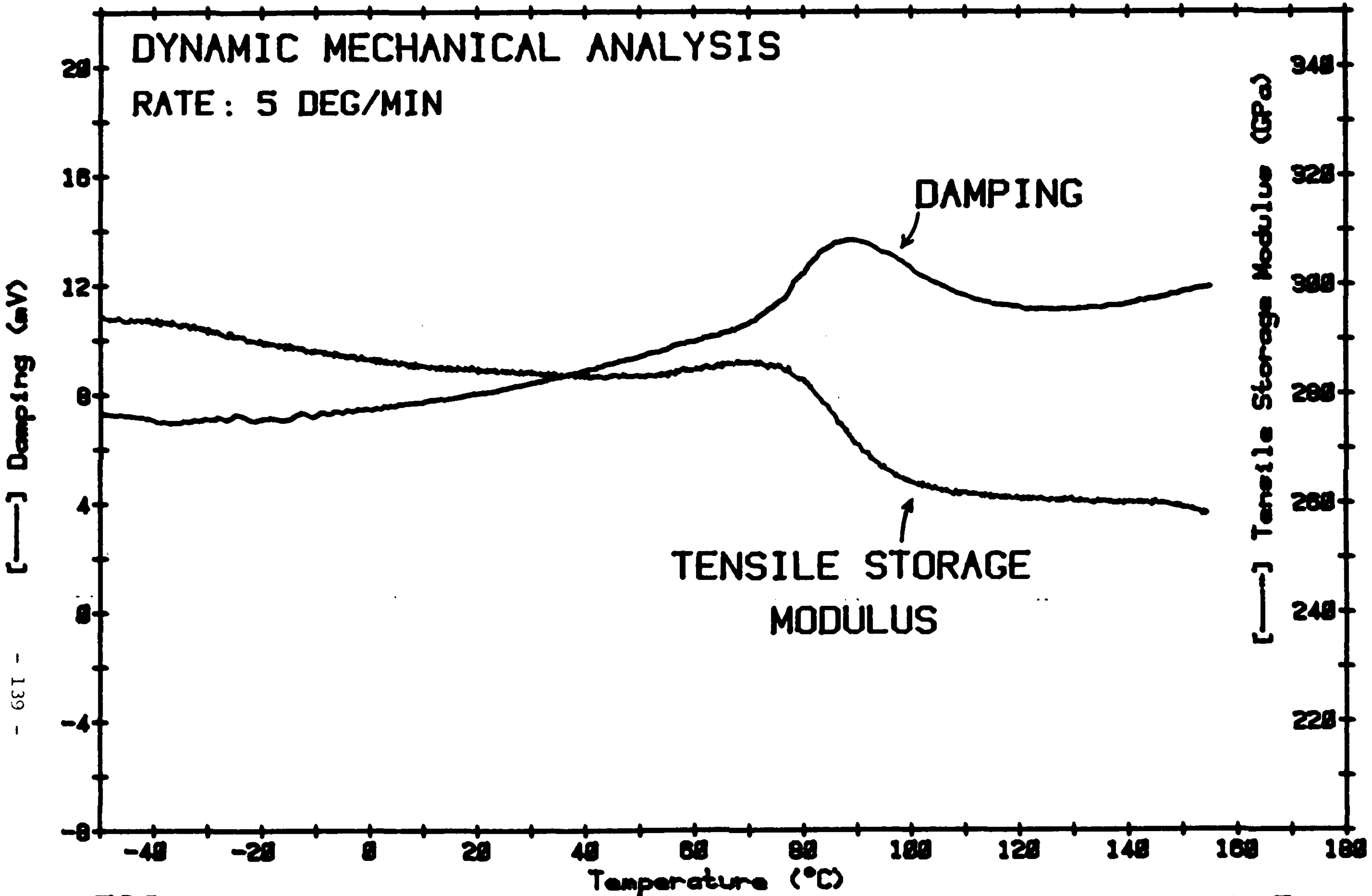


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 1000 HOURS

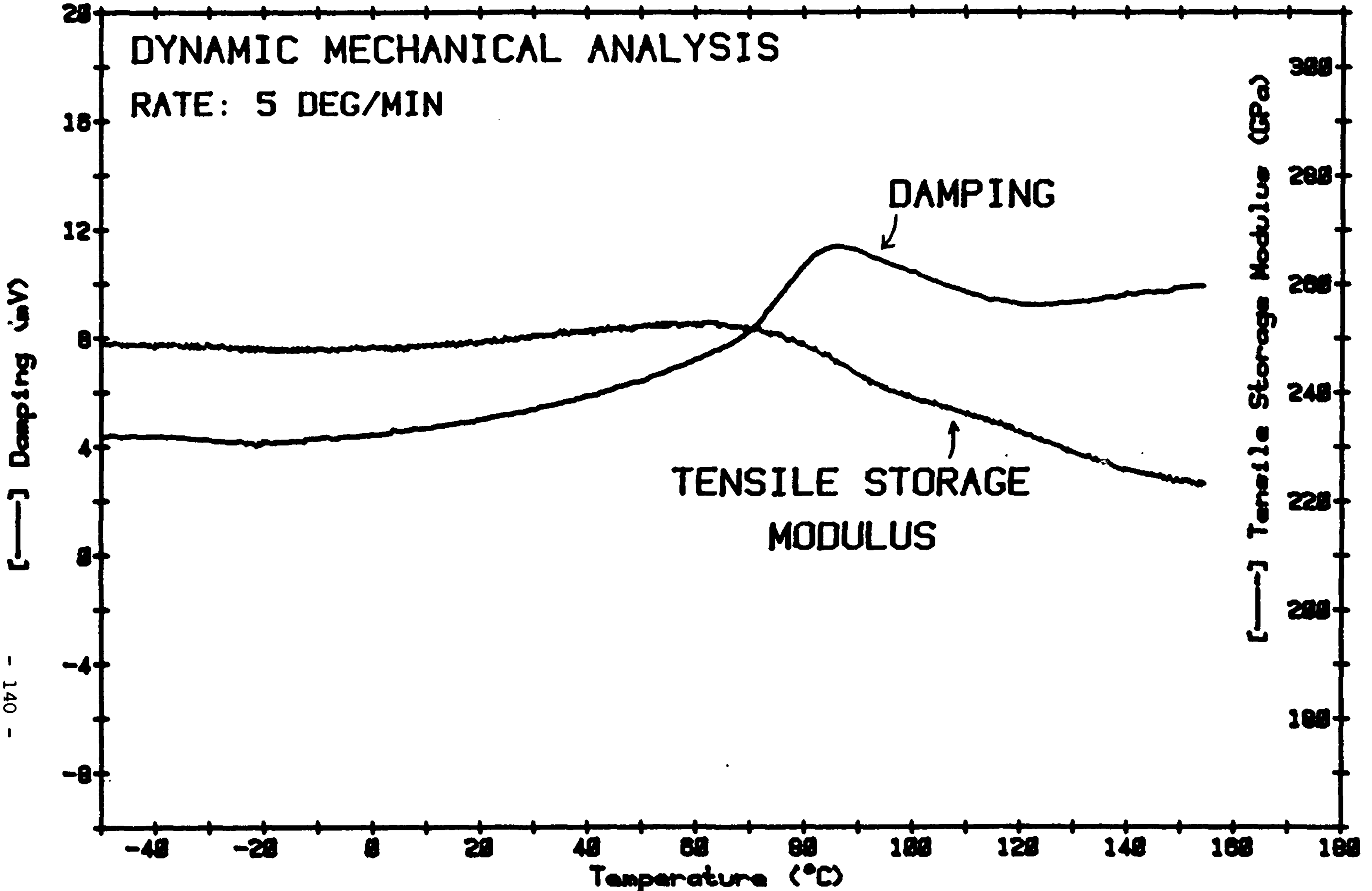


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 1500 HOURS

