REPORT

Contract No. F09603-90-D-2217-Q805

Experimental Evaluation of the Adhesive Degradation and Corrosion Potential of Silicone Fluids

To

Newark AFB

January, 1995

Battelle

Putt/rig Technology To Work

DTIC QUALITY INSPECTED 1

Battelle

505 King Avenue
Columbus, Ohio 43201-2693
Telephone (614) 424-6424
Facsimile (614) 424-5263

January 27, 1995

Mr. Tesfa Abraha
Chemical Engineer, AGMC/MAEL
813 Irvin Wick Drive., W
Newark AFB, OH 43057-0027

Dear Tesfa:

Contract No. F09603-90-D-2217-Q805
Study to Improve the Reliability and Maintainability
(R&M) of Inertial Navigation and Guidance System Components

Reference: Contract Data Requirements List (a) Sequence NO. A003

Enclosed are four (4) copies of our Final Report on your project referenced above. Our efforts have established that the siloxane fluids 0S-10 and 0S-30 have less impact on the physical properties of epoxy adhesives and metal substrates than the control solvent 1,1,1-trichloroethane (TCA).

Enclosed are two (2) copies of Form DD250. Please return one (1) signed copy to me indicating your acceptance of our Final Report.

We have enjoyed working on this timely and challenging project and are confident that the data generated will provide the information you need to make these solvents part of your maintenance process. If you have any questions, please call me at (614) 424-3294 or Dr. Mangaraj at (614) 424-6414.

Yours truly,

Robert H. Prause

Robert H. Prause
Senior Program Manager
AFMC Programs

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

RHP:jvd
Enclosures (6)

cc: Captain G. Letourneau (Letter Only)
DCMAO-Dayton (Letter Only)

19960520015

CONTENTS

Page

EXECUTIVE SUMMARY . . . . . .

1.0 INTRODUCTION 1

1.1 Background 1
1.2 Objective 2
1.3 Technical Approach 2

2.0 EXPERIMENTAL EVALUATION OF ADHESIVE DEGRADATION POTENTIAL 3

2.1 Test Materials 3
2.2 Test Matrix Design Considerations 5
2.3 Preparation of Adhesive Test Specimens 11
2.4 Preparation of MetaJ Test Specimens 13
2.5 Laboratory Testing ...,.... 14
2.5.1 Laboratory Testing Adhesive Degradation 14
2.5.2 Laboratory Testing of Metal Compatibility 19
2.6 Experimental Results 19
2.6.1 Results of Adhesive Degradation Study 19
2.6.2 Results of Metal Compatibility Study 19

3.0 STATISTICAL ANALYSIS OF THE RESULTS . . . . . , ... 27

3.1 Analytical Approach 27
3.2 Statistical Analysis of Results 35
3.2.1 Analysis of Adhesive Results 35
3.2.2 Analysis of Metal Compatibility Results 43
3.3 Review of the Results Analysis 43

4.0 INSTRUMENTAL ANALYSIS AND MECHANISM OF DEGRADATION . . . 46

4.1 Selection of Specimens for Analytical Study 46
4.2 Results of Instrumental Analysis 47
4.2.1 Differential Scanning Calorimetry 47
4.2.2 Scanning Electron Microscopy Study 57
4.2.3 Fourier Transform Infrared Spectrophotometry 74

5.0 SUMMARY AND CONCLUSIONS 79

6.0 REFERENCES 83

CONTENTS

Page

APPENDIX A. TEST PLAN . . . . . A-l

APPENDIX B. CATEGORICAL FACTORS AND RESPONSE FILENAMES B-1

TABLES

Table 1. Adhesive Inventory With Cure Schedules 4

Table 2. Data Entry Form 8

Table 3. Typical Results of Weight Change and Hardness Change After Soaking/Sonication 16

Table 4. Typical Results of Lap Shear Measurement Strength (psi) After Sonication in Siloxane Solvent 20

Table 5. Shore D Hardness of Bulk Specimens After Soaking in Cleaning Solutions and Drying 21

Table 6. Percent Weight Change of Bulk Specimens After Soaking in Cleaning Solutions and Drying 22

Table 7. Shore D Hardness of Bulk Specimens After Sonification in Cleanings Solutions After Drying. ., ...23

Table 8. Percent Weight Change After Sonification in Cleaning Solutions and Drying 24

Table 9. Average Lap Shear Strength (Psi) and Standard Deviation (Psi) of Specimens After Soaking in Siloxane Solvents 25

Table 10. Average Lap Shear Strength and Standard Deviation of Specimens After Sonification in Siloxane Solvents and Drying 26

Table 11. Summary of Significant Lap Shear Differences on Exposure of Test Specimens to Solvents and Cleaning Process . . . . . , . . 37

Table 12. Summary of Significant Shore D Differences on Exposure of Test Specimens to Solvents and Cleaning Process 38

TABLES

Page

Table 13. Summary of Significant Percent Weight Changes After Cleaning (Wet) Before Drying 39

Table 14. Brief Summary of Significant Percent Weight Changes After Cleaning and Drying 40

Table 15. Statistical Differences Between Solvents According to Weight Data 41

Table 16. Factors Leading to Apparent Changes and Techniques to Study 42

FIGURES

Page

Figure 1. Proposed Experimental Design.. 7

Figure 2. Specimen Exposure and Test Protocol 9

Figure 3. Test Matrix for Metal Compatibility Study 10

Figure 4. Form and Dimensions of Test Specimen 12

Figure 5. Weight Changed Observed on Exposure to Siloxane Cleaners (A12017) 28

Figure 6. Weight Changed Observed on Exposure to Siloxane Cleaners (Anodized A12017) 29

Figure 7. Weight Changed Observed on Exposure to Siloxane Cleaners (Beryllium) 30

Figure 8. Weight Changed Observed on Exposure to Siloxane Cleaners (Cartridge Brass) 31

Figure 9. Weight Changed Observed on Exposure to Siloxane Cleaners (Chromium Copper) 32

Figure 10. Weight Changed Observed on Exposure to Siloxane Cleaners (Chromium Steel) 33

FIGURES

Page

Figure 11. Weight Changed Observed on Exposure to Siloxane Cleaners (60/40 Solder) 34

Figure 12. DSC Trace of Adhesive A (Unexposed Control) 48

Figure 13. DSC Scan of Adhesive A Exposed to Siloxane Cleaner OS-10 for One Cycle 49

Figure 14. DSC Scan of Adhesive Unexposed Control 50

Figure 15. DSC Scan of Adhesive D Soakedin Siloxane Cleaner OS-10 for lHourat RT 51

Figure 16. DSC Scan of Adhesive E Unexposed Control. 53

Figure 17. DSC Scan of Adhesive E Exposed to OS-30 at 120 °F for 2 Cycles of Sonication 54

Figure 18. DSC Scan of Adhesive H Unexposed Control 55

Figure 19. DSC Scan of Adhesive H Exposed to Siloxane 0S-30 at 120 °F for 2 Cycles of Sonication 56

Figure 20. DSC Scan of Adhesive F Unexposed Control 58

Figure 21. DSC Scan of Adhesive F Exposed to Siloxane Cleaner 0S-10 for 2 Cycles of Sonication 59

Figure 22a. SEM Picture of Adhesive E, Soaked in 0S-30 for 1 Hour, at120°F, X=15 60

Figure 22b. SEM Picture of Adhesive E, Soaked in 0S-30 for 1 Hour, at120°F, X=500 60

Figure 23a. Scanning Electron Micrography of Adhesive A, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=15 61

Figure 23b. Scanning Electron Micrograph of Adhesive A, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=1000 61

FIGURES

Page

Figure 24a. SEM Picture of Adhesive C, Subjected to Ultrasonic Cleaning in OS-10 for 2 Cycles at RT, X=10 62

Figure 24b. SEM Picture of Adhesive C, Subjected to Ultrasonic Cleaning in OS-10 for 2 Cycles at RT, X=1000 62

Figure 25a. SEM Picture of Adhesive B, Subjected to Ultrasonic Cleaning in OS-lO at RT, X=10 63

Figure 25b. Scanning Electron Micrograph of Adhesive B, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=1000 63

Figure 26a. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning in OS-lOat RT, X=10 64

Figure 26b. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=1500 64

Figure 27a. SEM Picture of Adhesive E, Subjected to Ultrasonic Cleaning for 2 Cycles in OS-10, X=200 66

Figure 27b. SEM Picture of Adhesive E, Subjected to Ultrasonic Cleaning for 2 Cycles in OS-10, X=500 66

Figure 28a. SEM Picture of Adhesive E, Soaked in 0S-10 for 1 Hour, X=l0 67

Figure 28b. SEM Picture of Adhesive E, Soaked in 0S-10 for 1 Hour, X=500 67

Figure 29a. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning for 2 Cycles in TCA, X=10 68

Figure 29b. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning for 2 Cycles in TCA, X=1000 68

Figure 30a. SEM Picture of Adhesive E, Soaked for 1 Hour in 0S-30 at RT, X=1O 69

Figure 30b. SEMPicture of Adhesive E, Soaked for 1 Hour in OS-30 at RT, X=1 000 69

FIGURES

Page

Figure 3 la. SEM Picture of Adhesive H of Unexposed Control, X=12 70

Figure 3 lb. SEM Picture of Adhesive H of Unexposed Control, X=500 70

Figure 32a. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in OS-10 at RT, X=10 71

Figure 32b. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in OS-10 at RT, X=500 71

Figure 33a, SEM Picture of Adhesive H, Subjected to 1 Cycle Ultrasonic Cleaning in OS-30, X=10 72

Figure 33b. SEM Picture of Adhesive H, Subjected to 1 Cycle Ultrasonic Cleaning in OS-30, X=270 72

Figure 34a. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in OS-30, X=10 73

Figure 34b. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in OS-30, X=500 73

Figure 35. IR Spectra of Epoxy Resin Along With Curatives . . . . . , 75

Figure 36. FT-IR Spectra of Unexposed Adhesive E 76

Figure 37. FT-IR Spectra of the Extract of Adhesive H in 0S-10 77

Figure 38. FT-IR Spectra of the Extract of Adhesive H Exposed to 0S-10 78

Figure 39. FT-IR Spectra of Unexposed Adhesive H 80

Figure 40. FT-IR Spectra of Adhesive H Exposed to OS-30 at 120 F, 2 Cycles Ultrasonication 81

Figure 41. FT-IR Spectra of Adhesive E Exposed to 0S-30 at 120°F 82

EXECUTIVE SUMMARY

The Aerospace Guidance and Metrology Center located at Newark Air Force Base repairs and maintains navigation and guidance equipment for the United States Air Force and other components of the Department of Defense. During repair, the components are cleaned with solvents to remove hydrocarbons and other low molecular weight organic and metal organic compounds. It is important that these cleaning fluids not degrade the physical properties of the metal substrates and/or epoxy components. The Air Force has identified two environmentally compatible cleaning fluids, 0S-10 and 0S-30 as substitutes for the currently used CFC-113 and 1,1,1 -trichlorethane solvents that are ozone layer destroying chemicals. This program assessed the corrosion and adhesive degradation potential of OS fluids on the adhesives and metal substrates used in Air Force inertial navigation and guidance systems.

Bulk specimens of the adhesives and lap shear specimens were prepared and exposed under controlled conditions for up to 16 hours. Bare metals were also exposed to the solvents. Adhesive properties and the metal corrosion potential were evaluated and compared with the effects of the control solvents, 1,1,1 -trichloroethane and CFC- 113, on the same materials. The results show that OS- 10 and 0S-30 have an insignificant impact on the adhesives and metals. In all cases, the change in properties induced by 0S-10 and 0S-30 were less than the effects observed using the control solvents.

FINAL REPORT

for

EXPERIMENTAL EVALUATION OF THE ADHESIVE DEGRADATION AND CORROSION POTENTIAL OF SILICONE FLUIDS

1.0 INTRODUCTION

1.1 Background

The Aerospace Guidance and Metrology Center (AGMC) located at Newark Air Force Base (NAFB), Ohio repairs inertial navigation and guidance equipment for the United States Air Force and other Department of Defense (DoD) components. The critical tolerance requirements of these devices require controlled cleaning processes during repair. Currently many of these processes use chlorofluorocarbons (CFC) and chlorinated hydrocarbons (CHC) which the Montreal Protocol identified as ODCS and established agreements to eliminate their production. Driven by safety and environmental concerns, AGMC has been aggressively implementing new maintenance procedures and is replacing these environmentally unacceptable cleaning agents with more environmentally acceptable alternatives. Many of the new cleaning processes use deionized water and aqueous detergent solutions. Although some of these have worked very well, there are certain applications where aqueous processes are not suitable.

In a recent study, Dow Corning engineers have shown that hexamethyl siloxane and its oligomers are very good cleaners for grease and cutting fluids and they are environmentally benign. Initial testing at AGMC indicated that siloxane cleaners can adequately clean some of the components which cannot be cleaned by aqueous processes. However, it was necessary to evaluate the impact of these new solvents on adhesive and sealant performance and their compatibility with various metals before AGMC could implement siloxane-based cleaning procedures.

Battelle carried out an experimental evaluation of the adhesive degradation and corrosion potential of hexamethyl siloxane (OS-10) and one of its oligomers (0S-30) using

adhesives and metal substrates currently used in inertial guidance and navigation equipment. This report summarizes the experiments and the results of this evaluation.

1.2 Objective

The objective of this study was to assess potential adhesive degradation and metal compatibility problems which may be associated with the use of siloxane cleaners. Metals and adhesives in this context refer to materials used in the construction of inertial guidance and navigation equipment. Lack of compatibility between metal and siloxane cleaners refers to degradative interaction such as corrosion, pitting, discoloration, etc. Adhesive degradation refers to decrease or loss of adhesion between metal substrates and the adhesive or sealant following exposure to the cleaner. The scope of the program included exposure of the adhesive specimens in bulk and in lap shear specimens followed by instrumental analysis of adhesive degradation and corrosion. The siloxane solvents were compared to 1,1, 1-trichloroethane (TCA), which has been the traditional solvent of choice.

1.3 Technical Approach

To achieve the objectives of the program, a detailed work plan was prepared and submitted to AGMC (Appendix A). The work plan consisted of six tasks as follows:

- Selection of adhesives, metals, and siloxane cleaners and test parameters (Task 3.3)
- Test Plan - statistical design of test matrices and methodology for data analysis (Task 3.4)
- Preparation of adhesive and metal tests specimens (Task 3.5)
- Testing of adhesive degradation potential and metal compatibility (3.6.1, and 3.6.2)
- Analysis of results (3.6.3)
- Conclusions and recommendations.

2.0 EXPERIMENTAL EVALUATION OF ADHESIVE DEGRADATION POTENTIAL

The potential for adhesive degradation by siloxane cleaners was experimentally evaluated following the test plan.

The test plan consisted of the following five activities: selection of test materials, protocols for the preparation and exposure of adhesive test specimens, a test matrix, a data analysis and evaluation plan, and an implementation plan. Battelle devised a test matrix using statistical experimental design methodology in order to maximize the significance of the data generated while using a minimum number of experiments. Three replicates were used for each test condition.

2.1 (a) Test Materials

Two siloxane cleaners were used in conjunction with adhesives and sealants commonly used in guidance equipment repaired at AGMC. The two siloxane cleaners are hexamethy siloxane, 0S-10, and its oligomer, 0S-30. A control solvent, trichloroethane (TCA), was used for comparing the degradation potential of the new solvents with the old ones.

The adhesives and their descriptive chemistry are presented in Table 1. These materials represent different chemical types and performance (strength, cure, temperature, Tg) characteristics of commercially available epoxy adhesives. RTV silicone was eliminated from the program because it is very likely to be affected by siloxane solvents.

The seven metals selected for the metals compatibility study were 60 Sn-40 Pb solder, aluminum 2017, anodized aluminum 2017 per MIL-A-8625, beryllium CDA182, cartridge brass CDA260, chromium copper CDA 82, and chromium steel C521OO.

Table 1. Adhesive Inventory With Cure Schedules

Reference Letter Code	Manufacturer Adhesive/Material	Lot #	Ratio	Chemical Type	Cure Schedule Temperature/Time
"A"	Bacon Industries FA 8 Resin BA5 Hardener	 106 223	 100 13.5	Mixture of diglycidyl ether of bisphenol "A" and 2-2' bis (2,3 epoxy propyloxy) phenyl propyl bisphenol "A" cured with aminoethylamino ethyl imidazolidone	200°F/2.0 Hours
"B"	Bacon Industries LCA 4 BA 5	 307 223	 100 4.5	4,4 bismethylidine bisphenol polymer with chloromethyl oxirane cured with aminoethylamino ethyl imidazolidone	200°F/2.0 Hours
"C"	3M, Scotchweld (Gray) "Eccobond" 2216 B/A	 W4068R237 W4058R256	 7 5	Mixture of bisphenol "A" epoxy resin, alumina, and crystalline silica cured with tetraethylene-pentamine	200°F/30 Minutes
"D"	Bacon Industries FA 1 Resin BA 4 Hardener	 115 84	 100 3.2	Bisphenol "A" diglycidyl ether, bis(ethylene oxy) methane containing disulfide links, cured with tri(dimethylamino ethyl) phenol	200°F/2.0 Hours
"E"	Shell Epon 828 Versamid 125	 03THJ07 3M8895	 50 50	Bisphenol "A" diglycidyl ether cured bypolyamide	Room Temperature/24 Hours
"F"	Ciba Geigy Araldite CY 179 Hardener HT 907 Accelerator DY 183	 TF313082 0657092 NGG 101	 100 105 12	Cylcloaliphatic epoxy cured with hexahydrophthalic anhydride	Melt hardener at 120°C (245°F). Add CY179 resin and cool to room temperature. Add accelerator. Apply to coupons and cure 3.0 hours at 248°F
"G"	Grace Stycast 2760 "A" Stycast 2760 "B"	 714284106 714000506	 100 50	Copolymer of epoxy and polyurethane; casting resin	200°F/2.0 Hours
"H"	Tracon Trabon 2133 Resin Trabon 2133 Hardener	 4188 4188	 100 110	Bisphenol "A" epoxy cured with polysulfide hardener	Room Temperature/24 Hours

2.2 Test Matrix Design Considerations

In a previous study with aqueous cleaners, the criteria for the compatibility of the cleaning process were not quantitatively defined. The criteria for success were largely relative with respect to control samples. However, this effort was more sharply defined concentrating on fewer variables, thus permitting the evaluation of quantitative differences. Specifically, differences in adhesive mean property values attributable to experimental factors such as time, temperature, cleaning method and solvent type. The physical properties which were selected for evaluation include lap shear strength, "Shore" D hardness of bulk material and weight changes of bulk specimens. The specific factors for this effort were as follows:

(a) Solvent type: silicone fluids 0S-10 and 0S-30, and control solvent TCA (trichloroethane); these were designated S 1, S2, and Cl respectively.

(b) Cleaning method: two cleaning methods were simulated: sonication (U) and soaking (S).

(c) Time: if the cleaning method was soaking, the times were 1 or 16 hours; if ultrasonic cleaning was employed, then one or two 5-minute cycles were used.

(d) Temperature: specimens were exposed to OS-10, 0S-30, and TCA at approximately 75 °F; in addition, specimens were also exposed to 0S-30 at approximately 120°F.

(e) Adhesives: Eight commercial adhesives designated A through H were evaluated.

For this effort, all factors were considered categorical and all measured responses (measured physical properties) were interval level measurements. With the above considerations in mind, an experimental plan was designed to detect differences in mean

property values of approximately one standard deviation (or better) at the 95 percent confidence level.

Figure 1 graphically represents the experimental design repeated for each of the eight adhesives and for both lap shear and bulk specimens. Each design point (dot) represents a unique combination of experimental conditions, i.e., which solvent is used, whether the cleaning method is sonication (U) or soaking (S), if time is short or long and the applied temperature. In addition, a point has been included for the unexposed control specimens. This same design information is represented in Table 2 as a data entry form for Adhesive A.

Each design point was replicated three times (three specimens) for each of the eight adhesives for both lap shear and bulk properties testing. The 408 lap shear specimens as well as the bulk properties specimens were prepared and subsequently tested in random order.

The design illustrated in Figure 1 is a factorial design which can provide clear (unconfounded) contrasts between the various factor levels including the eight adhesive levels. Temperature was permitted a “high” level only with the 0S-30 solvent. Consequently, 2-way interactions including temperature could not be calculated and temperature effects can not be generalized but apply only to 0S-30.

Specimens were prepared and evaluated in random order in an effort to minimize the effect of any bias error which may occur during the experimental period. Each specimen was distinguished by a number consisting of the adhesive type (A to H), design point in the test matrix (1 to 17), replicate type (a, b, or c) and a serial number representing each specimen (1 to 918). The exposure and test protocol used in the experimental work is presented in Figure 2. The only difference between this protocol and the one proposed in the test plan is that the intermediate weight gain was measured in addition to the final weight gain to focus on the potential of each adhesive for absorbing the siloxane solvent. This could help in explaining the mechanism of adhesive degradation.

A small test matrix was used for the metal compatibility study. This included three solvents, two cleaning methods, two temperatures for TCA and 0S-30, but only room temperature for OS- 10. The cleaning times were the same as those in the adhesive degradation study. The test matrix is presented in Figure 3.

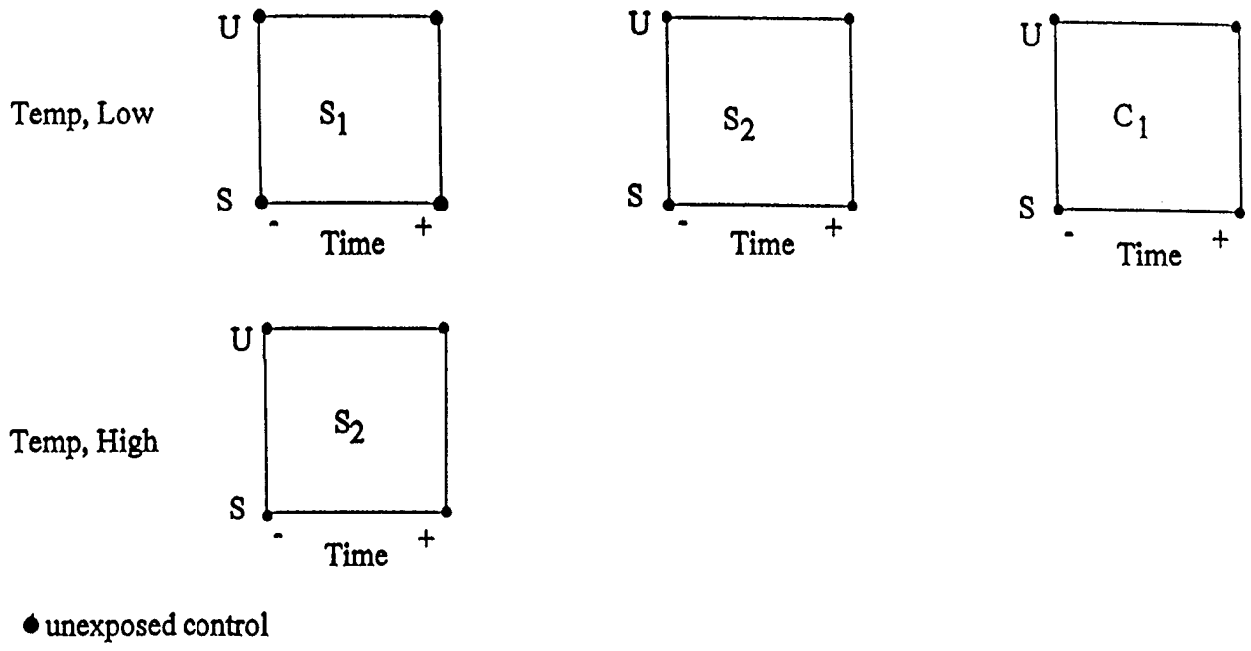


Figure 1. Proposed Exper tal Design

Table 2. Data Entry Form

Design ID	Adhe-sive	Tem-pera-ture	Solvent	Method	Time	Lap Shear	Shore D	Weight Change	DSC/ Tg*
1	Al	T1	S1	u	1				
2	Al	T1	S1	u	2				
3	Al	T1	S1	s	1				
4	Al	T1	S1	s	16				
5	Al	T1	S2	u	1				
6	Al	T1	S2	u	2				
7	Al	T1	S2	s	1				
8	Al	T1	S2	s	16				
9	Al	T1	c1	u	1				
10	Al	T1 ‘	cl	u	2				
11	Al	T1	c1	s	1				
12	Al	T1	cl	s	16				
13	Al	T2	S2	u	1				
14	Al	T2	S2	u	2				
15	Al	T2	S2	s	1				
16	Al	T2	S2	s	16				
17	A1	Unexposed control							

* Tg will be measured for selected samples.

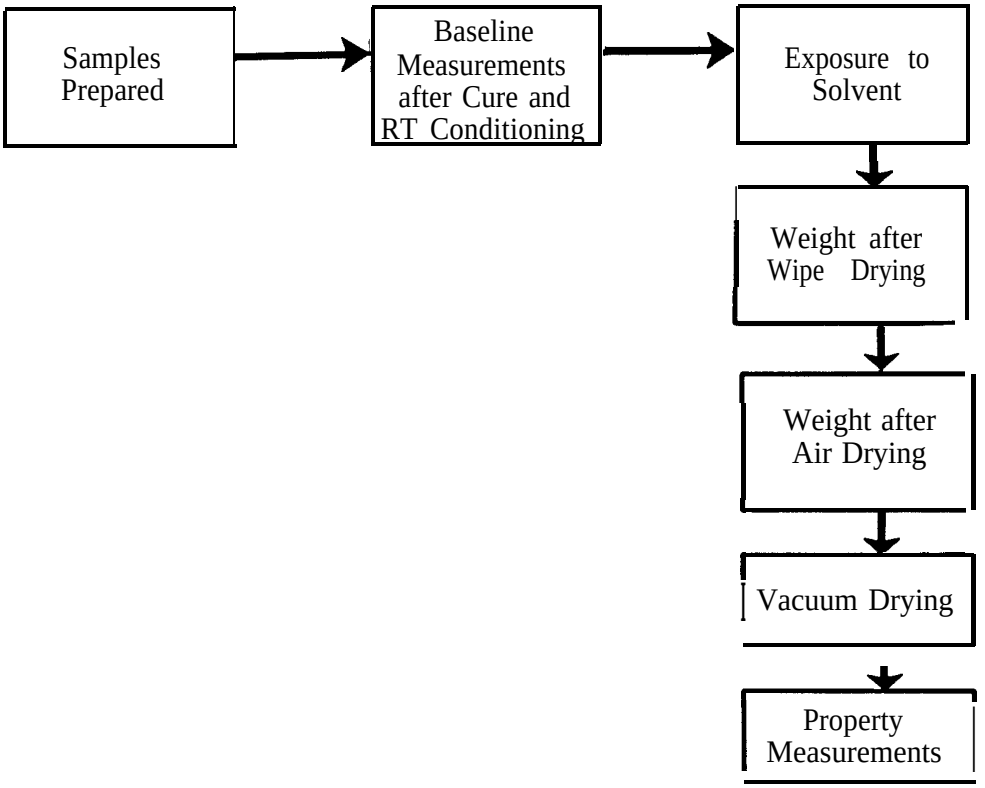


Figure 2. Specimen Exposure and Test Protocol

Experimental Design for Each of the Seven Metals			
Cleaner	Cleaner Method	Time	Temperature
TCA	Sonication	5 minutes	room
	Sonication	5 minutes	120°F
	Soak	16 hours	room
OS-10	Sonication	5 minutes	room
	Soak	16 hours	room
OS-30	Sonication	5 minutes	room
	Sonication	5 minutes	120°F
	Soak	16 hours	room

Figure 3. Test Matrix for Metal Compatibility Study

2.3 Preparation of Adhesive Test Specimens

Two types of test specimens, namely bulk and lap shear, were prepared. The following provides a brief description of the sample preparation procedure.

Bulk Specimen: Small aluminum containers were cleaned with toluene followed by cleaning with acetone and air drying. The two parts of the adhesives were then weighed and then placed into the containers in the ratio suggested by the manufacturer. The two parts were mixed thoroughly and then placed in a vacuum oven for degassing at room temperature for 5 minutes at 28 to 30 mm Hg pressure. The adhesives were then removed from the oven and carefully poured into a Teflon mold. After the adhesives leveled out, the mold was placed in an oven for curing at the temperature and for the time recommended by the adhesive manufacturer. Table 1 provides the names of different adhesives (Part A and B), the mixing ratio, and the time and temperature for cure. After the specimens cooled, they were removed from the mold and the excess material at the edges (flash) was carefully removed using 240-grit sand paper. The specimens were then numbered on the rough surface and stored in a desiccator in the constant temperature room at 23°C and 50 percent humidity.

Lap Shear Specimens: Aluminum coupons (0.063" x 1.0" x 4.0") (Q Panels from Q Panel Company) were used for preparing lap shear specimens. A 0.25" diameter hole was made in each specimen to hang it during etching. Approximately 1" to 2" length (not more than 2") were used for etching the specimens in a sodium bichromate, sulfuric acid solution, following MIL-HDBK-691A, 1965 (p. 26).

