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HIGH TEMPERATURE BONDING TECHNIQUES FOR SOLAR CELL ARRAY.

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An adhesive for solar cell attachment to spacecraft substrates has been sought with an unusually demanding combination of properties. These include 1) a basic resistance to decomposition at 600°C in vacuum, 2) retention of elastic properties at liquid nitrogen temperature, and 3) processibility as a bond line at conditions convenient to typical spacecraft fabrication. Of all the elastomeric materials available, the class of inorganic polymers termed poly (carboranesiloxanes) appears to be the only viable candidate. The ultra-

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high molecular species of this group have been found to be attractive, especially when blended or alloyed with low molecular weight versions. This promising assessment is based on high temperature thermo-vacuum stability studies, various characterization measurements, elasticity measurements at cryogenic temperatures, and 45° peel studies of thermally cycled bond lines with varying adherend combinations.

FOREWORD

This report was prepared by Hughes Aircraft Company Space and Communications Group, El Segundo, California, under Contract F33615-76-C-2032. The work was administered under the direction of J.E. Beam, POE-2, Air Force Aero Propulsion Laboratory. Contributors include M.F. Hawthorne of the University of California, Los Angeles; H. Hatwell, C. Hedaya, G. Dunks, D. Stewart, C. Peters, and G. Kwiatkowski of Union Carbide Corporation; and G. Lafontaine, F. Marsh, F. Sinsheimer, H. Levin, and G. Wolff of Hughes Aircraft Company. The report was submitted by the authors 15 November 1977.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

This report summarizes the work conducted under Air Force contract F33615-76-C-2032, High Temperature Bonding for Solar Cell Arrays, through the seventeenth contractual month of the program. This work has its origin in the fact that solar cell arrays are susceptible to damage when exposed to continuous wave laser irradiation. The primary failure mechanism is the delamination of cells from the substate. This failure is a direct result of the breakdown of the adhesive at the high temperatures induced by laser irradiation. The objective of this program is to develop techniques for bonding solar cell arrays so that they can withstand the high temperature extreme (600°C) anticipated for the laser exposure and yet remain sufficiently elastic at cryogenic temperatures (-190°C) to prevent thermomechanically-induced cell damage.

The work of the program has been divided into four phases as follows:

Phase I - Initial Investigation. Definition of adhesive requirements; literature search; investigation of state-of-the-art bonding techniques. Available inorganic and modified inorganic adhesives to be selected for experimental investigation.

Phase II - Coupon Tests. Coupon tests conducted to determine candidate adhesives' suitability for solar cell array fabrication.

Phase III - Solar Cell Array Technology Testing. Solar array segments representative of solar panel configurations tested.

Phase IV - Solar Array Segment Fabrication. Ten solar cell array segments fabricated for delivery to AFAPL/POE-2.

These phases were not scheduled to follow in strict chronological order because the investigation of adhesive characteristics and coupon testing must, given the nature of this development program, run almost concurrently.

Section II of this report details the work conducted on Phase I of the program effort. This activity was brought to completion in the twelfth contractual month of the program.

Section III describes the initiatory effort of Phase II, Coupon Tests. The essential activity of this phase has been delayed, and further experimental work suspended, because of the inavailability of the required adhesive materials.

SECTION II. INITIAL INVESTIGATION

The initial phase of the effort was designed to bound the requirements of the problem of high-temperature-stable adhesive bonding of solar cell arrays to spacecraft substrates. Both flexible and rigid substrates were considered. In this context, current developments in inorganic (backbone) polymer chemistry were investigated to identify candidate materials. Promising base materials were subjected to limited chemical modification and subsequent adhesive formulation experimentation. Selected formulations provided the basis for the coupon/adhesive evaluation test phase (Phase II). With the resumption and completion of the Phase II effort (see Section 6), the most promising adhesive formulations resulting from the coupon tests would be used in the solar cell array technology testing phase (Phase III), the final test phase of this effort.

II. 1 ADHESIVE REQUIREMENTS

The problem was considered a high temperature adhesive bonding one, not to be confused with metallic joining or mechanical attachment. In reality, it is a high temperature transient/low temperature soak problem, and therein lies the technology development task. The low temperature excursion requires either a low glass transition temperature T_g, or thermal expansion properties matching the cell/substrate, or both. Materials that do have low temperature capability typically cannot meet the high temperature requirements. In general, even advanced materials have a limited low/high temperature capability range, and efforts to extend one end of the range invariably require a tradeoff of properties at the other end. The intent here was to meet high temperature adhesion/outgassing requirements of the bond line and to accommodate all others. A compilation of these requirements for adhesive bonding of solar cell arrays to spacecraft substrates was made and is given in Table 1.

II. 2 LITERATURE SEARCH

Materials that are stable at 600°C and remain elastomeric at cryogenic temperatures were the object of this search. Very high molecular weight (M_w 10^6) inorganic polymers were known to provide high temperature stability; linear polymers provided elastomeric properties. The quest for linear, high molecular weight, inorganic polymers ruled out the soluble

TABLE 1. REQUIREMENTS FOR BONDING SOLAR CELLS AND SUBSTRATES

Parameter	Substrate	
	Flexible	Rigid
ADHESIVE FORMULATION		
Select high temperature base stock	Yes	Yes
Select curing system for minimum outgassing at upper use temperature	Yes	Yes
Select filler (type, size, shape etc.) for improved high temperature stability/thermal conductivity and reduced thermal expansion	Yes	Yes
Select pigment to improve α_S of substrate	Yes	–
APPLICATION OF FORMULATED ADHESIVE (UNCURED)		
Acceptable pot life	Yes	Yes
Easy application (liquid, paste, or dry film, with or without glass scrim cloth support)	Yes	Yes
Minimum weep of bond line into porous substrate	Yes	–
Rheological behavior permits control of bond line thickness	Yes	Yes
Curable at modest temperature and pressure ($\leq$15 psig)	Yes	Yes
Minimum curing shrinkage of bond line	Yes	Yes
FINAL PROPERTIES (CURED)		
Acceptable adhesion and outgassing during thermal transient to 600°C	Yes	Yes
Acceptable adhesion and elasticity during low temperature excursion to -190°C	Yes	Yes
Acceptable cell/substrate/bus adhesion (various metal, dielectric surfaces)	Yes	Yes
Not corrosive to cell/substrate/bus surfaces (i.e., introduces no electrochemical damage effects)	Yes	Yes
Hydrolytically stable (so as to minimize depolymerization)	Yes	Yes
Minimum hygroscopicity (so as to minimize bond line distortion during high temperature transient)	Yes	Yes
Introduces acceptable decrease in substrate flexibility	Yes	–
Retains flexibility after space particulate and/or nuclear irradiation (i.e., no major increase in shear modulus)	Yes	Yes
Resistant to chemical reversion (depolymerization) via thermal (to 600°C) or X-ray mechanism (nuclear)	Yes	Yes
Low space outgassing	Yes	Yes
Vacuum UV-stable (via backside irradiation)	Yes	–

silicate and phosphate systems. The nonreactive types in these latter systems were also known to suffer hydrolytic instability, introducing a problem in ground handling where such adhesives might be used.

State of the art developments in inorganic backbone, linear, high molecular weight polymers directed attention to the following polymer categories:

- Poly (carboranesiloxane) elastomers: Silicon-oxygen-carbonium ion backbone
- Poly (phosphazene) elastomers: Phosphorous-nitrogen backbone
- Poly (thiazyl) elastomers: Sulfur-nitrogen backbone

The chemistry of the first two categories was deemed sufficiently advanced to permit adhesive applications within the limited scope of this program. The search was accordingly directed at these categories, and the limited literature was supplemented by personal consultation with the leaders in this specialized field of inorganic polymer technology. Hughes contacted the companies and Government laboratories carrying on the basic research and development on those polymers of interest. In addition, Dr. M.F. Hawthorne (Professor of Chemistry, UCLA, and an international authority in inorganic chemistry) was enlisted as a part-time consultant to assist the inorganic polymer studies.

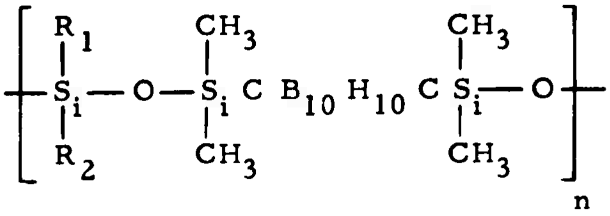
II.2.1 Poly D_2-m-Carboranesiloxanes)

In the early 1960's, it was discovered[1-4] that the introduction of the carborane moiety into the polysiloxane backbone (chain) greatly improves the thermal stability of the siloxane polymer. Important parameters affecting thermal stability have subsequently been identified as follows:

- Type of boron-carbon hydride cage structure ($-CB_xH_xC-$)
- Mole ratio of siloxy groups ($-Si\,R_1\,R_2-0-$) to $-CB_xH_xC-$ cage structure
- R_1 and R_2 constituency (i.e., methyl, phenyl, etc.)
- Molecular weight

Of the various HCB_xH_xCH cages discovered, the m-carborane structure ($HCB_{10}H_{10}CH$), designated as 1, 7-dicarba-closo-dodecaborane, has proven the most attractive. This is an icosohedral configuration. When inserted into the polysiloxane backbone, the 1, 7-dicarba-closo-dodecaborane-1, 7-diyl groups apparently stabilize S_i-O and S_i-C bonds as a result of the great electron withdrawing power of these $-CB_{10}H_{10}C-$ groups.

During the evaluation of these polymers over the past 10 years, those with a mole ratio = siloxy/m-carborane = 2 in the repeating unit seem to offer the best combination of physical properties and thermal stability. These are designated the "D_2-m-carborane-siloxane polymers" in the more recent Union Carbide group's work[5-8] and the 10-S_iB-2 polymers in Gillham, et al,[9-12] studies of the earlier Olin Chemicals polymers. The repeating unit is as follows:



$$\left[-\underset{R_2}{\overset{R_1}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\ C\ B_{10}H_{10}\ C\ \underset{CH_3}{\overset{CH_3}{Si}}-O- \right]_n$$

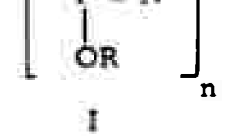
Sidechain siloxy constituents have been examined ranging from the all-methyl ($R_1 = R_2$ = methyl), methylphenyl, to the all-phenyl ($R_1 = R_2$ = phenyl). The preferred mole combination in Union Carbide work is as follows:

$$-[\text{all-methyl}]_{66}-[\text{methylphenyl}]_{33}-[\text{methylvinyl}]_{1}-$$

Synthetic procedures used in the earlier Olin work[1, 2] yielded network polymers of limited molecular weight, i.e., $\overline{M}_w < 50,000$. In contrast, Union Carbide has produced experimental lots of linear polymers with $\overline{M}_w \geq 10^7$. The screening evaluations in the reported Phase I and Phase II efforts have been based primarily on such ultra-high molecular weight UCARSIL specimens from Union Carbide. Unformulated gum stocks without vinyl constituency have been used primarily.

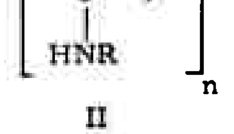
II. 2. 2 Polyphosphazenes (Phosphonitrilic Polymers)

Linear (also termed open-chain) polyphosphazene polymers are of interest to this program. These consist of phosphorous-nitrogen repeating units, each containing phosphorous substituents. It was known that the halogen substituted polymer chain, while elastomeric in properties, was hydrolytically unstable. Dr. H.R. Allcock[13-16] and colleagues are credited with discovering synthesis methods for producing polymer chains of enhanced hydrolytic stability associated with the following phosphorous substituents:



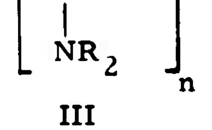
$$\left[-\underset{OR}{\overset{OR}{P}}=N- \right]_n$$

I ;



$$\left[-\underset{HNR}{\overset{HNR}{P}}=N- \right]_n$$

II ;



$$\left[-\underset{NR_2}{\overset{NR_2}{P}}=N- \right]_n$$

III

Considerable work has since been carried out with all three types of the poly(organo-phosphazenes) shown above. The letter R designates alkyl or aryl groups (in themselves often halogen- or alkyl-substituted). Selected members of type I have shown attractive combinations of low glass transition (T_G; a measure of elasticity), good thermal stability (350-400°C), and good hydrolytic stability. Such type I polymers have included poly(alkoxyphosphazenes) and poly(aryloxyphosphazenes), prepared as either homopolymers, copolymers, or mixed copolymers.

Excellent reviews of the preparation and properties of these poly(organo-phosphazenes) are given by Allcock[17, 18] and by Singler, et al.[19] Thermal and thermochemical behavior are reported by Connely and Gillham[20] and Singler, et al.[21] Molecular weight distribution measurements for poly(aryloxyphosphazenes) are reported by Hagnauer and LaLiberte.[22] Polymer syntheses are reported by Singler, et al[21] and Reynard, et al.[23]

II. 2. 3 Conclusions

Careful analysis of the published data, together with preliminary thermal-vacuum screening tests, lead to the conclusion that the poly(organo-phosphazenes) cannot survive transient heating to 600°C in vacuum. Of the categories of low-temperature-flexible, inorganic polymers for which the chemistry is in-place at this time, the only viable candidate as an adhesive polymer for this application appears to be the poly(carboranesiloxane).