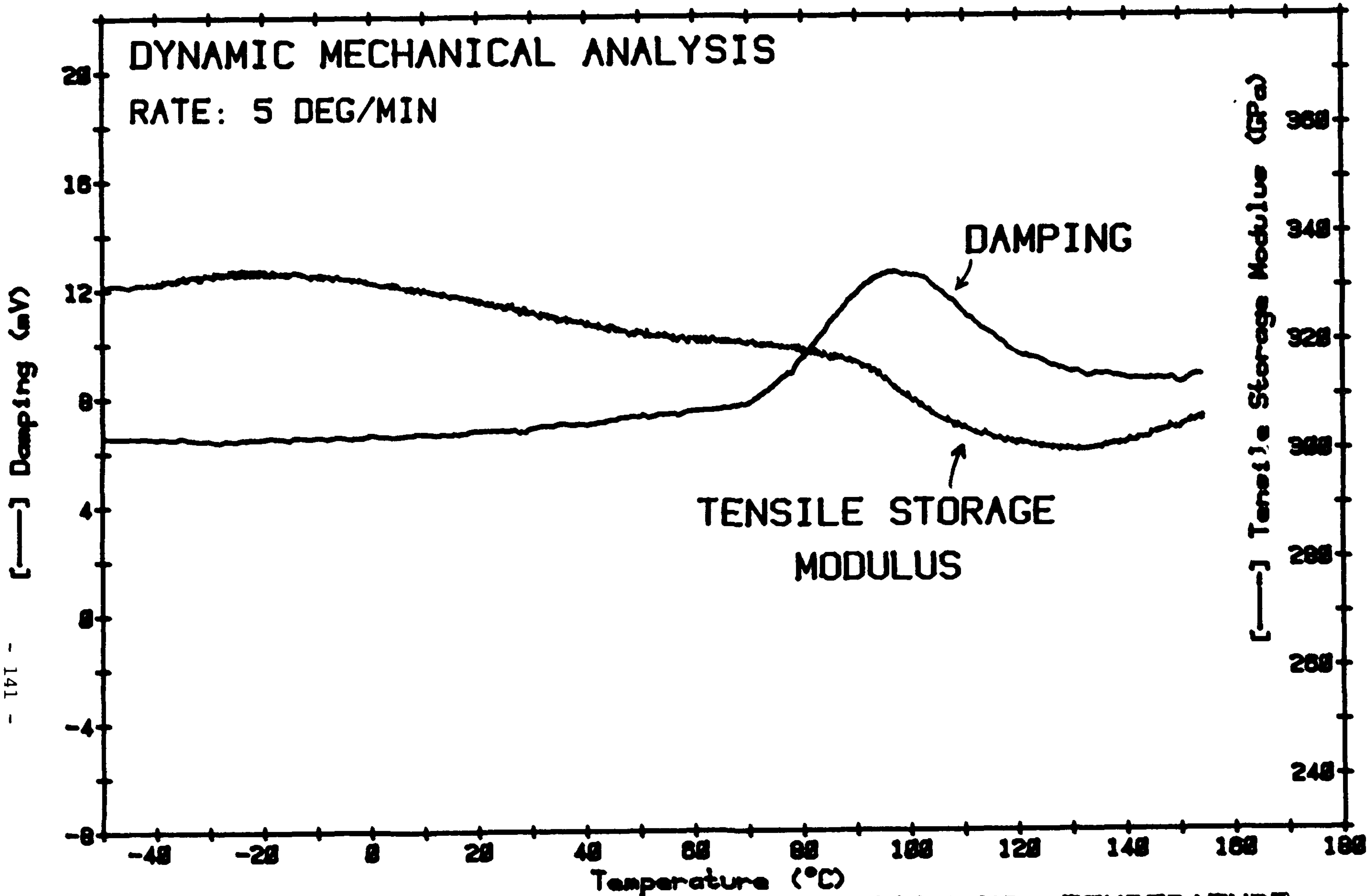


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 2000 HOURS

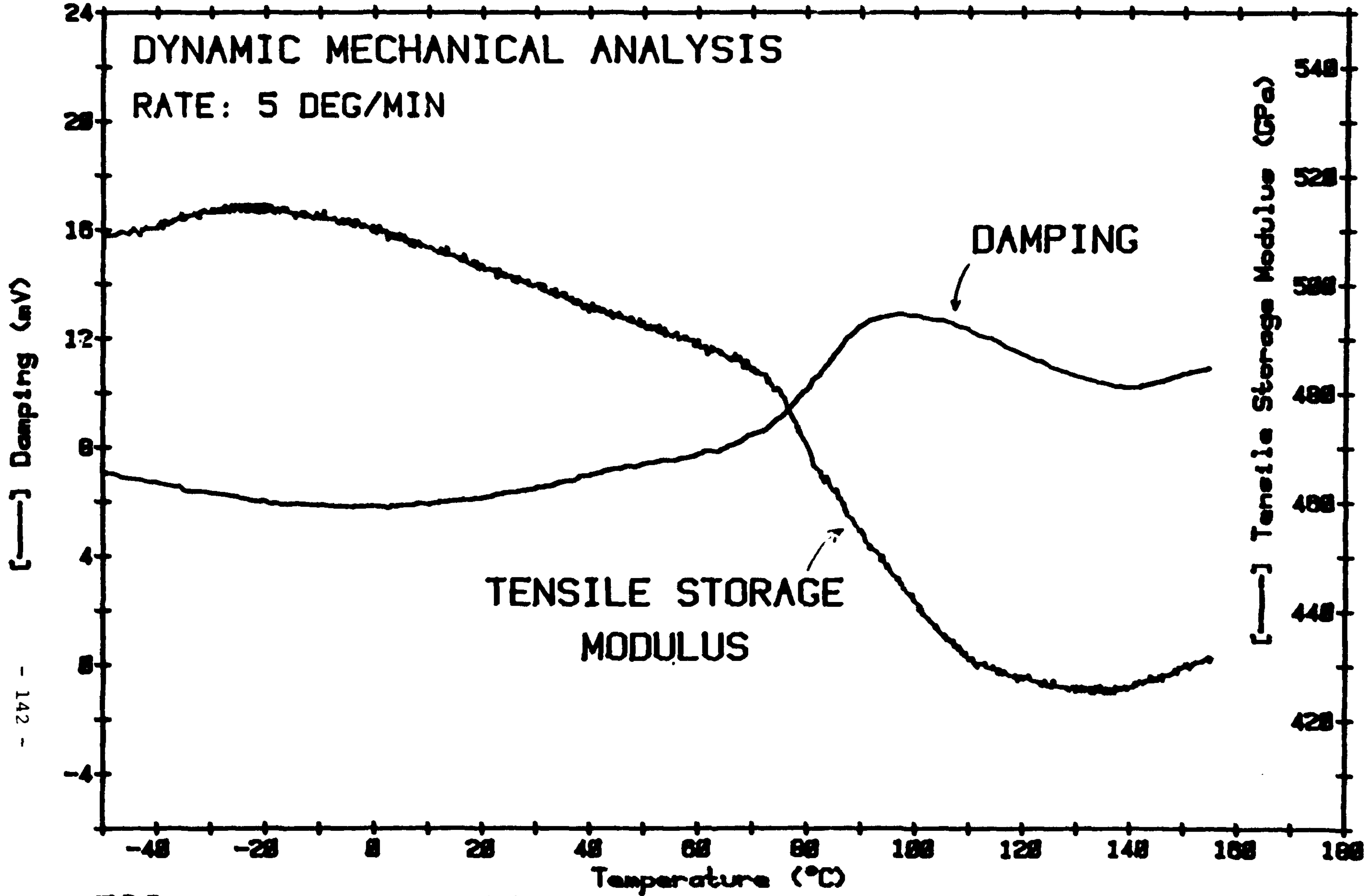


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 2500 HOURS