The coupons were then stored in a desiccator in the constant temperature room for 24 hours. The adhesives were prepared following the procedure described above. Adhesives were applied to slightly greater than a half-inch length of one end of each specimen. A few glass beads, 105 to 150 μm diameter, were sprinkled on the adhesive's surface to control the thickness. The adhesively-coated ends of the two specimens were then superimposed on each other to provide half-inch overlap joints as shown in Figure 4. The joint was then wrapped

ASTM D 1002-72

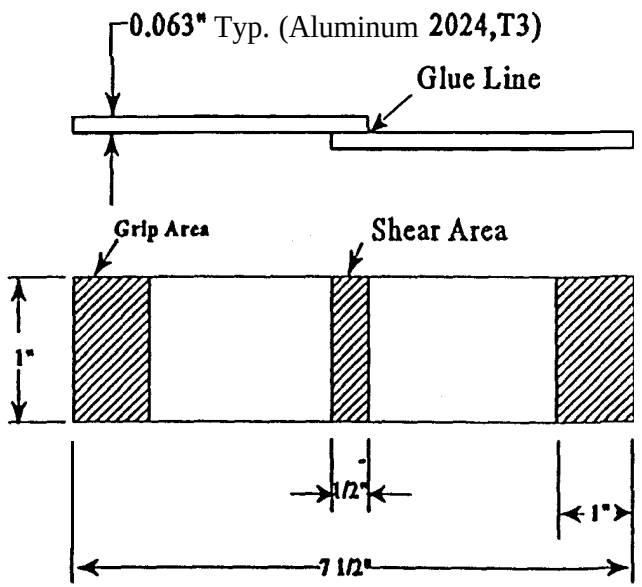


Figure 4. Form and Dimensions of Test Specimen

with a strip of polyethylene sheet and held in place with a binder clip. Specimens were then cured in an oven for the time and temperature specified by the adhesive manufacturer. They were then stored in a constant temperature room for 24 hours, after which the clips and the flashing at the glue line and at the sides of the bond line were carefully removed.

Randomization: To provide better statistically valid results, the samples were prepared at random. In other words, a set of samples as noted in our test matrix, using different adhesives and different replication, were prepared in a single day instead of preparing all samples of a particular adhesive in a single day. Each of the samples was given an ID number where the first letter describes the adhesive, the second number identifies the exposure condition from 1 to 17, the third letter describes the replication, and the fourth number describes the order in which the specimen was prepared. For example, the ID number B7 a41 denotes the specimen using Adhesive B, the test condition 7 (as described in our test plan), replication a and the 41st specimen prepared in a particular day. Spread sheets were prepared using the ID numbers to' introduce the exposure conditions and the test results, as they are obtained.

2.4 Preparation of Metal Test Specimens

The seven metals tested included aluminum 2017, anodized aluminum 2017, beryllium, CDA 182, CDA260, alloy 52100, and solder 60/40. The aluminum coupons were anodized according to MIL-A8625, Type 1. The nominal anodized layer was approximately 0.3 mil thick. and was dyed gold in color.

All the coupons except beryllium and solder 60/40 had a nominal surface roughness of 32 microinch, rms. The beryllium coupons had a surface roughness of approximately 5 to 10 microinch, rms. The 60/40 solder coupons could not be ground by traditional methods because of their soft surfaces and therefore were polished with Scotch Brite abrasive pads. The roughness of the 60/40 solder coupons was measured to be between 16 to 32 micro-inches, rms.

The nominal dimensions of all the coupons except beryllium were 2 inches long, 0.75 inch wide, and one-sixteenth to one-eighth inch thick. The beryllium coupons were supplied by AGMC. These coupons consisted of halves of PIGA accelerometers and were semi-circular in shape, with approximate dimensions of 2 inches high, 2 inches wide, and 2 inches deep.

2.5 Laboratory Testing

2.5.1 Laboratory Testing Adhesive Degradation

The test specimens were exposed to the test solvents and to the control solvent trichloroethane for different intervals of time at room temperature (≈ 75 ºF). For 0S-30, the exposure study was also carried out at 120°F. The specimens were then tested for changes in hardness, weight, and tensile shear strength. The procedure and the results are given below.

Bulk Samples: The bulk specimens in the form of discs were divided into 17 different design sets according to the design of the experimental test matrix. A number of disks were selected at random from each design set and dried in a vacuum oven for one hour at 155 ‘F and 20 mm Hg. The specimens were then allowed to cool for 1 hour in the desiccator and weighed individually to+O.0002 g using an analytical balance. The samples were then placed into 2 ounce glass jars with a Saran cap containing the designated solvent. The jars were placed on mixing rolls to provide for thorough exposure at room temperature. For 120°F exposure, thermal convection currents were enough to provide thorough exposure, so the specimens were not placed on mixing rolls. At the end of the time interval, the disks were wiped with a lintless Chem-Wipe, blow dried, and individually weighed using an analytical balance. The difference in the weight after blow drying and the initial weight gave the percent solvent absorption for each sample for a particular exposure to the solvent. The specimens were then subjected to drying in a vacuum oven at 155 “F at 30-mm Hg pressure for 1 hour. The specimens were taken out, cooled in a desiccator, and weighed individually

to give the final weight. The difference in the final and initial weight gave the amount of solvent retained after cleaning and drying the exposed specimen. Ultrasonic assisted exposure was carried out using an 85-watt "Baxter" ultrasonic bath for 5 minutes cycle at a time.

Shore D hardness was measured for each sample at the end of the exposure and compared with the hardness of control adhesive specimens not subjected to solvent exposure. ASTM Standard method D2240 was followed to measure hardness.

Typical results on percent solvent absorption (interim weight gain), the percent of residual solvent (final weight gain), and Shore D hardness after drying are given in Table 3.

Lap Shear Specimens:

Room Temperature Testing (No Ultrasonic Exposure)

1. A l-liter Berzelius beaker (no spout) was filled with trichloroethane. A second and third beaker were filled with 0S-30 and OS-10 cleaner. Beakers were then covered with "Saran" wrap and aluminum foil.

2. A polyethylene pan with lid was filled with enough water to come within 0.5 inches of the top of the beaker. The bath temperature was noted and recorded.

3. Randomly selected lap shear specimens chosen for evaluation at room temperature were then immersed in the appropriate cleaner in the polyethylene pan. The time of exposure was recorded.

4. Following the selected time of immersion, the lap shear specimens were then removed from the cleaner and were blow dried with "House Air" which is filtered through a CUNA 10 micron filter (oil trap), and then dried through a "Drierite" ($CaSO_4$) laboratory gas drying unit.

Table 3. Typical Results of Weight Change and Hardness Change After Soaking/Sonication

Adhesive	Temp., °F	Solvent	Cleaning Method	Time Exposure	Replica A % Weight Change Inter-mediate	Replica A % Weight Change Final	Replica A Shore D	Replica B % Weight Change Inter-mediate	Replica B % Weight Change Final	Replica B Shore D	Replica C % Weight Change Inter-mediate	Replica C % Weight Change Final	Replica C Shore D
G	T1	S1	U	1	-0.01	-0.03	85	-0.03	-0.03	88	0.03	-0.03	88
G	T1	S1	U	2	-0.05	-0.08	81	-0.02	-0.06	87	-0.06	-0.08	87
G	T1	S1	S	1	0.01	-0.04	85	0.00	-0.06	86	0.01	-0.03	85
G	T1	S1	S	16	0.01	-0.03	88	0.01	-0.03	88	0.00	-0.03	87
G	T1	S2	U	1	0.16	-0.04	87	0.10	-0.05	88	0.10	-0.04	86
G	T1	S2	U	2	0.13	-0.04	85	0.12	-0.05	85	0.07	-0.05	87
G	T1	S2	S	1	0.10	-0.07	87	0.05	-0.04	88	0.14	-0.02	88
G	T1	S2	S	16	0.09	-0.03	87	0.10	-0.03	88	0.10	-0.03	87
G	T1	C1	U	1	0.00	-0.02	88	-0.01	-0.04	88	-0.01	-0.05	86
G	T1	C1	U	2	0.01	-0.05	88	0.02	-0.04	87	0.01	-0.04	86
G	T1	C1	S	1	0.33	0.02	88	0.30	0.00	82	0.21	-0.01	85
G	T1	C1	S	16	2.83	1.57	81	2.19	1.23	85	1.77	0.86	83
G	T2	S2	U	1	0.04	-0.05	87	0.04	-0.06	88	0.02	-0.06	87
G	T2	S2	U	2	0.10	-0.02	88	0.06	-0.03	87	0.10	-0.03	87
G	T2	S2	S	1	0.04	-0.03	87	0.05	-0.03	87	0.04	-0.06	87
G	T2	S2	S	16	0.07	-0.03	87	0.11	-0.03	87	0.02	-0.03	--
H	T1	S1	U	1	0.01	-0.09	41	0.01	-0.15	46	0.01	-0.13	48
H	T1	S1	U	2	-0.33	-0.44	44	-0.26	-0.35	45	-0.47	-0.29	47
H	T1	S1	S	1	0.03	-0.13	42	0.02	-0.17	45	0.02	-0.13	49
H	T1	S1	S	16	0.02	-0.19	45	0.03	-0.12	43	0.02	-0.14	45
H	T1	S2	U	1	0.13	-0.22	45	0.10	-0.20	45	0.15	-0.09	40
H	T1	S2	U	2	0.07	-0.22	46	0.09	-0.23	43	0.03	-0.21	42
H	T1	S2	S	1	0.20	-0.13	43	0.17	-0.31	38	0.21	-0.14	41
H	T1	S2	S	16	0.19	-0.20	45	0.14	-0.17	40	0.17	-0.20	44
H	T1	C1	U	1	0.26	-0.14	46	0.28	-0.12	42	0.23	-0.14	44
H	T1	C1	U	2	0.30	-0.06	44	0.27	-0.06	47	0.31	-0.10	45
H	T1	C1	S	1	14.73	0.59	43	2.19	0.66	41	1.85	0.18	46
H	T1	C1	S	16	12.94	7.83	29	10.72	6.79	32	9.94	6.54	33
H	T2	S2	U	1	0.04	-0.30	47	0.11	-0.27	49	0.03	-0.16	41
H	T2	S2	U	2	0.15	-0.14	43	0.06	-0.12	47	0.06	-0.13	44
H	T2	S2	S	1	0.14	-0.20	44	0.08	-0.13	50	0.05	-0.16	44
H	T2	S2	S	16	0.00	-0.23	46	0.17	-0.18	44	0.05	-0.17	44

5. Lap shear specimens were then post dried under vacuum (30 mm Hg) at 155 “F for 60 minutes, and placed in the constant temperature room until time of tensile testing.

Elevated Temperature Testing (No Ultrasonification)

1. A l-liter Berzelius beaker (without spout) was filled with 0S-30 cleaner to within 0.5 inches of the beaker lip. The beaker was then covered with “Saran” wrap and aluminum foil. A water bath was prepared with enough water to cover the beaker containing the oS-30 cleaner to within 1.0 inch of the lip. The water bath heater was then set to maintain the bath temperature at 120°F.

2. Once the bath came to temperature, the water temperature was noted, and recorded. After the solvent attained the same temperature as the water bath, the randomly selected lap shear samples chosen for elevated temperature exposure were immersed in the 0S-30 cleaner. The time of exposure was recorded.

3. Following the selected time of immersion, the lap shear specimens were removed from the cleaner and were blow dried with “House Air”.

4. Lap shear specimens were then post dried under vacuum (30 mm Hg) at 155°F for 60 minutes and placed in the constant temperature room until time of tensile testing.

Ultrasonic Assisted Immersion Testing of Lap Shear Specimen

1. An 85-watt, “Baxter”, 4.6-quart capacity ultrasonic bath was filled with a sufficient volume of the candidate cleaners (1,1, 1-trichloroethane, 0S-10, and

0S-30) to cover the lap shear specimens by at least 2.0 inches. A CO_2 sparge was maintained throughout the ultrasonification cycle(s) to avoid the potential for explosion.

For Elevated Temperature

The 0S-30 cleaner was preheated in the 120°F bath. This bath was also used to heat the lap shear specimens to 120°F for the soak cycle(s). Two containers of 0S-30 cleaner were heated to carry out (1) and (2), 5-minute ultrasonic exposures separately. A CO_2 sparge was maintained throughout the ultrasonification cycle(s) to avoid the potential for explosion. The bath unit was then turned on to the required time setting (5 minutes).

Following the selected time of immersion, the lap shear specimens were removed from the cleaner and were blow dried with “House Air”.

Lap shear specimens were post dried under vacuum (30 mm Hg) at 155 ‘F for 60 minutes. They were removed from the oven and stored in the constant temperature room for tensile testing at a later time.

For lap shears requiring a second 5. O-minute cycle, the procedure noted above was repeated.

For Room Temperature Exposure

The procedure noted above was repeated, this time without heat.

The lap shear strength was measured using an Instron Testing Machine following ASTM Method D-002-72 (1983). The lap shear strengths were calculated by dividing the breaking load by the surface area of overlap, and the results are given as pounds per square

inch. In addition, the type of failure was noted for each specimen. Typical results are given in Table 4.

2.5.2 Laboratory Testing of Metal Compatibility

All the sonication and soaking tests of the metal coupons were carried out according to the experimental design shown in Figure 1. In this study, CFC-113 was used as a second control in addition to TCA.

The sonication tests were conducted in a timer-controlled, temperature-regulated Branson Model 5210 cleaner. Triplicate samples were used for each of the tests. Prior to testing, all the coupons were precleaned according to the Test Plan procedure, The precleaning procedure included sonication in TCA, blow-drying with filtered compressed air, and heating in a vacuum oven for 15 minutes at 155 ‘F. The specimens were desiccated after removal from the oven. The initial weights of the coupons were measured to 0.01 mg accuracy on an analytical balance. Testing and final rinsing were carried out by soaking or sonicating the coupons for selected time intervals in 1.8 liter beakers at the desired temperature followed by drying in the same manner described previously.

2.6 Experimental Results

2.6.1 Results of Adhesive Degradation Study

The average hardness and the average weight changes for soaking experiments (after drying) are given in Tables 5 and 6 and those for ultrasonic cleaning are given in Tables 7 and 8. The average results and standard deviation in lap shear strength measurements are presented in Tables 9 and 10 for soaking and ultrasonic exposure after drying.

2.6.2 Results of Metal Compatibility Study

The criteria used to evaluate metal compatibility included:

Table 4. Typical Results of Lap Shear Measurement
Strength (psi) After **Sonication** in **Siloxane** Solvent

Date	Specimen Design	Design I.D.	Temp., "F	Solvent	Method	Time	Bath Temp., "F	Date of Pull	Adhesive Area, Sq. In.	Lhs. at Break	PSI at Break	Type Failure
8-31-94	A14a14	14	T2	S2	u ,	2	48	9-12-94	0.60	1420	2,367	A
8-31-94	A14b184	14	T2	S2	u	2	48	9-13-94	0.50	1140	2,280	A
8-31-94	A14c354	14	T2	S2	u	2	48	9-12-94	0.55	1020	1,855	A
8-31-94	B14a48	14	T2	S2	u	2	48	9-12-94	0.60	1100	1,833	c
8-31-94	B14b218	14	T-2	S2	u	2	48	9-12-94	0.55	1100	2,000	c
8-31-94	B14c388	14	T2	S2	u	2	48	9-13-94	0.55	1060	1,927	c
8-31-94	C14a82	14	T2	S2	u	2	48	9-13-94	0.50	1550	3,100	c
8-31-94	C 14b252	14	T2	S2	u	2	48	9-13-94	0.50	1540	3,080	c
8-31-94	C14c422	14	T2	S2	u	2	48	9-13-94	0.50	1750	3,500	c
8-31-94	D14a116	14	T2	S2	u	2	48	9-13-94	0.55	1300	2,364	A
8-31-94	D14b286	14	T2	S2	u	2	48	9-13-94	0.55	1080	1,964	A
8-31-94	D 14c456	14	T2	S2	u	2	48	9-12-94	0.55	1120	2,036	A
8-31-94	E14a150	14	T2	S2	u	2	48	9-12-94	0.55	1150	2,091	A
8-31-94	E14b320	14	T2	S2	u	2	48	9-13-94	0.55	1680	3,055	A
8-31-94	E14c490	14	T2	S2	u	2	48	9-12-94	0.55	1480	2,691	c
8-31-94	F14a694	14	T2	S2	u	2	48	9-13-94	0.55	780	1,418	A
8-31-94	F14b762	14	T2	S2	u	2	48	9-13-94	0.55	570	1,036	A
8-31-94	F14c796	14	T2	S2	u	2	48	9-13-94	0.55	700	1,273	A
8-31-94	G14a524	14	T2	S2	u	2	48	9-13-94	0.55	1400	2,545	c
8-31-94	G14b592	14	T2	S2	u	2	48	9-13-94	0.55	1220	2,218	c
8-31-94	G14c626	14	T2	S2	u	2	48	9-13-94	0.60	1360	2,267	c
8-31-94	H14a558	14	T2	S2	u	2	48	9-13-94	0.55	930	1,691	A
8-31-94	H14b660	14	T2	S2	u	2	48	9-13-94	0.50	1250	2,500	A
8-31-94	H14c728	14	-T2	S2	u	2	48	9-13-94	0.55	980	1,782	A

T_2 = 120°F
δ_2 = D8-30
4 = ultrasonic
2 = 2 Cycles
Failure Type - A = adhesive, C = cohesive.

Table 5. Shore D Hardness[a] of Bulk Specimens After Soaking in Cleaning Solutions and Drying

Adhesive	Cleaner and Exposure Conditions								Unexposed Control[b]
	0s-10 (75°F)		0s-30 (75°F)		TCA (75°F)		0s-30 (120°F)		
	1 Hr	16 Hrs	1 Hr	16 Hrs	1 Hr	16 Hrs	1 Hr	16 Hrs	
A (FA8/BA5)	86	86	86	86	86	86	87	86	86
B (LCA4/BA5)	91	92	92	91	92	92	92	93	91
C (Eccobond 22K)	76	74	75	75	74	65	76	76	72
D (FA1/BA4)	85	85	86	85	86	85	86	85	74
E (Epon 828/ Versamid 125)	80	78	79	78	79	75	78	79	79
F (Araldite CY179)	87	87	87	87	87	87	87	87	86
G (Stycost 2760)	86	88	88	87	85	83	87	87	86
H (Tra-Bond 2133)	45	44	41	43	43	31	46	45	84

(a) ASTM D2240.
(b) Not exposed to cleaning solutions.

Table 6. Percent Weight Change of Bulk Specimens After Soaking in Cleaning Solutions and Drying

Adhesive Type	Cleaners and Exposure Conditions							
	0s-10 (75°F9		0s-30 (75°F)		TCA (75°F)		0s-30 (120°F9	
	1 Hr	16 Hrs	1 Hr	16 Hrs	1 Hr	16 Hrs	1 Hr	16 Hrs
A	-0.02	-0.03	-0.02	0	-0.004	+0.29	-0.01	-0.04
B	-0.02	-0.01	0	-0.01	-0.02	-0.01	-0.01	-0.01
c	-0.07	-0.08	-0.08	-0.08	+0.37	+5.06	-0.10	-0.10
D	-0.04	-0.05	-0.04	-0,04	-0.06	-0.04	-0.05	-0.06
E	-0.05	-0.05	-0.03	-0.02	+0. 14	+3.06	-0.05	-0.04
F	-0.09	-0.03	-0.04	-0.04	-0.10	-0.07	-0.05	-0.06
G	-0.04	-0.03	-0.05	-0.03	0	+1.22	-0.04	-0.03
H	-0.12	-0.15	-0.19	-0.19	+0.28	+4.79	-0.16	-0.19

Table 7. Shore D Hardness[a] of Bulk Specimens After Sonification in Cleaning Solutions After Drying

	Cleaners and Exposure Conditions								
	0S-10 (75°F)		0S-30 (75°F)		TCA (75°F)		0S-30 (120°F)		
Adhesive Type	1 Cycle	2 cycles	1 Cycle	2 cycles	1 Cycle	2 cycles	1 Cycle	2 cycles	Unexposed Control[b]
A	87	87	86	87	87	87	87	86	86
B	91	92	92	92	91	92	92	92	91
C	77	76	77	76	76	76	77	77	72
D	86	85	86	86	85	86	86	85	74
E	80	72	80	79	80	79	79	80	79
F	88	88	87	88	88	88	86	88	86
G	87	85	87	86	87	87	87	87	86
H	45	45	43	44	44	45	46	45	84

(a) ASTM D2240.

(b) Not exposed to cleaning solutions.

Table 8. Percent Weight Change After Sonification in Cleaning Solutions and Drying

Adhesive Type	Cleaners and Exposure Conditions							
	OS-10 (75°F)		OS-30 (75°F)		TCA (75°F)		OS-30 (120°F)	
	1 Cycle	2 Cycles	1 Cycle	2 Cycles	1 Cycle	2 Cycles	1 Cycle	2 Cycles
A	-0.02	-0.05	-0.03	-0.03	-0.003	-0.04	-0.06	0
B	-0.02	-0.04	-0.02	-0.02	-0.02	-0.03	-0.03	-0.01
C	-0.07	-0.19	-0.11	-0.12	-0.06	-0.04	-0.15	-0.09
D	-0.04	-0.09	-0.06	-0.06	-0.04	-0.05	-0.08	-0.04
E	-0.03	-0.11	-0.05	-0.08	-0.05	-0.04	-0.11	-0.04
F	-0.05	-0.10	-0.11	-0.10	-0.05	-0.08	-0.15	-0.07
G	-0.03	-0.07	-0.04	-0.05	-0.04	-0.04	-0.06	-0.03
H	-0.12	-0.36	-0.17	-0.22	-0.13	-0.07	-0.24	-0.13

T b 9 A rag Lap Shea S gth p d Sta d d D p
Specim ns A S k g S S ts

Adhesive	Lap S ıe S re gth p C rs d Exp re C d ns								Unexposed Control
	OS 0 F)		OS) F)		TCA F)		OS-30 (120°F)		
	1 Hour	16 Hours	1 Hour	16 Hours	1 Hour	16 Hours	1 Hour	16 Hours	
A (FA8/BA5)	2937 ± 311	3250 ± 420	2747 ± 532	2225 ± 92	2200 ± 141	2353 ± 473	2981 ± 757	2748 ± 555	2213 ± 138
B (LCA4/ BA5)	2000 ± 87	1983 ± 46	2031 ± 69	2033 ± 167	2030 ± 52	1990 ± 72	1986 ± 196	2005 ± 129	2160 ± 303
C (Eccobond 22K)	3406 ± 215	2944 ± 465	3452 ± 181	2985 ± 506	3058 ± 303	3101 ± 253	2562 ± 452	3307 ± 151	3145 ± 151
D (FA1/BA4)	2335 ± 58	2224 ± 252	2353 ± 222	2295 ± 199	2300 ± 131	2156 ± 203	2657 ± 160	2260 ± 16	2496 ± 181
E (Epon 828/ Versamid 125)	2745 ± 423	2761 ± 624	2349 ± 590	2662 ± 565	2690 ± 269	2249 ± 413	3175 ± 862	2338 ± 757	2025 ± 476
F (Araldite CY179)	1488 ± 127	1395 ± 116	1382 ± 30	1347 ± 112	1245 ± 152	1430 ± 48	1416 ± 230	1359 ± 88	1289 ± 10
G (Stycost 2760)	2663 ± 110	2352 ± 517	2563 ± 94	2428 ± 39	2455 ± 110	2504 ± 260	2514 ± 231	2473 ± 248	2571 ± 193
H (Tra-Bond 2133)	1570 ± 122	1945 ± 435	1892 ± 51	1591 ± 174	1567 ± 111	1465 ± 148	1612 ± 291	1902 ± 164	2984 ± 62

Table 10. Average Lap Shear Strength and Standard Deviation of Specimens After Sonification in Siloxane Solvents and Drying

Adhesive	Lap Shear Strength (psi) for Cleaners and Exposure Conditions								Unexposed Control
	OS-10 (75°F)		OS-30 (75°F)		TCA (75°F)		OS-30 (120°F)		
	1 Cycle	2 Cycles	1 Cycle	2 Cycles	1 Cycle	2 Cycles	1 Cycle	2 Cycles	
A (FA8/BA5)	2475 ± 89	2224 ± 420	2348 ± 433	2448 ± 477	2218 ± 219	2472 ± 555	2137 ± 234	2167 ± 224	2213 ± 138
B (LCA4/BA5)	1859 ± 171	2000 ± 0	1998 ± 57	1986 ± 150	1886 ± 146	1999 ± 123	1952 ± 62	1920 ± 68	2160 ± 303
C (Eccobond 22K)	3073 ± 332	3186 ± 134	2958 ± 339	2915 ± 191	2926 ± 215	3057 ± 494	3054 ± 347	3227 ± 193	3145 ± 151
D (FA1/BA4)	2552 ± 470	2164 ± 247	2102 ± 31	2102 ± 174	2315 ± 150	2097 ± 219	2056 ± 277	2121 ± 174	2496 ± 181
E (Epon 828/ Versamid 125)	2230 ± 774	1951 ± 471	2697 ± 312	2506 ± 557	2370 ± 509	2557 ± 387	2582 ± 452	2612 ± 397	2025 ± 476
F (Araldite CY179)	1418 ± 15	1578 ± 358	1402 ± 105	1453 ± 35	1404 ± 121	1167 ± 52	1361 ± 66	1242 ± 157	1289 ± 16
G (Stycost 2760)	2535 ± 78	2290 ± 33	2694 ± 120	2135 ± 70	2455 ± 136	2653 ± 88	2520 ± 121	2343 ± 144	2571 ± 19
H (Tra-Bond 2133)	2328 ± 206	1268 ± 444	2206 ± 668	1536 ± 187	1707 ± 323	1610 ± 85	2634 ± 111	1991 ± 361	2984 ± 62

- Weight loss less than 0.01 percent.
- Metal surface should not undergo a uniform color change.
- General corrosion should not be visible at a magnification of 200X.
- Pit depths should be less than 0.0005 inch (0.5 mil).

The results are presented in bargraphs in Figures 5 to 11.

3.0 STATISTICAL ANALYSIS OF THE RESULTS

3.1 Analytical Approach

Analysis Of Variance (ANOVA)[(1)*] was the primary tool employed to evaluate differences between the various compared means. The procedure One-Way[(2)], as well as the simple factorial ANOVA, was used extensively due to unique output and access to several multiple comparison procedures. A brief explanation of the method may aid the interpretation of the summary tables that will be described in the following section. For example, consider solvent effects on the lap shear strength of one of the adhesives. The 51 specimens were placed in four groups: the unexposed controls (CRTL), the TCA exposed specimens, the OS-10 and OS-30 exposed specimens. For each group (or treatment) a mean was calculated and then the question was raised concerning the differences in the observed mean values: are the differences due to random variation or due to the solvent treatment? The hypothesis to be tested is that the true treatment means are all the same; the alternative hypothesis is that they are different. If the hypothesis is indeed true, then there are several valid ways to estimate the population variance. One way is to calculate the variance for each treatment sample and then pool the results. This estimate is sometimes called the within-treatment mean square (S^2_R). It is an estimate of the internal consistency of the data and is not influenced by the spread in the treatment means.

---

* Superscripts refer to references listed in Reference Section of this report.