II. 3 DEVELOPMENT AND SELECTION OF ADHESIVES AND ADHESIVE FORMULATIONS

Adhesive development/candidate formulation constituted the central effort of this program. Pertinent basic materials were few in number. Thus, within the scope of an extensive prescribed evaluation effort, polymer modification/characterization and adhesive formulation efforts had to be kept to a modest scale. Sufficient materials effort was attempted, however, to ensure the success of the program. The adhesive development program was pursued in the following sequence:

- Selection of high temperature stable candidate materials (see section II. 2. 3)
- Materials formulation and exposure to high temperature stability (600°C) screening in vacuum
- Examination of viscoelastic properties at cryogenic temperatures of candidate formulations that survived ten high temperature cycles
- Examination of processibility as an adhesive of formulations that survived high and low temperature prescreening.

The procedures used to pursue the above tasks and the results obtained therefrom are described in the following paragraphs.

II. 3. 1 Thermal Stability

II. 3. 1. 1 Specimen Preparation

Early tests demonstrated the sensitivity of the poly(carborane-siloxanes) to thermally-induced cross-linking in the 500 to 600°C range, resulting in embrittlement of the adhesive film and loss of adhesive bond to the adherend. Since cross-linking appeared to be the primary thermal degradation mechanism in this temperature range of interest, it was decided to minimize all causative factors. To the extent possible, the following species were eliminated or minimized:

- Peroxide catalysts (cross-link promoters)
- Typical gum stock additives such as Al_2O_3 and silica (including the hydrophobic variety)
- Acidic contaminants
- Ambient and adsorbed moisture
- Vinyl or other unsaturated constituency in the polymer

In effect, since excessive thermal cross-linking represents the prime hazard, it was decided to use this linear polymer in its thermoplastic (uncured) state at the highest purity obtainable.

Film material suitable for adhesive bond lines was prepared from the polymer (typically termed gum stock) by solvent casting. The gum stock was cut into very small pieces and dissolved in spectral grade methylene chloride contained in a Teflon beaker. The mixture was then carefully stirred for 6 to 12 hours to ensure total dissolution. The resulting solution was cast into a flat petri dish lined with 1 mil Teflon film. After overnight drying, the deposited film (1 to 5 mils thick) was peeled away from the Teflon and stored in a dessicator. The entire procedure was performed in a laminar flow bench, with precautions taken to ensure cleanliness in the equipment.

Polymer film specimens were next cut in strips and sandwiched between two 0.5 in. x 4 in. x 0.010 in. tantalum foil strips. Inserted within this simulated bond line, 5 to 10 mils thick, was a fine (0.005 in.) iron/constantan thermocouple. This sandwich (Ta/film/thermocouple/film/Ta) was lightly wired together with fine constantan wire. Prior to assembly, the outer faces of the Ta strips were coated (1 to 2 mils thick) with graphite, using a graphite in water suspension.

II. 3. 1. 2 Thermal Cycling Screening Test

Using the sandwich configuration described above, the specimen was suspended vertically within a quartz cylindrical chamber (see Figure 1) from thermocouple feedthroughs (not shown). This chamber is attached (through a liquid nitrogen trap) to the manifold of a mercury-diffusion-pumped vacuum train. Just above the heated zone, the chamber is seen to contain a limbic (extended surface section) designed to promote condensation of room-temperature-condensable outgassing species.

Because of the uncertainty of the effect of residual casting solvent, adsorbed gases (e.g., H_2O, O_2, CO_2) etc., on cross-linking at high temperature, the specimen was subjected to vacuum outgassing prior to exposure to high temperature cycling. Prior to being mounted in the vacuum chamber, the specimen was baked in a vacuum oven ($\ll 100$ μm pressure) for 4 to 16 hours at 70 to 90°C. It was immediately transferred to the quartz vacuum chamber where it and the chamber walls were outgassed for 40 to 75 hours at 150 to 210°C and $\leq 10^{-5}$ torr. Specimen heating in the quartz chamber was accomplished by an external electric heating mantle. After the vacuum bakeout, this mantle was removed, and the specimen was allowed to cool to room temperature prior to thermal cycling.

Rapid thermo-vacuum cycling is accomplished by the two banks of high intensity, quartz-iodide (tungsten filament) lamps shown arranged for normal illumination of the sandwich faces in Figure 1. Typical thermal response of the I/C thermocouple embedded in polymer film is shown in Figure 2. Relative to the temperature at the polymer/metal interface which is of primary interest, these peak recorded temperatures are believed lower by an order of 10-20°C and are thus considered conservative values. Subsequent to each temperature peak, the specimen was allowed to cool to <200°C before recycling to high temperature. Rise time to the peak temperature (≈600°C) is seen to be of the order ≤10 sec., yielding an average heating rate of ~50°C/sec.

Ten thousand cycles to ~600°C were performed without interruption, as shown in Figure 2. Because of the severity of this excursion, no dwell time at peak temperature was used (or thought required) to assist the screening. After cycling and removal from vacuum, successful films were found to be converted to an adhesive bond line, and lap shear measurements could be made.

The requirement of an elastomeric material able to survive rapid cycling to 600°C (60°C below the melting point of aluminum) was of course the key requirement and proved extremely difficult to meet. It appears now that the poly(carboranesiloxane) polymer system can meet this thermal threat. Thermal stability studies with this system employed Union Carbide Corp. UCARSIL polymers. Because these were experimental materials, available only in very limited quantity (1-2 g), material variations, contaminants, and incomplete molecular characterization were factors that had

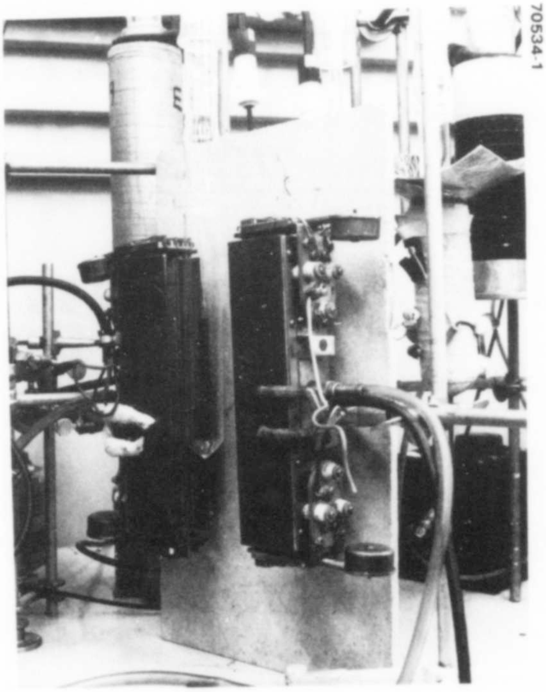


FIGURE 1. HIGH TEMPERATURE THERMO-VACUUM CYCLING ASSEMBLY (PHOTO FJM101)

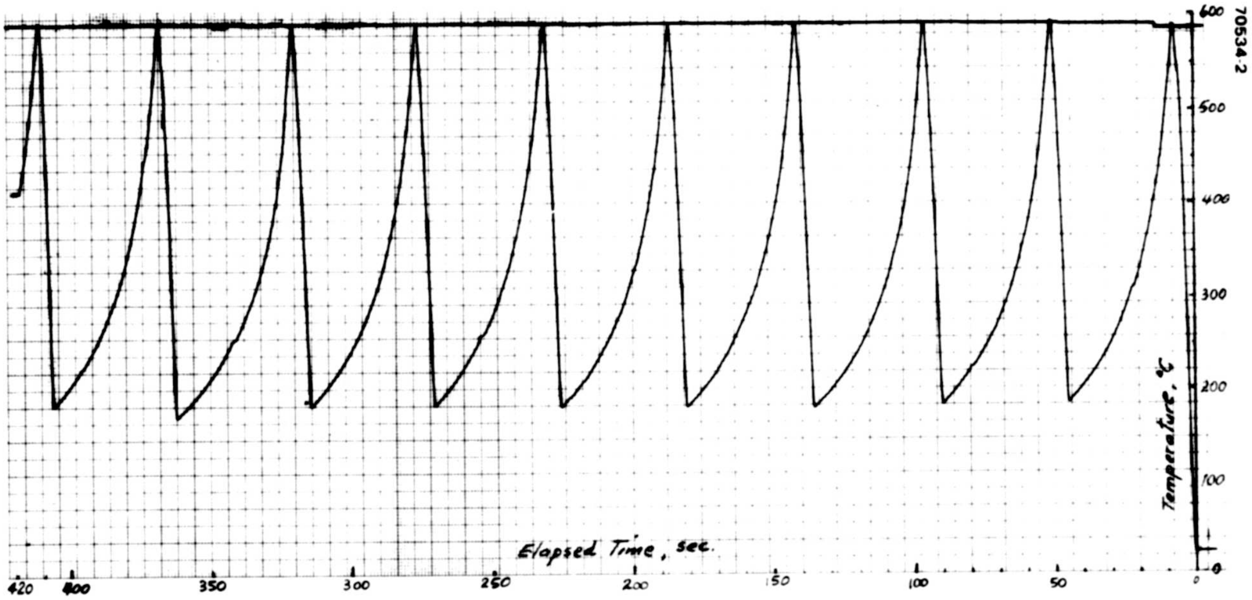


FIGURE 2. TYPICAL THERMAL CYCLING EXPOSURE IN VACUUM ($\sim 1 \times 10^{-5}$ TORR) FOR CARBORANE SILOXANE POLYMER (AND BLENDS) ADHESIVE BOND LINES BETWEEN TANTALUM (10 MIL) ADHERENDS

TABLE 2. EFFECT OF POLYMER TYPE, BLEND COMPOSITION, AND PEAK EXPOSURE TEMPERATURE ON THERMAL STABILITY OF CARBORANE SILOXANE POLYMER BLENDS

Specimen No.[a]	Polymer Blend Composition,[a] nominal % by weight						Acceptable High Temperature Stability at T_{max}	
	Ultra-Low Molecular Weight $\overline{M}_w \approx 5 \times 10^4$ (-104-2)[b]	Low Molecular Weight $\overline{M}_w \approx 1.4 \times 10^5$ (-111)[b]	High Molecular Weight $\overline{M}_w \approx 4 \times 10^6$ (-110)[b]	Ultra-High Molecular Weight $\overline{M}_w \approx 10^7$ (-80)[b]	Ultra-High Molecular Weight $\overline{M}_w \approx 10^7$ (-117)[b]	Ultra-High Molecular Weight $\overline{M}_w > 10^7$ (-98)[b]	Measured T_{max}, °C	Acceptable[c]
V6006	25.	—	—	75.	—	—	596	Yes
V6007	27.	—	—	73.	—	—	598	Yes
V6012	25.	—	—	—	—	75.	602	Yes
V6015	25.	—	—	—	—	75.	598	Yes
V6018	50.	—	—	—	—	50.	591	Yes
V6018A	50.	—	—	—	50.	—	600	Yes
V6019	75.	—	—	—	—	25.	595	Yes
V6020	50.	—	50.	—	—	—	600	No
V6021	75.	—	25.	—	—	—	590	Yes
V6022	25.	25.	—	—	50.	—	600	No
V6022A	25.	25.	—	—	50.	—	590	Yes
V6023	18.	32.	—	—	50.	—	595	Yes
V6024	—	49.	—	—	51.	—	602	No
V6024A	—	50.	—	—	50.		600	Yes
V6025	—	26.	—	—	74.	—	598	No
V6026	—	37.	—	—	63.	—	595	No
TPC-6	—	—	—	—	100.	—	591	No

NOTES:

a: Films of polymer blends (UCARSIL carborane siloxanes from Union Carbide Corporation) cast from methylene chloride solution.

b: UCARSIL (Union Carbide Corporation) designations, e.g. 10615-80, 10615-117, etc.

c: Retention of shear modulus less than an order of 20,000 psi (1.4×10^9 dyne/cm^2) after 10 thermal excursions to 600°C in vacuum ($\leq 10^{-5}$ torr), with no dwell at maximum temperature. Pre-thermo-vacuum high temperature cycling consisted of 1) 4-16 hr vacuum-oven outgassing at 70-90°C and ≤100 μm, followed by 2) 40-75 hr outgassing in a glass vacuum train ($\leq 10^{-5}$ torr) at 150-210°C. This pretreatment is designed to minimize residual casting solvent.

to be accepted. As a result, certain unexplained thermal stability behavior was encountered. Nevertheless, the pertinent stability data assembled in Table 2 appears credible in verifying requisite thermal stability. The most attractive thermoplastic polymer blends fall in the range 25 to 50% wt. ultra-low molecular weight combined with 75 to 50% wt. ultra-high molecular weight. Tradeoffs with intermediate molecular weight polymers designed to enhance adhesive processibility (i.e., viscous flow) seem neither warranted nor attractive.