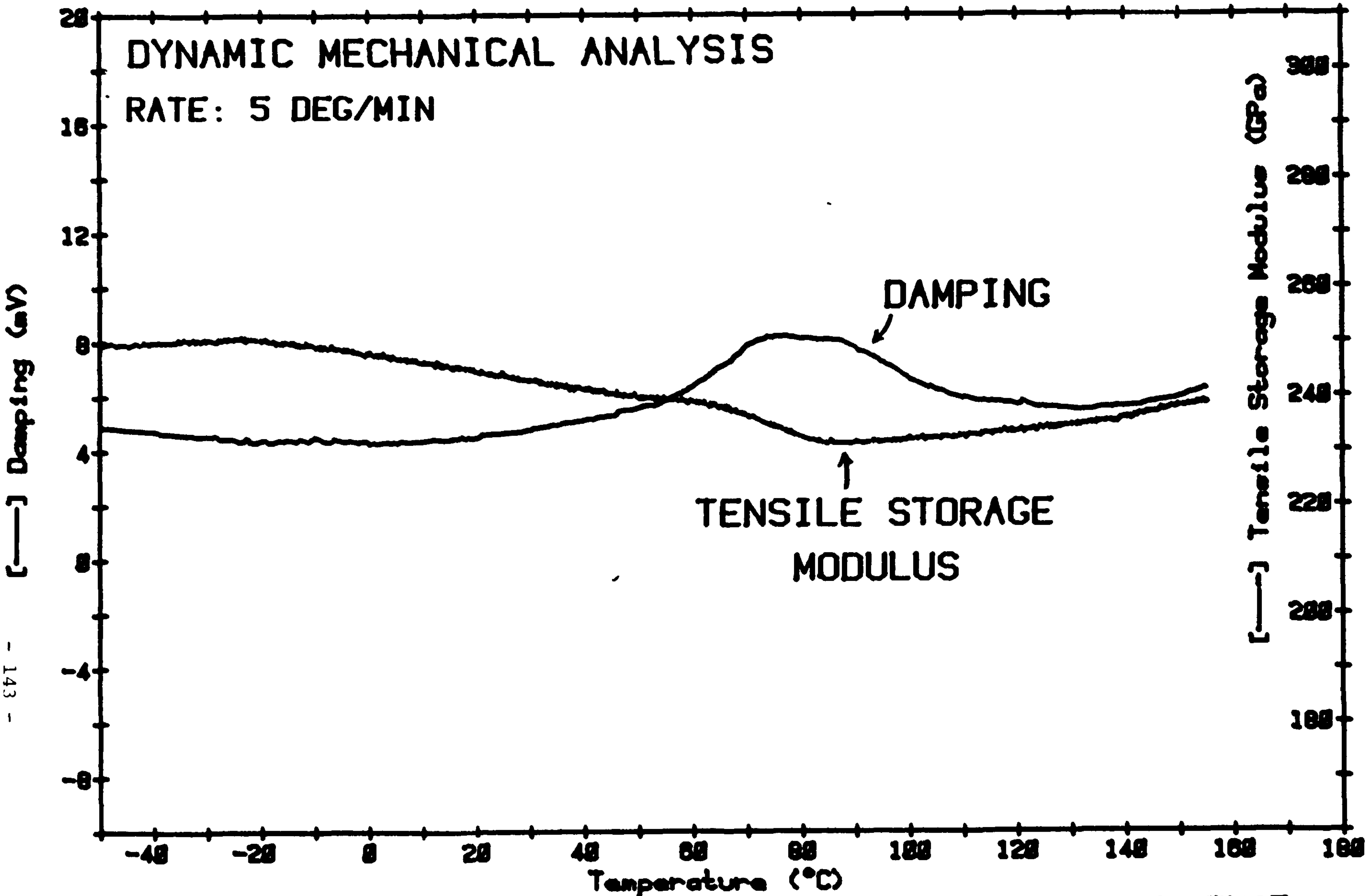


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 3000 HOURS

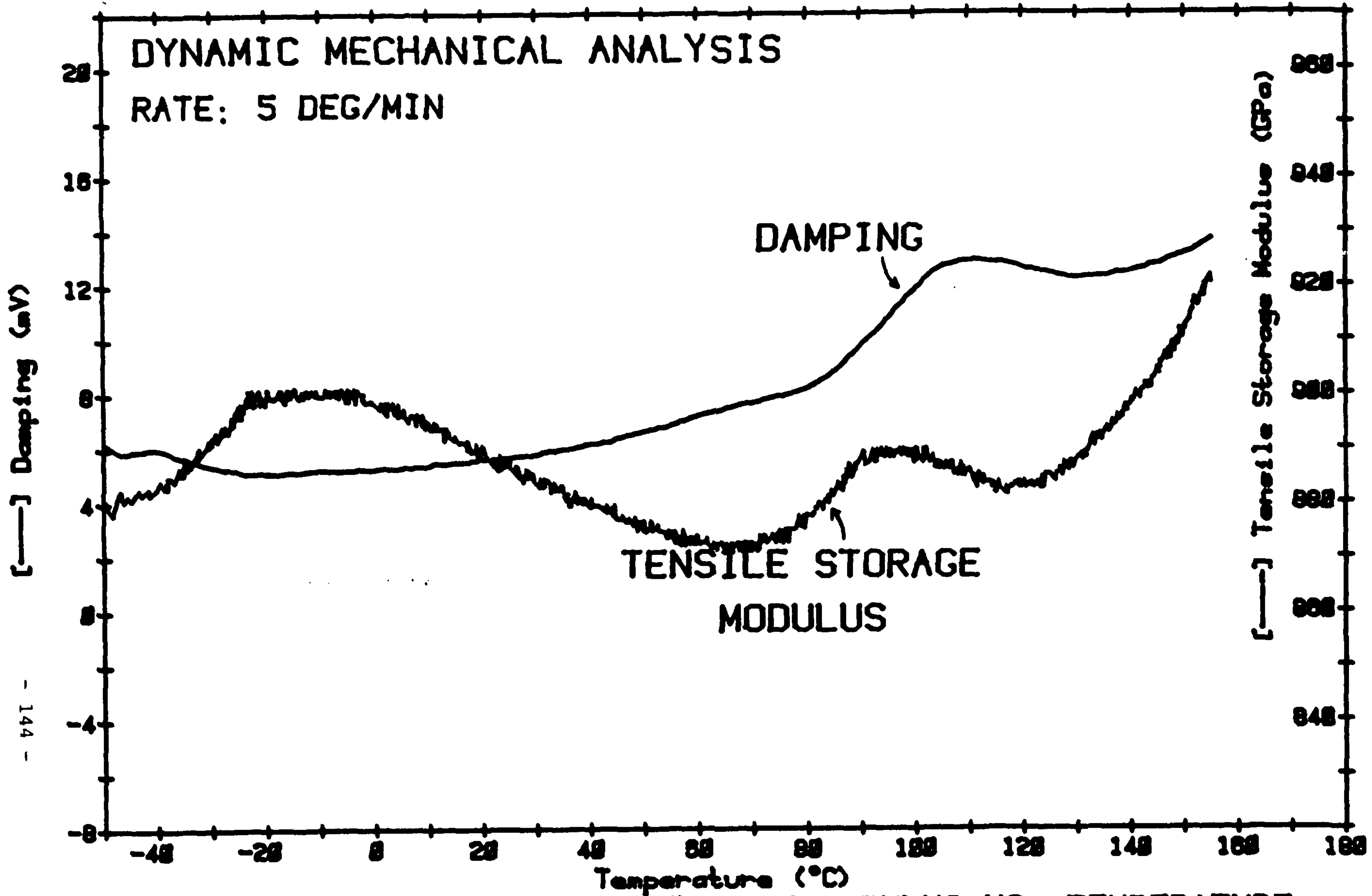


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 3500 HOURS