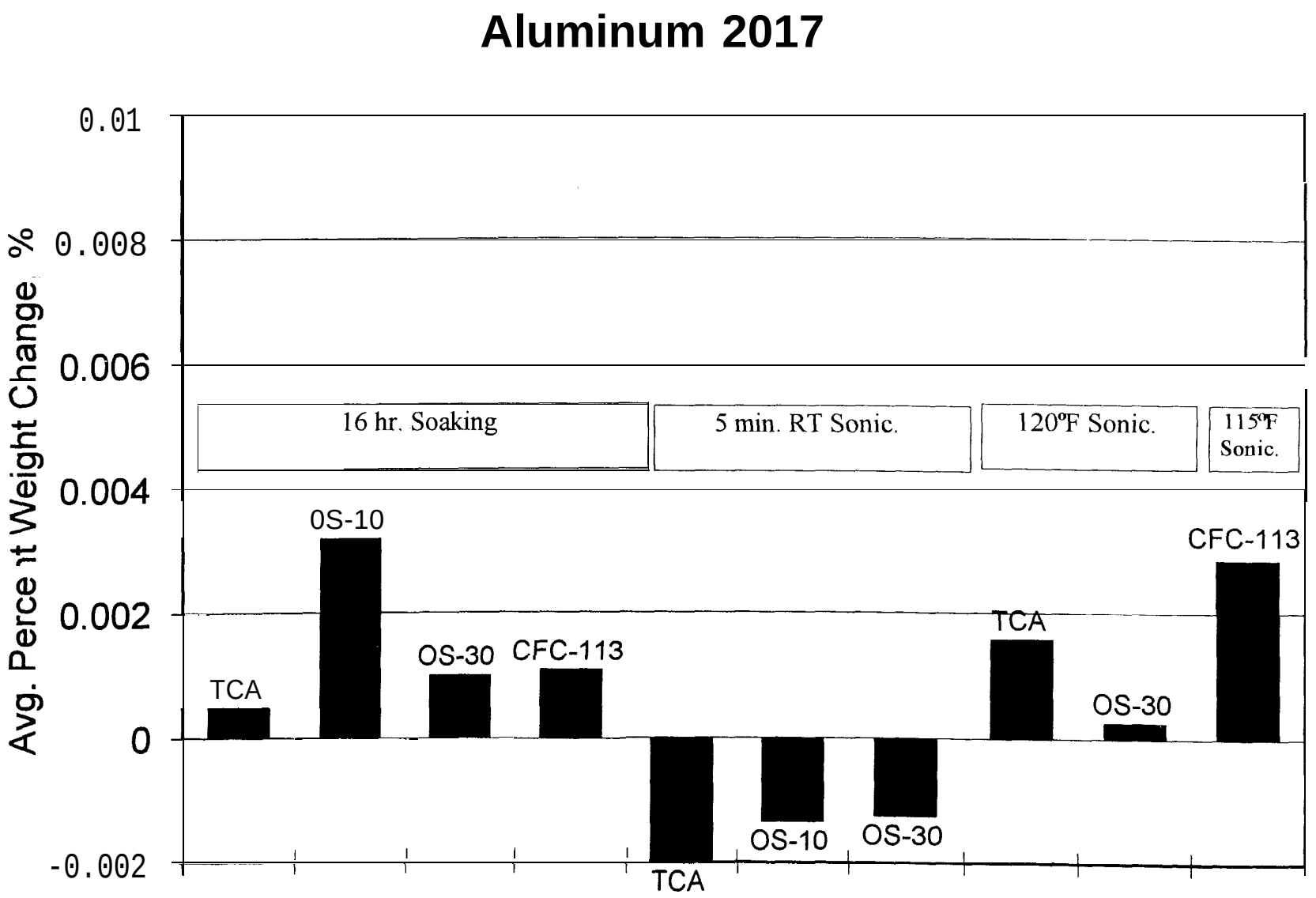
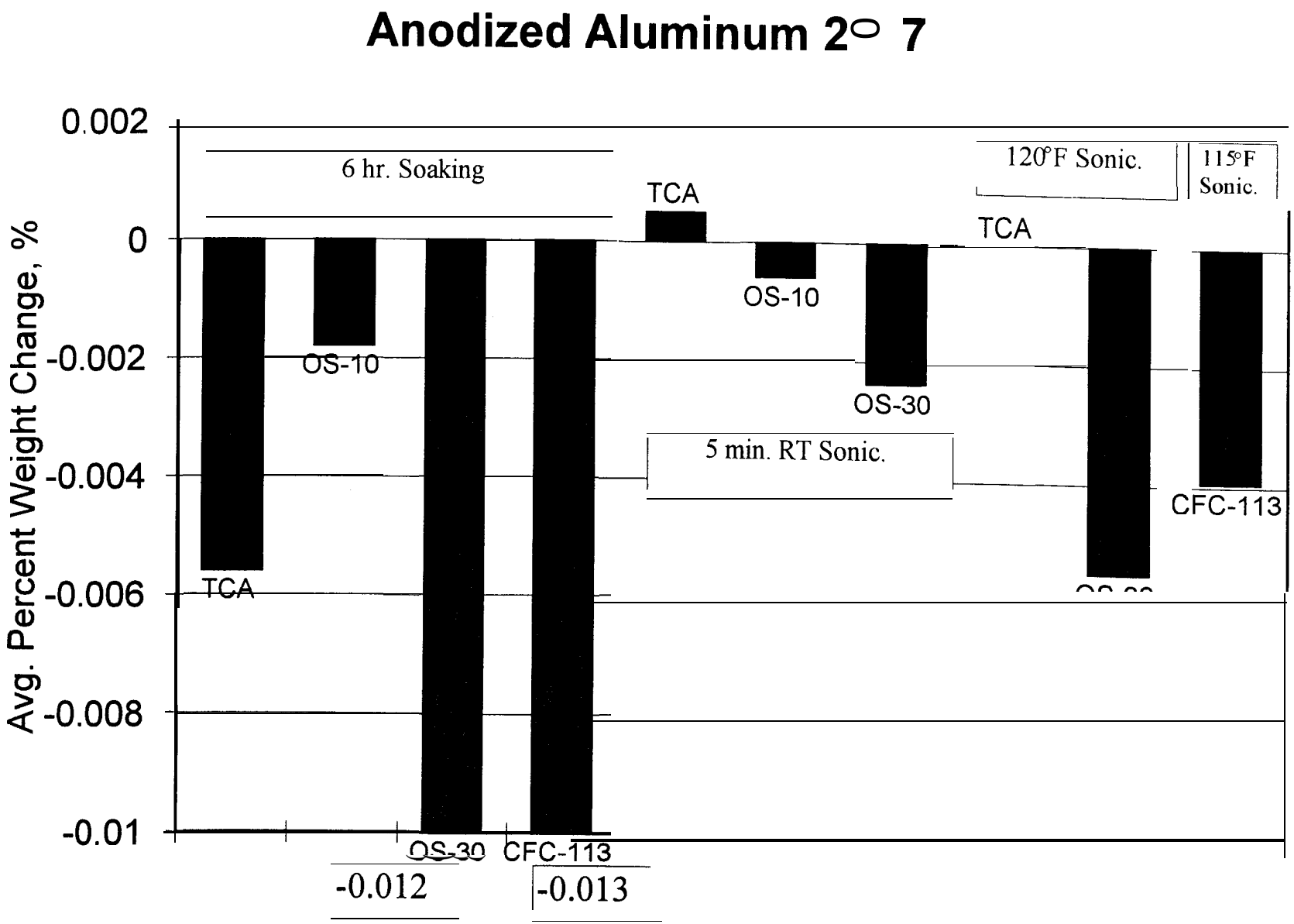


Figure 5. Weight Changes Observed on Exposure to Siloxane Cleaners (Al 2017)



F·gure 6. We·ght Changes Observed on Exposure to S·loxane C·eaners (Anodized Al 2017)

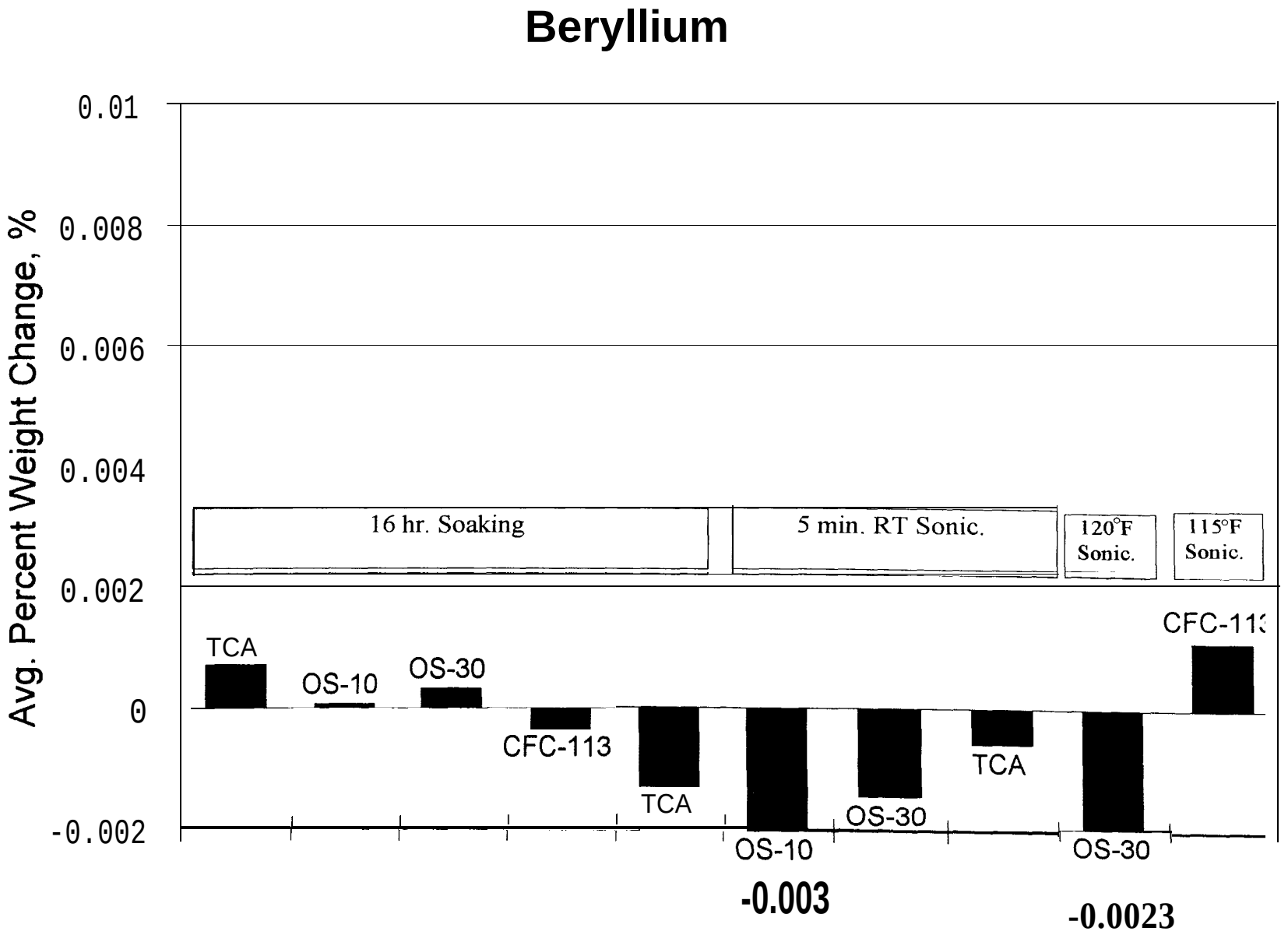


Figure 7. Weight Changes Observed on Exposure to Siloxane Cleaners (Beryllium)

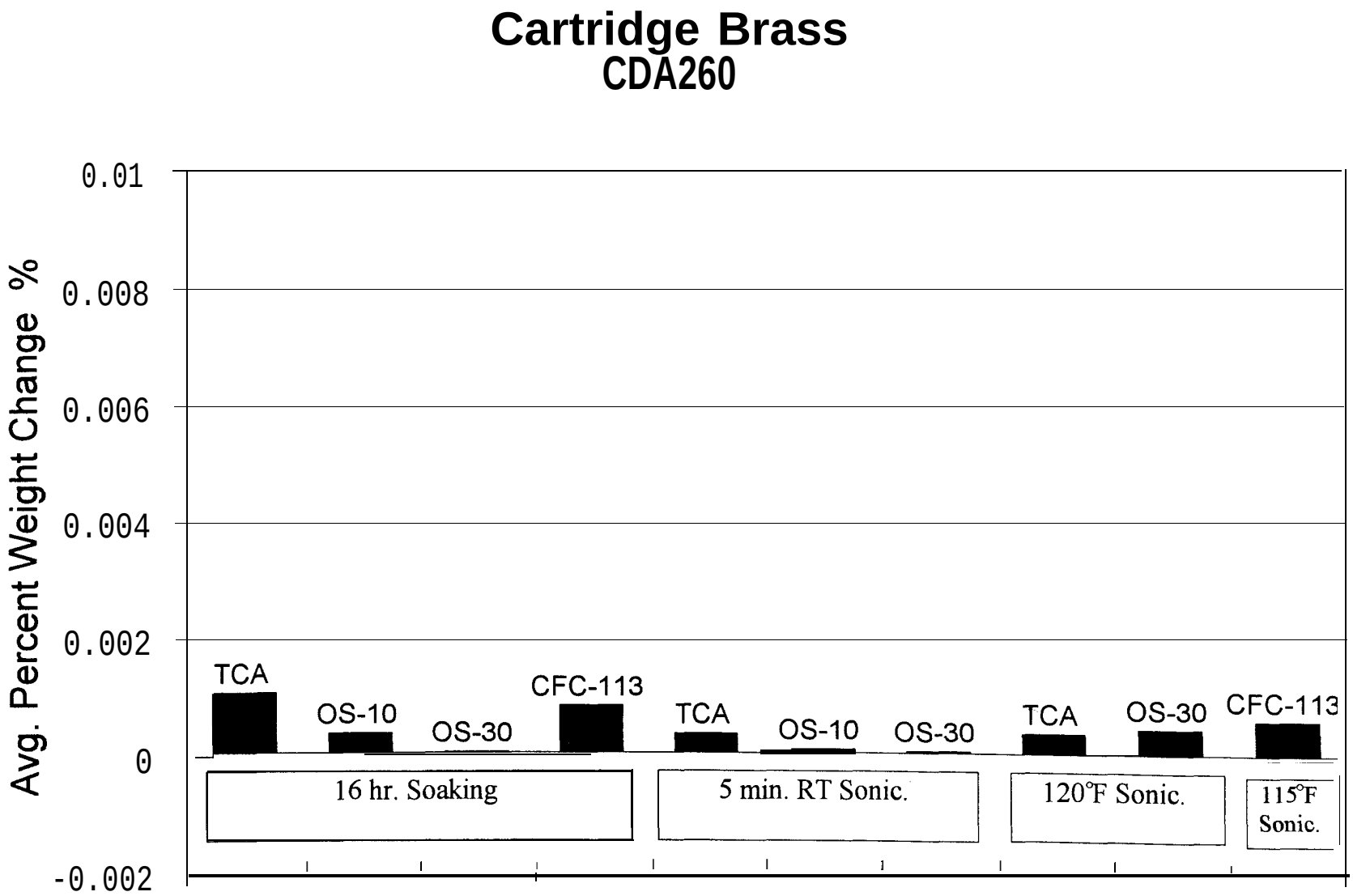


Figure 8. Weight Changes Observed on Exposure to Siloxane Cleaners (Cartridge Brass)

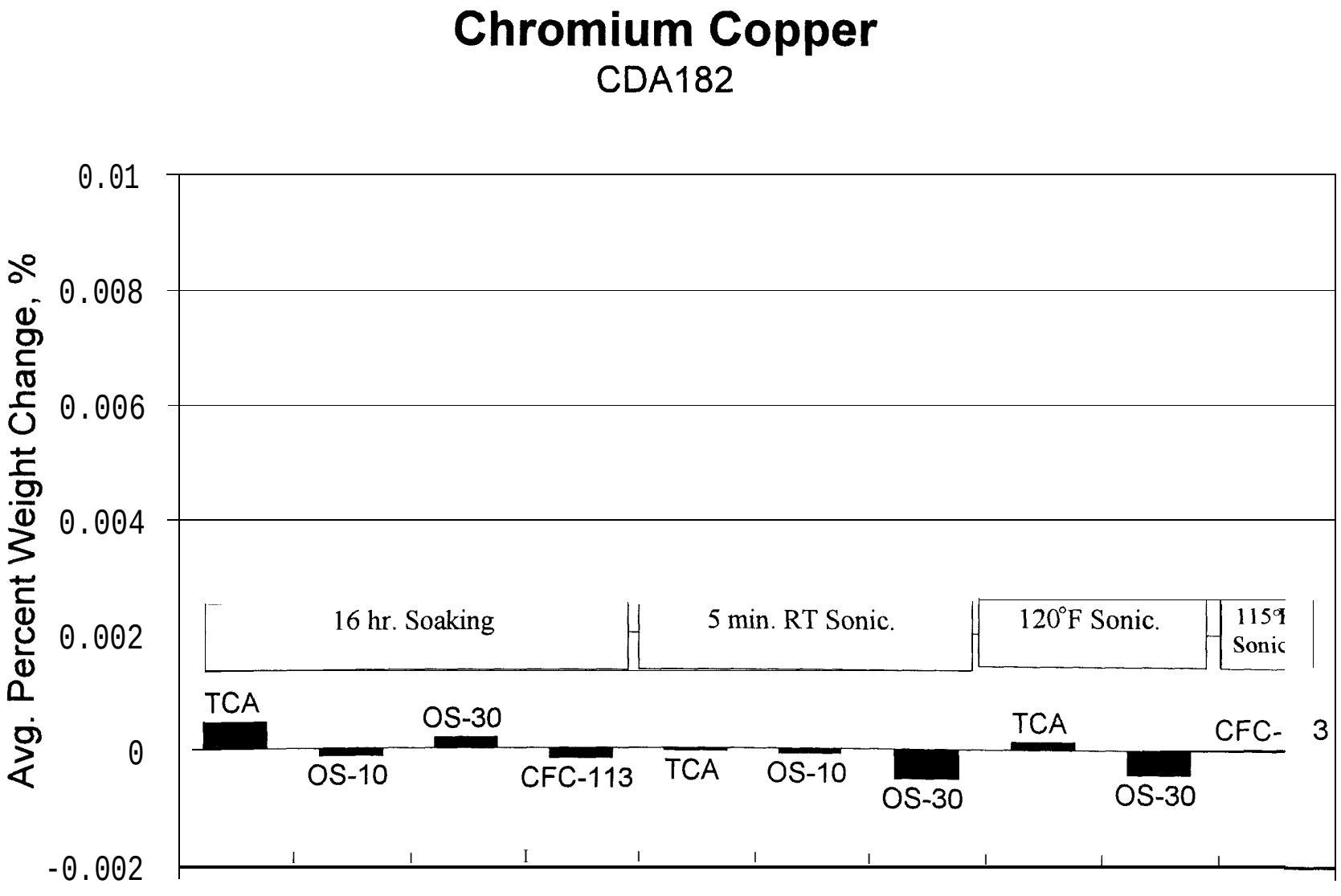


Figure 9. Weight Changes Observed on Exposure to Siloxane Cleaners (Chromium Copper)

Chromium Steel 52100

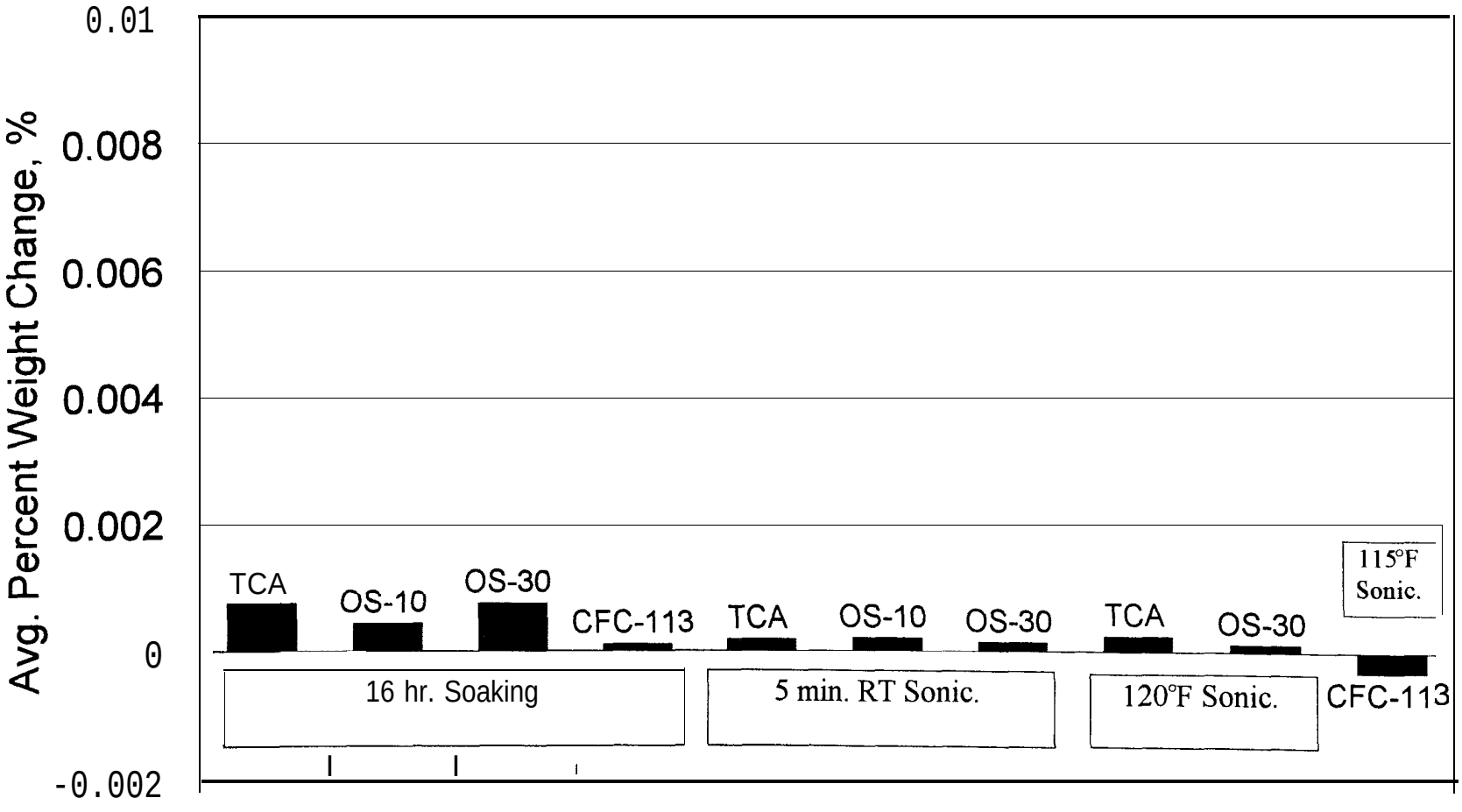


Figure 10. **Weight Changes Observed on Exposure to Siloxane Cleaners (Chromium Steel)**

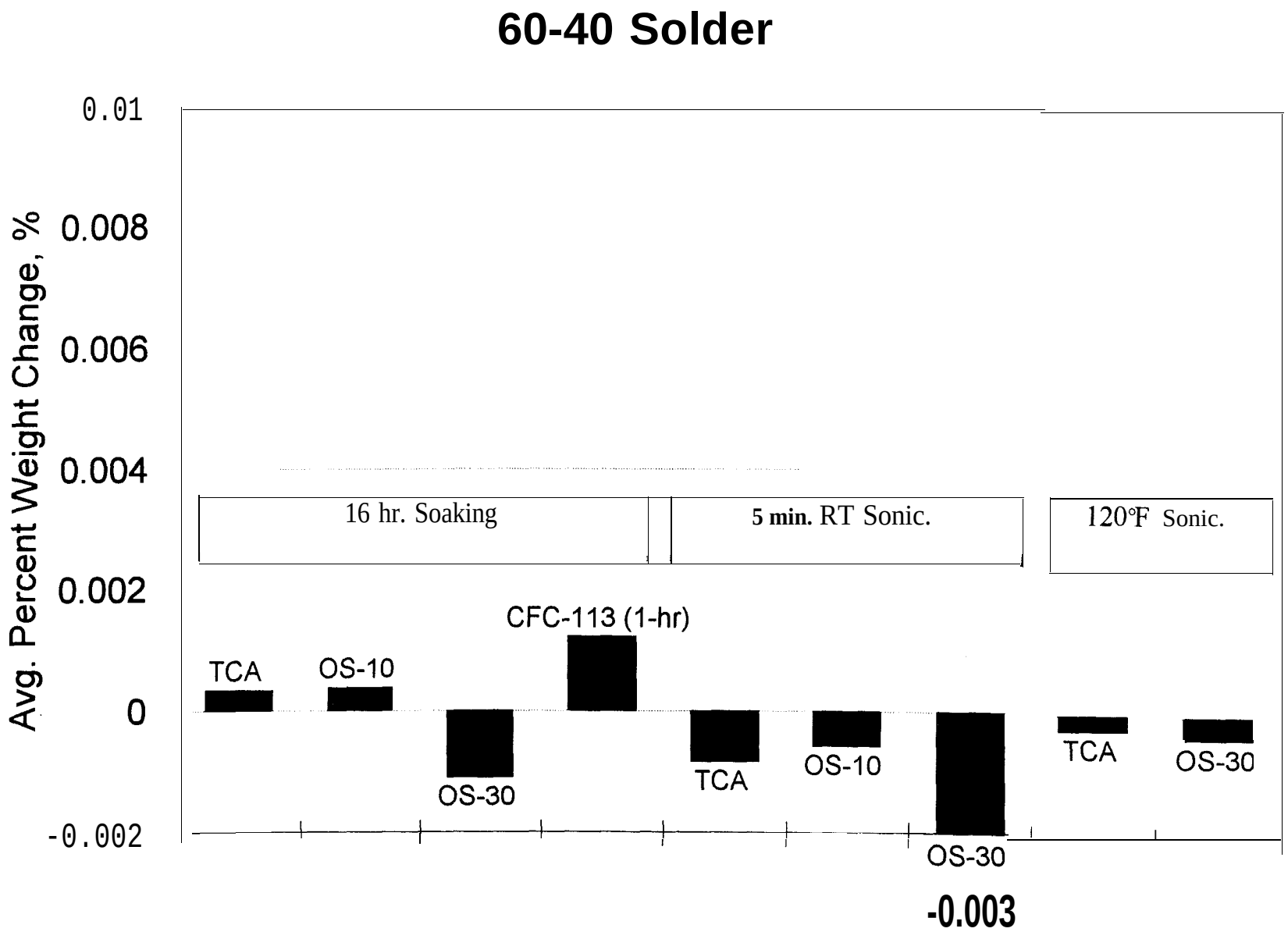


Figure 11. Weight Changes Observed on Exposure to Siloxane Cleaners (60/40 Solder)

A second estimate of population variance can be calculated based on differences between the overall mean and each of the treatment means; this estimate is usually called the between treatment mean square (S^2_T) and is influenced by the spread on the treatment means. If the (null) hypothesis is true and statistical assumptions have been met, then the ratio S^2_T/S^2_R (F statistic) will be relatively small, follow the F distribution and have a relatively high probability. When the ratio is high (relative to a table 'F' value with appropriate degree of freedom) and the probability is low (0.05, 0.01, 0.001), then it can be said that the data discredit the null hypothesis and we elect to accept the alternative that there is a difference in the treatment means. Our "confidence" is based on the likelihood of a particular "F" ratio occurring. A significant level for the F statistic of 0.050 indicates that the calculated ratio should occur 5 percent of the time when the null hypothesis is true. In other words, we are 95 percent confident in rejecting the hypothesis.

When two treatment means are compared, the analysis is essentially complete. When three or more treatments are involved, an additional evaluation is required to determine which treatment means are significantly different. As a group, these tests are called multiple comparison procedures. Of the procedures readily available, Fisher's Protected LSD[3] was selected.

3.2 Statistical Analysis of Results

3.2.1 Analysis of Adhesive Results

Data was developed using the previously described design relating to four responses: adhesive lap shear strength, bulk adhesive Shore "D" hardness, weight change (wet) measured before vacuum oven drying, and weight change (dry) measured after vacuum oven drying. All files that support this analysis have been included with this report in Appendix B as a hard copy and on IBM formatted 3.5-inch diskettes for computer viewing. The "Analysis Notes" at the beginning of Appendix C include the categorical factor names and levels, the response names and descriptions, and a listing of the file names with a brief

description. The files are organized with respect to the particular response. Results will be discussed with respect to each response.

Lap Shear Strength. The lap shear tensile strength was calculated for each specimen by dividing the breaking force in pounds by the lap area in square inches. This response was assigned the variable name BREAKPSI.

The first examination of the data was global in nature, including all of the data for all of the adhesives. The differences between the adhesives produced the most significant effect. The least significant effect was due to different temperatures. * Examination of cell means and a significant 2-way interaction suggested that the adhesives were responding to the cleaning simulations differently and that examination of the data on a per adhesive basis would provide greater clarity in understanding any cleaning simulation effects. Results from this analysis are summarized in Table 11.

Briefly, Table 11 shows that the shear strength of Adhesives B, C, and E was unaffected by the various simulated cleaning treatments. For these adhesives, the grand average represents the best estimate of adhesive performance irrespective of environment. Further, any variation in calculated treatment means is believed to be due to pure error variation, i.e., the hypothesis that the true means are equal, was not rejected. The "-" indicates that the treatment had no significant effect on the adhesive and allows one to quickly focus on the specific adhesive treatment combinations that were found to be significant.

Increasing the temperature of 0S-30 had no apparent effect on any of the adhesives, while Adhesive H was significantly effected by each of the other treatments.

By comparison, the analysis of bulk property responses including Shore D hardness, percent weight change (wet), and percent weight change (dry) was more interesting because the various treatments produced a much greater number of significant effects. Results for these responses are summarized in Tables 12 through 16. Although there are a considerable number of statistically significant differences, many of the differences are small and may be of no practical importance. The matter of importance will be discussed later in this report.

---

* ANOVA2.LST Appendix B for details.

Table 11. Summary of Significant[1] Lap Shear Differences on Exposure of Test Specimens to Solvents and Cleaning Process

Adhesive	Grand Average[2]	Mean for Each Solvent[1]				Mean for Each Cleaning Method[1]		Mean for Each Time[1]		Mean for Each Temperature[5]	
		CTRL[3]	TCA	OS-10	0S-30	Ultrasonic	Soaking	A[4]	B[4]	75°F	120°F
A	2479	2213±138	-	-	-	2311	2680	-	-	-	-
B	1995	2160±303	-	-	-	-	-	-	-	-	-
C	3080	3145±151	-	-	-	-	-	-	-	-	-
D	2269	2496±181	-	-	-	2188	2322	2334	2177	-	-
E	2500	2025±476	-	-	-	-	-	-	-	-	-
F	1375	1289±16	1312	1470	-	-	-			-	-
G	2479	2571±19	-	-	-	-	-	2550	2397	-	-
H	1862	2984[6]	1587	1778	1901[7]	1916	1668	1921	1664	-	-

(1) Significantly different at the 95 percent confidence level. Every "-" indicates the treatment had no significant effect on the adhesive and the grand average is the best estimate of adhesive performance.
(2) Average lap shear for each adhesive in PSI at the break point; based on 51 specimens to indicate relative strengths of each adhesive.
(3) Average lap shear for 3 unexposed control (Ctrl) specimens.
(4) A-1 hr ultrasonic cleaning or 1 hour soak, B-2 cycles of ultrasonic cleaning or 16 hour soak.
(5) Temperature effect was measured with OS-30 only (approximately 75°F and 120°F).
(6) Significant difference in variances of compared groups; the control group has a smaller variance than the other three groups.
(7) Mean values within bracket are not significantly different.