Similarly, beneficial effects of additives (or coproducts such as the "substituted urea") could not be demonstrated, despite earlier indications of benefits. On the contrary, "urea" contents should be suppressed. In this regard, Attachment I (see Appendix), describing a UV absorption technique for estimating "substituted urea" contents, was sent to Union Carbide to assist in monitoring this coproduct in the UCARSIL polymers. Note that this coproduct, trivially termed "substituted urea" here, is more correctly termed N-phenyl-1-pyrrolidinecarboxamide. This coproduct is labeled N-pyrrolidino-N'-phenylurea in Reference 6.

II. 3. 2 Characterization Studies

In addition to thermal cycling to high temperature in vacuum, other screening criteria used included 1) extensive spectral studies of the polymers (before and after thermal cycling) and their vacuum outgas products, 2) limited mass analysis of vacuum outgas products, 3) limited thermal analysis of polymers (before and after thermal cycling), and 4) selected physical characterization (see discussion of latter in II. 3. 3 and II. 3. 4).

II. 3. 2. 1 Spectral Studies

IR Analysis. Typical of the IR spectra characteristic of poly(carborane-methylphenylsiloxane) is that shown in Figure 3a for pure UCARSIL 10615-80. Comparison of the IR spectrum for the control with that of the thermally cycled material (i.e. as in II. 3. 1 above) is instructive. The major results of the prescribed thermo-vacuum exposure as interpreted from these spectra are as follows:

- Pronounced line broadening in the regions: Si—O/carborane resonance (9-10 μm), $-Si(CH_3)_2-$ and $>Si(CH_3)-$ resonance (11.7-12.9 μm), an undetermined resonance centered at 11 μm, and the benzene ring substitution pattern (13.3-14.4 μm)
- Small amount of Si—H (silane) substituent generated (4.6 μm)
- Methyl and phenyl side chains remain largely intact after cycling.

Figure 3b displays the effect of thermal cycling (as in II. 3. 1) on the IR spectrum of blend V6007 (see Table 2). This blend consists of the following:

No.	Polymer	% by Weight
-104-1	Ultra-low molecular weight poly(carborane-dimethylsiloxane)	27.
-80	Ultra-high molecular weight poly(carborane-methylphenylsiloxane)	73.
	Total	100.

Spectrally the results of thermo-vacuum cycling of this polymer blend appear quite similar to those displayed for the ultra-high molecular weight poly(carborane-methylphenylsiloxane) alone. Silane generation and line broadening do appear lower in the blend than in the pure polymer.

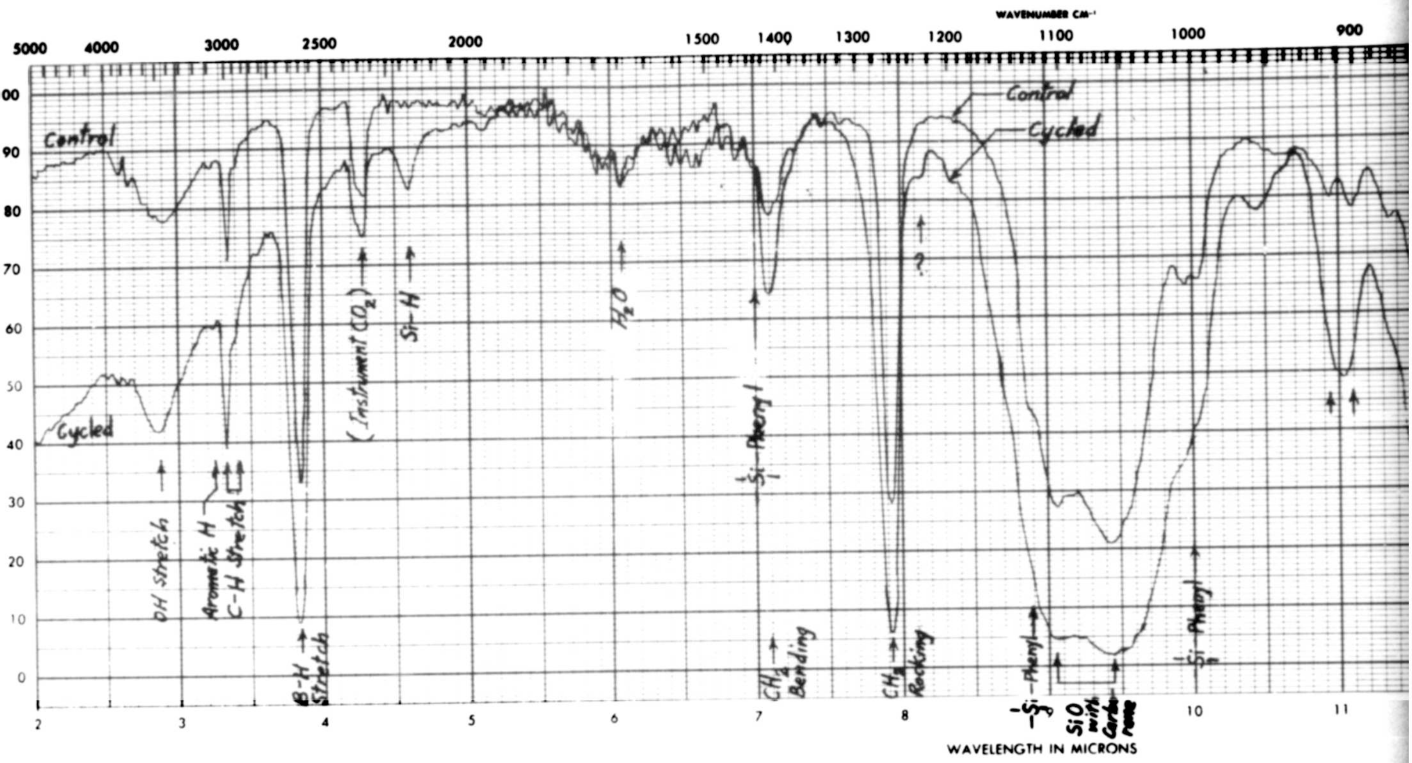
Summarizing, the Si-H generation indicates side chain scission which leads to cross-linking as evidenced by extensive broadening of characteristic bands. Enhanced suppression of this undesirable thermo-vacuum cross-linking is observed in the blend and is believed associated with the introduction (into the blend) of a low molecular weight version of the polymer.

Optical Transmission. This development effort is primarily aimed at an adhesive suitable for bonding solar cells to a substrate (rigid or flexible). As a consequence, its optical properties in the spectral range 0. 35 to 1. 2 μm (near-UV to near-IR region) would not impact the problem.

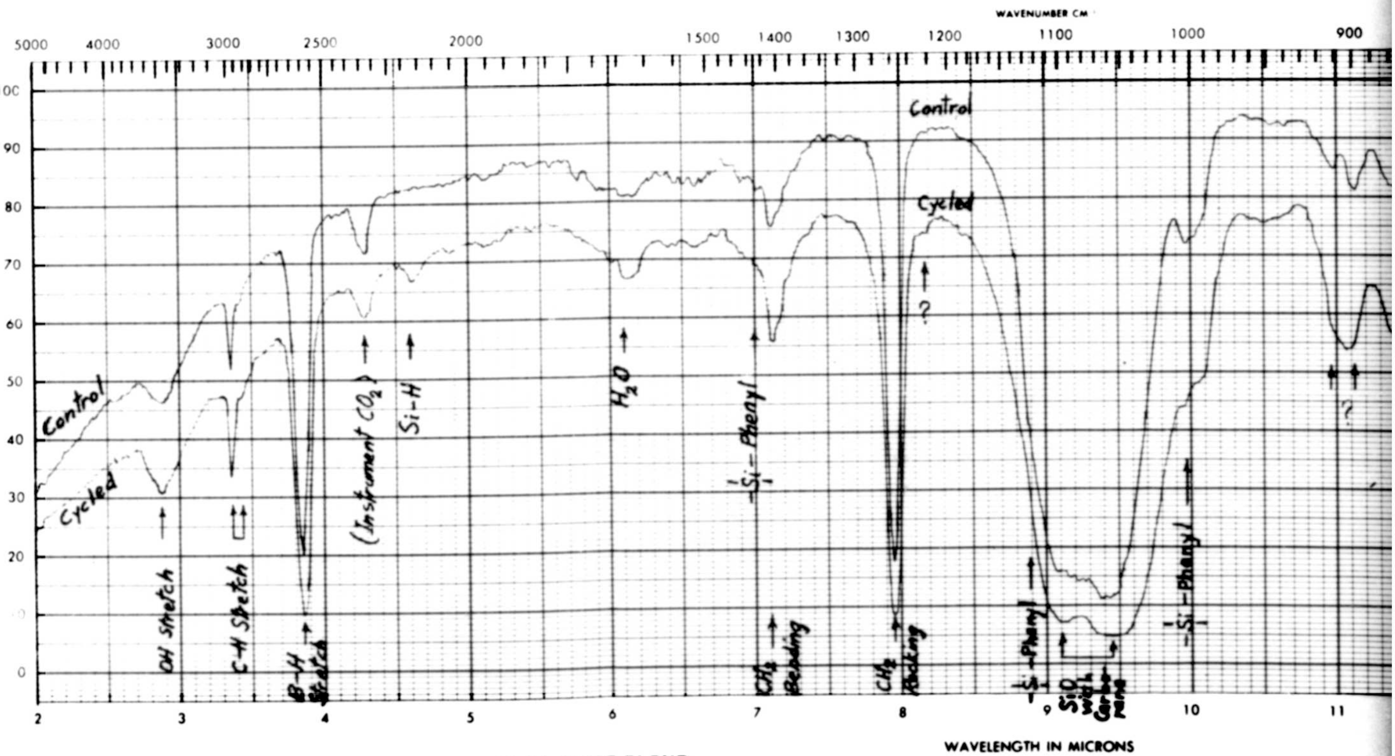
II. 3. 2. 2 Mass Analysis

Specimens typical of the -80 polymer and the -80/-104 polymer blend (V6002) were subjected individually to one 600°C excursion in vacuum during a 40 second interval. The pyrolysis gas was then introduced into a mass analyzer. The polymer vacuum pyrolysis chamber-mass analyzer assembly is shown in Figure 4. The results are shown in Table 3. The occurrence of hydrogen as the major gas constituent is indicative that hydrogen cleavage followed by cross-linking is the major thermo-vacuum degradation mechanism.

An indication of some main chain scission is indicated by the presence of low molecular weight silicone species in the pyrolysis gas. Silicone outgas species were also identified (by IR) in the room temperature condensate collected (in the limbic section) during thermo-vacuum screening tests (see II. 3. 1). However, since the parent polymers were not analyzed for residual carborane disilanol (one of the two comonomers), it is uncertain