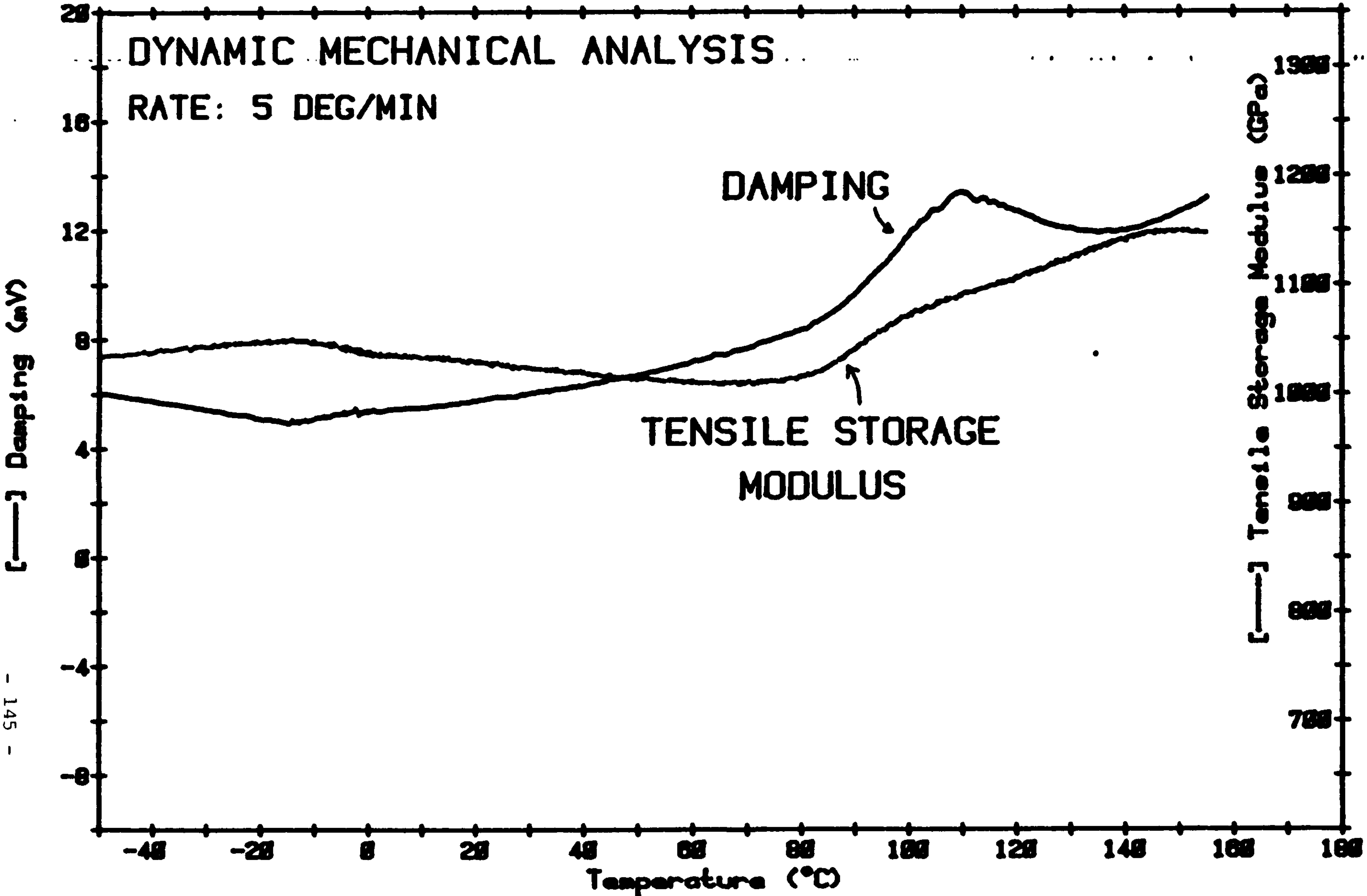


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 4000 HOURS

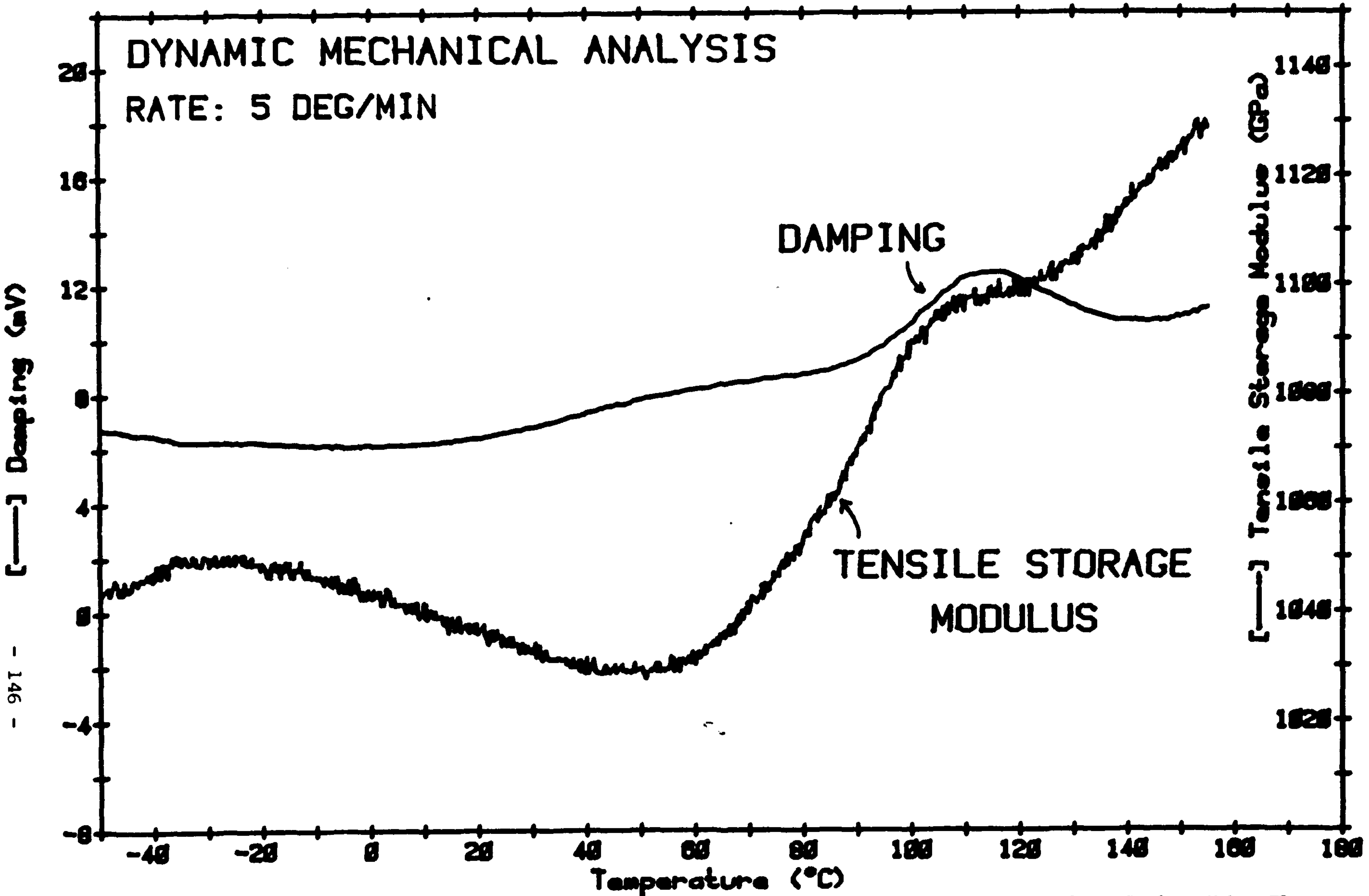


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE CLEAR TOPCOAT - QUV 4500 HOURS