Table 12. Summary of Significant[1] Shore D Differences on Exposure of Test Specimens to Solvents and Cleaning Process

Adhesive	Grand Average[2]	Mean for Each Solvent[1]				Mean for Each Cleaning Method[1]		Mean for Each Time[1]		Mean for Each Temperature[5]	
		CTRL[3]	TCA	OS-10	0S-30	Ultrasonic	Soaking	A[4]	B[4]	75°F	120°F
A	86.6	86	-	-	-	87.1	86.1	-	-	-	-
B	91.9	91	-	-	-	-	-	91.6	92.2	-	-
c	75.0	72 (71.7 72.9)*		(75.8 76.0)[6]		76.4	73.9*	76.0	74.4 *	-	-
D	84.8	74**	(85.6 85.3 85.5)			-	-	-	-	-	-
E	78.2	79	-	-	-	-	-	-	-	-	-
F	87.2	86	-	-	-	-	-	-	-	-	-
G	86.4	86	-	-	-	-	-	-	-	-	-
H	45.9	84**	41	(45 43)		44.6	42.3*	-	-	42.6	45.2

(1) Significantly different at the 95 percent confidence level. Every "-" indicates the treatment had no significant effect on the adhesive and the grand average is the best estimate of adhesive performance.
(2) Average Shore D value for each adhesive based on 51 samples (50 samples for adhesive G).
(3) Unexposed control (Ctrl) specimens.
(4) A-1 hr ultrasonic cleaning or 1 hour soak, B-2 cycles of ultrasonic cleaning or 16 hour soak.
(5) Temperature effect was measured with OS-30 solvent (only) at approximately 75°F and 120°F.
* Significant difference in variances of compared groups with "*" placed with the group with the higher variance; Levene Test for Homogeneity of Variances was applied.
** Zero variance measured.
(6) Mean values within bracket are not significantly different.

Table 13. Summary of Significant[1] Percent Weight Changes After Cleaning (Wet) Before Drying

Adhesive	Mean for Each Solvent			Mean for Each Cleaning Method		Mean for Each Time		Mean for Each Temperature[3]	
	TCA	OS-10	0S-30	Ultrasonic	Soaking	A[2]	B[2]	75°F	120°F
A	(0.07 -0.00)[4]		0.24	-	-	-	-	0.29	0.18
B	(-0.01 0.00)		0.17	-	-	-	-	0.22*	0.11
C	2.75	(-0.02 0.26)		0.22	1.41*	-	-	0.30	0.22
D	(0.01 -0.01)		0.20	-	-	-	-	-	-
E	2.46	(0.00 0.64)		0.50	1.38*	-	-	0.75	0.53
F	(0.01 -0.00)		0.54	-	-	-	-	-	-
G	0.64	(-0.01 0.08)		0.04	0.36*	-	-	0.10	0.06
H	4.50	(-0.07 0.11)		0.07	2.25	-	-	0.14	0.08

(1) Significantly different at the 95 percent confidence level. Every "-" indicates the treatment had no significant effect on the adhesive and the grand average is the best estimate of adhesive performance.
(2) A-1 hr ultrasonic cleaning or 1 hour soak, B-2 cycles of ultrasonic cleaning or 16 hour soak.
(3) Temperature effect was measured with OS-30 solvent (only) at approximately 75°F and 120°F.
(4) Mean values within bracket are not significantly different.
* Significant difference in variances of compared groups with "*" placed with the group with the higher variance; Levene Test for Homogeneity of Variances was applied.
** Zero variance measured.

Table 14. Brief Summary of Significant[1] Percent Weight Changes After Cleaning and Drying

Adhesive	Mean for Each Solvent			Mean for Each Cleaning Method		Mean for Each Time		Mean for Each Temperature[3]	
	TCA	OS-10	0S-30	Ultrasonic	Soaking	1[2]	2[2]	75°F	120°F
A	-	-	-	-0.03	-0.01	-	-	-	-
B	(-0.02	-0.02)[4]	-0.1	-0.02	-0.01	-	-	-	-
C	1.33*	(-0.10	-0.10)	-0.10[5]	0.61			-	-
D	-	-	-	-0.06	-0.05	-	-	-	-
E	0.78*	(-0.06	-0.05)	-0.06	0.37*	-0.03[5]	0.34*	-	-
F	-	-	-	-0.08	-0.06	-	-	-	-
G	0.29*	(-0.04	-0.04)	-0.04	0.13*	-0.04	*12	-	-
H	1.83	(-0.19	-0.19)	-0.18	0.81*	-0.09	0.72*		

(1) Significantly different at the 95 percent confidence level. Every "-" indicates the treatment had no significant effect on the adhesive and the grand average is the best estimate of adhesive performance.
(2) A-1 hr ultrasonic cleaning or 1 hour soak, B-2 cycles of ultrasonic cleaning or 16 hour soak.
(3) Temperature effect was measured with OS-30 solvent (only) at approximately 75°F and 120°F.
(4) Mean values within bracket are not significantly different.
* Significant difference in variances of compared groups with "*" placed with the group with the higher variance; Levene Test for Homogeneity of Variances was applied.
** Zero variance measured.
(5) Included numbers with "F" probability slightly greater than 0.050.

Table 15. Statistical Differences Between Solvents According to Weight Data

Allov	Differences Between Solvents Indicated by Brackets
Anodized 2017	[CFC, OS-10] [TCA, OS-10]
Cartridge Brass	[CFC] [OS-10, OS-30] [TCA] [OS-30]
Chromium Steel	[CFC] [TCA, OS-10, OS-30]

Table 16. Factors Leading to Significant Changes and Techniques to Study

Change	Factor	Technique
Weight gain	Residual solvent	DSC (Tg, Endotherm), FTIR
Weight loss	Leaching of unreacted components	FTIR of extractable
Hardness change	Additional x-linking	DSC (Tg), swelling
Increase in lap shear	Additional x-linking	DSC
	Change in fracture mode	SEM
Decrease in lap shear	Additional flaw (micropores)	SEM
	Change in fracture mode	SEM

3.2.2 Analysis of Metal Compatibility Results

The statistical methodology used for the adhesive degradation study was also used to analyze the weight change results obtained for evaluating metal compatibility. The effects of solvent type, cleaning method, and temperature are quantitatively illustrated in Table 15.

It appears that there is no statistical difference (at 95 percent confidence level) between solvents (TCA, OS-10, and 0S-30) for aluminum 2017, berylium, chromium copper and solder. However, there was statistically significant differences in weight changes between CFC 113, OS-10 versus TCA and OS-10. For cartridge brass, a significant difference in weight changes was found between TCA and 0S-30 and between CFC 113 and the two siloxane solvents. A significant difference was also found between the weight changes noted for CFC 113 and those for the group TCA, 0S-10, and 0S-30.

The effects of cleaning methods, sonication and soaking were observed for berrylium and chromium copper, and the higher temperature affected the results for aluminum 2017 and solder.

Although the differences measured were statistically significant, they are very small and within the specified limits for compatibility. This conclusion was further confirmed by ICP study and metallographic inspection of the coupons.

3.3 Review of the Results Analysis

The statistical analyses described in the previous sections identified statistically significant differences on measured properties as a function of solvent effects, cleaning method effects, time effects and temperature effects. While making this analysis, the statistical means of 51 specimens for each adhesive and each property were taken into consideration instead of the means of each test point for each adhesive. Further, the inherent experimental accuracy of each test procedure was not taken into consideration. Therefore, we wanted to look at the results from a different perspective; namely, the mean deviation of each test point and how important these differences are to the overall objective of

determining if the siloxane solvents have greater degradation potential than TCA under any of the test conditions evaluated in the program.

The average data for Shore D hardness and weight change (after drying) are presented in Tables 5 and 6 and those for sonication experiments are given in Tables 7 and 8. The average values for lap shear strength are given in Tables 9 and 10 for soaking and sonication, respectively.

The hardness test is not very precise. Usually the indentation is carried out at 8 to 10 points on the surface and the average is used as a reading. In addition to the subjective factor, the accuracy of the hardness test depends on the planarity of the specimen, surface uniformity, and surface imperfection. The hardness data, therefore, can vary between 2 to 3 units in Shore D.

The adhesive specimens used for weight changes are approximately 1.2 to 1.3 gms each. The weights are measured to ± 0.0002 g. Hence, the error in weight change measurement could be 0.25 to 0.5 percent.

The lap shear strength measurement is very sensitive to flaws and defects. It largely depends on test specimen preparation, i.e., how well the specimens are etched and how they have been handled during bonding, curing and testing. In addition, the effect of flaws will also depend on the nature of the adhesive. If the adhesive is brittle, then the effect can be large. For a ductile adhesive, there will be a smaller effect. We have, therefore, calculated standard deviations for each test condition, although the number of specimens for each mean was limited to three. The standard deviations are given for each test condition in Tables 10 and 11.

We may re-examine the statistically significant effects (solvent type, cleaning method, time and temperature of exposure) within the experimental accuracy of each test procedure. The solvent effects on percent weight change (Table 14) are within the experimental error except for the control solvent TCA for Adhesive C and H where significant weight changes (1.33 and 1.83 percent, respectively) have been observed. In the case of Adhesive E, the TCA residual weight change of 0.78 percent is also appreciable. The weight changes for 0S-10 and 0S-30 are significantly smaller (0.04 to 0.19 percent) for all adhesives and are very much within experimental error. The effects of time and cleaning methods identified in

Table 14 are within experimental error except for Adhesive H. Similarly the solvent, cleaning method, time and temperature effect on hardness identified in Table 12 are within experimental error (± 2 units) except in the case of Adhesive H where there is a significant drop in the hardness from 84 Shore D for the unexposed specimen to approximately 46 when exposed to three solvents under different conditions. However, the differences in hardness identified for each effect are not very large even for Adhesive H.

Examination of individual means also reflects a similar trend. The weight changes (Tables 6 and 8) are significant only for Ahesives C, E, and H when soaked for 16 hours in the control solvent TCA. The effect on hardness (Tables 5 and 7) is significant only for Adhesive H where the hardness dropped from 84 shore D to 41 to 46 under all exposure conditions. For 16 hour exposure to TCA, the hardness for Adhesive H dropped even more (31 shore D).

The effect on lap shear strength (Table 9 and 10) is appreciable for Adhesives A, E, and H. In case of Adhesives A and E, there was a significant increase in lap shear strength when soaked with OS-10 and OS-30 (except for OS-30 at 75°F for 16 hours for Adhesive A; at 75°F for 1 hour, and 120°F for 16 hours for Adhesive E.) For Adhesive H, there was a significant decrease in lap shear under all conditions of soaking and sonication. The lap shear strength when exposed to OS-10 and OS-30 under sonification conditions (except OS-10 at 75°F and TCA at 75°F for 1 cycle) is somewhat higher than the lap shear strength seen under soaking condition. On the other hand, Adhesive D shows a decrease in lap shear strength when exposed to OS-10 for 2 cycles, OS-30 for both 1 and 2 cycles at 75°F and OS-30 at 120°F. The failure mode for Adhesives B, C, and G was a cohesive under all conditions, whereas the failure mode for the rest of the five adhesives was adhesive under the same conditions. The standard deviation was significantly high in most cases when differences are observed. The residual strength of the joints for all adhesives exposed to OS-10 and OS-30 were higher than those exposed to TCA, and substantially high except for Adhesive H. Hence, the adhesive degradation potential of siloxane solvents can be considered small for the epoxy adhesives and less than the degradation potential of the control solvent, trichloroethane.

4.0 INSTRUMENTAL ANALYSIS AND MECHANISM OF DEGRADATION

The objective of this task was to identify the degradation mechanism for test conditions where significant degradations occurred. Instrumental techniques were used to identify the molecular mechanism underlying the degradation phenomenon. To carry out this task, we reviewed the results of weight changes, hardness change and changes in lap shear specimens and identified methods suitable for identifying the mechanism.

4.1 Selection of Specimens for Analytical Study

Based on earlier review, we selected three criteria for selecting specimens for instrumental analysis. They were:

- Weight change (gain or loss) greater than 0.5 percent.
- Hardness change greater than 2 to 3 Shore D units.
- Change in lap shear strength greater than 20 percent.

Selecting the best instrumental techniques requires understanding both the nature of the change and the factors leading to the change. The weight gain from exposure to siloxane solvents could be due to residual solvent being held up by the adhesive specimen, whereas weight 1oss could be ascribed to the leaching of unreacted components from the test specimens. Surface hardness, which is a rough measure of modulus, could be caused by increased crosslinking during cleaning and drying or due to loss of low molecular weight components which act as plasticizers. The lap shear strength can increase due to additional crosslinking or by microtoughening of the adhesive. The specimens were, however, more likely to lose strength due to introduction of flaws in the specimens during testing. Each of these factors can be analyzed by a suitable analytical technique. Table 16 lists the different changes, their possible cause, and the most suitable technique for identifying the cause of this change.

Based on the criteria mentioned previously, Specimens A, D, E, and H were selected for differential scanning calorimetry (DSC) analysis, Specimens E and H were selected for Fourier Transform Infrared (FT-IR) analysis, and Specimens A, E, and H were selected for scanning electron microscopy (SEM) analysis. Specimens B and C were also included in this test because the nature of failure of B and C were different (cohesive) from A, D, E, F, and H (adhesive).

The bulk specimens selected for DSC and FT-IR analysis were either soaked or sonicated depending on the treatment which produced the observed change in hardness or weight. The fractured lap shear specimens were examined by electron microscope without any further treatment.

4.2 Results of Instrumental Analysis

4.2.1 Differential Scanning Calorimetry

Figures 12 and 13 present the DSC traces of Adhesive A unexposed and exposed to 0S-10 sonication for one cycle. The two scans for each specimen show the heat flow in the first heating cycle and the second scan represents heat flow in the second cycle after the sample is coated and reheated. There does not appear to be any major difference between the DSC traces of unexposed and exposed specimens. The glass transition temperature of the exposed specimens are somewhat lower 910 C and 97°C compared to 93 “C and 102 “C for the unexposed specimen. The higher lap shear strength obtained for Adhesive A could not be ascribed to additional crosslinking. The small decrease of Tg may have improved the flexibility of the interracial bonding between the adhesive and the metal leading to higher lap shear strength.

The DSC traces of unexposed and exposed (soaked in OS-10 for 1 hour) for Adhesive D are presented in Figures 14 and 15. Both traces are very similar and there is no apparent difference in Tg. Therefore, the increase in surface hardness cannot be ascribed to increased crosslinking. A very small loss of some low molecular weight volatile components from the

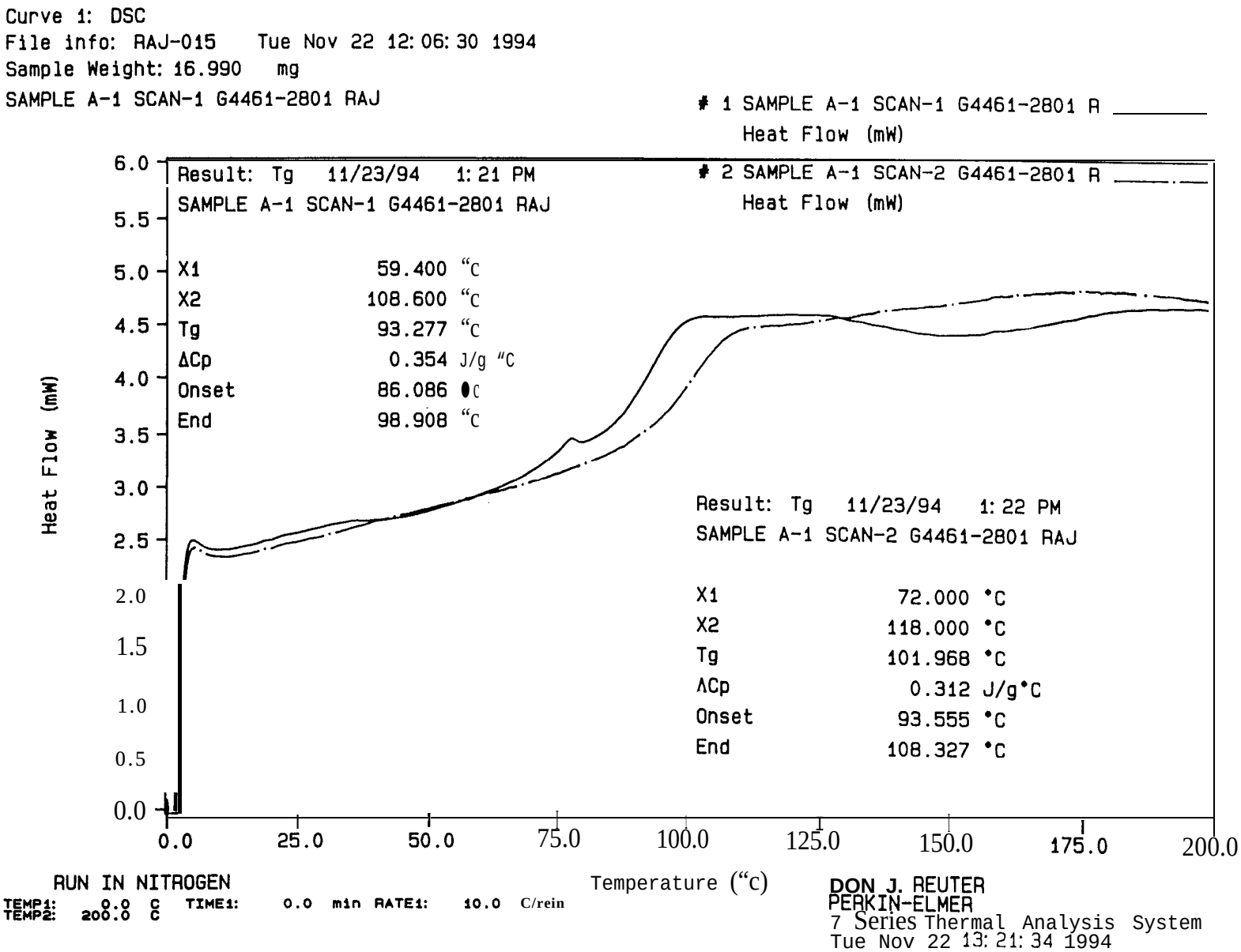


Figure 12. DSC Trace of Adhesive A (Unexposed Control)

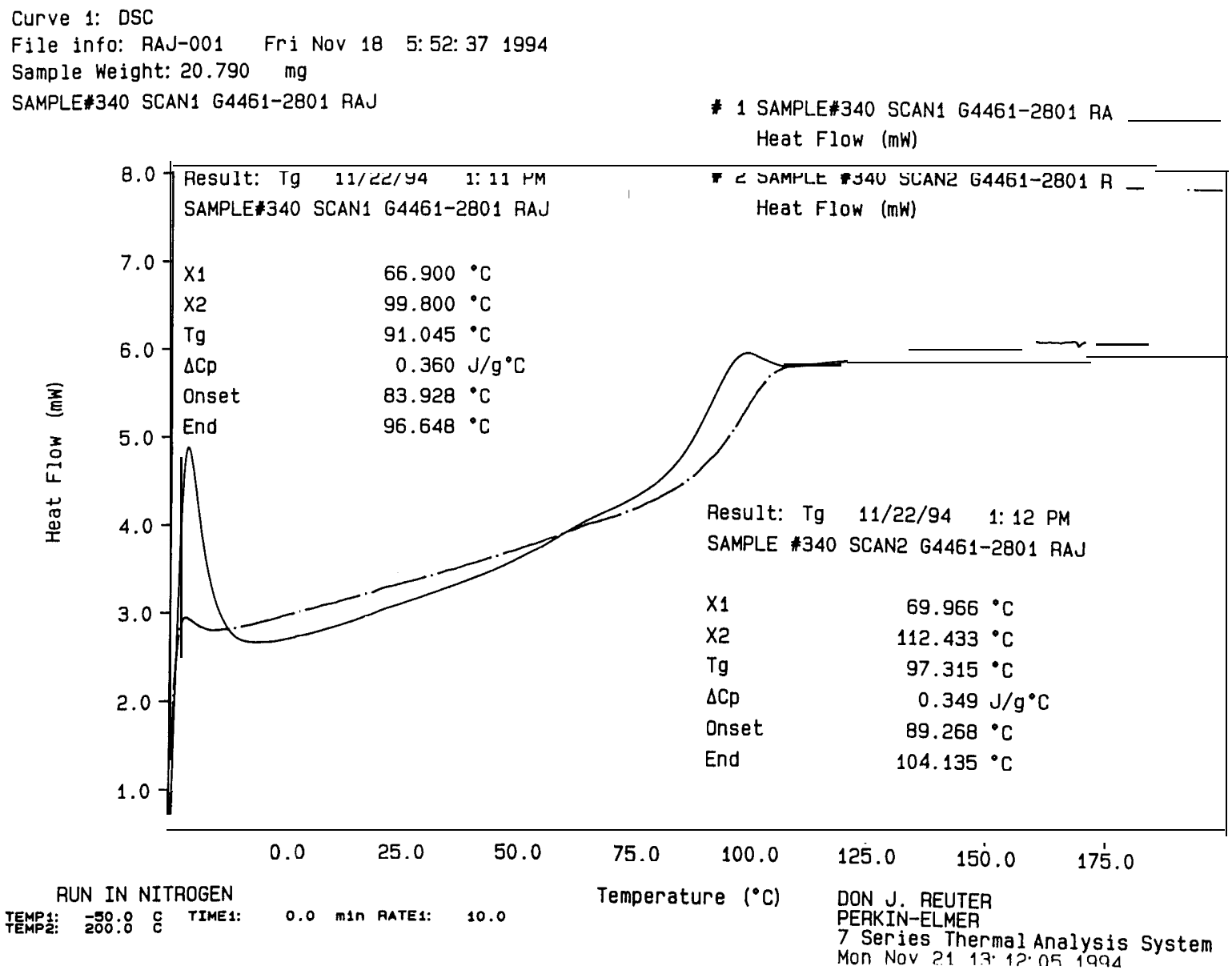


Figure 13. DSC Scan of Adhes ve A Exposed to Siloxane Cleaner OS-10 for One Cyc e

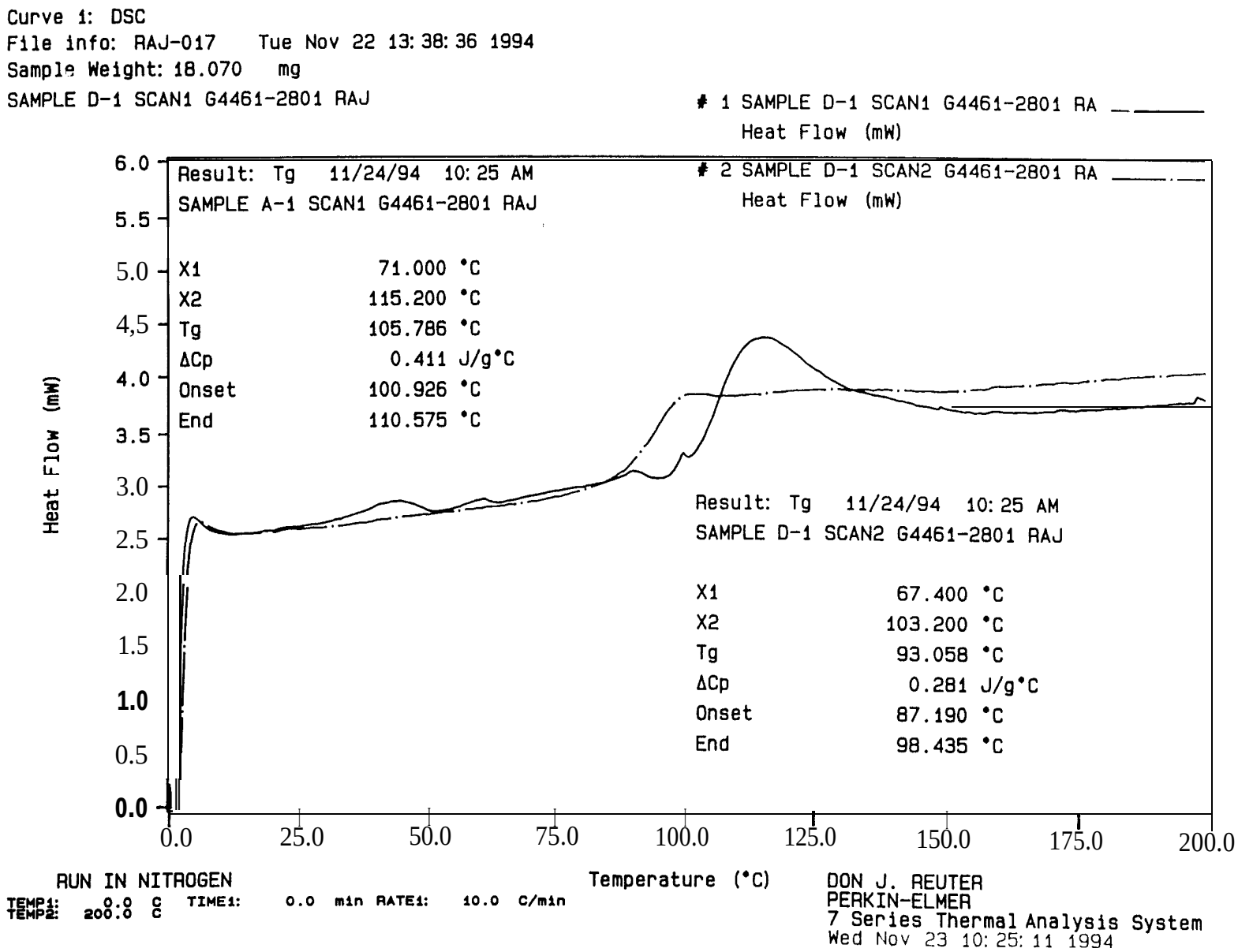


Figure 14. DSC Scan of Adhesive D Unexposed Control

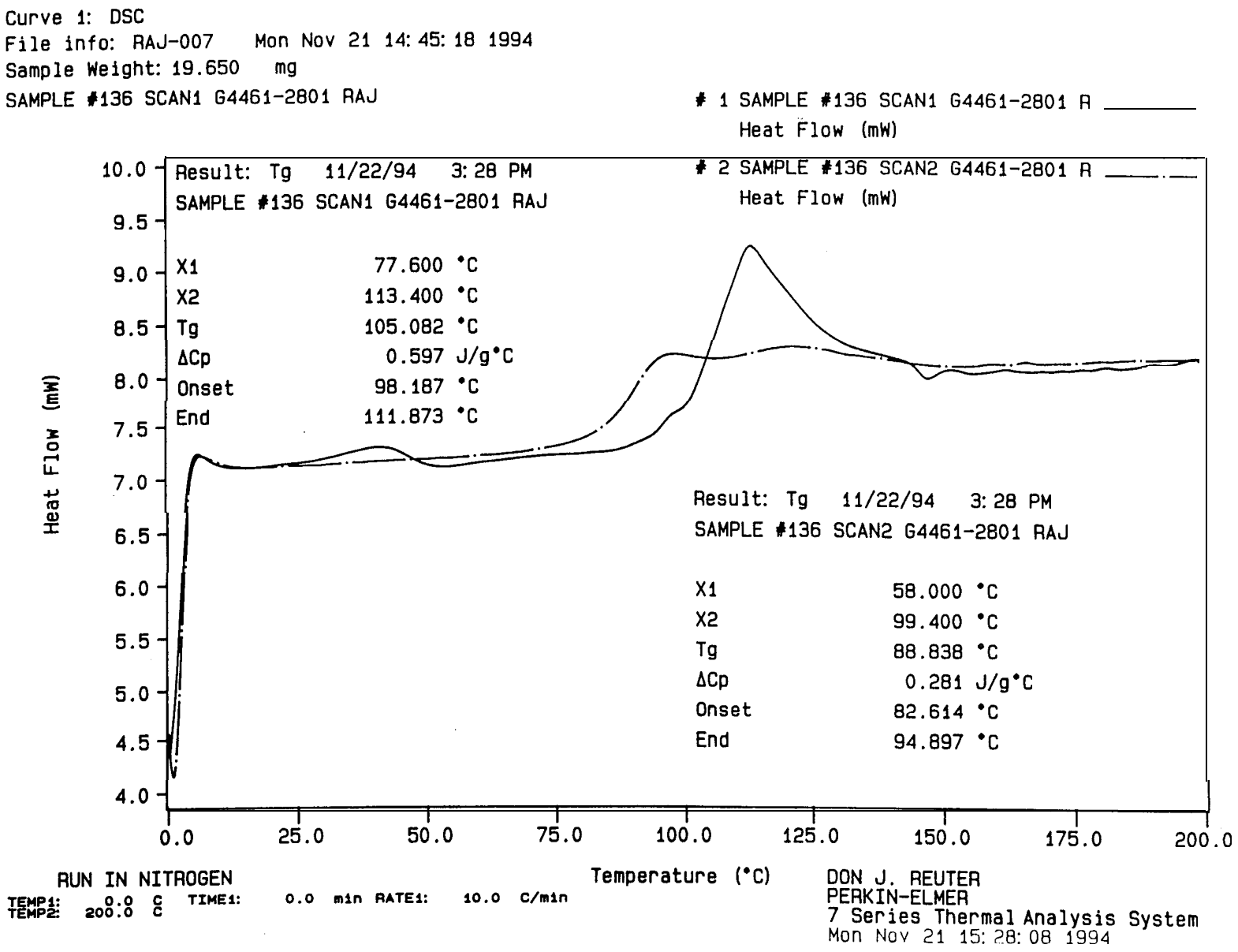


Figure 15. DSC Scan of Adhesive D Soaked in Siloxane Cleaner OS-10 for 1 Hour at RT

surface may explain the increase in hardness. Note that there was no substantial change in the lap shear strength for Adhesive D.