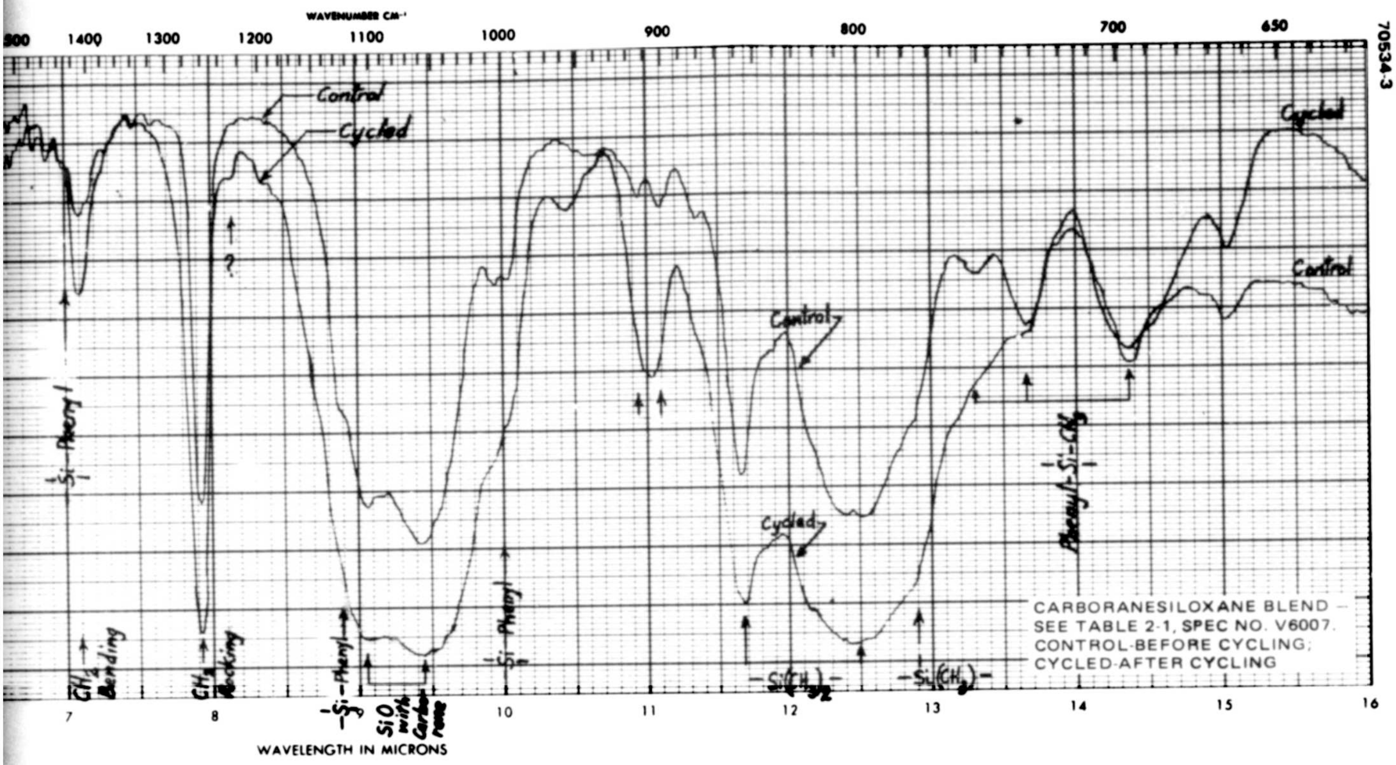


a) PURE POLYMER

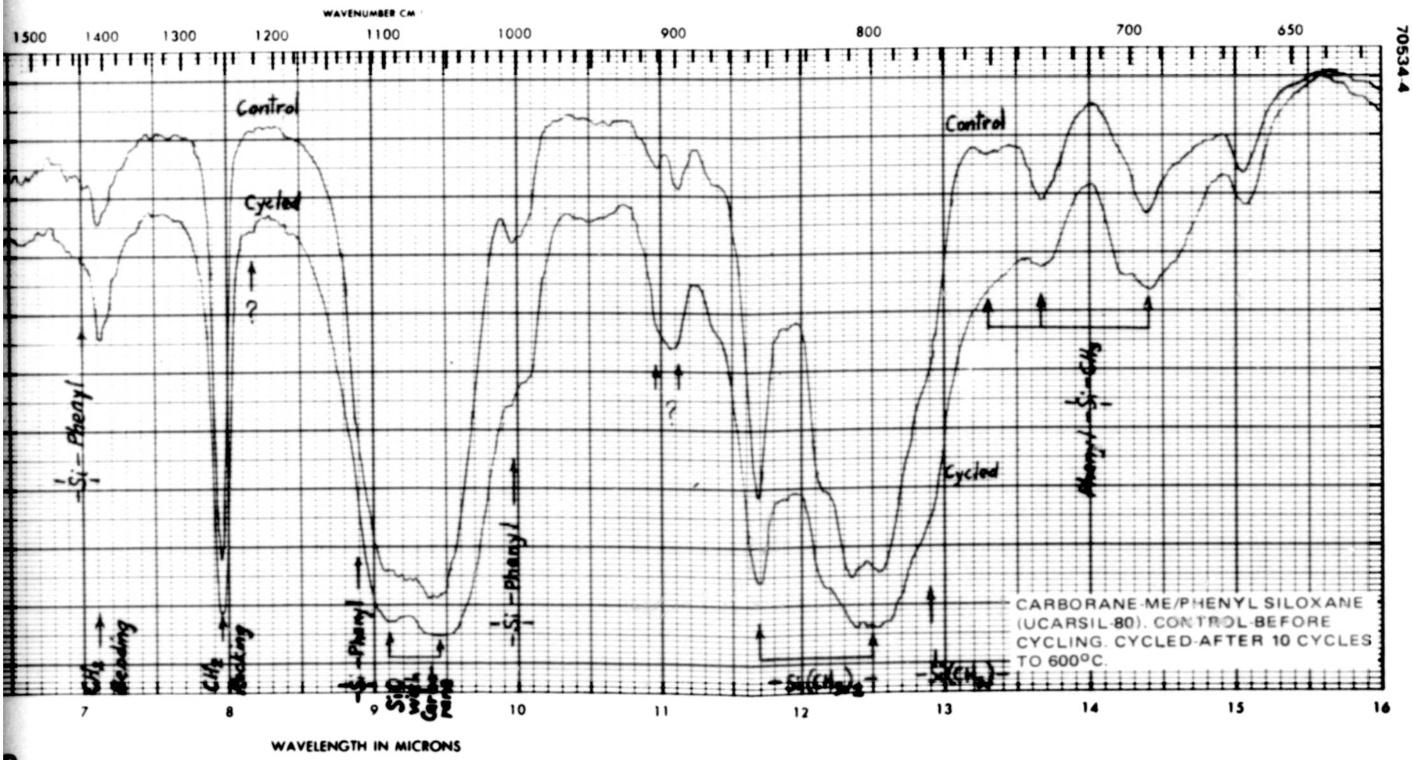


b) POLYMER BLEND

FIGURE 3. SELECTED IR SPECTRA



CARBORANESILOXANE BLEND — SEE TABLE 2-1, SPEC NO. V6007. CONTROL-BEFORE CYCLING; CYCLED-AFTER CYCLING



CARBORANE-ME/PHENYL SILOXANE (UCARSIL-80). CONTROL-BEFORE CYCLING. CYCLED-AFTER 10 CYCLES TO 600°C.

D

SPECTRA

2

TABLE 3. MASS ANALYSES OF POLYMER PYROLYSIS GASES

	Composition, Mole %	
	Polymer* -80	Polymer Blend* -80/-104
Hydrogen	89.257	82.453
Methane	4.100	4.188
Silicone (unidentified)	0.734	0.093
N_2/CO	2.450	5.008
Benzene	1.100	2.945
Toluene	0.012	0.029
Unsaturated hydrocarbons (as butene)	0.299	0.528
Saturated hydrocarbons (as butane)	0.136	0.229
i-propanol	0.028	0.000
CO_2	0.563	3.958
O_2	0.009	0.029
Ar	0.082	0.144
Decacarborane	0.002	0.003
Water	1.228	0.393
Total	100.	100.

*See column headings in Table 2 for description. The blend contains 73% by wt. polymer-80 (methylphenyl type; ultra-high molecular weight) and 27% by wt. polymer-104 (all-methyl type; ultra-low molecular weight; relatively high content of "substituted urea" coproduct ≈1.9% by wt.).

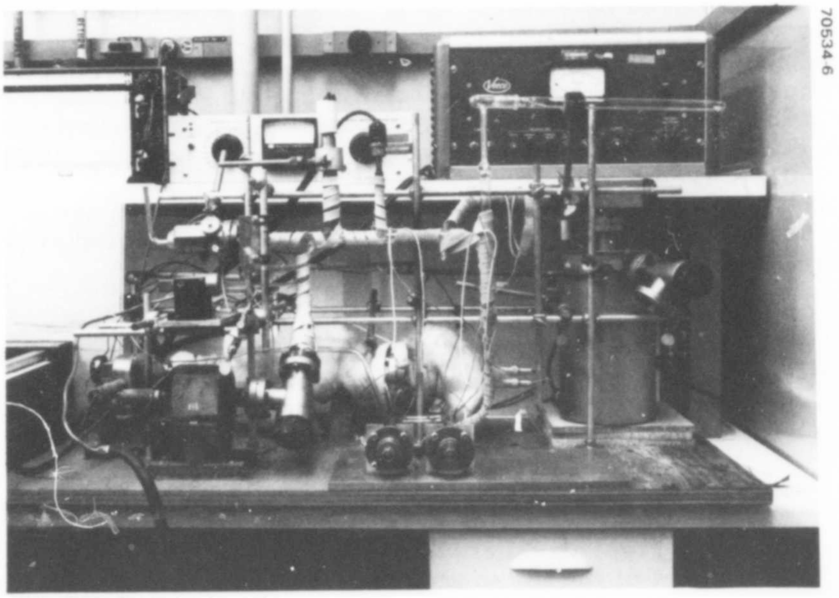


FIGURE 4. POLYMER VACUUM PYROLYSIS CHAMBER--MASS ANALYZER ASSEMBLY (PHOTO FJM100)

whether the silicone outgas species derive from this comonomer or from main chain scission. It is of interest to note suppression of the silicone outgas species by blending a relatively high mole content of the ultra-low with the ultra-high molecular weight polymer. The fact that the decacarborane content of the pyrolysis gas is very low in the case of both the pure ultra-high molecular weight polymer (-80) and its blend (-80/-104) increases the likelihood that the silicone outgas species result from main chain scission rather than residual silicone-containing monomer in the polymer.

Meaningful comparison of aliphatic versus aromatic gas content as a means of estimating relative thermal stability of methyl versus phenyl side chains is prevented by the presence of the thermally decomposable, "substituted urea" coproduct in the polymers, 0.14% by wt. in the polymer -80 and 0.62% by wt. in the -80/-104 blend.

II. 3. 2. 3 Thermal Analysis

Characterization by techniques of thermal analysis was found useful in studying high temperature stability as well as low temperature viscoelastic behavior. Despite limitations imposed by the scope of the effort, the data obtained will be observed to complement those obtained by other means. Thermogravimetric analysis (TGA) was performed with a DuPont 900 Thermal Analyzer. Differential scanning calorimetry (DSC) studies were carried out at low temperature with a Mettler instrument; a single high temperature run was made with the DuPont analyzer. TGA data are indicative of thermal volatilization (outgassing — both condensable and noncondensable) and DSC data display changes in viscoelastic properties.

TGA data reported by Peters, et al[8] are shown in Figure 5. Unfortunately, these were obtained in air at heating rates roughly 300 times slower than appropriate for this application. Even though exact comparison with this application is not possible, relatively high thermo-oxidative stability is verified up to the 600°C region, especially for the phenyl-containing polymer. A TGA curve for N_2 gas exposure (also slow heating) using polymer blend V6018A (see Table 2; 50% by wt. all-dimethyl/50% by wt. methylphenyl) is included in Figure 5 for comparison. At a temperature greater than 500°C, preferential decomposition of the all-dimethyl polymer component in the blend seems to occur.

Further indication of the relative thermal stability of these poly(carboranesiloxanes) is the high temperature DSC scan shown in Figure 6 made with polymer -80 (33 mole %-methylphenyl polymer) in N_2 gas at a heating rate of 0.083°C/sec. The major, thermal decomposition endotherm appears at ~584°C in this low rate of rise thermal excursion.

DSC heating scans of individual poly(carboranesiloxane) polymers and a blend of all-dimethyl (27% by wt. -104) and methylphenyl (75% by wt.) polymers are shown in Figures 7 and 8, before and after thermovacuum cycling. Values of the glass transitions (T_g) and melting endotherms

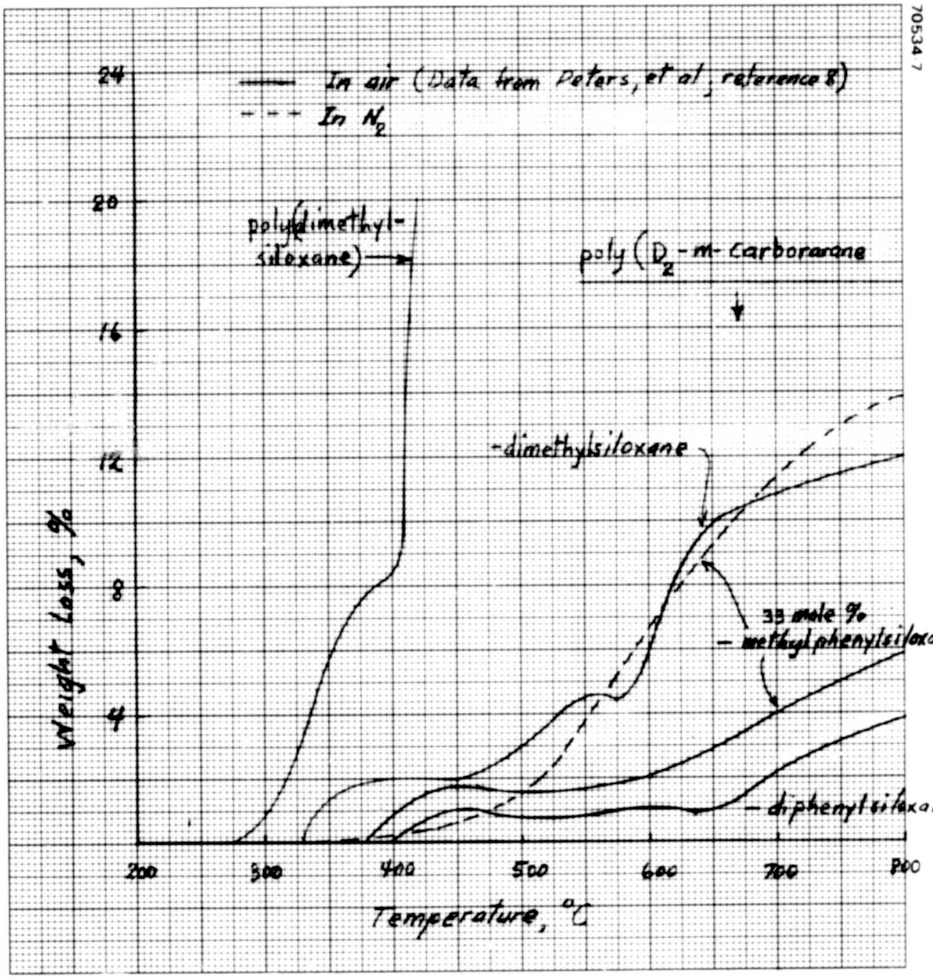


FIGURE 5. TGA OF POLY(D_2M-CARBORANE-SILOXANES) AND TYPICAL POLY(DIMETHYLSILOXANE)