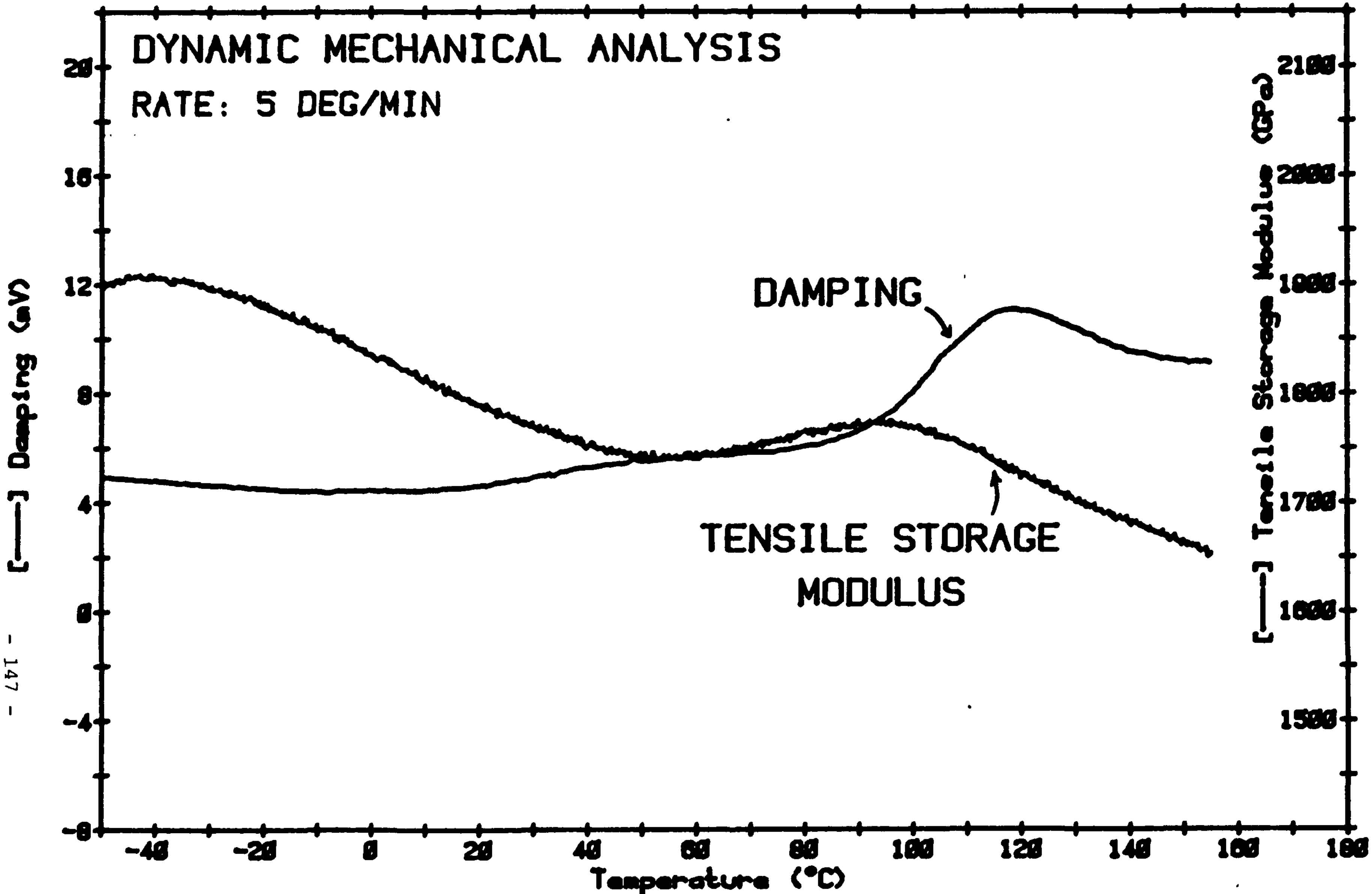


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 5000 HOURS

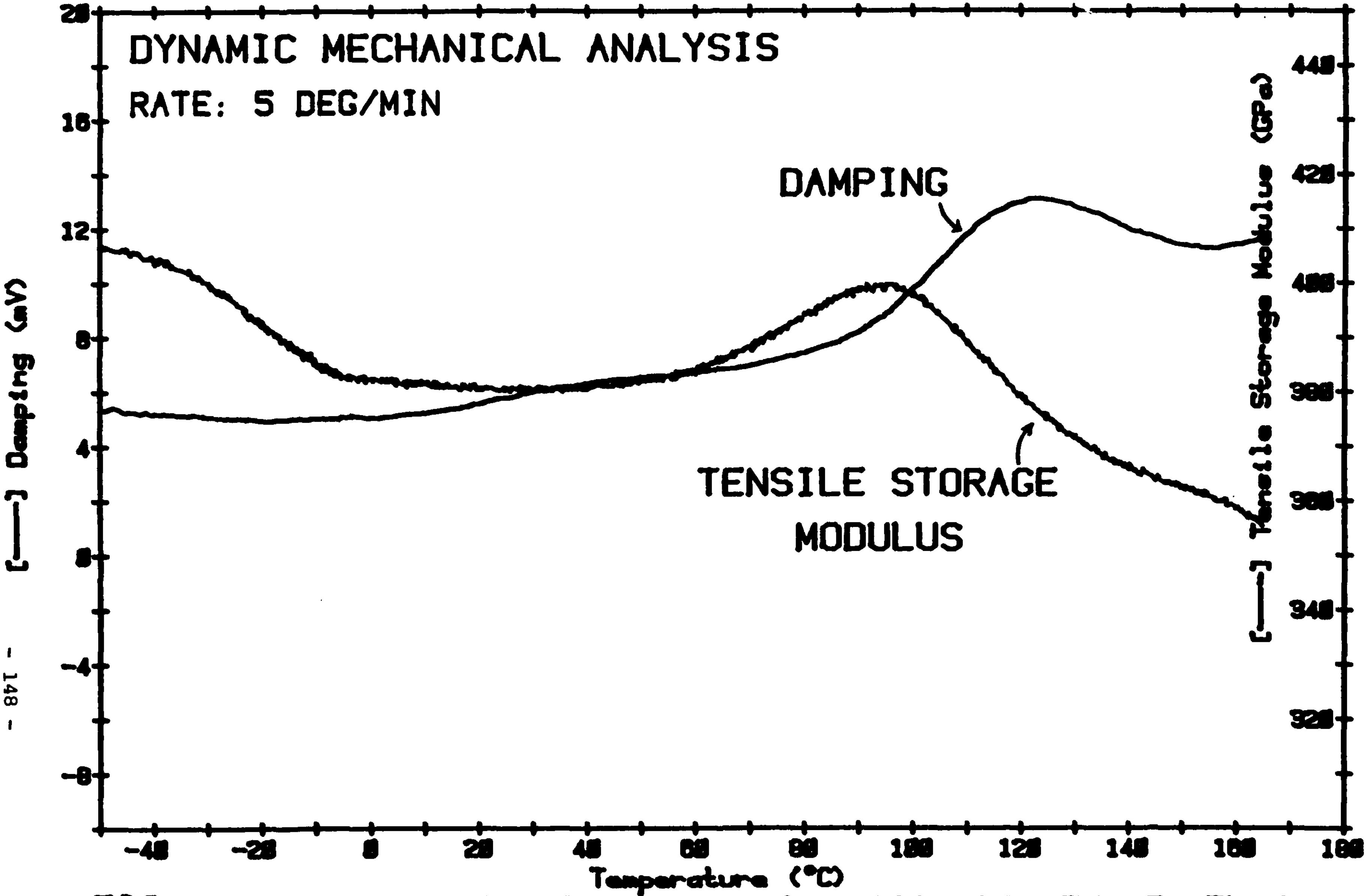


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 5500 HOURS

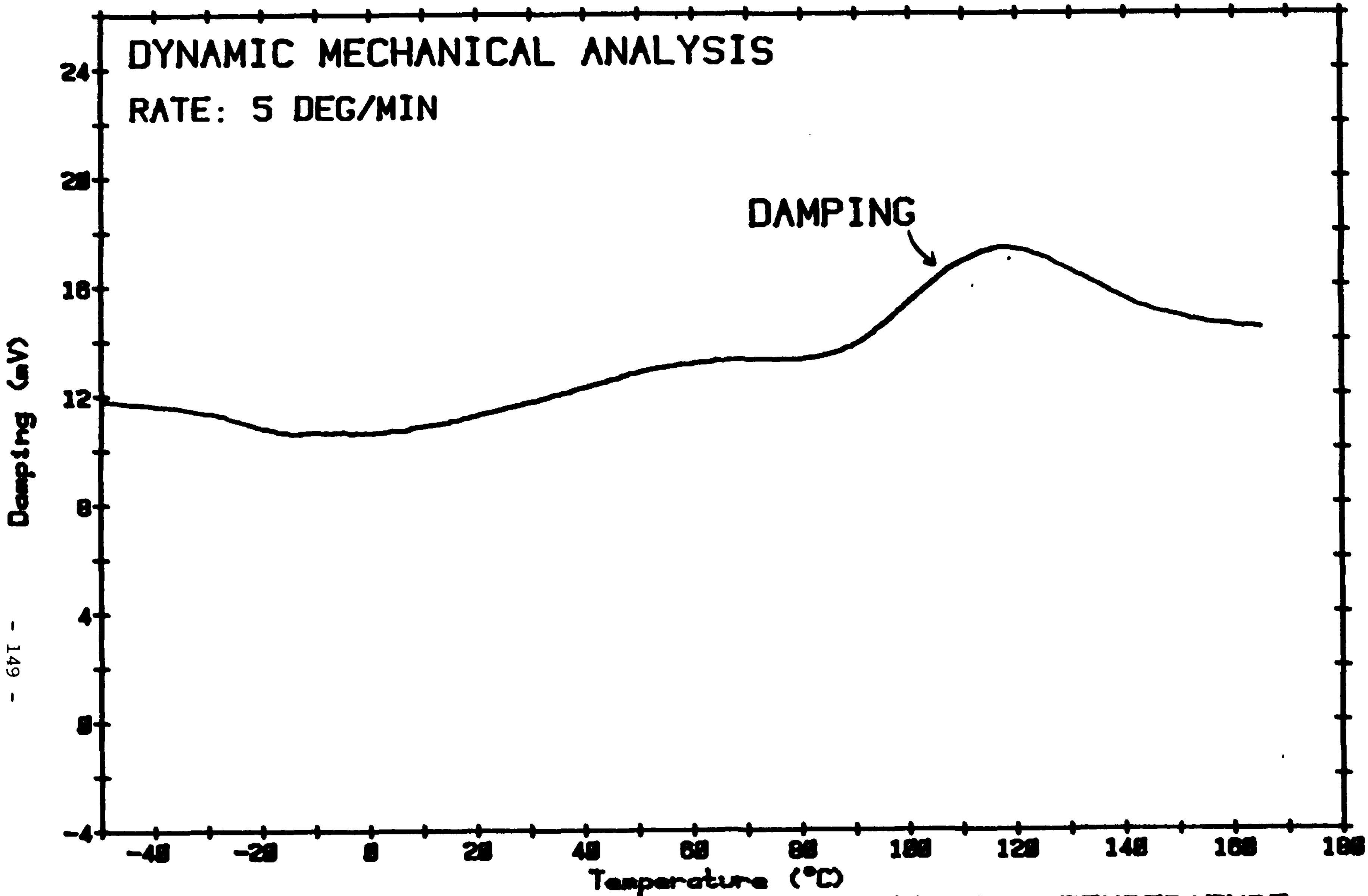


FIG. DAMPING AND TENSILE STORAGE MODULUS VS. TEMPERATURE
CLEAR TOPCOAT - QUV 5000 HOURS

SECTION VII

REFERENCES

[1]. Osawa, Z. "Photodegradation and Stabilization of Polyurethanes" in "Developments in Polymer Photochemistry", Allen, N. S. ed; *Applied Science*: London 1981; Vol 3, Chapter 6.

[2]. Ranby, B. and Rabek, J. F. *Photodegradation, Photo-oxidation and Photostabilization of Polymers*; John Wiley and Sons: London, 1975.

[3]. Schnabel, W. *Polymer Degradation*; Hanser International: Munich 1981.