Adhesive E shows an increase in lap shear strength and appreciable absorption of liquid on soaking, particularly when the liquid is OS-30. DSC traces of the unexposed and soaked specimen of Adhesive E are presented in Figures 16 and 17. The glass transition temperature seen for the first and second scan of the unexposed specimen are 31°C and 42°C, respectively. This is smaller compared to Tg of conventional epoxy adhesives, approximately 100°C. The solvent intake can be ascribed to low Tg. The increase in Tg and sharp change in the DSC trace for the scans of the exposed sample indicates additional curing in the heating cycle of the DSC measurement. The Tg increase is more prominent in the DSC traces of the exposed specimen (Tg = 86°C and 67°C compared to 31°C and 42°C for the unexposed specimen). This definitely indicates additional curing of the adhesive during drying of the specimen at 155°F. The higher state of cure probably contributes to increased lap shear strength. The singular decrease of hardness from 79 to 72 Shore D on exposure to OS-10 for 16 hours could not be explained because increased crosslink density usually increases modulus and hardness.

Adhesive H showed maximum decrease in hardness and lap shear strength and in many cases appreciable absorption of the solvent. The DSC traces of this adhesive with and without exposure to siloxane cleaner are given in Figures 18 and 19. The traces appear very similar to each other and there is no significant difference between the first and second scan traces. However, the Tg is very low, -5°C and -6°C for the unexposed specimen and 12°C and -3°C for the exposed specimen. The low Tg for the polysulfide cured epoxy indicates that it is a very flexible epoxy-polysulfide copolymer, having a solubility parameter much lower than that of conventional epoxy polymer. This possibly explains the greater tendency of this adhesive to absorb the siloxane cleaner. The additional mobility provided by low Tg and the closeness of the solubility parameter of the epoxy-polysulfide copolymer to that of siloxane solvents contribute to greater solubility. (The solubility parameter of siloxanes are close to 7 $(cal/cc)^{1/2}$.) Absorption of solvent on the skin of the specimen and the interfacial layer and leaching probably contribute to its lower hardness and lower lap shear strength, respectively.

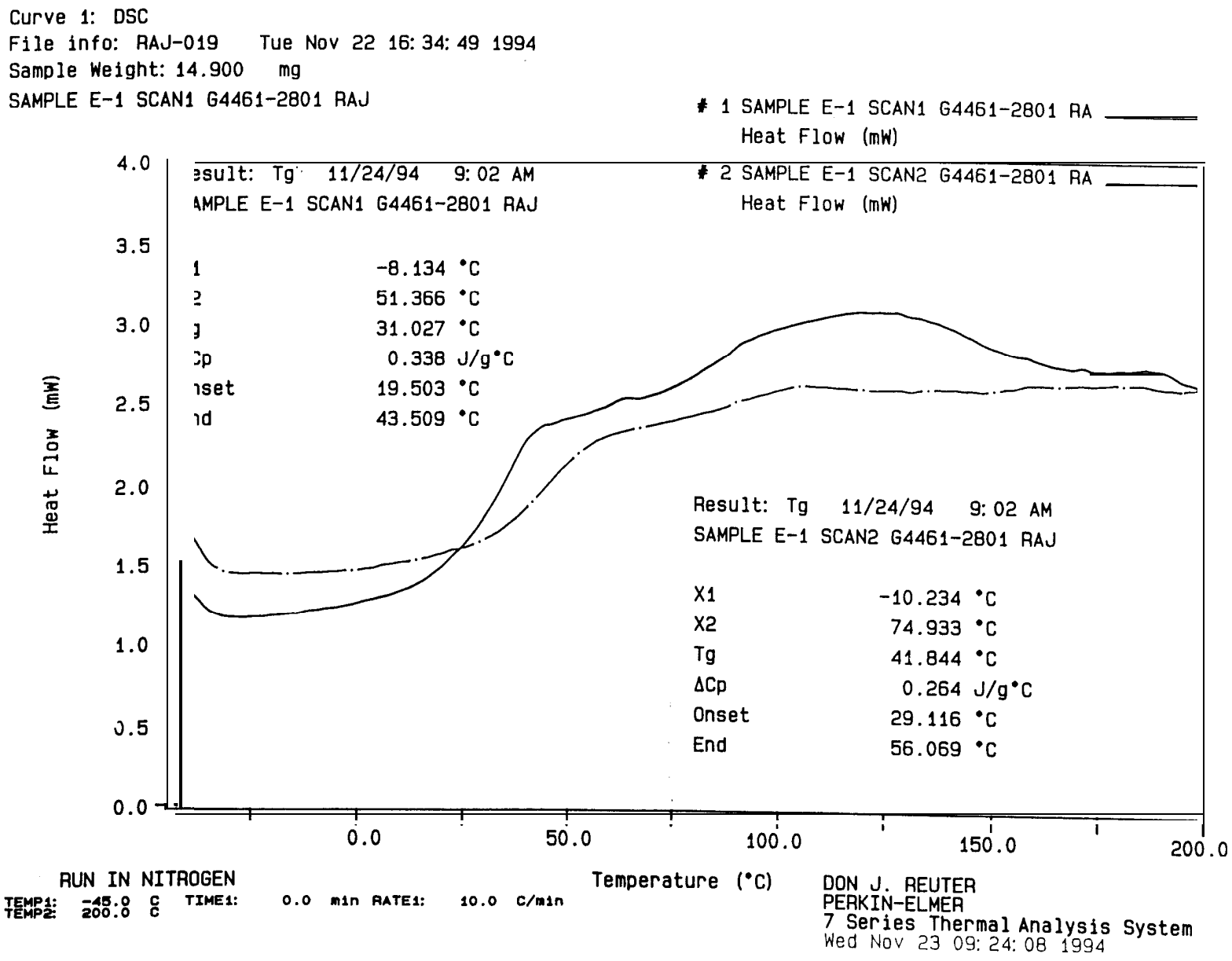


Figure 16. DSC Scan of Adhesive E Unexposed Control

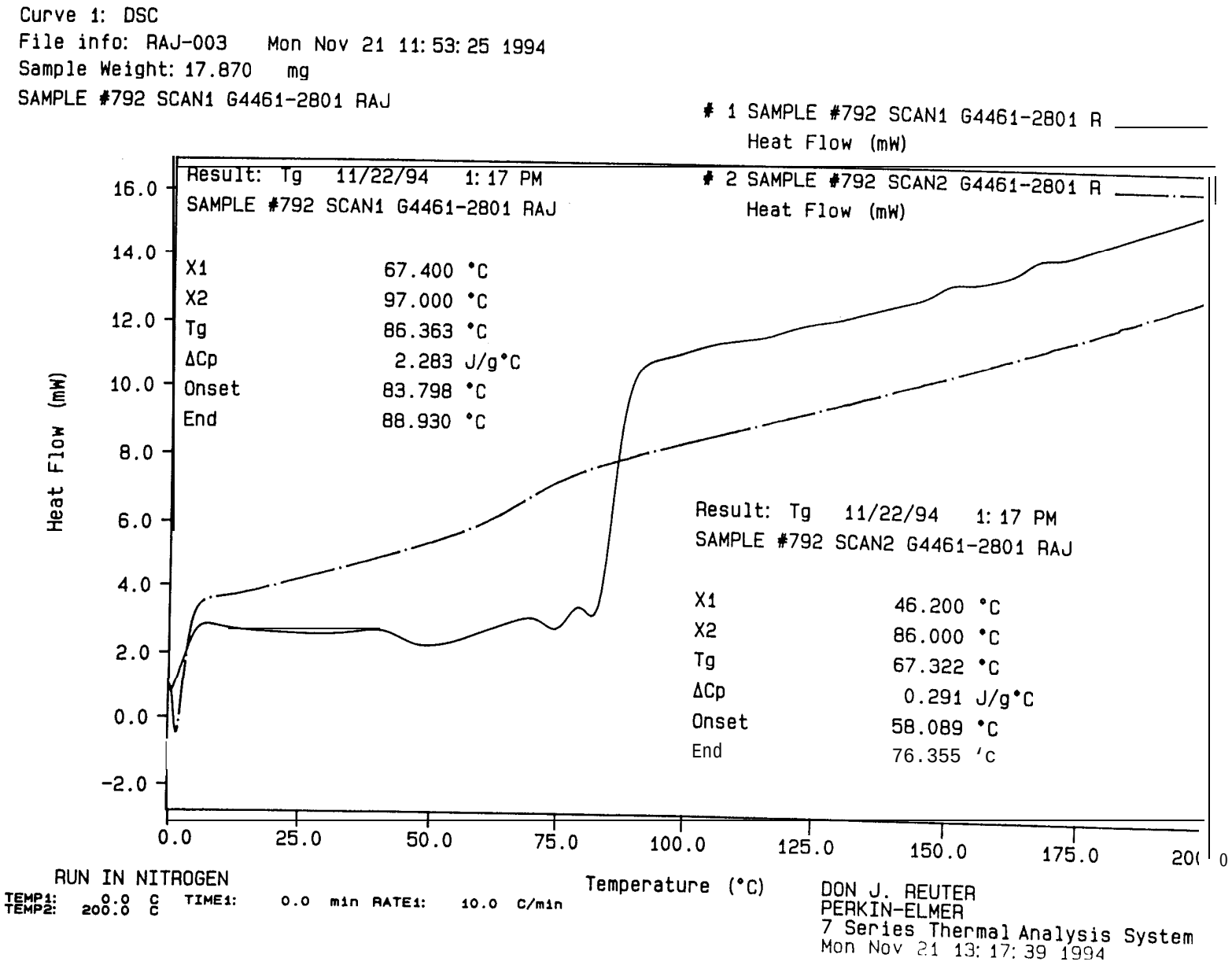


Figure 17. DSC Scan of Adhesive E Exposed to OS-30 at 120°F for 2 Cycles of Sonication

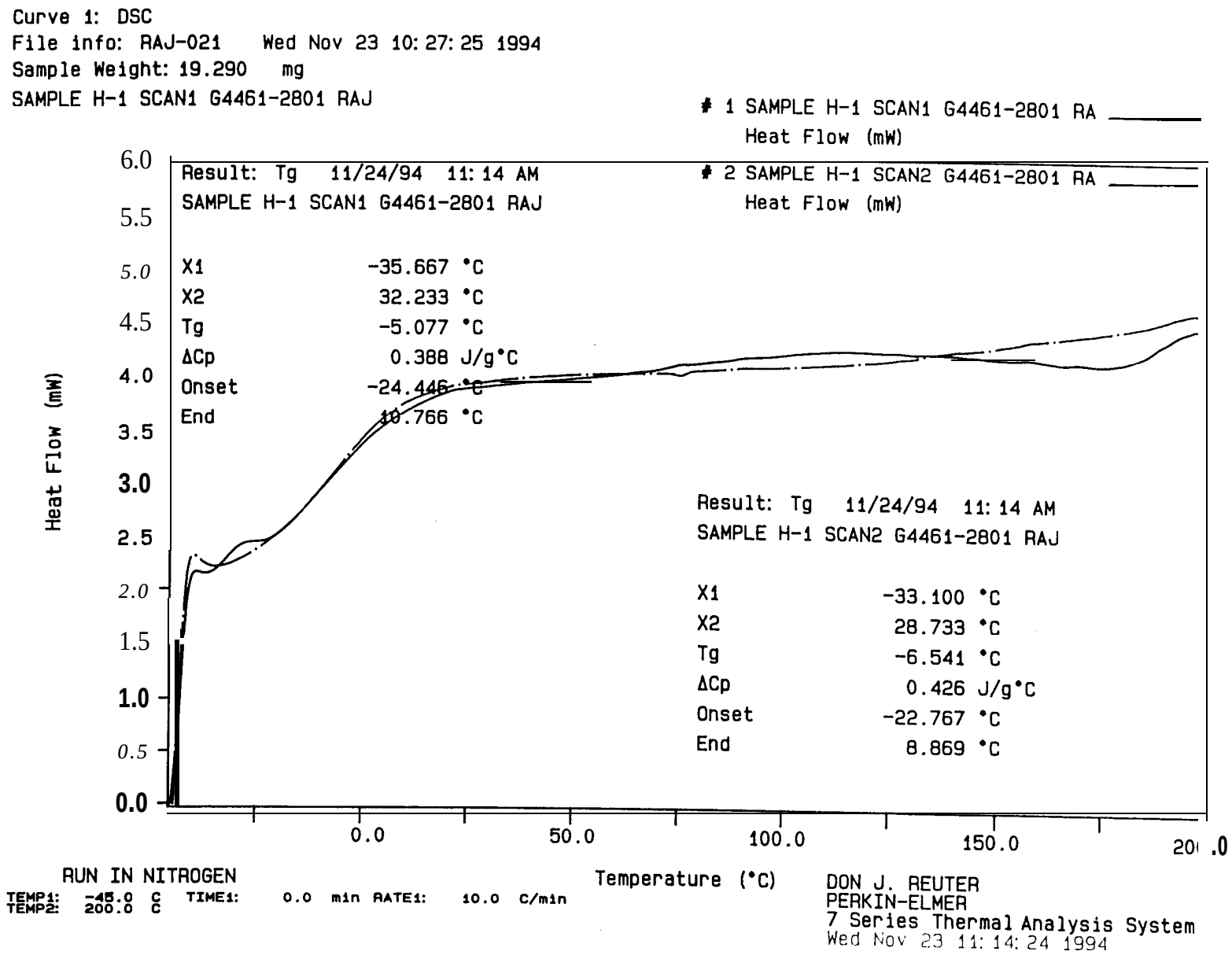


Figure 18. DSC Scan of Adhesive H Unexposed Control

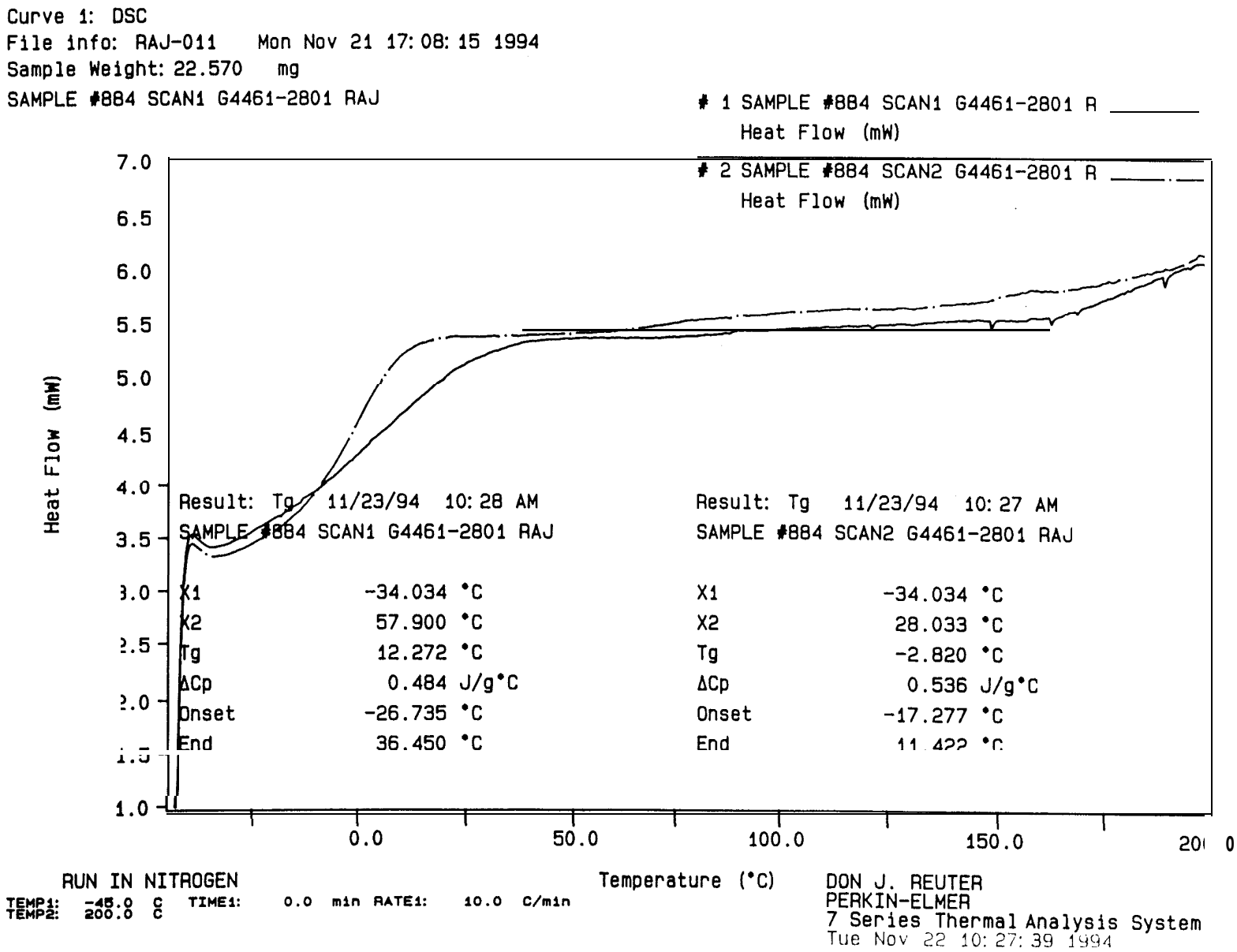


Figure 19. DSC Scan of Adhesive H Exposed to Siloxane OS-30 at 120°F for 2 Cycles of Sonication

Figures 20 and 21 show the DSC scans of Adhesive F. This is an anhydride cured epoxy. Unlike other epoxies, the glass transition temperature of this epoxy is very high, 179°C for the unexposed control and 187°C for the specimen exposed to 0S-10. The higher glass transition temperature could be due to additional cure during drying of the specimen.

4.2.2 Scanning Electron Microscopy Study

The objective of this study is to examine the surface morphology of the fractured specimens and relate it to the failure mechanism.

As mentioned earlier, out of the eight adhesives studied in the program, five (A, D, E, F, and H) of them failed adhesively; i.e., the failure took place as the adhesive stripped away from the metal surface. Three (B, C, and G) failed cohesively; i.e., the failure took place in the body of the adhesive. Figure 22a presents the SEM scan of Adhesive E at small magnification (X = 15). The adhesive appeared to have peeled away from the metal surface possibly due to poor adhesion. As the fracture travels from the interface it breaks, leaving ridges and valleys on the surface (Figure 22b, X = 500). This specimen was soaked in OS-30 for 1 hour at 120°F.

Similar cleavage is also seen in Adhesive A (Figure 23a and 23b). The increase in lap shear strength could be related to the microtoughening phenomenon leading to ductile failure in some areas.

Figures 24a and 24b present the fracture surface of Adhesive C at 10 and 1000 times magnification. This specimen was subjected to ultrasonic cleaning in OS-10 at room temperature for 2 cycles. The absence of bare metal surface shows cohesive failure as compared to adhesive failure in Figure 22a. The fracture took place in a mixed mode, partly ductile, partly brittle (Figure 24b). Adhesive B (Figures 25a and b) also shows adhesive failure like Adhesive C, except the failure is probably more brittle than that for Adhesive C.

Figures 26a and b present the fracture morphology of Adhesive A after soaking for 1 hour. Although the fracture is brittle in nature, it does not have the cleavage valleys seen for Adhesive A (Figures 22 and 23).

Curve 1: DSC
File info: RAJ-014 Tue Nov 22 11:24:19 1994
Sample Weight: 19.410 mg
SAMPLE F-1 SCAN2 G4461-2801 RAJ

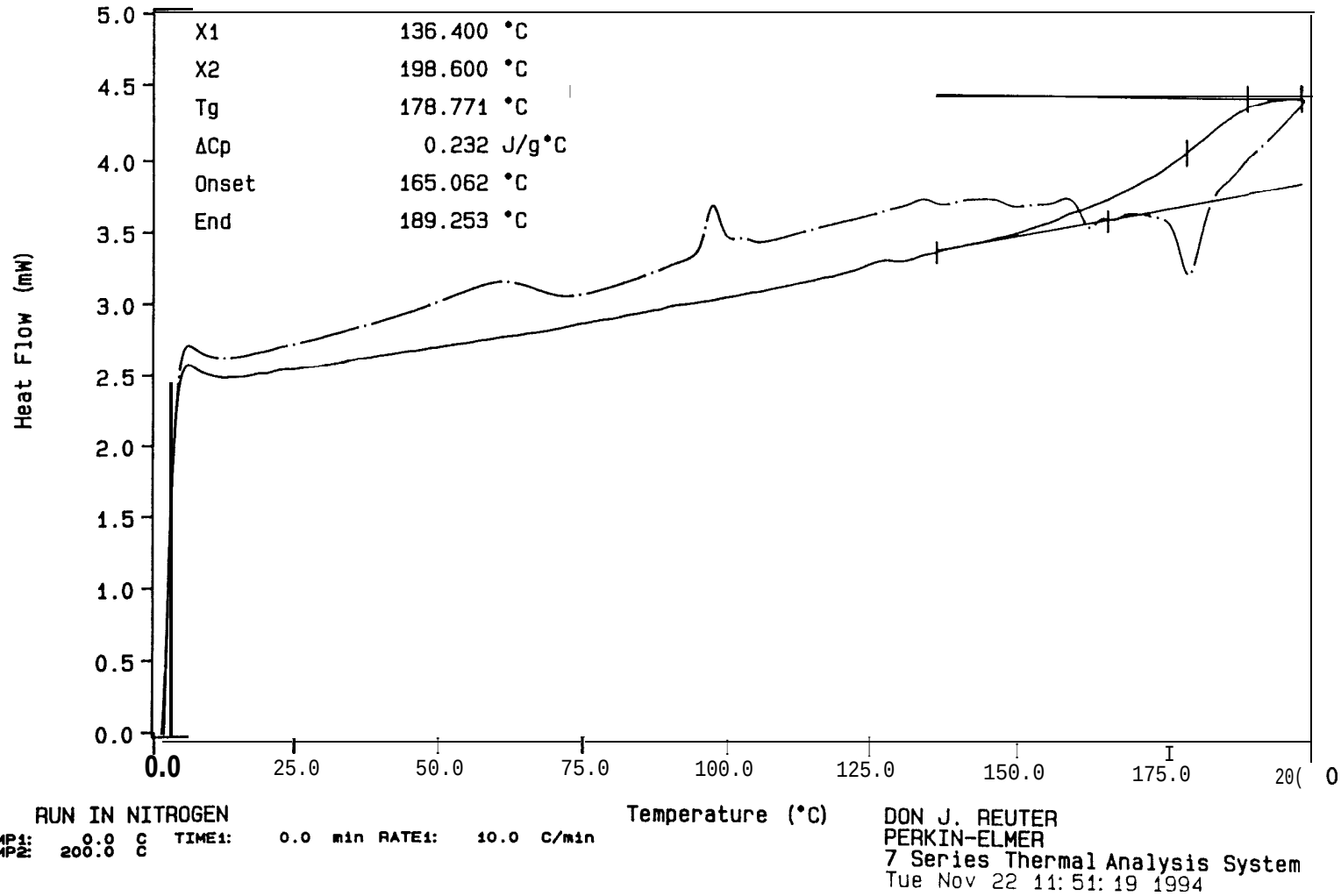


Figure 20. DSC Scan of Adhesive F Unexposed Control

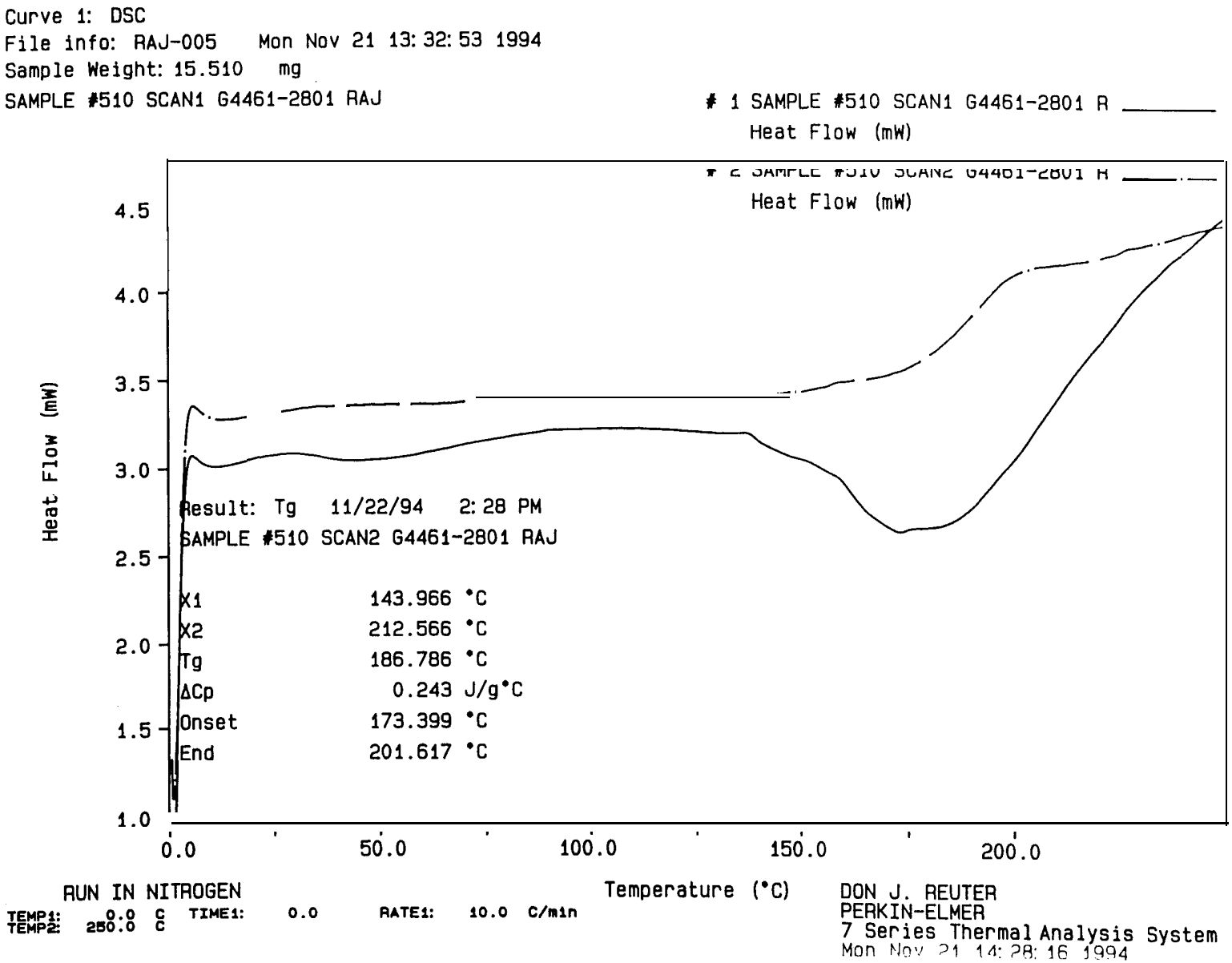


Figure 21. DSC Scan of Adhesive F Exposed to Siloxane Cleaner OS-10 for 2 Cycles of Son cation

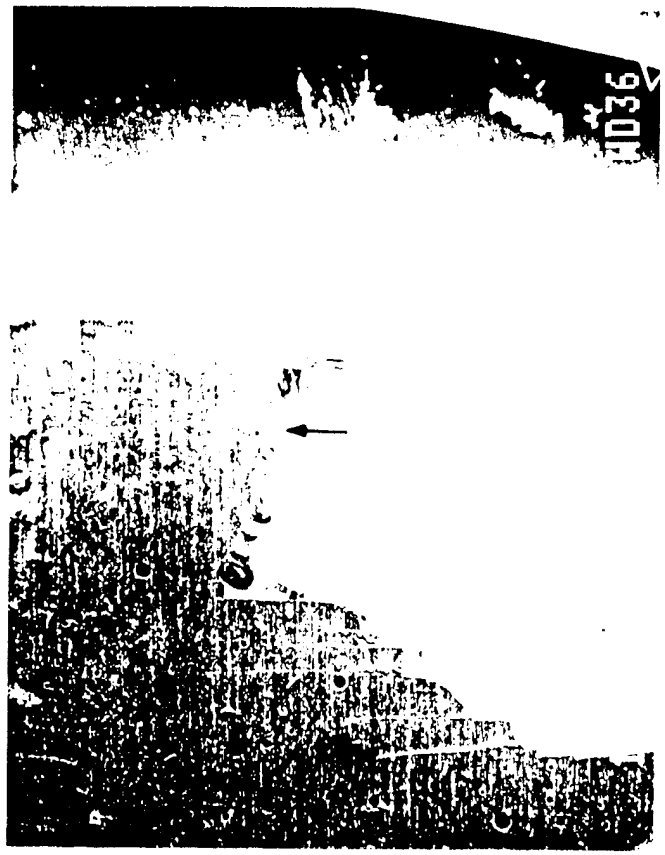


Figure 22a. SEM Picture of Adhes ve E, Soaked in OS-30 for 1 lour at 120°F, X=15

Figure 22b. SEM Picture of Adhesive E, Soaked n OS-30 for 1 lour at 120°F, X=500

Figure 23a. Scanning Electron Micrography of Adhesive A, Subjected to Ultrasonic Cleaning in 0S-10 at RT, X=15

Figure 23b. Scanning Electron Micrograph of Adhesive A, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=1OOO

Figure 24a. SEM Picture of Adhesive C, Subjected to Ultrasonic Cleaning in 0S-10 for 2 Cycles at RT, X=1O

Figure 24b. SEM Picture of Adhesive C, Subjected to Ultrasonic C" caning in 0S-10 for 2 Cycles at RT, X=1000

Figure 25a. SEM Picture of Adhesive B, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=10

Figure 25b. Scanning Electron Micrograph of Adhesive B, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=1000

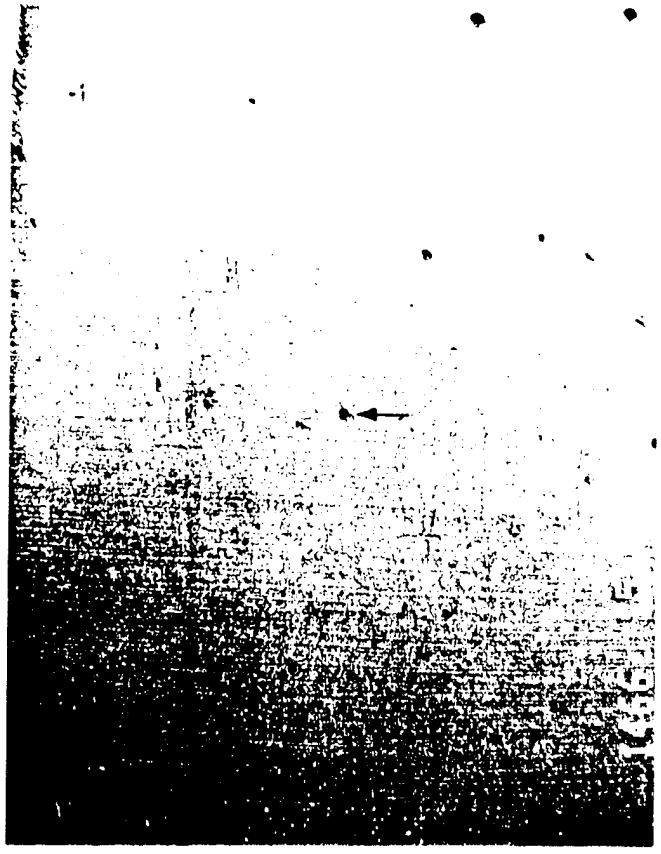


Figure 26a. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=10

Figure 26b. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning in OS-10 at RT, X=1500

A similar but less distinct difference is seen for Adhesive E, subjected to ultrasonic cleaning (Figure 27) for 2 cycles in OS-10 versus the one subjected to soaking for 1 hour in the same solvent, both at room temperature (Figure 28). The lap shear strength of the specimen subjected to ultrasonic cleaning is somewhat lower than that for soaking. This may indicate that either microtoughening occurs when the specimen is exposed to solvent over a longer period of time as in soaking or ultrasonic vibration creates weakening between the adjacent layers of the adhesives. The plane where the fracture started does not show any sipping and undercut. The fracture surface of Adhesive A when sonicated for 2 cycles in trichloroethane (TCA) showed a slightly different morphology of the surface and some undercut, probably due to sipping (Figures 29a and b) of the solvent at the metal-adhesive interface.