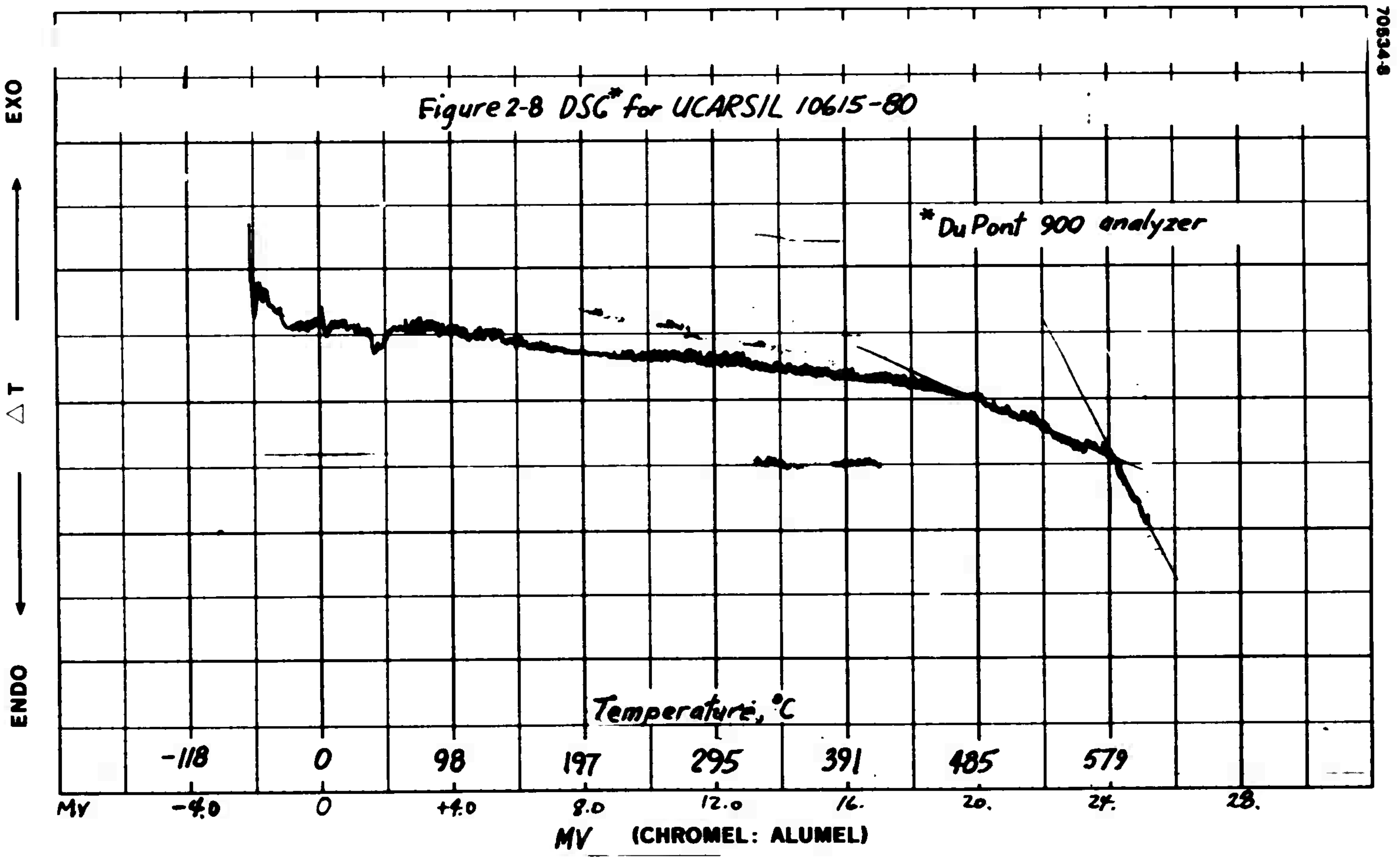
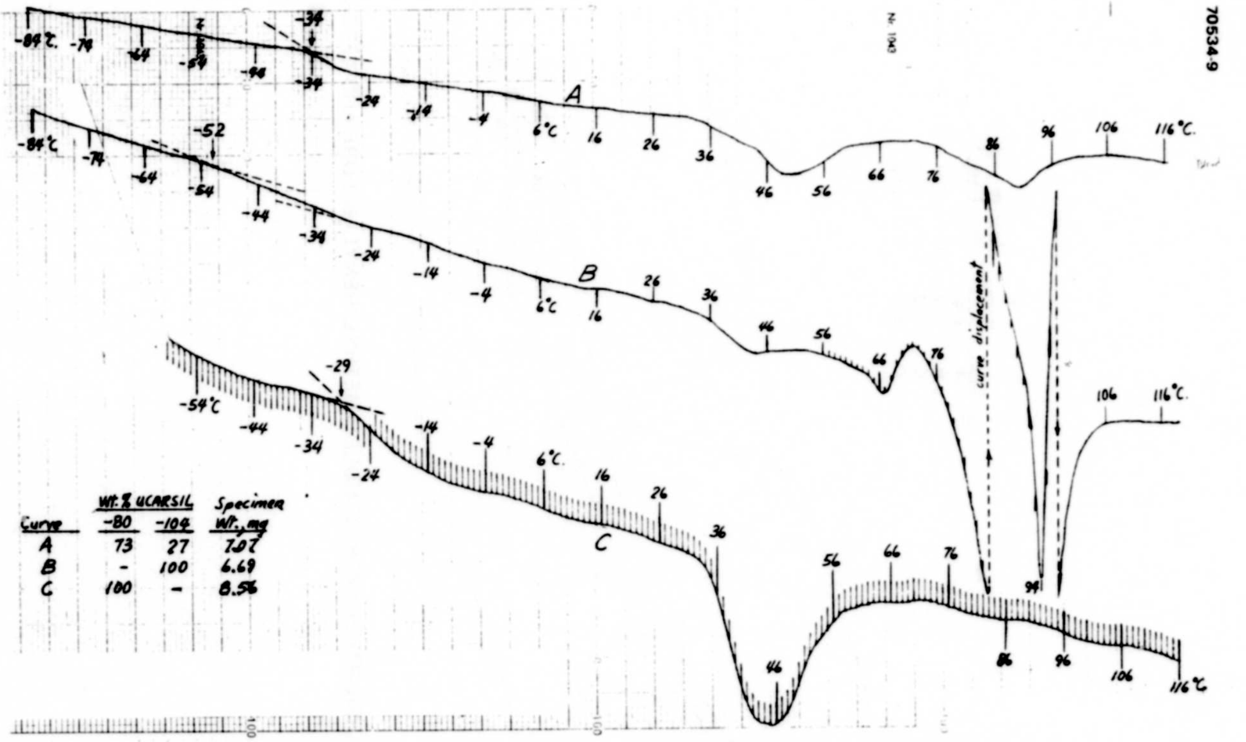


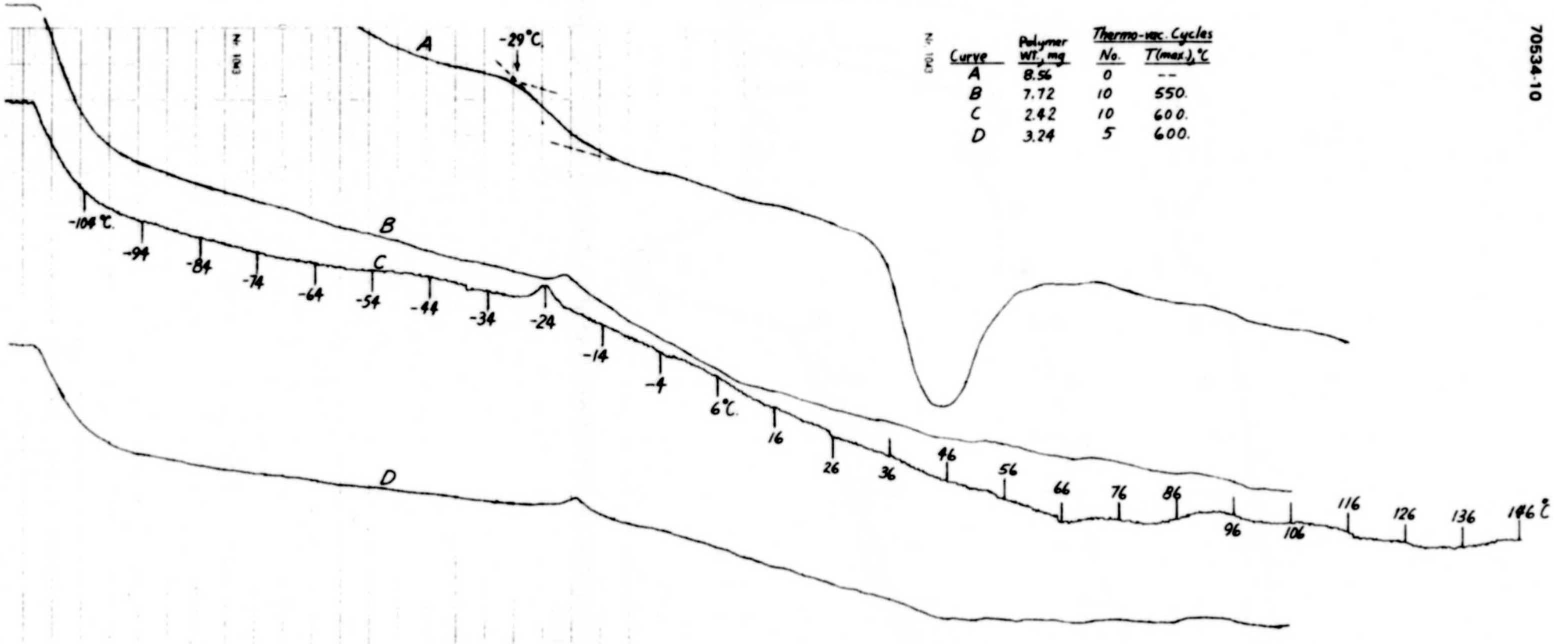
FIGURE 6. DSC FOR UCARSIL 10615-80 (DUPONT 900 ANALYZER)



Curve	Wt.% UCARSIL -80	Wt.% UCARSIL -104	Specimen Wt., mg
A	73	27	7.07
B	-	100	6.69
C	100	-	8.56

FIGURE 7. DSC SCANS (10°C/MIN) OF POLY(CARBORANESILOXANE) POLYMERS AND BLENDS BEFORE THERMAL CYCLING

70534-10



Curve	Polymer WT., mg	Thermo-vac. Cycles No.	Thermo-vac. Cycles T(max.), °C
A	8.56	0	--
B	7.72	10	550.
C	2.42	10	600.
D	3.24	5	600.

FIGURE 8. DSC SCANS OF UCARSIL-80 POLYMER (33 MOLE % METHYLPHENYL) BEFORE AND AFTER THERMO-VACUUM CYCLING

(T_m) derived from these scans are given in Table 4. Conclusions that may be drawn are as follows:

- For the individual, uncycled polymers, the measured T_G and T_m values are in reasonable agreement with Reference 8 values. The only serious discrepancy was a measured (DSC cooling scan not shown) crystallization exotherm (T_c) for the -104 of 7°C, as compared to a value of 37°C reported in Reference 8.

- Transition values measured for the blend were not averages of the values of individual components as was anticipated. This failure of the polymer alloy to display averaged properties may stem from inadequate specimen size or other instrumental deficiency.

- Thermo-vacuum cycling to 550-600°C significantly modifies the thermal transitions of the virgin blends, a result probably associated with cross-linking.

- As pointed out by Peters, et al (Reference 8), the introduction of phenyl side chains effectively suppresses polymer crystallization, thus promoting elastomeric behavior. (e.g., compare -104 with -80 polymers in Table 4).

- For polymers which exhibit crystallinity, the ratio T_g/T_m is typically found to have a value of 0.5 to 0.66. This rule seems to apply to UCARSIL -104.