[4]. Tarakanov, O. G., Nevskji, L. V., Beljakov, V. K. J. Poly. Sci. Part C. 1968, No. 23 pp 193-99.

[5]. Beachell, H. C., and Chang, I. L., J. Poly. Sci. Part A. 1972, 10, 503-20

[6]. Yamagata, T., et. al., Kobunshi Ronbunshi 1979, 26(11), 767-71.

[7]. McCallum, J. R. and Wright, W. W.,"Polymer Degradation" in *Macromolecular Chemistry* Royal Society of Chemistry: London 1982.

[8]. Fowkes, F. M. ed.;"Contact Angle, Wettability and Adhesion"; American Chemical Society: Washington, D.C., 1964.

[9]. Box, G. E. P., Hunter, W. G., Hunter, J. S. *Statistics for Experimenters*; John Wiley and Sons: New York, 1978.

[10]. Fish, R. A. and Morris, R. L. J., J. Oil Col. Chem. Assoc. 1972, 55, 189-206.

[11]. DuPont Analytical Instruments Division, "DuPont 982 Dynamic Mechanical Analysis System"; 1983.

[12]. Turi, E. A., ed.; *Thermaly Characterization of Polymeric Materials*; Academic Press: New York, 1981.

[13]. Chiang, C. P., and Rehfeldt, T. K., "Abstracts of Papers", 26th Annual Technical Conference of the Cleveland Society for Coatings Technology, Cleveland OH April 28, 1983.

[14]. Chiang, C. P., and Rehfeldt, T. K., "Scanning Laser Acoustic Microscopic Study of the Internal Structure of Latex Paint Films" presented at the Annual Meeting of the Federation of Coatings Societies, Chicago, October 1984.

[15]. Hopfenberg, H. B., North Carolina State University, personal communication, 1983.

References (Continued)

[16]. Klemchuk, P. P., Polymer Photochemistry 1983, 3, 1-27.

[17]. Wagner, C. D., Anal. Chem. 1972, 44, 1050.

[18]. Dilks, A., and Clark, D. T., J. Poly. Sci., Poly. Chem., 1981, 19, 2847-60.

[19]. Kinell, P-O., Ranby, B., Runnstrom-Reio, V., eds.; ESR Applications to Polymer Research; John Wiley and Sons: New York, 1973.

[20]. Gerlock, J. L., Anal. Chem.; 1983, 54, 1520-22.

[21]. Gerlock, J. L., Van Oene, H., Bauer, D. R., Eur. Poly. J.; 1983, 19, 11-18.

[22]. Gerlock, J. L., Bauer, D. R., and Briggs, L. M., "Electron Spin Resonance (ESR) of Photodegradation in Polymer Networks" in "Characterization of Highly Cross-linked Polymers", Labana, S. S. and Dickie, R. A., eds.; ACS Symposium Series 243, American Chemical Society: Washington, D. C., 1984.

[23]. Rosencwaig, A., Photoacoustics and Photoacoustic Spectroscopy; John Wiley and Sons: New York, 1980.

[24]. Box, G. E. P., and Jenkins, G. M., Time Series Analysis Forecasting and Control, Holden-Day: San Francisco, 1976.

[25]. Meeker, W. Q., Jr., "TSERIES- A User Oriented Computer Program for Identifying, Fitting, and Forecasting ARIMA Time Series Models"; in Proceedings of the Statistical Computing Section, American Statistical Association, 1977.

[26]. Nelson, C. R., Applied Time Series Analysis; Holden-Day: San Francisco, 1973.

[27]. Durban, J. and Watson, G. S., Biometrika, 1951, 38, 159-78.

[28]. Mosteller, F. and Tukey J. W., Data Analysis and Regression; Addison-Wesley: Reading, MA, 1977.

[29]. Neter, J., and Wasserman, W., Applied Linear Statistical Models; Richard D. Irwin, Inc.: Homewood, IL, 1974.

[30]. Draper, N. R., and Smith, H., Applied Regression Analysis, 2nd Edition; John Wiley and Sons: New York, 1980.

[31]. Mann, N. R., Schafer, R. E., Singpurwalla, N. D., Methods for Statistical Analysis of Reliability and Life Data; John Wiley and Sons: New York, 1974.

[32]. Martz, H. F.and Waller, R. A., Bayesian Reliability Analysis; John Wiley and Sons: New York, 1982.

References (Continued)

[33]. Martin, J. W., Durability Build. Mater. 1982, 1(2), 175-194.

[34]. Kececioglu, D., Jacks, J. A., Reliability Engineering, 1984, 8, 1-9.

[35]. C. A. Lucchesi, Northwestern University, personal communication, 1984.

[36]. Wehry, E. L. ed., Modern Fluorescence Spectroscopy; Vol. 2 Plenum Press: New York, 1976.

[37]. R. Haidle and C. A. Lucchesi, Northwestern University, personal communication, 1984.

[38]. Czanderna, A. W., Methods of Surface Analysis; Elsevier: Amsterdam, 1975.

[39]. Clark, D. T., and Feast, W. J., Polymer Surfaces; John Wiley and Sons: New York, 1978.

BIBLIOGRAPHY

Apicella,A.,Nicolais,L.,Astarita,G.and Drioli,E.
Polymer Engineering and Science ,Jan.1981,vol.21,no.1
"Hygrothermal History Dependence of Moisture Sorption
Kinetics in Epoxy Resins"

Appleman,B.and Campbell,P.
Journal of Coatings Technology ,march 1982,vol.54,no.686
"Salt Spray Testing for Short Term Evaluation of Coatings"

ASTM Committee E.44 on Solar Energy Conversion
E44.04.02, Oct.1980,pp.1-22
"Performing Accelerated Outdoor Weathering Using Concentrated
Natural Sunlight"

Back,E.and Sandstrom,E.
Holz als Roh-und Werkstoff,40 (1982)
"Critical Aspects on Accelerated Methods for Predicting
Weathering Resistance of Wood Based Panels"

Bailey,D.and Vogl,O.
J. Macromol. Sci.-Rev. Macromol. Chem.,C14(2),1979,pp.267-293
"Polymeric Ultraviolet Absorbers"

Bauer,D.R.
Journal of Applied Polymer Science, 1982,vol.27,pp.3651-3662
"Degradation of Organic Coatings"

Berens,A.R.and Hopfenberg,H.B.
Journal of Polymer Science,1979,vol.17,pp.1757-1770
"Induction and Measurement of Glassy-State Relaxations
by Vapor Sorption Techniques"

Berner,G. and Rembold,M.
FATIPEC,82
"New Lightstabilsers for High Solid Coatings"

Brand,B.G.,Nowacki,L.J.,Mirik,W.and Mueller,E.R.
Journal of Paint Technology, Sept.1968,vol.40,no.524
"Predicting Service Life of Organic Coatings"

Brown,D.W.,Lowry,R.E.and Smith,L.E.
Macromolecules,March-April 1980,vol.13,no.2,pp.248-252
"Kinetics of Hydrolytic Aging of Polyester Urethane
Elastomers"

Cassidy,P.and Aminabhavi,T.
J. Macromol. Sci. 1981,pp.89-133
"Enhanced Environmental Degradation of Plastics"

Bibliography (Continued)

Cheu,E.and Osawa,Z.
Journal of Applied Polymer Science,1975,vol.19,pp.2947-2959
"Study of the Degradation of Polyurethane. I. The Effect of Various Metal Acetylacetonates on the Photodegradation of Polyurethanes"

Chiang,S.S.,Marshal,D.B.and Evans,A.G.
Lawrence Berkeley Laboratory,1980
"A Simple Method for Adhesion Measurements"
Coating Films Which Are Pigmented with Titanium Dioxide"

Christensen,R.M.
Journal of Rheology,25(5),1981,pp.529-536
"Residual-Strength Determination in Polymeric Materials"

Christensen,R.M.
Journal of Rheology,25(5),1981,pp.517-528
"Lifetime Predictions for Polymers and Composites under

Colling,J.H.and Dunderdale,J.
Progress in Organic Coatings,1981 v 9 ,pp.47-84
"The Durability of Paint Fibers Containing Titanium Dioxide"

Colling,J. and Dunderdale,J.
Advances in Organic Coatings Science and Technology,vol.IV,1980
"The Durability of Paint Films Containing Titanium Dioxide-Contraction, Erosion and Clear Layer Theories"

Connelley,R.W.,Parsons,W.F.and Pearson G.H.
Journal of Rheology,25(3),1981,pp.315-328
"Prediction of Peel Adhesion using Extensional Rheometry"

Cooney,J.D.
Polymer Engineering and Science,June 1982,vol.22,no.8
"The Weathering of Engineering Thermoplastics"