Figure 30 presents the scanning electron micrograph of Adhesive E subjected to soaking for 1 hour in OS-30 at room temperature. This may be compared with Sample E subjected to soaking for 1 hour at 120°F (Figures 22a and b). The fracture surface of both specimens appear to be very similar except the valleys in the specimen subjected to higher temperature are somewhat wider compared to the valleys of the specimen subjected to exposure at lower temperature. Higher temperature may be causing additional weakening leading to a small decrease in lap shear strength.

Adhesive H showed the maximum decrease in lap shear strength and hardness for all conditions of solvent exposure. Figures 31a and b present the scanning electron micrographs of unexposed Adhesive H specimen and Figures 32a and b present the same for Adhesive H subjected to two cycles of ultrasonic cleaning at room temperature. Both cleavage surfaces look very similar. The failure apears to be brittle in spite of low Tg. The low magnification picture, however, shows more small holes in the ultrasonically cleaned specimen (Figure 32a) than compared to those in the unexposed specimen (Figure 31a). This indicates that some material loss may be occurring and micropores are being formed when Adhesive H is exposed to siloxane cleaners. The lowering of lab shear strength could also be attributed to leaching and microhole formation particularly at metal-adhesive interface. The SEM pictures of Specimen H subjected to one cycle of ultrasonic cleaning in OS-30 versus two cycles cleaning are shown in Figures 33 and 34, respectively. Whereas there are few holes after

Figure 27a. SEM Picture of Adhesive E, Subjected to Ultrasonic Cleaning for 2 Cycles in 0S-10, X=20

Figure 27b. SEM Picture of Adhesive E, Subjected to Ultrasonic Cleaning for 2 Cycles in 0S-10, X=500

Figure 28a. SEM P·cture of Adhesive E, in OS-10 for 1 Hour, X=10

Figure 28b. SEM Picture of Adhesive E Soaked in OS-10 for 1 Hour, X=500

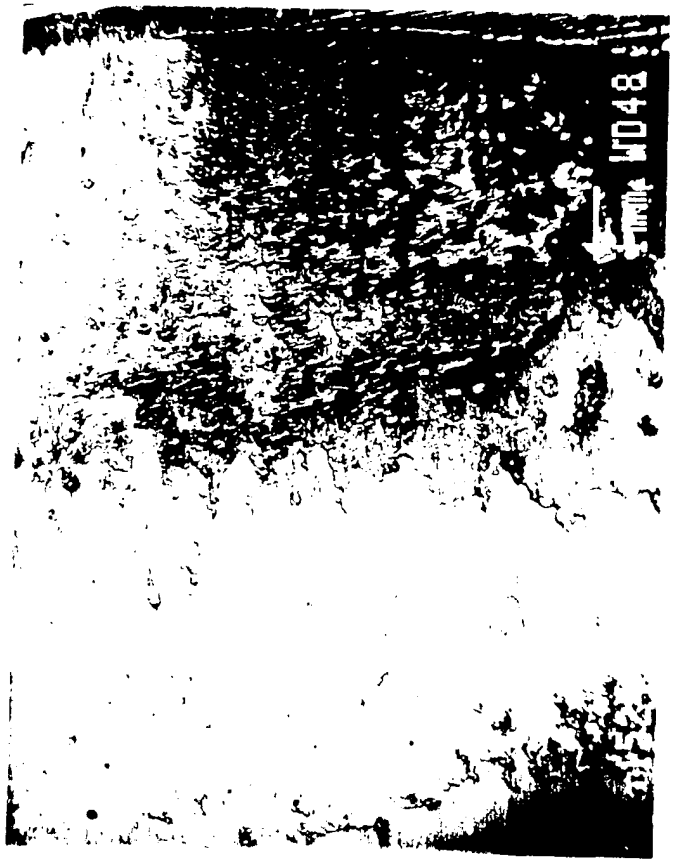


Figure 29a. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning for 2 Cycles in TCA, X=10

Figure 29b. SEM Picture of Adhesive A, Subjected to Ultrasonic Cleaning for 2 Cycles in TCA, X=1OOO

Figure 30a. SEM Picture of Adhesive E, Soaked for 1 Hour in 0S-30 at RT, X=10

Figure 30b. SEM Picture of Adhesive E, Soaked for 1 Hour in 0S-30 at RT, X=1OOO

Figure 31a. SEM Picture of Adhesive H of Unexposed Control, X=12

Figure 31b. SEM Picture of Adhesive H of Unexposed Control, X=500

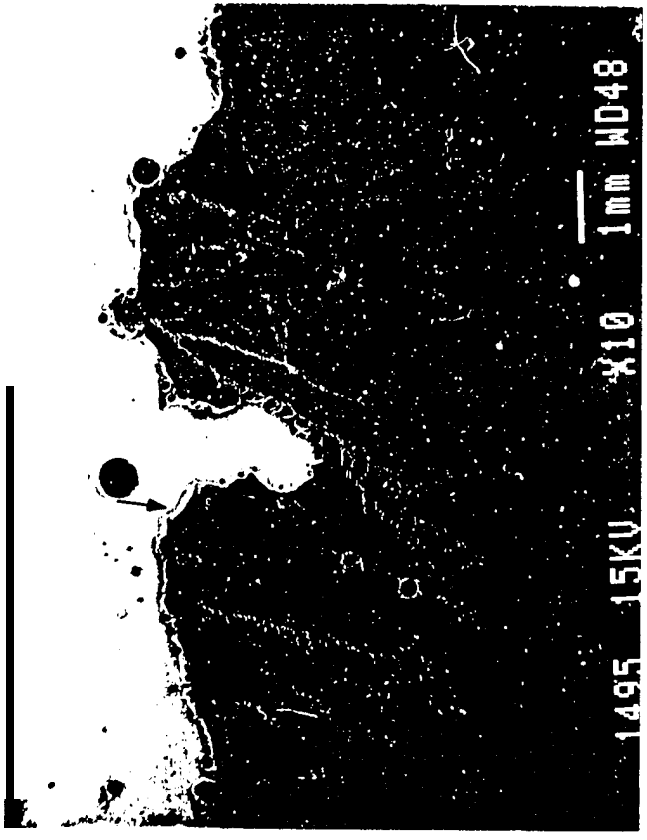


Figure 32a. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in 0S-10 at RT, X=1O

Figure 32b. SEM Pictue of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in 0S-10 at RT, X=500

Figure 33a. **SEM Picture of Adhesive H, Subjected to 1 Cycle Ultrasonic Cleaning in 0S-30, X=10**

Figure 33b. SEM Picture of Adhesive H. Subjected to 1 Cycle Ultrasonic Cleaning in 0S-30, X=270

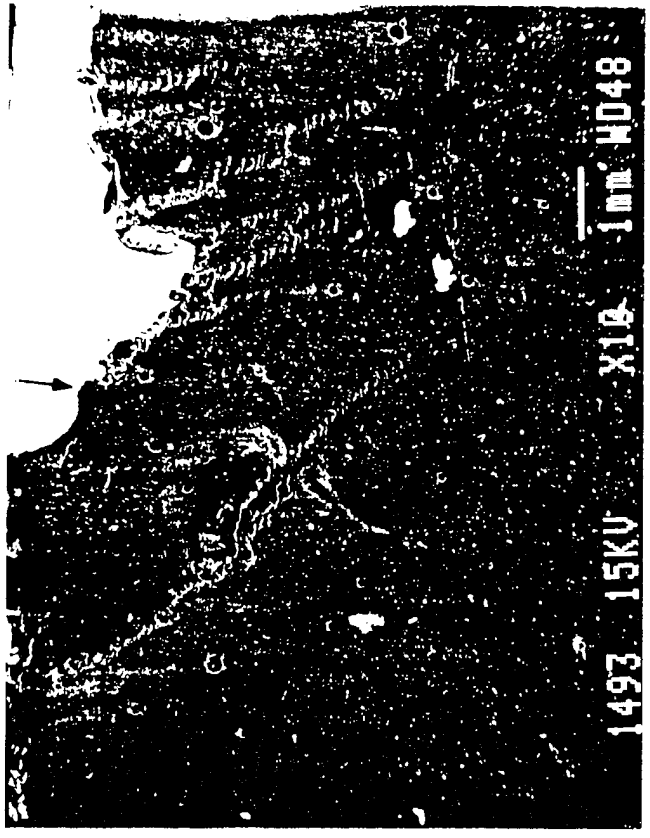


Figure 34a. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in 0S-30, X=1O

Figure 34b. SEM Picture of Adhesive H, Subjected to 2 Cycles of Ultrasonic Cleaning in 0S-30, X=500

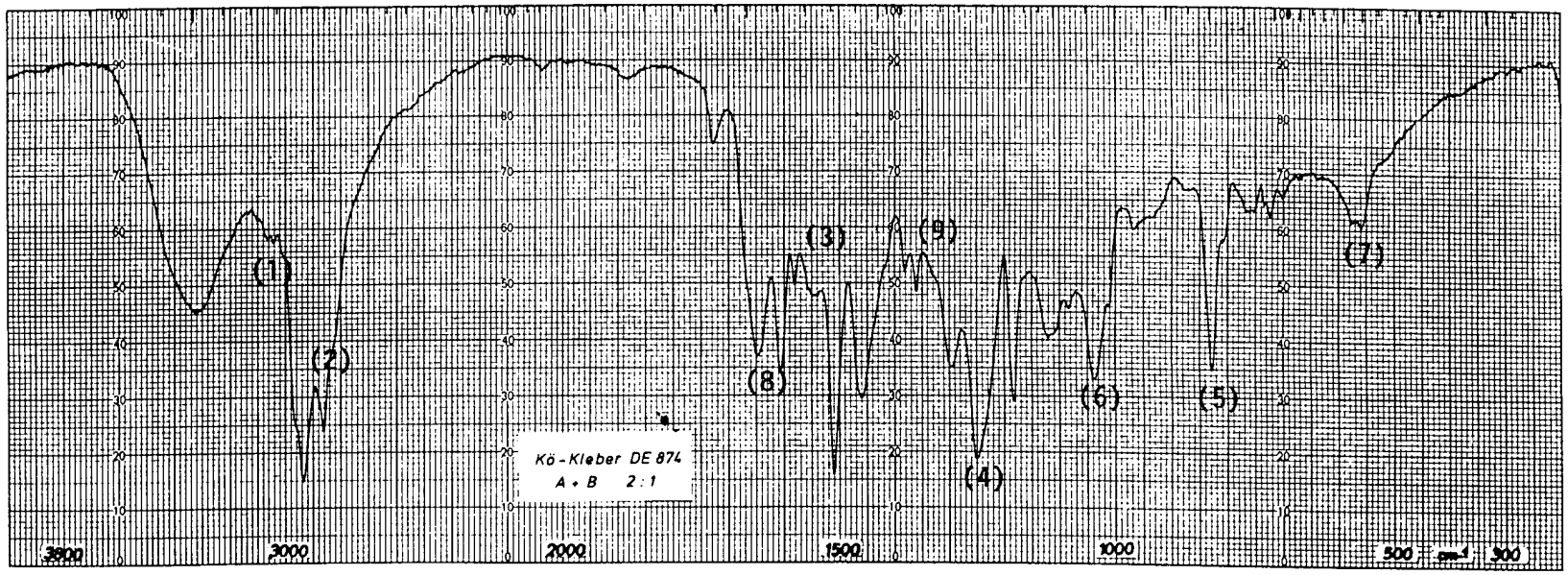
ultrasonic exposure for one cycle, there are an appreciable number of holes after two cycles of exposure.

In conclusion, it may be said that the scanning electron micrograph successfully explains some of the results discussed earlier. The difference in failure type, adhesive or cohesive, depends more on the interracial adhesion than on the mode of failure, brittle, or ductile. The increase in strength due to solvent exposure as seen in Adhesive A and E can be traced to a microtoughening mechanism which introduces some ductile failure. The reduction in lap shear strength in case of Adhesive H could be due to a small amount of leaching of components and formation of microholes, particularly at the interface. The decrease in surface hardness can be ascribed to formation of microholes on the surface, making it spongy. The leaching probably takes place in a few minutes after solvent exposure. Further ultrasonic cleaning may introduce some weakening between the adjacent layers of the adhesive joint and a similar weakening effect may be caused by exposure to higher temperature.

4.2.3 Fourier Transform Infrared Spectrophotometry

FTIR provides molecular details of the changes that may take place in the adhesive or the siloxane cleaner as the adhesive is exposed to the cleaner. Hence, this analysis was carried out for adhesive specimens which exhibited weight gain or loss. Figure 35 presents a typical spectra of an epoxy adhesive (Ciba Geigy Araldite B) combined cured with a polyamide curing agent. The spectra of Adhesive E (Figure 36) not exposed to siloxane cleaners is very similar to this spectra. The main peaks such as amido (NHCo) and aromatic hydrocarbons, aromatic ether, and carbonyl groups are noted in the figure. The IR spectra of the siloxane cleaner 0S-30 is given in Figure 37. The siloxane peaks are quite distinct and are seen between 800 to 1100 wave numbers.

The solution obtained from exposing Adhesive H to 0S-10 was evaporated off the solvent and IR spectra was taken of the film left on the surface (Figure 38). It can be seen that the volatile solvent OS- 10 evaporated completely leaving no trace of silicone. It also does not have typical epoxy peaks. However, it does have amine and hydrocarbon peaks



(1) **Kö-Kleber DE 874, Komponenten A + B (2:1)**
(2) Kömmerling Chemische Fabrik, Pirmasens
(3) Epoxidharz, mit Amidamin gehärtet
(4) gelber, transparenter Film
(6) kapillare Schicht zwischen CsI, 24 h bei 50 °C gehärtet

(1) **Kö-Kleber DE 874, components A + B (2:1)**
(3) epoxy resin cured with amidoamine
(4) transparent, yellow film
(6) capillary film between CsI, cured for 24 h at 50 °C

Figure 35. IR Spectra of Epoxy Resin Cured With Amido Amino

(1) Aromatic Hydrocarbon
(2) Aliphatic Hydrocarbon —C—H
(3) Aromatic Hydrocarbon (breathing)
(4) Aromatic Ether
(5) Bi Substituted Aromatic
(6) Carbon Oxygen C—O Band
(7) Aliphatic Ether —C—O—C—
(8) Amido —NH—C=O
(9) Hydrocarbon C—H (bending)

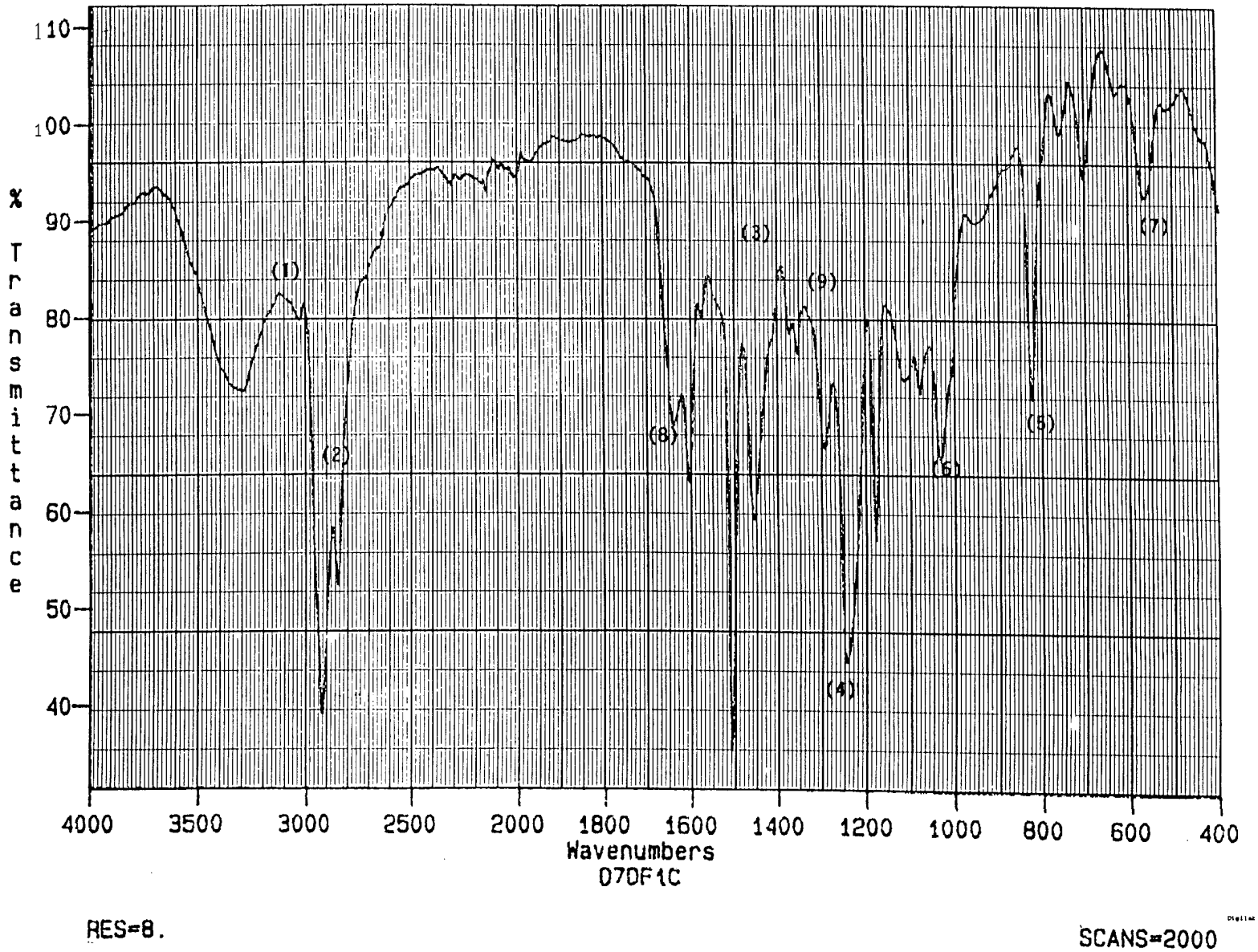
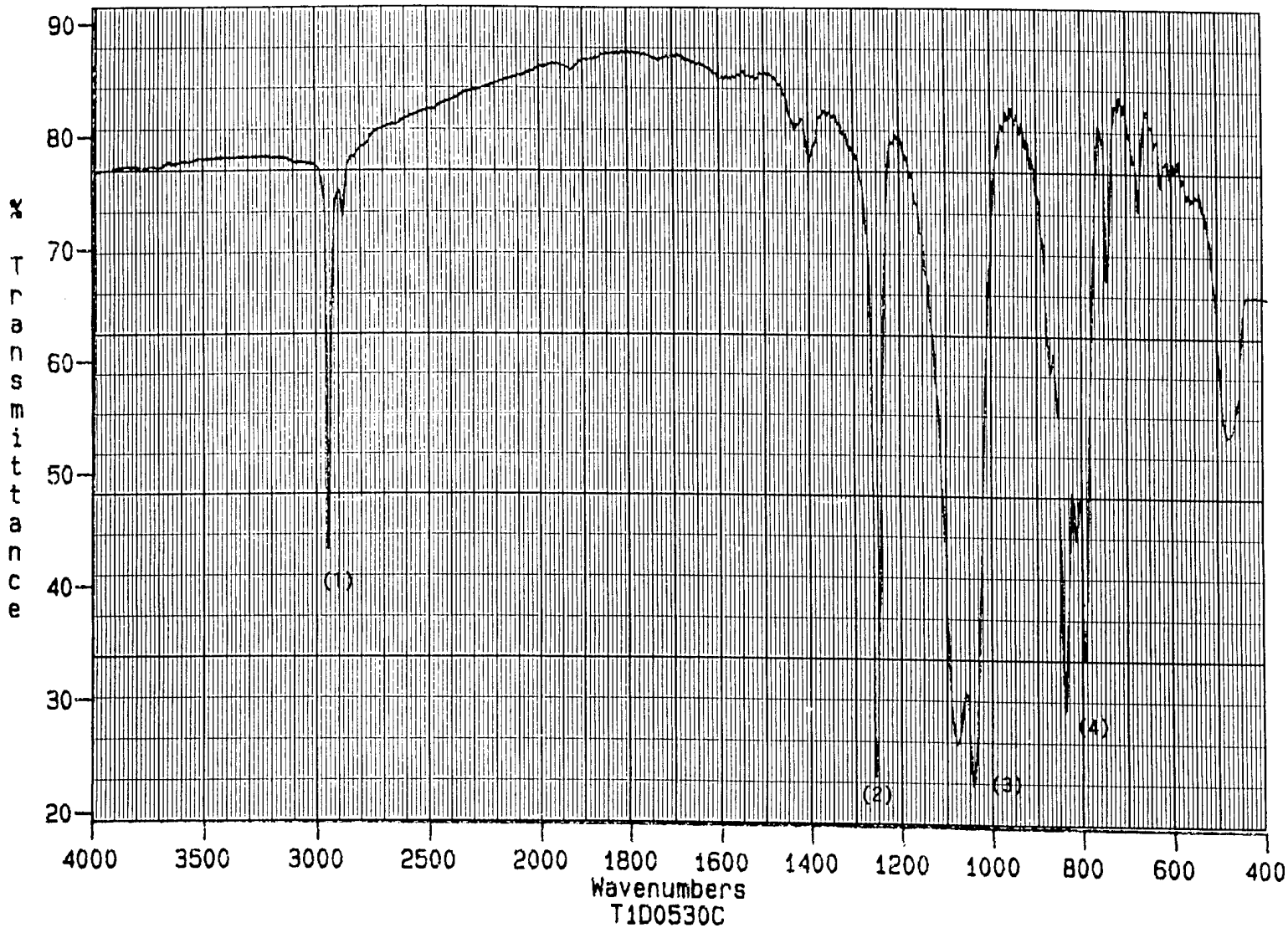


Figure 36. FT-IR Spectra of Unexposed Adhesive E

(1) Aromatic – C–H
(2) Aliphatic –C–H
(3) Aromatic –C–H (breathing)
(4) Aromatic Ether (-⬡-o-)
(5) Bi Substituted (-⬡-) Aromatic
(6) Carbonyl (–C=O
(7) –C–O–C– Aliphatic Ether
(8) Amido (–NH–CO–) stretch
(9) –CH– bend



RES= **Figure 37. FT-IR Spectra of the Extract of Adhesive H in 0S-10** SCANS=2000

(1) Aliphatic –CH
(2) Methyl Siloxane (–Si –CH_3)
(3) Silicon Ether (Si–O–Si)
(4) Silicon Carbon Bond Si–C and Methyl CH_3

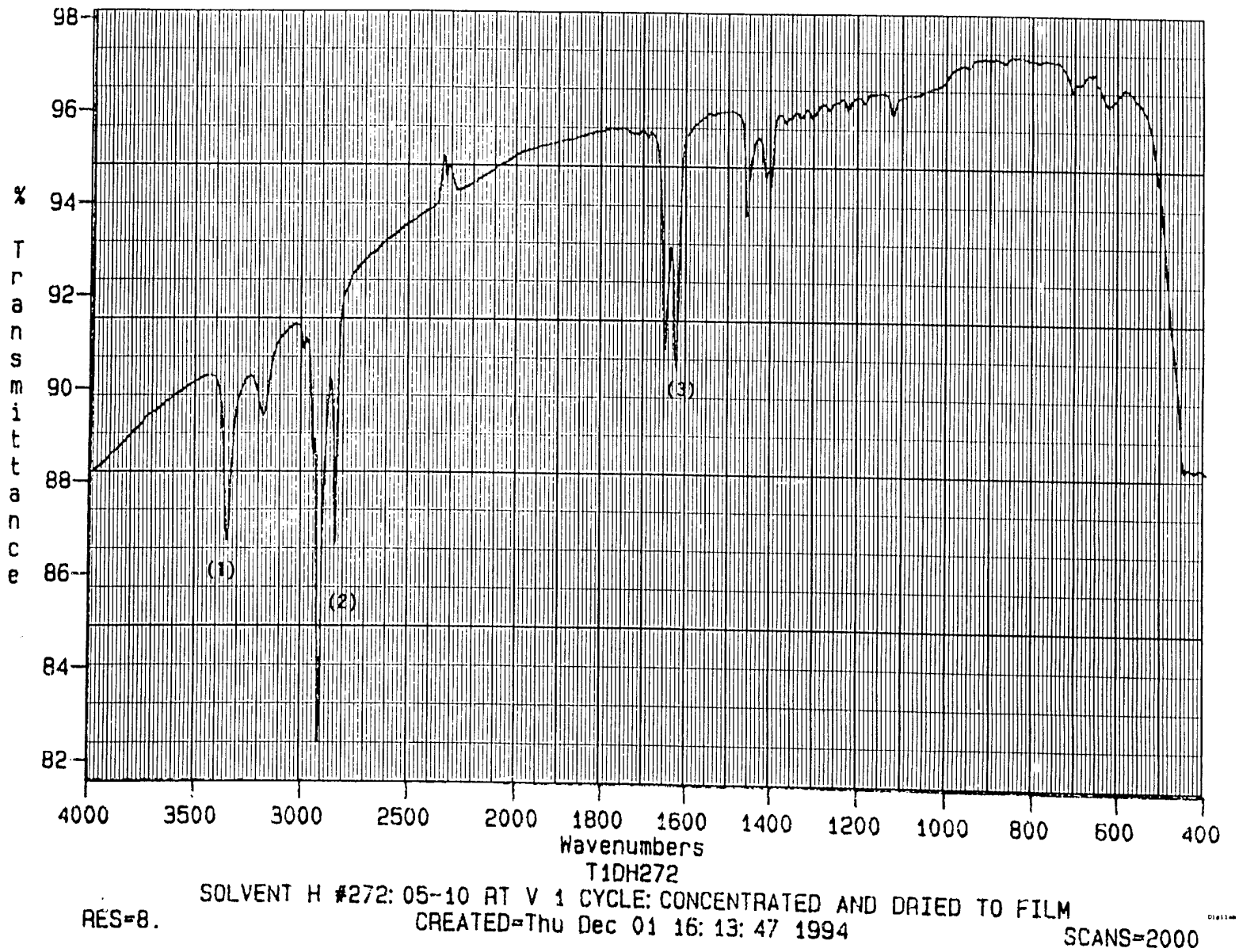


Figure 38. FT-IR Spectra of the Extract of Adhesive H Exposed to OS-10

(1) Amine –NH
(2) Aliphatic –CH
(3) Carboxylate or Carbon-Carbon Double Bond

characteristic of the amine curing agent. The polysulfide peak which appears around 600 is also clearly absent showing that the epoxy-polysulfide copolymer is not extracted.