II. 3. 3 Elasticity at Cryogenic Temperature

The next issue addressed was that of cryogenic elasticity. Ta coupon sandwiches, bonded as a result of high temperature cycling (10 times to ~600°C), were used as test specimens. Stress relaxation behavior in the adhesive bond line was examined by "instantaneously" applying a low but constant strain (0.5% in this case) and observing the load during the next 2 minute interval. It was presumed that the shear modulus ratio, E(-185°C)/E(RT), would be an order of 10^2 to 10^3, since it would be elastomeric at room temperature ($T > Tg$) and a glass at -185°C ($T < Tg$). Note also that the modulus ratio = load ratio, since the shear area remains unchanged. Surprisingly, this ratio was much smaller (see column 5 of Table 5). There is no ready explanation for the inferred very low Tg values so indicated, but the phenomenon is advantageous to this particular

TABLE 4. SUMMARY OF THERMAL ANALYSIS DATA

Polymer		Thermo-Vacuum Cycling		T_g, °C		T_m, °C*		Unidentified	
UCARSIL No.	Type	No.	T(max), °C	Measured	Reference 8	Measured	Reference 8	Endotherm	Exotherm
-104	All dimethylsiloxane	—	—	-52.	-50.	67, 94	68, 90	44	—
-80	33 mole % methylphenylsiloxane	—	—	-29.	-37.	—	—	45	—
-80/-104	Blend	—	—	-34.	—	90	—	49	—
-80/-104	Blend	10	550	—	—	—	—	—	-21
-80/-104	Blend	10	600	—	—	—	—	—	-24
-80/-104	Blend	5	600	—	—	—	—	—	-19

*Minimum of melting endotherm. Heating rate 10°C/min.

TABLE 5. STRESS RELAXATION AND SHEAR STRENGTH DATA FOR VARIOUS CARBORANE SILOXANE BLENDS PREVIOUSLY THERMAL CYCLED TO ~600°C IN VACUUM (10 TIMES)

Specimen	Blend Weight Ratio $[(M_w)_1/(M_w)_2$ etc.$]$	Load at Room Temperature, 10^7 dyne*	Load at -185°C, 10^7 dyne*	Load Ratio -185°C/R.T.	Load to Failure at -185°C 10^7 dyne	Adhesive Shear Area (est.) cm^2	Adhesive Shear Strength at -185°C 10^7 dyne/cm^2	Shear Modulus at -185°C 10^9/dyne/cm^2	Type of Failure
V6015A	75/25 $[10^7/5 \times 10^4]$	0.23	2.7	12	4.9	1.7	2.9	3.2	35% cohesive 65% adhesive
V6018	50/50 $[10^7/5 \times 10^4]$	1.6	4.3	2.6	16.5	4.5	2.6	1.9	Cohesive
V6018A	50/50 $[10^7/5 \times 10^4]$	0.22	0.58	2.6	5.0	2.0	2.5	1.7	35% cohesive 65% adhesive
V6019	25/75 $[10^7/5 \times 10^4]$	0.83	1.9	2.3	19.2	4.8	4.0	0.8	Cohesive
V6021	25/75 $[4 \times 10^6/5 \times 10^4]$	0.82	2.7	3.3	32.	1.8	18.	3.0	Cohesive
V6023	50/32/18 $[10^7/1.4 \times 10^5/5 \times 10^4]$	Failed during mounting in grips		—	—	—	—	—	Adhesive

*2 minute load readings at 0.5% constant strain adhesive application. The shear modulii, estimated as follows, confirm this inference:

Example: Specimen V6018

$$\text{shear modulus} = (E_s)_{-185^\circ\text{C}} = \frac{\text{shear stress in dynes}}{\text{constant strain}}$$

$$= \frac{(4.27 \times 10^4 \text{ g} \times 981)/4.5 \text{ cm}^2}{0.005}$$

$$= 1.9 \times 10^9 \text{ dyne/cm}^2$$

Thus, glass-like shear modulii are typically of the order 10^{10} dyne/cm^2. In contrast, the measured values (column 9, Table 5) of shear modulus at -185°C are an order of magnitude lower, i.e., ~10^9 dyne/cm^2, indicating a leathery behavior.

Shear strengths are of such magnitude that the modest peel requirements are not expected to pose a problem.

II.3.4 Viscous Behavior

The problem of thermally-induced embrittlement as a result of cross-linking in the range 500-600°C necessarily confines consideration to thermoplastic species. Resort to thermoplastic species, however, introduces the problem of striking a balance between 1) 600°C viscosity sufficiently high to minimize creep and plastic flow and 2) processing viscosity (at, say, 150°C maximum) sufficiently low to permit adhesive bonding at moderate pressure and dwell (say 15 psi and 24 hours). In other words a compromise is required to assure acceptable dimensional stability at 600°C and acceptable processibility at lower temperature, both factors being considered in the context of the dominant consideration of acceptable resistance to high temperature embrittlement. Thus there is an apparent need to restrict consideration to a very viscous thermoplastic material. The data thus far seem to indicate that a mutually compatible blend of low and high molecular weight polymers is attractive. The low molecular weight constituents inhibit high temperature embrittlement. The high molecular weight constituents introduce the necessary viscosity to minimize creep or plastic flow at service temperatures. Thus, ultrahigh molecular weight polymers are advantageous because they permit use of maximum contents of low molecular weight species without loss of requisite viscoelastic properties at processing (say 150°C max.) and service (say 50°C max.) temperatures. This results from the strong dependency of viscosity η on molecular weight, MW, as follows:

$$\eta = k(MW)^{3.4}$$

It is conceived that upper limits on adhesive processing variables are of the order 150°C, 15 psi and 24 hour dwell. On this basis, the required 150°C value for viscosity of the high molecular weight species is estimated to be $\sim 10^9$ dyne-sec/cm^2 (= 10^9 poise). This obviously directs attention at the ultrahigh (e.g., -98) rather than the high (e.g., -110) molecular weight species. A lap shear specimen was prepared from -98 polymer at the above processing conditions, and the load-displacement relationship determined at constant strain rate ($\dot{\gamma}$ = 0.0194 sec^{-1}) as shown in Figure 9. The viscosity η is estimated as follows for -98 material by itself:

$$\eta = \frac{\sigma(\infty)}{\dot{\gamma}} = \frac{\text{Extrap. load x 981/shear area}}{0.0194}$$

$$= \frac{(225 \times 981)\ \text{dyne}/0.91\ \text{cm}^2}{0.0194\ \text{sec}^{-1}}$$

$$= 1.2 \times 10^7\ \text{dyne sec/cm}^2$$

$$= 1.2 \times 10^7\ \text{poise}$$

Thus even the ultrahigh molecular weight species has an estimated η lower than desirable, in view of the desired large dilution with low viscosity species, e.g., -104 and/or -111. Additional viscosity values for individual polymers were determined in a similar manner and are presented in Table 6.

Blend viscosities can be estimated by weight averaging as follows:

$$\eta_{Blend} = (w\eta)_1 + (w\eta)_2$$

where w is the weight fraction of each component. Although blend values of the order of 10^9 poise would be preferred, the blend values estimated from Table 6 appear acceptable.

TABLE 6. VISCOSITIES OF POLY(CARBORANE SILOXANE) INDIVIDUAL POLYMERS AT ANTICIPATED PROCESSING TEMPERATURE (150° MAXIMUM)

Polymer		Temperature, °C	Viscosity η, Poise
No.	$\overline{M}_w$		
-98	$>10^7$	150	1.2×10^7 8.2×10^7
-117	$\sim 10^7$	150	8.4×10^7
-110	4×10^6	150	3.1×10^6
-111	1.4×10^5	20	5×10^5

II. 3. 5 Conclusions

Specimens V6018A, V6022A, and V6024A (representing a broad variation in polymer blend compositions) were thermally cycled in an effort to determine whether an acceptable compromise between high temperature chemical and dimensional stability and lower temperature processibility prevailed. The concern was that, during an initial excursion to 600°C (and prior to onset of any thermal cross-linking, at say 400°C), the viscosity of the thermoplastic bond line might drop low enough to permit plastic flow or substrate delamination. The test specimens were prepared as lap shear sandwiches, i.e., Ta (10 mil)/polymer film/Ta (10 mil), with bond lines measuring 0.5 cm wide x 1 cm long x 6 to 18 mils thick. At a shear load of 1.6 g/cm^2, each bond line was heated (in vacuum) from 20 to 600°C in ~10 seconds. There was no evidence of bond line deformation, translation, or delamination. Similar tests carried out at 50°C for over 6 months yielded equally encouraging results.

The foregoing review of experimental studies to determine practical tradeoffs between acceptable thermo-vacuum stability and acceptable viscous behavior leads to the following conclusions:

- Binary blends of ultralow molecular weight, all-methyl carborane siloxane polymer with ultrahigh molecular weight, methylphenyl carborane siloxane polymer are preferred. Preferred compositions are of the order 50%-50% by weight.
- Polymers with RV* > 3.5 are preferable to those with RV < 3.5 for the ultrahigh molecular weight species.
- Ternary polymer blends containing low molecular weight methylphenyl species (e.g., UCARSIL 10615-111) lose more in high temperature stability than might be gained in improved viscous behavior.

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*RV = reduced viscosity at 25.00°C, using 0.2000 g polymer per dl chloroform solution.

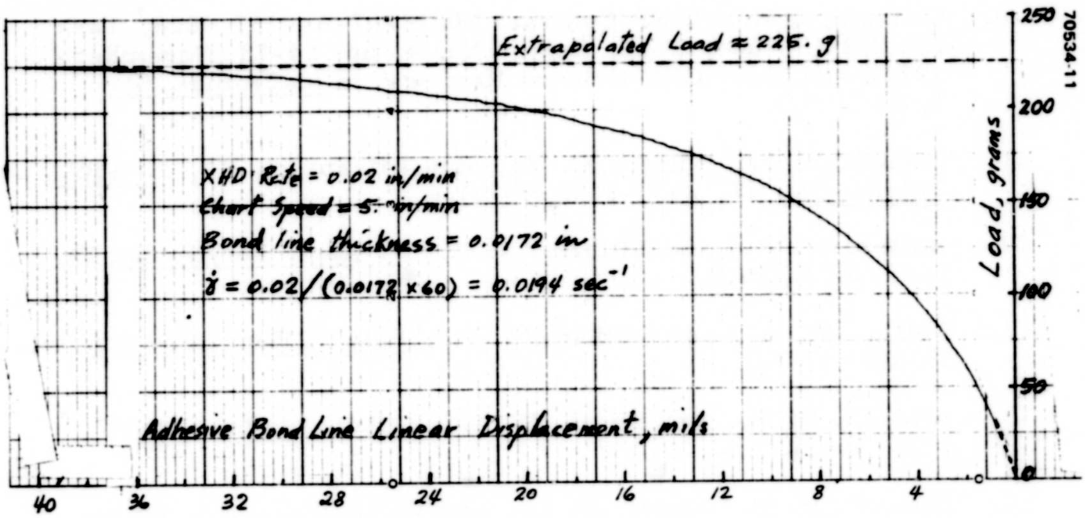


FIGURE 9. LOAD-DISPLACEMENT CURVE AT 150°C FOR ULTRAHIGH MOLECULAR WEIGHT UCARSIL POLYMER (-98) ADHESIVE BOND LINE

II. 4 REFERENCES

1. Schroeder, H. A., Schaffling, O. G., Larcha, T. B., Frulla, F. F., and Heying, T. L., Rubber Chem. and Technol. 39 (No. 4, Pt. 2), 1184-1199 (1966).

2. Pappetti, S., Schaeffer, B. B., Gray, A. P., and Heying, T. L., J. Polymer Sci A-1 (Pt. 4), 1623 (1966).

3. Knollmueller, K. O., Scott, R. N., Kwasnik, H., and Sieckhaus, J. F., J. Polym. Sci. A-1, 9 (4), 1071-1088 (1971).

4. Dietrich, H. J., Alexander, R. P., Heying, T. L., Kwasnik, H., Obenland, C. O., and Schroeder, H. A., Makromol. Chem. 175 (2), 425-440 (1974).

5. Dunks, G. B., Hedaya, E., Kawakami, J. H., Kopf, P. W., Kwiatkowski, G. T., McNeil, D. W., and Tulis, R. W., "Union Carbide Rept." UCRI-735 (30 July 1973).

6. Peters, E. N., Hedaya, E., Kawakami, J. H., Kwiatkowski, G. T., McNeil, D. W., and Tulis, R. W., Rubber Chem. and Technol. 48 (1), 14-18 (1975).

7. Peters, E. N., Stewart, D. D., Bohan, J. J., Kwiatkowski, G. T., Beard, C. D., Moffitt, R., and Hedaya, E., "Union Carbide Rept." CRL-T828 (4 December 1975).

8. Peters, E. N., Kawakami, J. H., Kwiatowski, G. T., Hedaya, E., Joesten, B. L., McNeil, D. W., and Owens, D. A., J. Polym. Sci. Polym. Phys. Ed. 15, 723-732 (1977).

9. Gillham, J. K., "ONR Contract N0014-67-A-0151-0024, Task No. NR 356-504, Tech. Rept." No. 4, pp. 54-73 (November 1971); see also "CRC Critical Reviews" in *Macromol. Sci.* 1, 83 (1972).

10. Mohadger, Y., Roller, M. B., and Gillham, J. K., *J. Appl. Polym. Sci.* 17, 2635-2652 (1973).

11. Roller, M. B., and Gillham, J. K., *J. Appl. Polym. Sci* 17, 2623-2652 (1973).

12. Roller, M. B., and Gillham, J. K., *Polym. Engr. and Sci.* 14, 567-572 (1974).

13. Allcock, H. R., and Kugel, R. L., *J. Am. Chem. Soc.* 87, 4216 (1965).

14. Allcock, H. R., Kugel, R. L., and Valan, K. J., *J. Inorg. Chem.* 5, 1709 (1966).

15. *Ibid.*, p. 1716.