Cunningham,J.and Hodnett,B.
J. Chem. Soc.,Faraday Trans.1,1981,77 pp.2777-2801
"Kinetic Studies of Secondary Alcohol Photo-oxidation on ZnO and TiO_2 at 348 K Studied by Gas Chromatographic Analysis"

Cunningham,G.and Hansen,C.
Journal of Coatings Technology,Nov.1981,vol.53,no.682
"Examination of Weathered Coatings by Photoelectron Spectroscopy and Fourier Transform Infrared Spectroscopy"

Davis,A.and Gardiner,D.
Polymer Degradation and Stability,1982,vol.4, pp.145-157
"An Ultraviolet Radiation Monitor for Artificial Weathering Devices"

Bibliography (Continued)

Demjaneko,M.and Dusek,K.
Macromolecules,June 1980,vol.13,no.3,pp.571-579
"Statistics of Degradation and Cross-Linking of Polymer Chains with the Use of the Theory of Branching Processes"

Derringer,G.C. and Markham,R.L.
ACS Meeting-March 1982
"A Computer Based Methodolgy for Matching Polymer Structures with Required Properties"

Dwight,D.W., Nockengost,K.W.and Nockengost,R.F.
Environ. Degrad. Eng. Mater.Hydrogen,Proc.Int.Conf.,2nd, 1981,pp.483-94
"Failure of Protective Coatings: Field Test and Laboratory Simulation"

Feist,W. and Rowell,R.
American Chemical Society,1982
"UV Degradation and Accelerated Weathering of Chemically Modified Wood"

Gledhill,R.A., Kinloch,A.J.and Shaw,S.J.
J. Adhesion,1980,vol.11,pp.3-15
"A Model for Predicting Joint Durability"

Haken,J.K.
Progress in Organic Coatings,1979,vol.7,pp.209-252
"The Characterization of Polymer and Coatings Materials Using Gas Chromatography and Chemical Degradation"

Holland,R.V,and Santangelo,R.A.
Journal of Applied Polymer Science,1982,vol.27,pp.1681-1689
"Spectrophotometric Determination of Water Vapor Permeation through Polymer Films"

Huisman,H.F. and Linden,J.
FATIPEC,82
"Degradation of Polyurethanes in Organic Solvents"

Joint Services Research and Development Committee on Paints and Varnishes
Journal of the Oil & Colour Chemists' Association,Feb.1964, vol.47,no.2
"Accelerated Weathering of Paint Films"

Kaempf,G.,Voelz,H,G.,Klaeren,A.and Papenroth,W.
Advances in Organic Coatings Science and Technology,vol.IV
"Degradation Behavior of Pigmented Organic Coatings as a Function of the Spectral Energy Distribution of the Incident Radiation"

Kaempf,G.,Papenroth,W.and Holm,R.
Farbe und Lack 73,no.7,pp.606-618
"Observation and Interpretation of the Micromorphological Degradation Process During the Weathering of

Koros,W.J., Chern,R.T. Stannett,V.and Hopfenberg,H.B.
Journal of Polymer Science,1981,vol.19
"A Model for Permeation of Mixed Gases and Vapors in Glassy Polymers"

Leaver,Ian H.
Journal of Polymer Science,1982,vol.20,pp.2417-2427
"The Action of a Benzotriazole Light Stabilizer in Wool"

Major,Mike
Major Enterprises
"Boeing Takes Paint Testing One Step Beyond"

Martin,J.
National Bureau of Standards
"The Transformation Function Commonly Used in Life Testing Analysis"

Martin,K.and Rolles,R.
Journal of Paint Technology, July 1967,vol.39,no.510
"Durability of Precoated Aluminum Products"

Mayhew,K.G.
2nd Annual SEM Symposium,April 1969
"A Look at Polymer Morphology, Poly-(Ethylene Terepthalate)"

Mead,J.W.,Mead,K.E.,Auerbach,I.and Ericksen,R.
Ind.Eng.Chem.Prod.Res.Dev.,1982,21,pp.158-163
"Accelerated Aging of Nylon 66 and Kevlar 29 in Elevated Temperature,Elevated Humidity,Smog,and Ozone"

Mijovic,J.
Ind, Eng. Chem. Prod. Res. Dev., 1982,21,pp.290-296
"Structure-Property Relationships in Neat and Reinforced

Minsker,K.S.,Lisitsky,V.V.and Koleson,S.V.
J. Macromol. Sci.-Rev.Macromol. Chem.,C20(2),1981,pp.243-308
"New Developments in Degradation and Stabilization of Polymers Based on Vinyl Chloride"

Muller,K.,Barth,T.and Boxhammer,J.
Farbe Und Lack,87,(1981),no.4,pp.253-261
"The Quality Profile of Clear Acrylic Melamine Lacquer Systems as a Measure of the Behavior of Materials During Artificial and Natural Weathering"
Epoxy Resins Exposed to Aggressive Environment"

Bibliography (Continued)

Murray,J.B.,Perry,G.J.and Vertessy,M.T.
J. Macromol. Sci.-Chem.,A 17(2),1982, pp.265-272
"In-Service and Weather Station Exposure of Grey and Black Pvc Covered Conductors"

Nash,R.J.,Jacobs,D.M.and Selig,R.F.
Journal of Colloid and Interface Science,June 1979,v.70,no.2
"Substrate Effects on the Mechanochemical Degradation of Thin Polymeric Coatings"

Nilsson,E.and Hansen,C.
Journal of Coatings Technology,Sept.1981,vol.53,no.680
"Evaporation and Vapor Diffusion Resistance in Permeation Measurements by the Cup Method"

Oesterle,K.M.
Advances in Organic Coatings Science and Technology,vol.III
"New Insights in the Structure and Behavior of Polymers and Pigmented Polymer Films"

Oldfield,D.
J. Macromol. Sci.-Chem.,A 17(2),1982,pp.273-285
"Weathering of a Thermoplastic Elastomer"

Osawa,Z.,Cheu,E.and Ogwara,Y.
Polymer Letters Edition,1975,vol.13,pp.535-542
"Study of the Degradation of Polyurethane. II. ESR Study on the Photodecomposition of Polyurethanes and Ethylphenylcarbamate"

Osawa,Z.,Cheu,E.and Nagashima,K.
Journal of Polymer Science,1977,vol.15,pp.445-450
"Study of the Degradation of Polyurethanes. III. Mechanism of the Photodegradation of Polyurethane."

Osawa,Z.and Nagashima,K.
Polymer Degradation and Stability
"Study of the Degradation of Polyurethanes-Part 5: Photo-Decomposition of Ethyl N-Phenylcarbamate, Methylene Bis (Ethyl N-Phenylcarbamate) and Polyurethane in Solution"

Osawa,Z.,Nagashima,K.,Ohshima,H.and Cheu,E.
Journal of Polymer Science,1979,vol.17,pp.409-413
"Study of the Degradation of Polyurethanes. VI. The Effect of Various Additives on the Photodegradation of Polyurethanes"

Piens,M. and Verbist,R.
Lehigh University-Corrosion Prevention by Organic Coatings Aug.1980
"Electrochemical Values-Their Significance When Applied to a Coated Substrate"

Bibliography (Continued)

Popov,A.A.,Blinov,N.N.,Krisyuk,B.E.and Zaikov,G.E.
Eur. Polym. J.1982,vol.18,pp.413-420
"Oxidative Destruction of Polymers Under Mechanical Load"

Princen,L.H.,Baker,F.L.and Stolp,J.A.
ACS-April,1973
"Monitoring Coatings Performance Upon Exterior Exposure"

Prosser,J.L.
Modern Paint and Coatings, July 1977,pp.47-51
"Internal Stress Studies"

Pukanszky,B.,Nagy,T., Kelen,T.and Tudos,F.
Journal of Applied Polymer Science,1982,vol.27,pp.2615-2623
"Comparison of Dynamic and Static Degradation of Poly(vinyl Chloride)"

Rehacek,K.
Fatipec 78,pp.573-580
"Crack Propagation in the Paint Film,Its Measurement and Importance for the Study of Paint Film Structure"

Ruggeri,R.T.and Beck,T.R.
Electrochemical Technology Corp., Seattle,WA
"An Investigation of the Mass Transfer Characteristics of Polyurethane Paint"

Saarnak,A. Nilsson,E.and Kornum,L.O.
J.Oil Col. Chem. Assoc., 1976,59,pp.427-432
"Usefulness of the Measurement of Internal Sresses in Paint Films"

Schneider,M.H.
Journal of Paint Technology,Aug.1970,vol.42,no.547
"Coating Penetration into Wood Substance Studied with Electron Microscopy Using Replica Techniques"

Shalaby, S.W.
Journal of Polymer Science,1979,vol.14,pp.419-458
"Radiative Degradation of Synthetic Polymers"

Stanton,J.M.
Journal of Paint Technology,1967,vol.39,no.514
"Evaluation of the Dew Cycle Method of Accelerated Testing"