Figure 39 presents the spectra of bulk Specimen H. Note the -C-S- (carbon-sulphur) C-S bond peaks at approximately 700 wave numbers, respectively. The spectra of Specimen H8654 exposed to OS-30 at 120°F is presented in Figure 40. This spectra shows no peak at 700 wave number which may indicate the loss of -C-S bond in epoxy-polysulfide copolymer. In other words, this adhesive may be undergoing degradation when exposed to the siloxane solvent. However, these observations are very rudimentary and require further work to come to any definite conclusion.

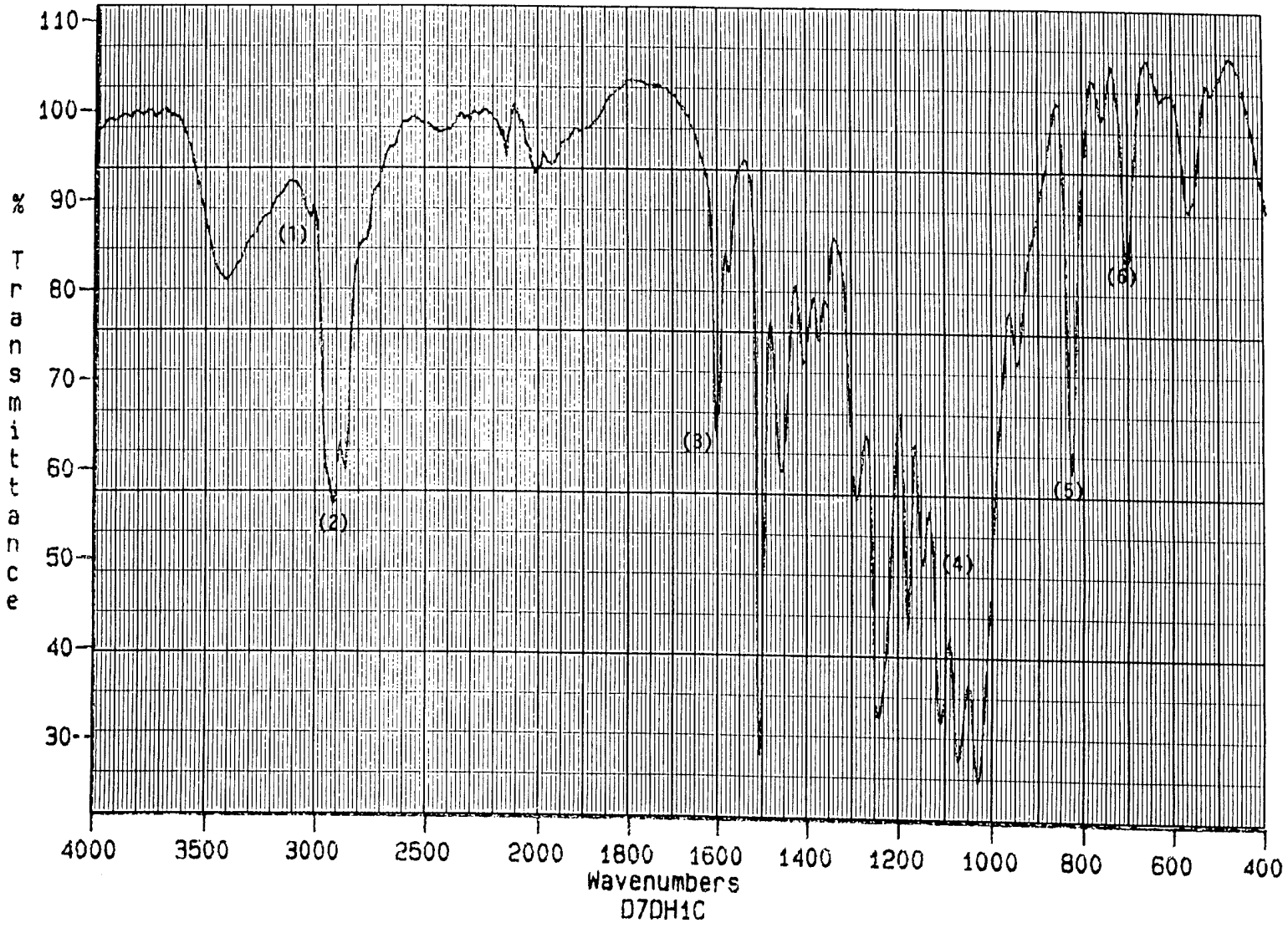
Figure 41 presents the spectra for a bulk specimen of Adhesive E subjected to OS-30 at 120°F for two cycles of sonication. It is very similar to Control E (Figure 36). The higher lap shear strength of the cleaned specimens compared to that of the unexposed specimen could not be attributed to any change in the molecular level.

In conclusion, it can be said that exposure of adhesive specimens to silicone solvents does not extract any polymer except in the case of Adhesive H. In the case of Adhesive H, some residual low molecular components leach into the solvent. In addition, there is some evidence of molecular degradation of Adhesive H, which could give low molecular weight products. The leaching of unreacted additives and low molecular weight degradation products probably leads to microhole formation on the specimen surface and the interface, thus lowering both hardness and lap shear strength.

5.0 SUMMARY AND CONCLUSIONS

The adhesive degradation potential of two cleaners has been examined for a range of epoxy adhesives differing both in chemical structure and performance. The compatibility of these cleaners with seven metallic substrates have also been examined during the course of this program.

The two siloxane cleaners, 0S-10 and 0S-30, appear to have little adhesive degradation potential on most adhesives currently used by AGMC for the repair of navigation



RES=8. Figure 39. FT-IR Spectra of Unexposed Adhesive H SCANS=2000

(1) Aromatic CH
(2) Aliphatic -CH
(3) Amido -CO-NH-
(4) Aromatic Ether
(5) Bi Substituted Aromatic
(6) Carbon-Sulphur -C-S-

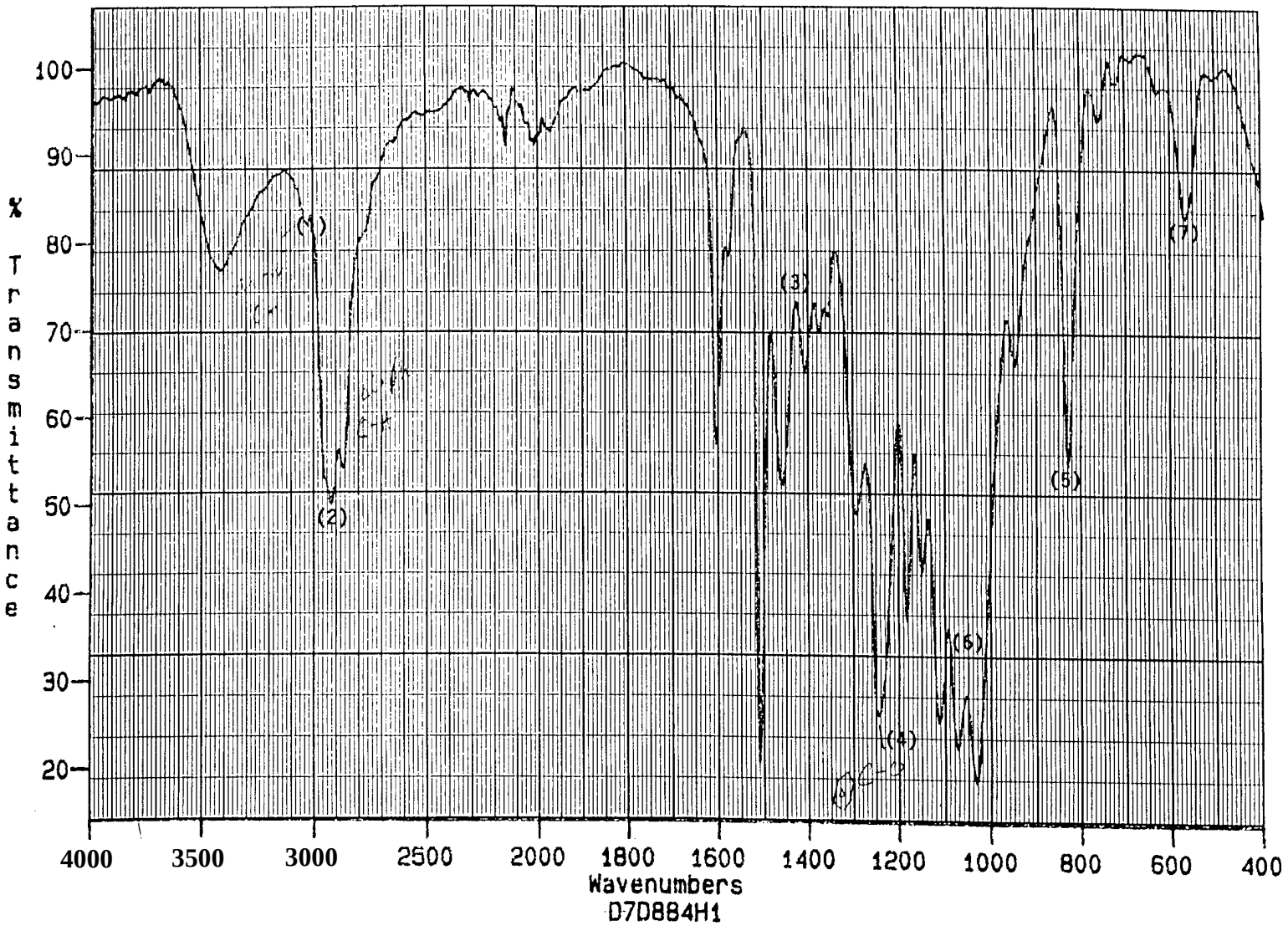


Figure 40. FT-IR Spectra of Adhesive H Exposed to OS-30 at 120°F, 2 Cycles Ultrasonication

(1) Aromatic Hydrocarbon
(2) Aliphatic Hydrocarbon
(3) Aromatic Breathing
(4) Aromatic Ether
(5) Bi Substituted Aromatic
(6) –Si–O–Si– (Siloxane)
(7) Aliphathc Ether

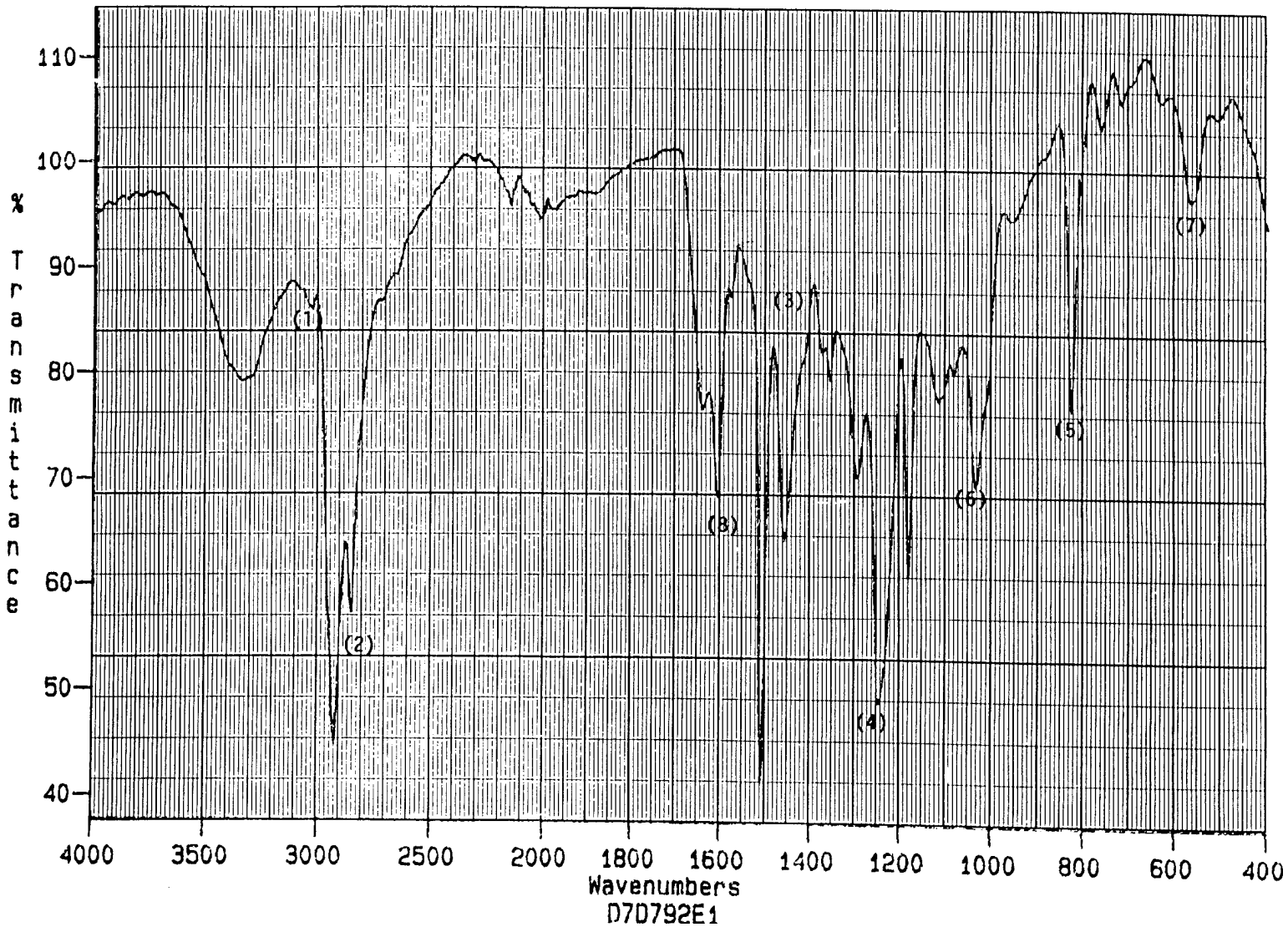


Figure 41. FT-IR Spectra of Adhesive E Exposed to OS-30 at 120°F

(1) Aromatic –C–H
(2) Aliphatic –C–H
(3) Aromatic –C–H (breathing)
(4) Aromatic Ether
(5) Bi Substituted Aromatic
(6) Carbonyl –C=O
(7) –C–O–C– Aliphatic Ether
(8) Amido –NH –CO–

and guidance systems. They are, however, to a very small extent under most cleaning conditions. Under the same conditions, TCA is absorbed to a larger extent than the OS-10 and OS-30. This is in agreement with the large difference between the lower solubility parameter (≈ 7 cal/cc$^{1/2}$) of the siloxane cleaners and those of the epoxy resins (≈ 10.6 cal/cc$^{1/2}$). The solubility parameter of trichloroethane (96 cal/cc$^{1/2}$) is closer to that of epoxy, which leads to greater solubility and absorption. However, Adhesive H has a lower solubility parameter and dissolves to a small extent in OS-10 and OS-30. This lowers the lap shear strength and hardness of Adhesive H, probably because the low molecular weight components on the surface and interracial layer are solubilized. There also is some evidence of degradation of this polymer by the breakage of the -C-S- bond, which may contribute to enhanced leaching. However, 1,1, 1-trichloroethane has a more deteriorating effect on this adhesive than the siloxane cleaners. Also, Adhesive is not currently used at AGMC and is less likely to be used in the future because of its very low glass transition temperature.

The siloxane cleaners are also compatible with the seven metals examined in this study. There is a very thin layer of silicone left on the anodized aluminum which may weaken the adhesion of the cleaned substrate to the epoxy adhesive. This requires further examination.

In summary, the results obtained in this program do not indicate any serious problem with the use of siloxane cleaners for metal cleaning and decreasing at AGMC.

6.0 REFERENCES

1. Statistics for Experimenters, "An Introduction to Design, Data Analysis, and Model Building", by G.E.P. Box, W. G. Hunter, and J. Stuart Hunter, published by John Wiley & Sons, 1978, pp. 165-207.

2. Analysis Performed Using a Software SPSS for Windows, Release 6.0 (June 17, 1993).

3. "Design and Analysis of Experiments, " by Roger G. Petersen, Oregon State University, Corvallis, Oregon, by Marcel Dekker, Inc. (1985), pp. 77, 84-85.

APPENDIX A

TEST PLAN

TEST PLAN

for

EXPERIMENTAL EVALUATION OF THE ADHESIVE DEGRADATION AND CORROSION POTENTIAL OF SILICONE FLUIDS

1.0 BACKGROUND, OBJECTIVE, AND SCOPE

The Aerospace Guidance and Metrology Center (AGMC) located at Newark Air Force Base (NAFB), Ohio, repairs inertial navigation and guidance equipment for the United States Air Force and other Department of Defense (DoD) components. The critical tolerance requirements of these devices require that extensive controlled cleaning processes be used during the repair process. Currently many of these processes use chlorofluorocarbons (CFC) and chlorinated hydrocarbons (CHC) to clean oil, grease and other contaminants from electronic components and equipment casings. However, these solvents with ozone depleting potential have been banned by the Montreal Protocol and the Clean Air Act of the Environmental Protection Agency. Driven by safety and environmental concerns, AGMC has been aggressively implementing new maintenance procedures and is replacing these environmentally unacceptable cleaning agents with more environmentally acceptable materials. Many of the new processes use deionized water and aqueous detergent solutions. Although some of these processes have worked very well, there are certain applications where aqueous processes lead to corrosion and adhesive degradation. In a recent study, Dow Coming engineers have shown that hexamethyl siloxane and its oligomers are very good cleaners for grease and cutting fluids and they are environmentally benign. Initial testing at AGMC indicates that siloxane cleaners can adequately clean and dry off the components which are adversely affected by aqueous cleaners. However, the impact of these new solvents on adhesive and sealant performance and their compatibility with various metals needs to be examined before AGMC can fully implement siloxane based cleaning procedures.

The objective of this study is to assess the degree of any adhesive degradation and metal incompatibility which may be associated with the use of siloxane cleaners in the precision cleaning processes of inertial guidance and navigation system equipments. The study will identify the basic material/process combinations which will or will not induce adhesive degradation and metal corrosion problems, allowing AGMC to select the appropriate metal/adhesive/siloxane process combinations in their precision cleaning processes. The scope of this project is to design and conduct a series' of experiments, evaluate the results, and to draw conclusions regarding the potential for adhesive degradation and metal corrosion that may result from replacing the solvent systems currently used with two of the siloxane fluids recommended by Dow Coming.

Battelle has developed a draft test plan to evaluate adhesive degradation and metal compatibility problems associated with siloxane cleaners. While doing this, Battelle has

taken into consideration the Test Plan and Test Matrices used in the earlier studies at Battelle on adhesive degradation and metal compatibility. However, unlike the earlier study, this study will examine some adhesives in addition to those currently used by AGMC. The emphasis will be to measure and understand the potential of siloxane cleaners to interact, degrade and extract the adhesive or parts of it during the cleaning process. In general, the cured adhesive and sealant samples will be exposed to silicone-based cleaning agents under application conditions similar to those used at AGMC. This will be followed by physical and analytical testing to evaluate adhesive degradation and corrosion. Instrumental analysis of selected samples will be performed by Battelle to understand the chemical nature and the mechanism of the degradation process. Battelle shall analyze and evaluate the results of these experiments and submit a written final report to AGMC describing the nature and extent of any resulting degradation. The metal compatibility study will be carried out by exposing selected metals to siloxane solvents following a well-designed test matrix and examining the weight loss and the corrosion effects such as pitting, cracking and discoloration. The test plans for adhesive degradation and metal compatibility are presented in two separate sections.

2.0 ADHESIVE DEGRADATION STUDY

The test plan for the assessment of adhesive degradation potential consists of the following parts: selection of test materials, protocols required to prepare and expose adhesive test specimens, a test matrix, a data analysis and evaluation plan, and an implementation plan. This is followed by results analysis, conclusions and recommendations. Battelle has devised a test matrix using statistical experimental design methodology in order to maximize the information generated while using the minimum number of experiments to control cost. Three replicates will be used for each test.

2.1 (a) Selection of Test Material

The test matrix will use two siloxane cleaners in conjunction with nine adhesives. These will include adhesives commonly used as structural adhesive, particularly those used in repairing inertial equipment at AGMC and epoxy adhesives of different chemical types. As mentioned earlier, the emphasis is to observe the interaction of siloxane cleaners with a variety of epoxy resins, curing agents and additives. Hence, epoxies containing a variety of chemical types such as aliphatic and aromatic diglycidyl ethers and rubber modified bisphenol diglycidyl ethers have been included in the program. Commonly used curing agents such as amines and polysulfides have also been included in the study. The two cleaners are hexamethyl disiloxane, 0S-10 and its oligomer 0S-30 with trichloroethane used as control for comparing the degradation potential of the new solvents. 1,1, 1-Trichloroethane (TCA) has been chosen, in preference over CFC 113, because it is more commonly used in the industry for metal cleaning. Earlier stud y on adhesive degradation potential of aqueous cleaners has shown little difference between the adhesive degradation potential of CFC- 113 and TCA. Battelle has selected nine adhesives covering a variety of epoxies. The details of the adhesive

composition are presented in Table A-1. The first six adhesives were selected from the series of adhesives currently used by AGMC and were a part of the twelve adhesives used in earlier investigation on adhesive degradation potential of aqueous cleaners. The last three were selected because they provide a variety in the chemical structure of epoxy backbone and additives such as flexibilizers and curing agents. Materials which are known to interact with siloxanes such as RTV silicone have not been included in the program.

2.2 Preparation of Adhesive Test Specimens

Two types of test specimens, namely lap shear specimens and bulk specimens will be used in the adhesive degradation study.

- The lap shear specimens will be assembled on aluminum coupons used in acceptance and certification testing (ASTM D 1002). Cleaning procedures as given in Mil-HDBK-691A, 1965 (p. 26) will be followed to prepare the specimens for adhesive coating.
- The coupons will be coated with the adhesive to a controlled thickness and will be overlapped to provide specimens for lap shear testing.
- Curing will be carried out following manufacturer's specifications.
- Bulk samples will be cast in specially designed molds in the test form (approximately 1/8" thickness) required for weight loss and hardness evaluation and will be cured using manufacturers' specifications.

2.3 Test Matrix

Both lap shear and bulk specimens will be exposed to two cleaning simulation procedures, three different solvents (OS-1O, 0S-30, and control), one or two temperatures and for two different times or number of cycles. Whereas OS- 10 will be tested at room temperature, OS-30 will be tested both at room temperature and 120 F. Cleaning will be carried out by immersion soaking for 1 hour or 16 hour periods, or by sonication for one or two cycles, each lasting for 5 minutes. Subsequently, the specimens will be examined by optical microscopy and evaluated for various properties including lap shear strength, "Shore" D hardness, weight change, and selectively other analytical procedures as needed to explain observed property changes. Additional unexposed specimens will be prepared and evaluated to provide a basis for comparison between this experimental effort and previous efforts, and to provide a performance baseline for previously unevaluated adhesives. With the above in mind, a balanced experimental design was constructed to provide adequate resolution during subsequent analysis of the results while controlling the total number of experiments.

Table A-1. Adhesive Test Candidates

Adhesive	Chemical Type	Supplier
FA8/BA5	Mixture of diglycidyl ether of bisphenol A and 2-2' bis(2,3 epoxy propoloxy) phenyl propyl bisphenol A cured with aminoethylamino ethyl imidazolidone	Bacon Industries, Inc.
LCA4/BA5	4,4 bismeth ylidine bisphenol polymer with chloromethyl oxirane cured with aminoethyl imidazolidone	Bacon Industries, Inc.
Ablestik 724/14C	Toluene diisocyanate based polyurethane	National Starch, Inc.
Epon 8281 Versamid 125	Bisphenol diglycidyl ether cured by polyamide	Miller-Stephenson Chemical Company
Eccobond 2216	Mixture of bisphenol "A" epoxy resin, alumina, and crystalline silica cured with tetraethylene-pentamine	3M, Inc.
FA1/BA4	Bisphenol A diglycidyl ether, bis(ethylene oxy) methane containing disulfide links, cured with tri(dimethylamino ethyl) phenol	Bacon Industries, Inc.
Araldite CY179/Araldite Hardener 907	Cycloaliphatic epoxy cured with hexahydrophthalic anhydride	Ciba Geigy
Masterbond EP72M3 or equivalent	Bisphenol epoxy cured with polysulfide	Masterbond, Inc.
Epoxy ER 2287 or equivalent	Flexibilized epoxy adhesive	TACC International Company

Specific factors for this experiment are as follows:

Solvents. Two experimental solvents OS- 10 and 0S-30, and a control solvent TCA; these will be designated S 1, S2, and C 1, respectively.

Cleaning Simulation. Two cleaning methods will be simulated: sonication (U), and soaking (S).

Cleaning Temperature. Separate specimens will be exposed to each of the three solvents at room temperature (approximately 75°F). In addition, specimens will be exposed to the OS-30 solvent at 120°F.

Cleaning Time. For soaking, times will be 1 or 16 hours; for sonication, one or two 5-minute cycles will be used.

Adhesives. Nine commercial adhesives designated Al through A9 will be evaluated.

Control. Unexposed specimens will be evaluated for subsequent analysis.

Each adhesive will be evaluated according to the experimental design matrix illustrated in Figure A-1 graphically and in Table A-2 as a data entry form. As may be seen in Figure A-1, there are 16 experimental design points used to introduce variation and one point included as a control. Three lap shear specimens and three bulk specimens will be prepared for each of the design points. This arrangement will produce 459 lap shear and 459 bulk specimens.

Specimens will be prepared and evaluated in random order in an effort to minimize the effect of any bias error which may occur during the experimental period.

2.4 Cleaning Protocols

The lap shear test specimens prepared in 2.2 will be exposed to cleaning agents based on the test matrix following an exposure protocols as follows. Exposure of the test samples shall consist of 5 minutes of sonication in the cleaning agent followed by drying of the samples with clean air until visually dry. Subsequently, the specimens will be oven dried for 1 hour at 155 ‘F at 30 mm Hg. We do not anticipate degradation of adhesive at this temperature. Figure A-2 presents a schematic of exposure cycle. Soaking for 1 hour or 16 hours will be carried out by hanging the specimens in the solvent in a closed container. Drying will be the same as for the sonicated samples. The contractor shall use bench top type sonication equipment currently available at Battelle. The type and power used should be close to

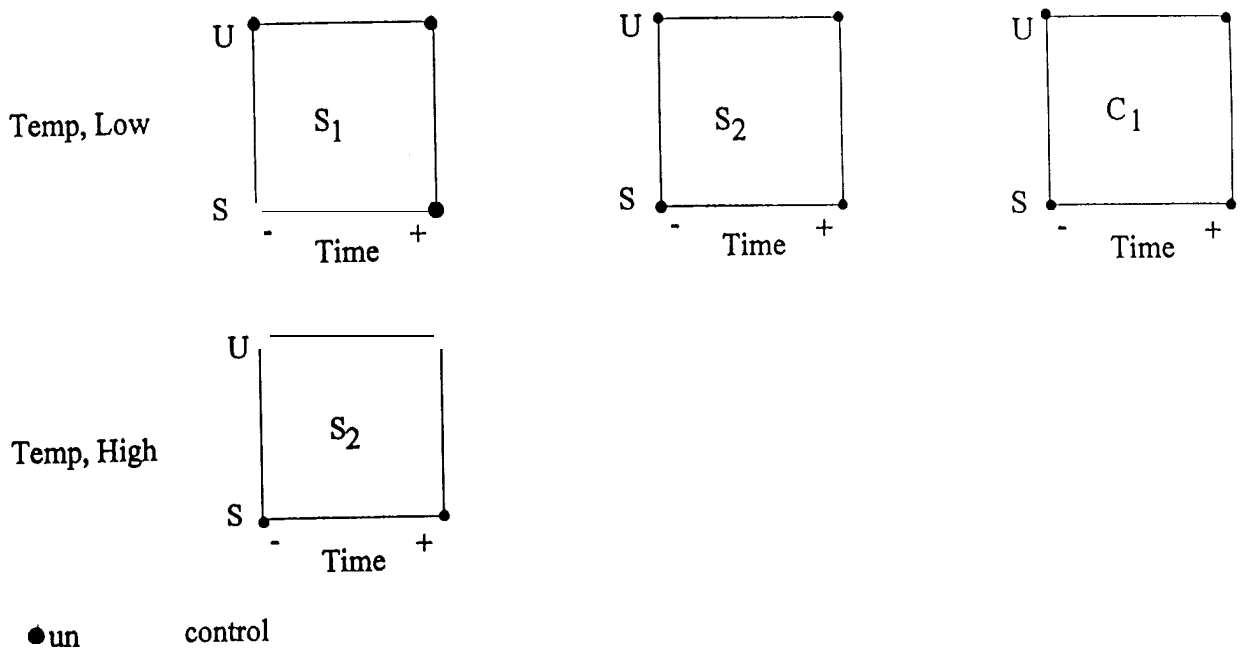


Figure A-1. Proposed Experimental Design

those used by AGMC. Exposure temperatures of room temperature or 120°F will be used in OS-30 study and only room temperature for OS-10 and TCA. A separate set of bulk samples will be prepared and exposed to the three solvents, following a similar test protocol for evaluation of changes in bulk properties.