16. Allcock, H. R., and Cook, W. J., *Macromolecules* 7, 284 (1974).

17. Allcock, H. R., *Phosphorous-Nitrogen Compounds,* Academic Press, New York (1972).

18. Allcock, H. R., *Chem. Rev.* 72, 315-356 (1972).

19. Singler, R. E., Schneider, N. S., and Hagnauer, G. L., *Polym. Engr. and Sci.* 15 (5), 321-338 (1975).

20. Connely, T. M., Jr., and Gillham, J. K., *J. Appl. Polym. Sci.* 20, 473-488 (1976).

21. Singler, R. E., Hagnauer, G. L., Schneider, N. S., LaLiberte, B. R., Sacher, R. E., and Matton, R. W., *J. Polym. Sci. Polym. Chem. Ed.* 12, 433 (1974).

22. Hagnauer, G. L., and LaLiberte, B. R., *J. Polym. Sci. Polym. Phys. Ed.* 14, 367-371 (1976).

23. Reynard, K. A., Gerber, A. H., and Rose, S. H., *AMMRC CTR* 72-29, Dec. 1972 (AD755188).

SECTION III

COUPON TESTS

III. 1 PHASE II PLAN

The coupon tests are relatively simple screening tests designed to provide practical indications of any deficiencies in 1) candidate adhesive formulation and application to adherend surfaces, 2) adherend wetting, 3) bond line control (thickness/location), 4) adherend-adhesive interaction, 5) bond line curing, and 6) properties of the cured bond line. In this latter regard, adhesive bond strength (via 45° pull test) and its separate resistance to degradation by 1) thermal cycling of 600°C and 2) hydrolytic attack are the primary evaluation criteria.

III. 1. 1 Adherend Material Matrix

The adherend material test matrix (see Table 7) is designed to simulate anticipated adherend combinations that would be typical of a high temperature solar cell array design. Thus, both flexible and rigid substrates are simulated in both monolayer, multilayer, and sandwich constructions. Cell rear contact simulation is limited to silver and aluminum surfaces; bus simulation is limited to aluminum (>99 percent purity) foil. In accordance with the statement of work, four different adherend combinations (plus one variation) are included as the minimum requirement.

TABLE 7. ADHEREND COMBINATIONS FOR COUPON TESTING

Adherend (Simulated Substrate)	Counter Adherend Simulation		
	Cell Rear Contact	Electric Bus	Multilayer or Sandwich Construction Substrate
Fused silica fabric[a]	Aluminum[b]	Aluminum[c]	Fused silica fabric
Fused silica fabric[a]	Silver[b]	–	–
Aluminum face sheet[d]	–	–	Aluminum honeycomb core[d]

[a] HASPS program fabric: 5 μm diameter "Astroquartz" filament; 900 1/2 yarn count; 186 warp x 150 fill woven as double faced warp satin.

[b] Vapor deposit on convenient substrate.

[c] Alloy EC foil or similar.

[d] Aluminum alloy.

III. 1. 2 Test Parameter Matrix

III. 1. 2. 1 Visual Examination

Background documentation will include written description of pertinent visual observations supplemented by such microscopic detail (photomicrographs) as appears warranted. Such efforts will be conducted before and after coupon tests.

III. 1. 2. 2 Pull Test

An attempt to correlate adhesive bond strength (to varying adherend surfaces) with simulated degradation test parameters will be made. In accordance with the statement of work, a 45° pull test will be used to evaluate bond strength. This test combines both tensile and shear failure forces.

The test configuration visualized is shown in Figure 10. The tests will be conducted at room temperature. Because mechanical manipulation effects are such a hazard in correlating test data, it is tentatively planned to test a replicate group of reference specimens ("before" condition) in parallel with thermally exposed (or hydrolytically exposed) specimens. Where possible, adherend A will be selected from the flexible materials (fabric or metal foil).

Adherend A — Flexible. The failure mode is likely to be a continuous peel. In this case, a satisfactory grip separation rate should fall in the range of 5 to 15 cm/min. The tab at adherend A may be via 3M pressure sensitive tape No. 250 (Fed. Std. 101B, Method 2050).

Adherend A — Rigid. This case would also include the rigid solar cell array test elements. Failure is likely to occur via adhesive cleavage. It is proposed to attach 3M tape No. 250 on the outer face of adherend A to function as a flexible pull tab. This would be done after electrical output measurements. Where it is deemed necessary to make electrical measurements after pull testing, careful peel-removal of the tape (perhaps at 50°C) followed by solvent removal of residuals at room temperature (methyl i-butyl ketone, acetone, and last methanol) should restore surface transparency. Such tape removal should not be necessary for the rigid coupon tests. In these cases where cleavage is anticipated, tensile loading is tentatively proposed as 50 to 100 g/min. This is believed associated with a grip separation rate of the order of 0.05 mm/min.

III. 1. 2. 3 High Temperature Cycling

Coupon test specimens will be cycled from ambient to 600°C a total of ten times. Depending on laser intensities of interest and whether front or back irradiation is being simulated, thermal excursion rates in the bond line at the cell rear face have been found in previous studies to range from

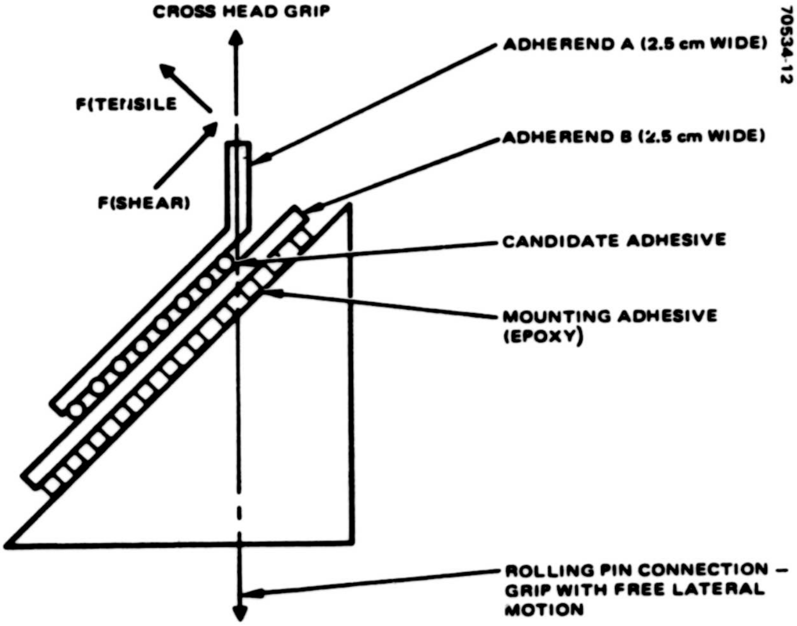


FIGURE 10. PULL TEST CONFIGURATION

~10°C/sec to 100°C/sec. One of the following options will be selected to perform this thermal cycling of coupon size adherend combinations:

- 10.6 μm laser exposure in vacuum at a convenient intensity to attain 600°C
- High intensity lamp heating (quartz/iodide) in vacuum
- Air heating in electric furnance at ~1000°C

A thermocouple (chromel-alumel, 0.0127 cm wire diameter) in the bond line will be used to designate the 600°C exposure. Pull tests (see above) will be run before and after thermal cycling.

III. 1. 2. 4 Storage Test

Hydrolytic stability will be evaluated by coupon storage for 10 consective days at T≥60°C and a relative humidity of 95 percent. Pull tests will be run before and after this humidity exposure.

III. 2 PHASE II STATUS

III. 2. 1 Preliminary Activity – Coupon Thermal Cycling Apparatus Design/Fabrication/Operation

The cycling chamber was fabricated from glass (Corning 7052) and contained two 2-3/4 OD Varian vacuum flange closures. One was connected to an 8 ℓ/sec vac-ion pump through a butterfly valve; a 3 inch OD (minimum) by 0.5 inch thick polished NaCl window was mounted (via Viton O-ring) on the other flange. Kovar feed-throughs were mounted in the chamber walls to permit connection of specimen thermocouples (located in the adhesive bond line) to a recording two-output potentiometer. A single test coupon was mounted on a copper pedestal within the chamber. This pedestal was sealed to the chamber through a Kovar tubulation which formed a cavity directly under the pedestal back face. This was arranged as an LN_2 cold finger on the pedestal back face; while the front face (containing the mounted coupon) was arranged for direct exposure (though the salt window) to a laser beam, CO_2 (CW). This arrangement permitted exposure of coupon specimens to thermal excursions of ~-190°C to ~600°C in vacuum (~10^{-5} torr) in times of <10 seconds.

Such rapid cycling seemed relevent because the polymer blends studied will not retain flexibility after extended dwell at temperatures of 550 to 600°C. In the necessarily confined experimental chamber geometry used, thermal losses and radiation/conduction effects can retard the thermal rate of rise over this $\Delta T = 790°C$ as well as maintenance of the low temperature extreme. Precautions used include the following:

- Careful location/mounting of thermocouples (5 mil OD chromel/alumel used)

- Careful location/mounting of test specimen on cold finger pedestal (specimen mount)
- Careful prior inspection and subsequent handling of thermocouple interconnects within chamber
- Increase in laser raw power (to maximum of 325 watts)
- Insertion of radiation shield (quartz fabric/tantalum foil/quartz foil) between irradiated specimen surface and internal feed-through pins in chamber
- Maintenance of large LN_2 reservoir behind cold finger pedestal

III. 2. 2 Program

Coupon testing was initiated; the results are discussed below. The lack of availability of additional required ultra-high molecular weight polymers caused suspension of this effort and prevented acquisition of confirmatory test data.

III. 2. 3 Initial Coupon Test Results

II. 2. 3. 1 Polymer Processibility

The adhesive bond time processibility study was limited to a minimum effort necessary to yield acceptable and reproducible test coupons. In this regard, a small portion of V6018A (~3 mils thick; see Table 2) was committed to a brief examination of adhesive bonding, using quartz fabric/quartz fabric and quartz fabric-stainless steel coupons. It was hoped that these test combinations would provide a preview of pertinent factors and potential problems as follows:

- Processing conditions that prevent "weep" through quartz fabric, yet generate acceptable initial peel strength
- Processing conditions for acceptable wetting of nonporous (metal) adherend
- Anticipated level of peel strength prior to thermal cycling and type of bond failure

The results of the tests are given in Table 8.

Additional bond specimens were processed from V6018A and quartz fabric/quartz fabric and quartz fabric/silver adherend combinations. At the processing conditions 135°C/~16 hour/15 psia, pre-cycling bond failure appeared to be mostly cohesive. This is confirmed by examination of the photomicrographs (Figures 11, 12, and 13). These conditions thus are useful in guiding the fabrication of coupon specimens for cyclical exposure.

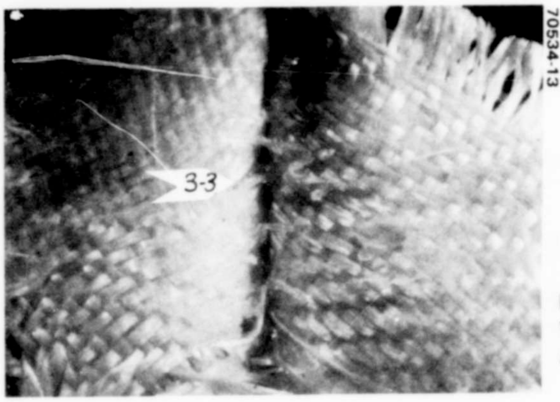


FIGURE 11. COHESIVE FAILURE (DURING PEEL) OF V6018A ADHESIVE BOND LINE BETWEEN QUARTZ FABRIC ADHERENDS (MAGNIFICATION: 8X; ETCH: NONE)

FIGURE 12. COHESIVE FAILURE (DURING PEEL) OF V6018A ADHESIVE BOND LINE BETWEEN QUARTZ FABRIC ADHERENDS (MAGNIFICATION: 22X; ETCH: NONE)

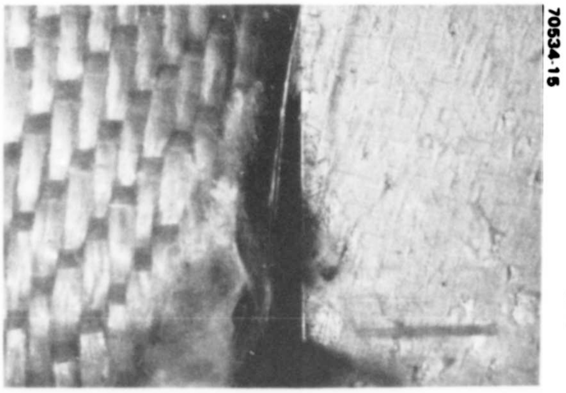


FIGURE 13. COHESIVE FAILURE (DURING PEEL) OF V6018A ADHESIVE BOND LINE BETWEEN QUARTZ FABRIC AND SILVER ADHERENDS (MAGNIFICATION: 14X; ETCH: NONE)

TABLE 8. BRIEF BONDING TESTS WITH V6018A THERMOPLASTIC FILM ADHESIVE

Adhesive Bond Line Process Conditions			Adherend Combination			
			Quartz Fabric/Quartz Fabric		Quartz Fabric/Stainless Steel	
Temperature, °C	Time, hr	Pressure, psia	Quartz Fabric Weep	180° Peel Strength* (Estimated), g/cm	Quartz Fabric Weep	180° Peel Strength* (Estimated), g/cm
150	62	15	Yes	--	--	--
125	~20	15	No	>1600	No	~1430 (Failure: ~25% cohesive ~75% adhesive)
100	~20	15	No	--	No	--

*Before thermal cycling.