Tahan,M.,Molloy.R.,and Tighe,B.
Journal of Paint Technology,March 1975,v.47,no.602
"Comparison of Reflectance and Related Methods for Studies of Film Surface Deterioration"

Tooke,W.R.and Montalov,J.R.
Journal of Paint Technology,1966,vol.38,no.492
"Coatings Adherence Measurement by an Angular Scribe-Stripping Technique"

Bibliography (Continued)

Tsuda,M.and Oikawa,S.
Journal of Polymer Science,1979,vol.17,pp.3759-3773
"Theoretical Aspect of the Radiation Effects of Polymers"

Voulgarides,E.V.and Banks,W.B.
Journal of the Institute of Wood Science,1981,vol.9
"Degradation of Wood During Weathering in Relation to Water Repellent Long-Term Effectiveness"

Wilska,S.
Journal of Paint Technology,April 1971,vol.43,no.555
"Solvent Etching: New Technique for Electron Microscope Studies of Dry Paint Films"

Winslow,F.H.
Makromol. Chem., Suppl. 2,1979,pp.27-34
"Recent Studies of Polymer Degradation and Stabilization"

Yamagata,T.,Jshii,T.,Takanaka,Y.and Handa,T.
Kobunshi Robunshu, Nov.1979,vol.36,no.11,pp.767-771
"The Effect of Antioxidants on the Photodegradation of Polyurethane Paints"

Yan,Johnson
Science,Msrch 1982,vol.215
"Kinetics of Delignification : A Molecular Approach"

Zicherman,J.B. and Thomas,R.J.
Journal of Paint Technology,July 1972,vol.44,no.570
"Scanning Electron Microscopy of Weathered Coatings on Wood"

Azarov, V. A., et.al., Korroz. Zashch. Neftegazov. Prom-sti. Date: 1982 Number: 10, Pages 19-20 Method for the accelerated study of structural changes in the aging of polymeric film coatings.

Camina, Martin; Report Date: 1981 Number: Order No. Paintra-82/07 Pages: 14pp. Evaluation of some artificial weathering cycles.

Chapman, J. D.; Aust. Occa Proc. News Date: 1981 Volume: 18 Number: 12 Pages: 4-6, 8-9 Durability of automotive surface coatings.

Chase, D. B., et.al.; Appl. Spectrosc. Date: 1982 Volume: 36 Number: 2 Pages: 155-157 Applications of diffuse relectance FT-IR to pigment photodecomposition in paint.

Colling, J. H. et.al., Date: 1982 Volume: 4 Number: Int. Conf. Org. Coat. Sci. Technol., Proc., 6th 1980 Pages: 205-238 The durability of paint films containing titanium dioxide- contraction, erosion and clear layer theories.

Bibliography (Continued)

Cunningham, Glenn P.; Hansen, Charles M., Technol. Imiebi Rurf.: Relat. Form., Weld. Painting, Proc. Conf. Date: 1982 Pages: 297-313 Examination of weathered coating by photoelectron spectroscopy and Fourier transfrom infrared spectroscopy.

Denisenko, L. V., et. al.; Kompoz. Polim. Mater. Date: 1982 Volume: 14, Pages: 37-39 New polyurethane coating materials and the effectiveness of their use in the national economy.

Fukushima, Toshio; Durability Build. Mater. Date:1983 Volume: 1, Number: 4, Pages: 327-343 Deterioration processes of polymeric materials and their dependence on depth from surface.

Gerlock, J. L. et.al, Date: 1983 Volume: 19 Number: 1 Pages: 11-18 Nitroxide kinetics during photodegradation of acrylic/malamine coatings

Goering, Wolfgang, et.al., Corros. Control Org. Coat. Date: 1981 Pages: 255-262 Comparative investigations of corrosion performance of coating systems for automobiles by different methods of accelerated weathering.

Grentzer, Thomas H., et.al., Polym. Prepr. Date: 1981 Volume: 22 Number: 1 Pages: 318-319 Quantitative reaction kinetics by differential scanning calorimetry.

Ishimura, Hidekazu; Fushoku Boshoku Bumon Iinkai Shiryo Date: 1982 Volume: 21, Number: 5, Pages: 17-35 Corrosion resistance and durability test of coated films.

Kaempf, Guenter; Papenroth, Wolfgang; Kunststoffe Date: 1982 Volume: 72 Number:7 Pages: 424-429 Parameters influencing the accelerated weathering of pigmented plastics and paints.

Kaempf, G., et.al., Congr. Fatipec Date: 1982 Volume: 16th Number: Vol. 3 Pages: 167-174 Accelerated observation of chalking under the electron microscope.

Kaempf, G., et.al., Adv. Org. Coat. Sci. Technol. Ser. Date: 1982 Volume: 4 Number: Int. Conf. Org. Coat. Sci. Technol., Proc., 6th, 1980 Pages: 239-255 Degradation behavior of pigmented organic coatings as a function of the spectral energy distribution of the incident radiation.

Kiryu, Haruo; Kogyo Toso Date: 1982 Volume: 59, Pages: 83-88. Heterogeneous structure and defect of film forming polymers. III

Konovalov, O. K., et. al; Lakokras. Mater. Ikh Primen Date:1983 Number 1 Pages: 42-43 Accelerated method for estimating the oxidation rate of coating materials.

Kosuge, Norio; Mukaihara, Fuminori; Shikizai Kyokaishi Date: 1982 Volume: 55 Number: 10, Pages: 709-714 Study on thermal degradation mechanism of epoxy-amine resin coatings by torsional braid analysis.

Bibliography (Continued)

Kumanotani, Ju; Kinzoku Hyomen Gijutsu Date: 1981 Volume: 32 Number: 11 Pages: 579-586 Degradability of organic coating films-chemical reaction in degradation.

Liu, Tony; Corros. Control Org. Coat., Date: 1981 Pages: 247-254 Is the salt fog test an effective method to evaluate corrosion resistant coatings?

Maiorova, N. V., et.al., Modif. Polim. Mater. Date: 1980 Volume: 9 Pages: 152-158 Study of the structure and properties of polyurethane films in the aging process.

Nikitin, P. V.; Pirogov, A. E.; Inzh.-Fiz. Zh. Date: 1981 Volume: 41 Number: 6 Pages: 1078-1082 Determination of the characteristics of polymer decomposition by the semi-infinite body method.

Oesterle, K. M.; Congr. FATIPEC Date: 1982 Volume: 16th Number: Vol. 4 Pages: 41-90 Qualification and prediction of the behavior of organic coatings by means of micromechanical analytical methods (interference factors)

Okuda, Satoshi; Iguchi, Takayuki; Adv. Org.Coat. Sci. Technol. Ser. Date: 1982, Volume: 4 Number: Int. Confl Org. Coat. Sci. Technol., Proc., 6th 1980 Pages: 256-266 Electrical measurement of liquid penetration into organic coatings.

Opiela, Karl Heinz; Kunstharz-Nachr Date: 1983 Volume: 19, n Pages: 17-19 Correlation between accelerated and natural weathering of dispersion paints with varying levels of pigmentation.

Pini, G. Oberflaeche-Surf Date: 1982 Volume: 23, Number: 11 Pages: 391-396 Selection and testing of coating systems.

Rouchaudhury, A. N., et.al., Paintindia, Annu. Date: 1981 Pages: 111-114 Study on surface coating durability in exterior exposure.

Sano, Tsunoru; Kenkyu Hokokushu-Tokushima-ken Kogyo Shikenjo Date: 1980 Pages: 44-51 Study on degradation of free paint film.

Shvartsman, I. S., et, al.; Lakokras. Mater. Ikh Primen Date: 1983 Number 1 Pages: 30-32 Prediction of the protective action of weather-resistant coatings.

Skledar, S., et.al., Congr. Fatipec Date: 1982 Volume: 16th Number: Vol. 2 Pages: 335-350 Investigation of the coatings degradation by Auger electron spectroscopy.

Takeshima, Eiki,et.al, Nisshin Seiko Giho Date: 1982 Volume: 47, Pages: 37-50 Forcast of longevity of paint coated and plastc film laminated steel sheets. Part 3. Analysis of degration of organic coatings by FT-IR.

Bibliography (Continued)

Troyanovskaya, G. I.; Zelenskaya, M. N., Teor. Prikl. Zadachi Treniya, Iznosa Smazki Mash. Date: 1982 Pages: 96-103 Calculation of the force of friction between a polymer and a metal.

Webb, J. D. ,et.al., Report Date: 1981 Number: Seri/Tp-255-1408; Order No. De82006069 Pages: 3 pp Photochemical degradation of polymeric coatings on mirrors as studied in situ using FT-IR reflection-absorption spectroscopy.

☆U.S. Government Printing Office:1992—750-113/80010