Table A-2. Data Entry Form

Design ID	Adhe-sive	Tem-pera-ture	Solvent	Method	Time	Lap Shear	Shore D	Weight Change	DSC/ Tg*
1	Al	Tl	Sl	U	1				
2	Al	Tl	Sl	U	2				
3	Al	Tl	Sl	S	1				
4	Al	Tl	S1	S	16				
5	Al	Tl	S2	U	1				
6	Al	Tl	S2	U	2				
7	Al	Tl	S2	S	1				
8	Al	Tl	S2	S	16				
9	Al	Tl	Cl	U	1				
10	Al	Tl	Cl	U	2				
11	Al	Tl	Cl	S	1				
12	Al	Tl	Cl	S	16				
13	Al	T2	S2	U	1				
14	Al	T2	S2	U	2				
15	Al	T2	S2	S	1				
16	Al	T2	S2	S	16				
17	Al	Unexposed control							

* Tg will be measured for selected samples.

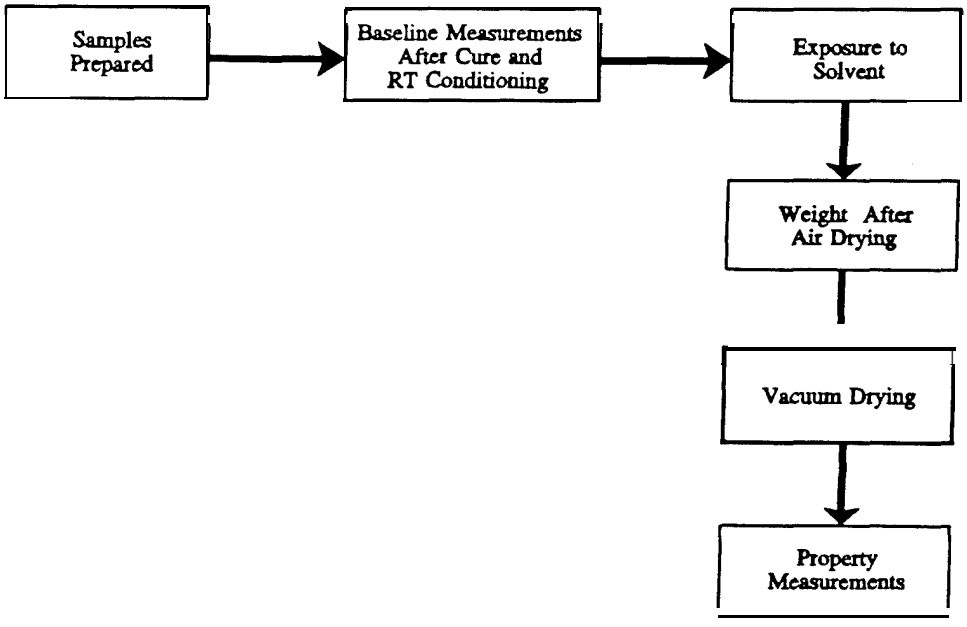


Figure A-2. Specimen Exposure Cycle

2.5 Evaluation of Adhesive Degradation Potential

The exposed samples will be evaluated after exposure for changes in both bulk and interracial properties. It is anticipated that the adhesives may absorb the solvents and may dissolve or swell depending on whether they are crosslinked or not. Absorption may plasticize the adhesive, thereby lowering its surface hardness and mechanical properties. Hence, the bulk samples will be evaluated for solvent absorption and shore hardness. The aluminum to aluminum lap shear specimens will be tested for their lap shear strength following ASTM D1OO2. The bulk samples will be examined by optical microscopy to observe visual degradation, if any. Selected samples, showing significant degradation, will be examined to reveal the type and mechanism of degradation. We anticipate two types of mechanism, physical and chemical. The physical mechanism may involve plasticization, thus lowering Tg, and environmental stress cracking (ESC). The chemical degradation may include extraction of the adhesive components and chemical interaction of the solvent with specific structural groups in the adhesive. Plasticization will be examined by differential scanning calorimetry (DSC), environmental stress cracking (ESC), by seaming electron microscopy (SEM), and loss or gain of inorganic additives by ESCA. The chemical degradation and interaction will be evaluated by FTIR and NMR analysis of the adhesives and the residual cleaning solution. Table A-3 lists response factors along with test procedures which will be used to measure each of these factors. whereas all adhesive specimens will be subjected to Tests 1 to 4, Tests 5 to 8 will be carried out for selected samples in order to explain the mechanism of degradation. For costing purposes, we have estimated approximately 80 DSC, 60 FTIR and 30 NMR, 20 ESCA and 20 SEM measurements.

Table A-3. Measured Responses and Analytical Procedures

	Measured Responses	Analytical Procedure
1.	Solvent absorption/adhesive extraction	Weighing
2.	Shore hardness	ASTM D2240
3.	Visual changes	Optical microscopy
4.	Lap shear	ASTM D1OO2
5.	Glass-transition temperature (Tg)	Differential scanning calorimetry
6.	Selective extraction	Weight loss and ESCA of bulk specimens NMR and FTIR of residual cleaner
7.	Chemical interaction	FTIR of bulk samples FTIR and NMR of residual cleaner
8.	Environmental stress cracking	Optical and scanning electron microscopy of bulk and lap shear samples

Plasticization takes place by the absorption of the cleaning liquid by the polymeric adhesive. The insertion of solvent molecules in the polymer network reduces the overall intermolecular force density which in turn reduces the glass transition temperature (Tg) and the softening point. The overall impact of plasticization on Tg will depend on the amount of solvent absorbed per unit volume of the adhesive and the cohesive energy density (CED) of the cleaner solvent. Since the volubility parameter (square root of CED) of the siloxanes are much lower than those for the adhesive, we do not anticipate substantial absorption of the solvent. However, small amount of absorbed liquid can affect Tg significantly. 3 to 5 percent absorption of the siloxane cleaner may lower the Tg appreciably. Hence, samples showing significant absorption of cleaners will be subjected to Tg measurement.

Built-in residual stress in the test specimen coupled with softening (lowering of compliance) gives rise to crazing which ultimately initiates cracks leading to failure. This is generally described as ESC. The presence of a microcracks can substantially lower the lap shear strength 20 to 25 percent or greater. The magnitude of the impact of ESC will, however, depend on the level of residual stress, plasticizing effect of the solvent and exposure time and temperature. One can detect ESC by looking for microcracks by optical microscopy of the bulk samples and by SEM of the fractured surface of the lap shear specimen.

Chemical degradation may take place in many ways. For example, the crosslink points may be attacked thus lowering compliance and increasing solvent absorption. Alternatively the additives such as fillers, catalyst residues and unreacted materials can be extracted creating flaws in the adhesive joint and lowering its strength. Substantial weight gain or loss (3 or 5 percent) and decrease in lap shear strength should provide necessary indication for chemical degradation. The change in the chemical structure of the adhesive and the loss of additives can be followed by FTIR and ESCA of the adhesives and by NMR examination of the extracted materials in the residual cleaner.

We, therefore, plan to carry out NMR, FTIR, ESCA, and glass transition temperature measurement for samples which show the most weight gain or loss and SEM examination for samples which show the most changes in compliance and lap shear strength. The objective of this study will be to explain the mechanism of adhesive degradation.

2.6 **Criteria of Compatibility**

In the earlier study with aqueous cleaners, the criteria of compatibility of the cleaning process were not quantitatively defined. The criteria of success were largely relative, compared to the control samples. However, the current study is more sharply defined, concentrating on fewer variables, thus permitting the evaluation of quantitative differences. Specifically, differences in mean property values that may be caused by the experimental factors defined as time, temperature, cleaning simulation, or solvents. The Battelle experimental plan is designed to detect mean property value differences of approximately one standard deviation at the 95 percent confidence level. For example, in the prior study on adhesive degradation unexposed lap shear data provided a mean of 2452 psi and a pooled standard deviation of 366 psi. If there is similar variation in the lap shear data generated during the current study, then a change in average lap shear of approximately 366 psi will be significant at the 95 percent confidence level. Significant differences in weight loss/gain, hardness, glass transition temperature and lap shear strength of adhesives exposed to solvents as compared to the control will be considered as indicators of incompatibility.

3.0 METAL COMPATIBILITY **STUDY**

This section describes the experimental approach and the statistical design recommended for the evaluation of the compatibility of siloxane cleaners with metallic substrates. As in Section 2.0, it will consist of solvent and metal selection, design of test matrix, sample preparation, exposure and evaluation of the results. The technical approach will be similar to the metal compatibility study* using aqueous cleaners that has recently been completed by

---

* Metals-Detergent/Cleaner Compatibility Study, Battelle Final Report to AGMC, Newark AFB, Newark, Ohio, January 1994.

Battelle. The major differences are that coupons will not be rinsed, and the sonication tests will use bench top ultrasonic tanks. The evaluation for metal degradation will be the same as in the previous study, namely weight change, pitting, cracking, and discoloration. The details of the plan are presented in the following paragraphs.

3.1 Selection of Test Materials

The three proposed cleaners are OS-10, OS-30, and TCA (as a control). 0S-10 and 0S-30 will be supplied by AGMC.

Seven representative metals and alloys will be used in this program for testing their compatibility with siloxane cleaners. They are shown in Table A-4.

Table A-4. List of Proposed Metals to be used for Compatibility Tests

Original AGMC Specification	Name of Equivalent Metal to be used
Aluminum 2017	Aluminum 2017
Anodized Aluminum 2017	Anodized Aluminum 2017
Beryllium per MC-1400	Beryllium per MC-1400
CDA260	Cartridge brass (70Cu-30Ni), CDA260
CDA182	Chromium copper alloy, CDA182
Tin-Lead, 63 percent tin	60Sn-40Pb solder
Chromium Steel 52100	C521OO

3.2 Metal Coupon Preparation

All the metal coupons, except beryllium, will be supplied and machined by the Metal Samples Corporation of Munford, Alabama. The nonberyllium coupons will have dimensions of 2-inches (50.4 mm) long, 0.75-inch (19.1 mm) wide. The thicknesses for all of the Metal Sample coupons will be approximately O. 10-inch (2.5 mm). All the flat coupons will have a 0.25-inch (6.4 mm) diameter hole machined and centered 0.25-inch from one end to facilitate hanging them in their test solutions. An identification number will be stamped in each coupon with a tungsten carbide die.

All the beryllium specimens will be supplied by AGMC. These specimens are halves of threaded, machined, circular parts that originally formed the PIGA main housing of a missile guidance system.

The surfaces of the flat coupons will be ground to a finish of 32 microinches rms, the value specified by the parts list supplied by AGMC. This finish will be achieved by using a double-disc grinding method on the coupons. The coupons to be used in this study were used in an earlier metals compatibility study. Any surface degradation that had occurred in these coupons will be ground out by Metals Samples Corporation. The expense of regrinding used coupons is less than half the cost of buying and machining new coupons.

New coupons of nonanodized aluminum 2017 will be anodized according to Mil-A-8625 (Type II) by Lancaster Electroplating. The anodized layer will be approximately 0.3 mil (0.0003 inch) thick and dyed gold in color.

The surface finish of the beryllium specimens will be somewhat smoother than the surfaces of the flat coupons and will be used in the as-received condition.

3.3 Cleaning Protocols

Precleaning

All the coupons will be handled with latex rubber gloves to avoid the possibility of contamination by finger prints. The flat coupons will be received individually wrapped with paper impregnated with a corrosion inhibitor to prevent any corrosion of the coupons during shipping. All the coupons will be precleaned in the same manner prior to subjecting them to either the soaking or sonication tests. Teflon racks will hold the coupons during their precleaning, cleaning, and drying procedures. The precleaning procedure will be as follows:

1. Sonicate coupons in a Branson ultrasonic cleaner* containing room temperature TCA for 1 minute.

2. Remove coupons from Branson tank and blow dry coupons with filtered compressed air**.

3. Place dried coupons in a vacuum oven (30 mm Hg) for 15 minutes at 155 “F.

---

* Branson Model 3200.

**Shop air will be filtered by a Wilerson Desiccant Dryer, Type C Coalescer filter and Type D absorption filter. This combination of filters are rated to reduce water below 0.03 ppm, oil below 0.003 ppm, and particle size below 0.01 micron in the compressed air.

4. After 15 minutes, turn off the oven heater and vacuum pump and fill the oven with the filtered compressed air. This will allow the coupons to cool within a reasonable time of several hours. The coupons will be removed from the oven when our temperature of the oven is about 80°F.

5. Remove the coupons from the vacuum oven and place them in a desiccator for at least 1 hour prior to initial weighing.

6. Remove the coupons from the desiccator and weigh with an analytical balance* to an accuracy of 0.01 mg.

The next several sections detail the cleaning test procedure for each coupon after their initial weighing.

The soak cleaning will consist of immersing a set of triplicate coupons in the cleaners according to the following procedures:

1. Fill two-liter pyrex beakers with 1.8 liters of the cleaner. Stir the cleaner using magnetic stirrers. Immerse the triplicate group of a test alloy completely in the solution. The coupons will be suspended in the solution by teflon racks which will prevent the coupons from coming in contact with each other or the sides of the beaker. All soaking tests will be conducted at room temperature.

2. Remove the coupons from the cleaners after the immersion period and blow dry with filtered, high purity compressed air.

3. Follow Steps 3 through 6 in the drying procedure of the precleaning section.

An initial soaking period of 16 hours will be used to ensure that any deleterious effects of the cleaners on the metals would become evident and to simulate the condition of a user inadvertently leaving components in the cleaner overnight. Metals not exhibiting degradation after 16 hours of soaking will certainly be compatible when exposed to the cleaner for shorter times. In the unlikely event where degradation does occur during 16 hours of exposure, new coupons of the metal will be tested for a period of 1 hour. If degradation occurs in 1 hour, then specimens will be exposed to solvent for 30 minutes and monitored for degradation. Half hour soak periods are usually the maximum time users would soak components in cleaners.

---

* Mettler Model AT250.

The sonication cleaning method will consist of exposing a set of triplicate coupons to their cleaners according to the following procedures:

1. A bench-top ultrasonic tank, either provided by AGMC or Battelle, will be filled with a cleaner. The holding tank will be adjusted to the temperature specified in the experimental design i.e., 120°F or left at room temperature.

2. A triplicate set of coupons of a test alloy will be completely immersed in the sonication cleaning tank for a period of 5 minutes. The suspended coupons will not be allowed to contact each other or the walls of the sonication tank.

3. After 5 minutes of sonication, the coupons will be dried with filtered compressed air.

4. Follow Steps 3 through 6 in the drying procedure of the precleaning section.

A time of 5 minutes will be used for all the sonication tests. The sonication time used in most cleaning procedures is anywhere from several seconds to several minutes. Five minutes was chosen to simulate the extreme end of sonication exposure periods.

A Branson table-top ultrasonic cleaner (or other ultrasonic cleaner supplied by AGMC) will have a nominal ultrasonic frequency of 40 Khz. Though the actual ultrasonic energy to reach an immersed coupon will not be measured in this study, it is expected that the power density in the tank will be between 10 and 40 W per gallon.

3.4 **Test Matrix**

A statistical grid of experiments has been designed for cleaning and evaluating the metal compatibility for each of the 7 metallic substrates (Table A-5). This design consists of 8 trials each, using triplicate coupons for each metal (duplicates in case of beryllium). A total of 56 trials will be needed to complete the tests assuming that no soak times of 1 hour are needed.

3.5 **Evaluation of Metal Compatibility**

Weight change and visual observation of pitting and discoloration will be used to evaluate metal compatibility with siloxane cleaners. The tested coupons will undergo a final weighing to a precision of 0.01 mg after they have gone through their drying procedure. Differences measured between the initial and final weights of each tested and control coupons will be used in assessing whether any corrosion has occurred in the tested coupons during their cleaning process. Optical microscopy and photography will be used to document any surface

Table A-5. Proposed Experimental De-sign for Each of the Seven Metals

Cleaner	Cleaning Method	Time	Temperature
TCA	u	5 minutes	room
	u	5 minutes	120°F
	s	16 hours	room
0S-10	u	5 minutes	room
	s	16 hours	room
II 0s-30	u	5 minutes	room
	u	5 minutes	120°F
	s	16 hours	room

degradation found on the tested coupons by monitoring pitting, cracks, or any surface discoloration that might have occurred during solvent exposure.

3.6 Compatibility Criteria

Samples of siloxane cleaners will be analyzed by the inductively coupled plasma (ICP) technique before and after they are used to clean the metal coupons. This technique will allow detection of very small concentrations of metals (5O ppb) in the cleaners that otherwise would be undetected by weight-loss measurements. This technique could also detect corrosion of metals in cases where the coupons gain weight after cleaning. Detection of the constituents of the coupons' metal in the cleaner solution after testing, when they were not present before testing, would indicate that corrosion did in fact occur.

Several types of measurements will be made on the metals to determine whether they are compatible with the various cleaners. Compatibility is here defined as a metal undergoing an acceptable level of degradation when exposed to a cleaner for a specified time at a specified temperature using a specified cleaning method. An "acceptable level" of degradation is not a absolute quantity but rather is based on various criteria, when taken as a whole, would allow a metal to be used in a cleaner without any deleterious changes to its surface properties. What is an acceptable level of degradation for one application or user may not be acceptable for another. Accordingly the acceptability or compatibility criteria must be defined for each application or user.

The compatibility criteria that will be used to evaluate the coupons will be the same as those used in the previous metal-cleaner study and is listed in Table A-6. The weight loss criterion

was based on the approximate value for a coupon that does not exhibit corrosion damage under 200X magnification, when that damage is uniformly distributed over its entire surface. The second criterion assumes that a uniform color change is a result of a surface film that was deposited on the coupons during the cleaning process. The third criterion is based on greatly improving the common practice of inspecting coupons at a magnification of 30X for evidence of corrosion damage and instead inspection them at 200X. The final criterion is based on the surface roughness of the coupons (32 microinch, rms) having natural defects on the same order as the maximum pit depths. If any of the coupons do not meet these criteria, then the metal will be judged incompatible with the cleaner under the conditions tested.

Table A-6. Compatibility Criteria for Metals Tested in Cleaners
Weight loss less than 0.01 percent
Metal surface should not undergo a uniform color change
General corrosion should not be visible at a magnification of 200X
Pit depths should be less than 0.0005 inch (0.5 roil)

4.0 REPORTING TEST DATA

The experimental results and their analysis will be documented in Battelle's laboratory notebooks, specifically identified for this program and be reported to AGMC in letter reports every month. At the end of the program, all experimental and nonexperimental data will be included in a comprehensive final report along with recommendations, identifying in particular those metal/cleaner/adhensive process combinations which do not degrade the adhesives and metal surface quality.

APPENDIX B

CATEGORICAL FACTORS AND RESPONSE FILE NAMES

ANALYSIS NOTES

Categorical Factors and Levels

Adhere 8 = 1 if Adhesive A
Adhere 8 = 2 if Adhesive B
Adhere 8 = 3 if Adhesive C
Adhere 8 = 4 if Adhesive D
Adhere 8 = 5 if Adhesive E
Adhere 8 = 6 if Adhesive F
Adhere 8 = 7 if Adhesive G
Adhere 8 = 8 if Adhesive H

Solvent 1 = O if unexposed control (CTRL)
Solvent 1 = 1 if TCA (Cl)
Solvent 1 = 2 if OS-1 O (S 1)
Solvent 1 = 3 if OS-30 (S2)

Clean 1 = O if unexposed control (CTRL)
Clean 1-1 if sonication (U)
Clean 1-2 if soaking (S)

Time 1 or 2 = O if unexposed control (CTRL)
Time 1 or 2 = 1 if 1 sonication cycle or 1 hour soaking
Time 1 or 2 = 2 if 2 sonication cycles or 16 hour soaking

Temp 1 = O if unexposed control (CTRL)
Temp 1 = 1 if room temperature (T1)
Temp 1 =2 if -120 F (T2)

Response Names and Descriptions

am	D
BREAKPSI	Lap shear tensile strength at the break
SHORED	Shore D hardness
WETPRCNT	Percent weight change measured after immersion prior to vacuum oven drying
DRYPRCNT	Percent weight change measured after immersion and vacuum oven drying

File Related to Lap Shear Data[a] Analysis[b]

Name	Description
SINGLE List	Cell means, all factor combinations
ANOVA2.LST	Analysis of variance, all factors
ANOVA5.LST	Analysis of variance, all factors minus Temp 1, plus 2-way interactions
ANOVA7.LST	Analysis of variance, by Clean 1, Time 2, Adhere 8 plus 2-way interaction
ANOVA8.LST	Analysis of variance; by Solvent 1, Clean 1 and Time 2 for each adhesive A through H
Oneway1.LST	Oneway analysis of variance, by Solvent 1 for each adhesive A through H
Oneway3..LST	Oneway analysis of variance, by Clean 1 for each adhesive A through H
Oneway4.LST	Oneway analysis of variance, by Time 2 for each adhesive A through H

(a) NAFBLSA.SAV SPSS readable data file
NAFBLSA.WK1 Spreadsheet readable data file

(b) Analysis performed using SPSS for Windows Release 6.0 (June 17, 1993)

File Related to Shore D Data[a] Analysis[b]

Name	Description
BANOVAA.LST	Analysis of variance, adhesive A
BANOVAB.LST	Analysis of variance, adhesive B
BANOVAC.LST	Analysis of variance, adhesive C
BANOVAD.LST	Analysis of variance, adhesive D
BANOVAE.LST	Analysis of variance, adhesive E
BANOVAF.LST	Analysis of variance, adhesive F
BANOVAG.LST	Analysis of variance, adhesive G
BANOVAH.LST	Analysis of variance, adhesive H
BONEA.LST	Oneway analysis of variance by solvent, adhesive A
BONEB.LST	Oneway analysis of variance by solvent, adhesive B
BONEC.LST	Oneway analysis of variance by solvent, adhesive C
BONED.LST	Oneway analysis of variance by solvent, adhesive D
BONEE.LST	Oneway analysis of variance by solvent, adhesive E
BONEF.LST	Oneway analysis of variance by solvent, adhesive F
BONEG.LST	Oneway analysis of variance by solvent, adhesive G
BONEH.LST	Oneway analysis of variance by solvent, adhesive H
BONEA1.LST	Oneway analysis of variance by clean method, adhesive A
BONEB1.LST	Oneway analysis of variance by time method, adhesive B
BONEC1.LST	Oneway analysis of variance by time method, adhesive C
BONEC2.LST	Oneway analysis of variance by clean method, adhesive C
BONEH1.LST	Oneway analysis of variance by clean method, adhesive H
BONEH3.LST	Oneway analysis of variance by temperature method, adhesive H
BANOVA5.LST	Analysis of variance, all factors and 0S-30 only
BANOVA6.LST	Analysis of variance by adhesive and solvents

(a) NAFBBD.SAV.WK1, SPSS and spreadsheet readable data files
(b) Analysis performed using SPSS for Windows Release 6.0 (June 17, 1993)

File Related to "Wet" Percent Weight Change Data[a] Analysis[b]

Name	Description
BANOVA1.LST	Analysis of variance, all factors
BANOVA2.LST	Analysis of variance, all factors on 0S-30 only
BANOVA3.LST	Analysis of variance, all factors and 2-way interaction
BWETONEA.LST	Oneway analysis of variance, by Solvent 1, adhesive A
BWETONEB.LST	Oneway analysis of variance, by Solvent 1, adhesive B
BWETONEC.LST	Oneway analysis of variance, by Solvent 1, adhesive C
BWETONED.LST	Oneway analysis of variance, by Solvent 1, adhesive D
BWETONEE.LST	Oneway analysis of variance, by Solvent 1, adhesive E
BWETONEF.LST	Oneway analysis of variance, by Solvent 1, adhesive F
BWETONEG.LST	Oneway analysis of variance, by Solvent 1, adhesive G
BWETONEH.LST	Oneway analysis of variance, by Solvent 1, adhesive H
BWETOWA1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive A
BWETOWB 1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive B
BWETOWC1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive C
BWETOWD1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive D)
BWETOWE1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive E
BWETOWF1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive F
BWETOWG1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive G
BWETOWH1.LST	Oneway analysis of variance, Temp 1, 0S-30 only, adhesive H
BWDOWCEA.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive A
BWDOWCEB.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive B
BWDOWCEC.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive C
BWDOWCED.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive D
BWDOWCEE.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive E
BWDOWCEF.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive F
BWDOWCEG.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive G
BWDOWCEH.LST	Oneway analysis of variance, Clean 1, 0S-30 only, adhesive H

Name	Description
BWDOWTEA.LST	Oneway analysis of variance, Time 1, adhesive A
BWDOWTEB.LST	Oneway analysis of variance, Time 1, adhesive B
BWDOWTEC.LST	Oneway analysis of variance, Time 1, adhesive C
BWDOWTED.LST	Oneway analysis of variance, Time 1, adhesive D
BWDOWTEE.LST	Oneway analysis of variance, Time 1, adhesive E
BWDOWTEF.LST	Oneway analysis of variance, Time 1, adhesive F
BWDOWTEG.LST	Oneway analysis of variance, Time 1, adhesive G, H

(a) NAFBBD.SAV.WK1, SPSS readable data files
NAFBBD.WK1 Spreadsheet readable data file

(b) Analysis performed using SPSS for Windows Release 6.0 (June 17, 1993)

File Related to "Dry" Percent Weight Change Data[a] Analysis[b]

Name	Description
BDRYANVA.LST	Analysis of variance, adhesive A
BDRYANVB.LST	Analysis of variance, adhesive B
BDRYANVC.LST	Analysis of variance, adhesive C
BDRYANVD.LST	Analysis of variance, adhesive D
BDRYANVE.LST	Analysis of variance, adhesive E
BDRYANVF.LST	Analysis of variance, adhesive F
BDRYANVG.LST	Analysis of variance, adhesive G
BDRYANVH.LST	Analysis of variance, adhesive H
BDRYONEB.LST	Oneway analysis of variance by Solvent 1, adhesive B
BDRYONEC.LST	Oneway analysis of variance by Solvent 1, adhesive C
BDRYONEE.LST	Oneway analysis of variance by Solvent 1, adhesive E
BDRYONEG.LST	Oneway analysis of variance by Solvent 1, adhesive G
BDRYONEH.LST	Oneway analysis of variance by Solvent 1, adhesive H
BWDOWTEA.LST	Oneway analysis of variance, Time 1, adhesive A
BWDOWTEB.LST	Oneway analysis of variance, Time 1, adhesive B
BWDOWTEC.LST	Oneway analysis of variance, Time 1, adhesive C
BWDOWTED.LST	Oneway analysis of variance, Time 1, adhesive D
BWDOWTEE.LST	Oneway analysis of variance, Time 1, adhesive E
BWDOWTEF.LST	Oneway analysis of variance, Time 1, adhesive F
BWDOWTEG.LST	Oneway analysis of variance, Time 1, adhesive G, H
BWDOWCEA.LST	Oneway analysis of variance, Clean 1, adhesive A
BWDOWCEB.LST	Oneway analysis of variance, Clean 1, adhesive B
BWDOWCEC.LST	Oneway analysis of variance, Clean 1, adhesive C
BWDOWCED.LST	Oneway analysis of variance, Clean 1, adhesive D
BWDOWCEE.LST	Oneway analysis of variance, Clean 1, adhesive E
BWDOWCEF.LST	Oneway analysis of variance, Clean 1, adhesive F
BWDOWCEG.LST	Oneway analysis of variance, Clean 1, adhesive G

Name	Description
BWDOWCEH.LST	Oneway analysis of variance, Clean 1, adhesive H
BANOVA2.LST	Analysis of variance, all factors in 0S-30 only
BANOVA4.LST	Analysis of variance, all factors

(a) NAFBBD.SAV SPSS readable data files
NAFBBD.WK1 Spreadsheet readable data file

(b) Analysis performed using SPSS for Windows Release 6.0 (June 17, 1993)

Notes and Files Related to Metals Data[a] Analysis[b]

Notes

Response Name and Description

WTPCTOOO Coupon percent weight change multiplied by 1000

Categorical Factors and Levels

METALI = 1 if Al 2017
METAL1 = 2 if anodized Al 2017
METAL 1 = 3 if beryllium
METAL 1 = 4 if brass
METAL 1 = 5 if chromium copper
METAL 1 = 6 if steel
METAL 1 = 7 if solder

METHOD1 = 1 if sonicate and 2 if soak
TEMP1 = 1 if lowand 2 if high
SOLVENTI = O if CFC 113
SOLVENT1 = 1 if TCA
SOLVENT1 = 2 if 0S-10
SOLVENT1 = 3 if OS-30

File Related to Metals Data[a] Analysis[b]

Name	Description
MANOVA1.LST	Analysis of variance, all factors
MANOVA2.LST	Analysis of variance, all factors
MIANOVA.LST	Analysis of variance, Al 2017
M2ANOVA.LST	Analysis of variance, anodized Al 2017
M3ANOVA.LST	Analysis of variance, beryllium
M4ANOVA.LST	Analysis of variance, brass
M5ANOVA.LST	Analysis of variance, chromium copper
M6ANOVA.LST	Analysis of variance, steel
M7ANOVA.LST	Analysis of variance, solder
U1ONE.LST	Oneway analysis of variance, by Solvent 1, Al 2017
M2ONE.LST	Oneway analysis of variance, by Solvent 1, anodized Al 2017
M30NE.LsT	Oneway analysis of variance, by Solvent 1, beryllium
M40NE.LsT	Oneway analysis of variance, by Solvent 1, brass
M50NE.LsT	Oneway analysis of variance, by Solvent 1, chromium copper
M60NE.LST	Oneway analysis of variance, by Solvent 1, steel
M70NE.LsT	Oneway analysis of variance, by Solvent 1, solder

(a) METAL.SAV SPSS readable data files
METAL.WK1 spreadsheet readable file

(b) Analysis performed using SPSS for Windows Release 6.0 (June 17, 1993)