In an effort to reveal shear creep tendency under low stress (~1.6 g/cm^2), lap shear coupons of V6018A, V6022A, and V6024A were exposed to 50°C in vacuum. After ~4000 hours exposure, no evidence of creep was noted.

While too much should not be read into the above data, indications are that film of the polymer blend with the best thermo-vacuum stability, e.g., V1018A, can be processed into a bond line acceptable for nonporous and porous adherends and providing acceptable initial adhesive strength.

III. 2. 3. 2 Initial Coupon Tests

Specimen Preparation. Approximately 0.075 g of candidate polymer blend V6018A was committed to these tests. The intent was to scope the area of material compatibility and attempt to identify unforseen problems of adhesion or quartz fabric, quartz fabric/silver, and quartz fabric/aluminum foil (10 mil). At a film thickness of 2.5 mils ±0.5 mil and a bond line 1.0 cm wide by 2.0 cm long, there proved to be sufficient polymer blend to prepare five specimens only. These were labeled CT-3 through CT-7.

Only the aluminum was subjected to chemical etch prior to adhesive bonding. The quartz fabric and silver adherends were solvent cleaned only with acetone and methanol prior to bonding. Bonding was carried out in a vacuum oven at 135°C/~16 hours/~15 psia. Brief previous tests had indicated satisfactory processing at these conditions. Unfortunately, a small amount of adhesive weep did occur (from the bond line to outer surfaces) in the specimens. The net result of high temperature exposure was some carbonization on the exposed quartz surface together with quartz fabric embrittlement. While this problem is more than cosmetic, it did not seem to impair the conclusions drawn from the coupon test data obtained from these specimens.

Thermal Cycling. Temperatures during typical thermal cycling excursions are shown in Figures 14, 15, and 16. The high temperature thermocouple was located at the interface between the adhesive and top peel fabric (quartz). The low temperature thermocouple was located on the substrate pedestal (a LN_2 cold finger). Depending on substrate thickness, separation of the two thermocouples varied by only 4 to 8 mils. Previous screening tests had shown the adhesive to be critically sensitive to embrittlement at $T>600°C$, hence the use of a separate high temperature thermocouple as indicated. Temperature extremes are given in Table 9 for the ten cycles the test coupons were exposed. The visible appearance of coupon test specimens may be observed in Figure 17.

Peel (45°) Measurements. Each exposed specimen was carefully removed from the cycling chamber. It was then bonded (with a room temperature curing epoxy resin) to an aluminum coupon (1 by 4 by 0.125 inches). This supported specimen was subsequently mounted on the 45° peel fixture shown in Figure 18 and then transferred to the peel apparatus shown in Figure 19.

The type of bond line failure may be observed for both exposed and unexposed specimens in Figures 20 through 25. Failure appears to be primarily cohesive in nature. Carbonization on and embrittlement of the

TABLE 9. COUPON TESTS: RESULTS OF THERMAL CYCLING OF PEEL SPECIMENS PREPARED WITH V6018A ADHESIVE

Coupon Test No.	Adherend Combination		Thermal Cycling Range (Each of 10 Cycles)		Room Temperature Peel (45°) Strength, g/cm[c]	Bond Line Failure[d]
	Peel Member[a]	Substrate	Minimum Temperature,[b] °C	Maximum Temperature,[b] °C		
CT-6	Quartz fabric	Quartz fabric	--	--	1340	Cohesive
CT-7	Quartz fabric	Silver[e]	--	--	980	60% – adhesive 40% – cohesive
CT-2	Quartz fabric	Quartz fabric	-125 to -190	570 to 630	>450	Cohesive
CT-3	Quartz fabric	Quartz fabric	-170 to -190	574 to 602	~550	Cohesive
CT-4	Quartz fabric	Silver[e]	-170 to -190	581 to 597	~900	Cohesive
CT-5	Quartz fabric	Aluminum	-170 to -190	588 to 607	640	Cohesive

[a] HASPS design, fused silica fabric in every case; high thread count, lightweight.

[b] Range over 10 cycles.

[c] Estimated from Figure 26. Peeling force (in grams) per centimeter of leading edge of adhesive; measured at ambient temperature and pressure. Crosshead rate = 0.05 in./min.

[d] See Figures 20 through 25.

[e] Silver-plated copper foil (2 mil thickness).

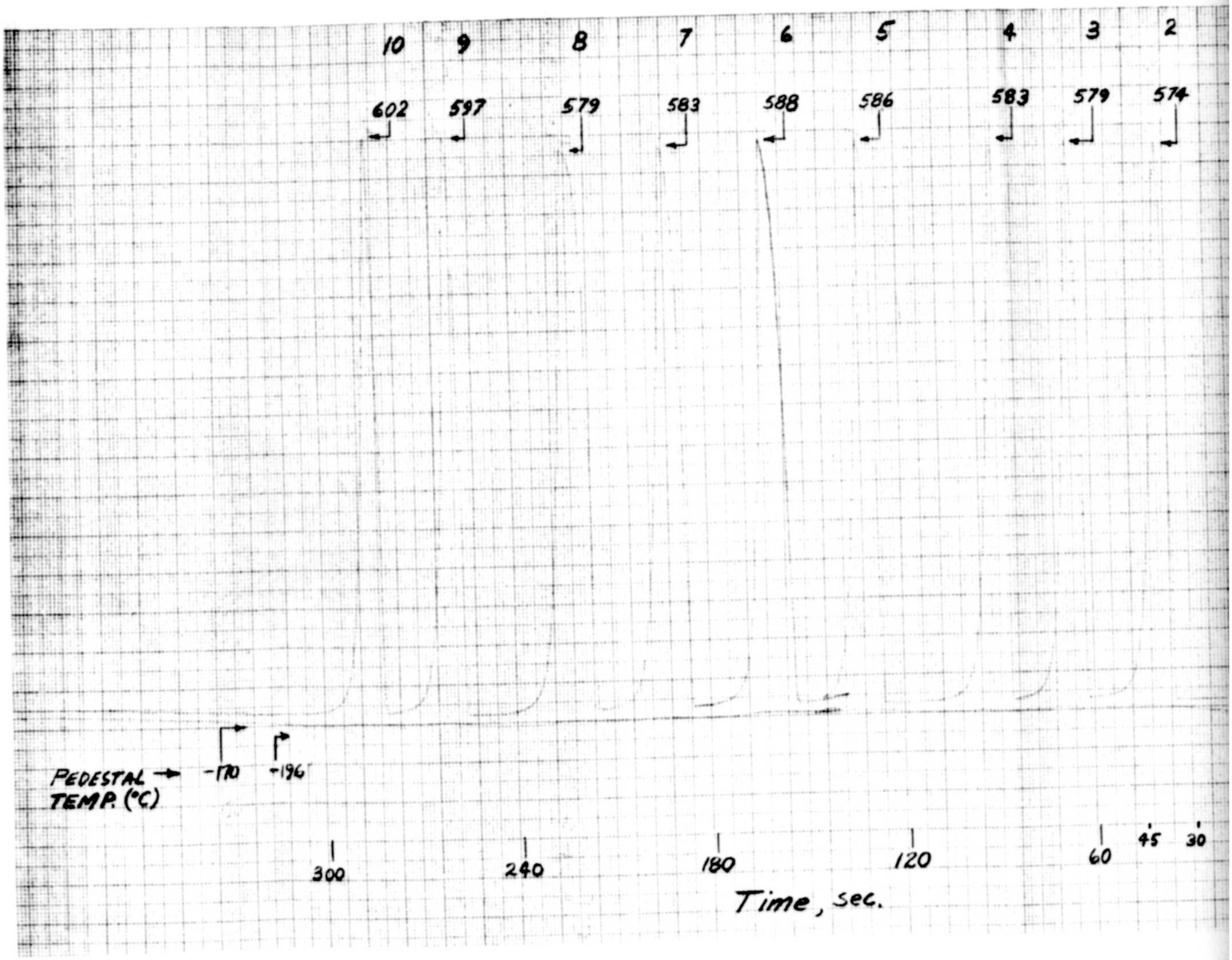
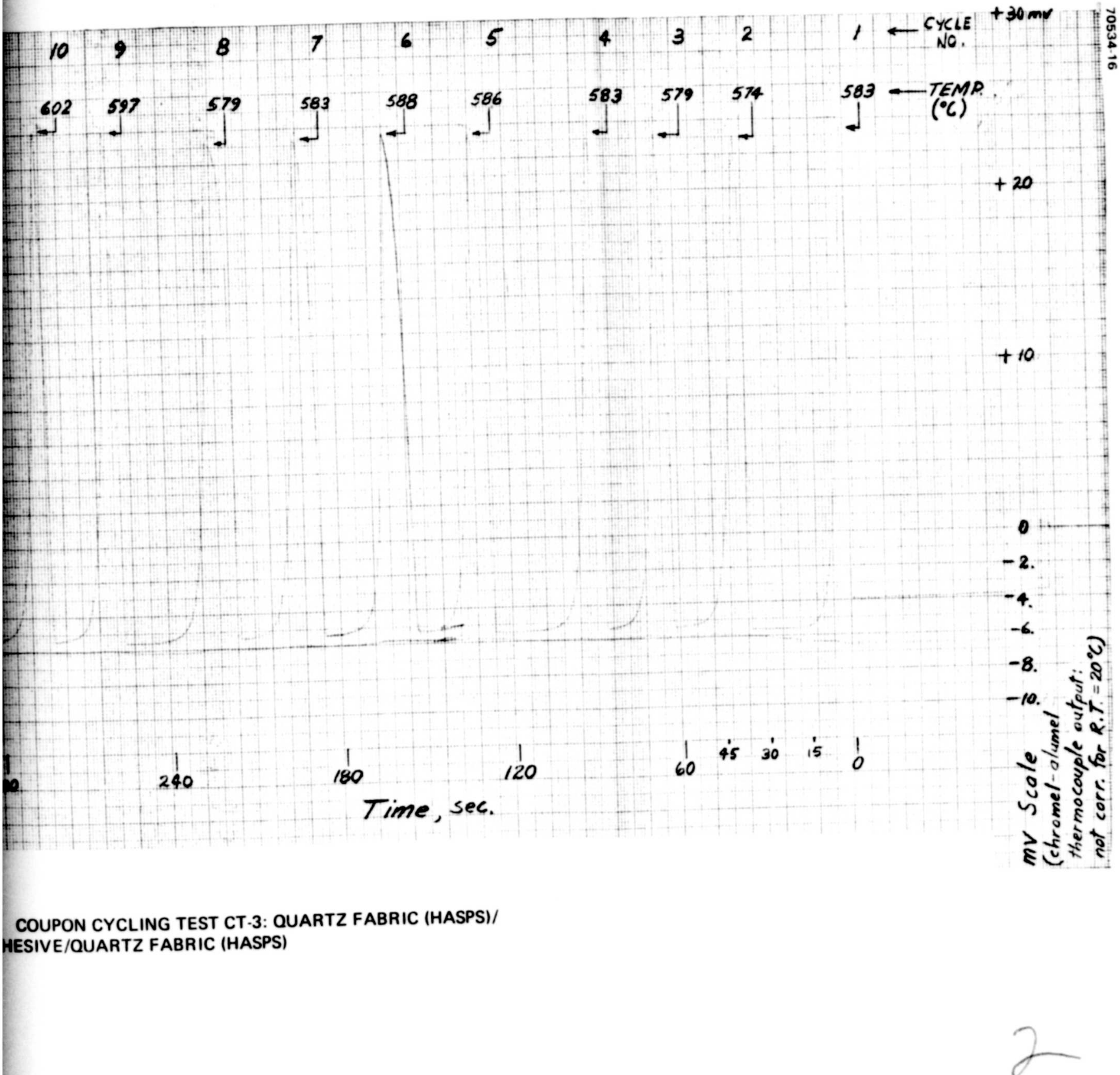


FIGURE 14. COUPON CYCLING TEST CT-3: QUARTZ FABRIC (HASPS)/ V6018A ADHESIVE/QUARTZ FABRIC (HASPS)



COUPON CYCLING TEST CT-3: QUARTZ FABRIC (HASPS)/
HESIVE/QUARTZ FABRIC (HASPS)

2

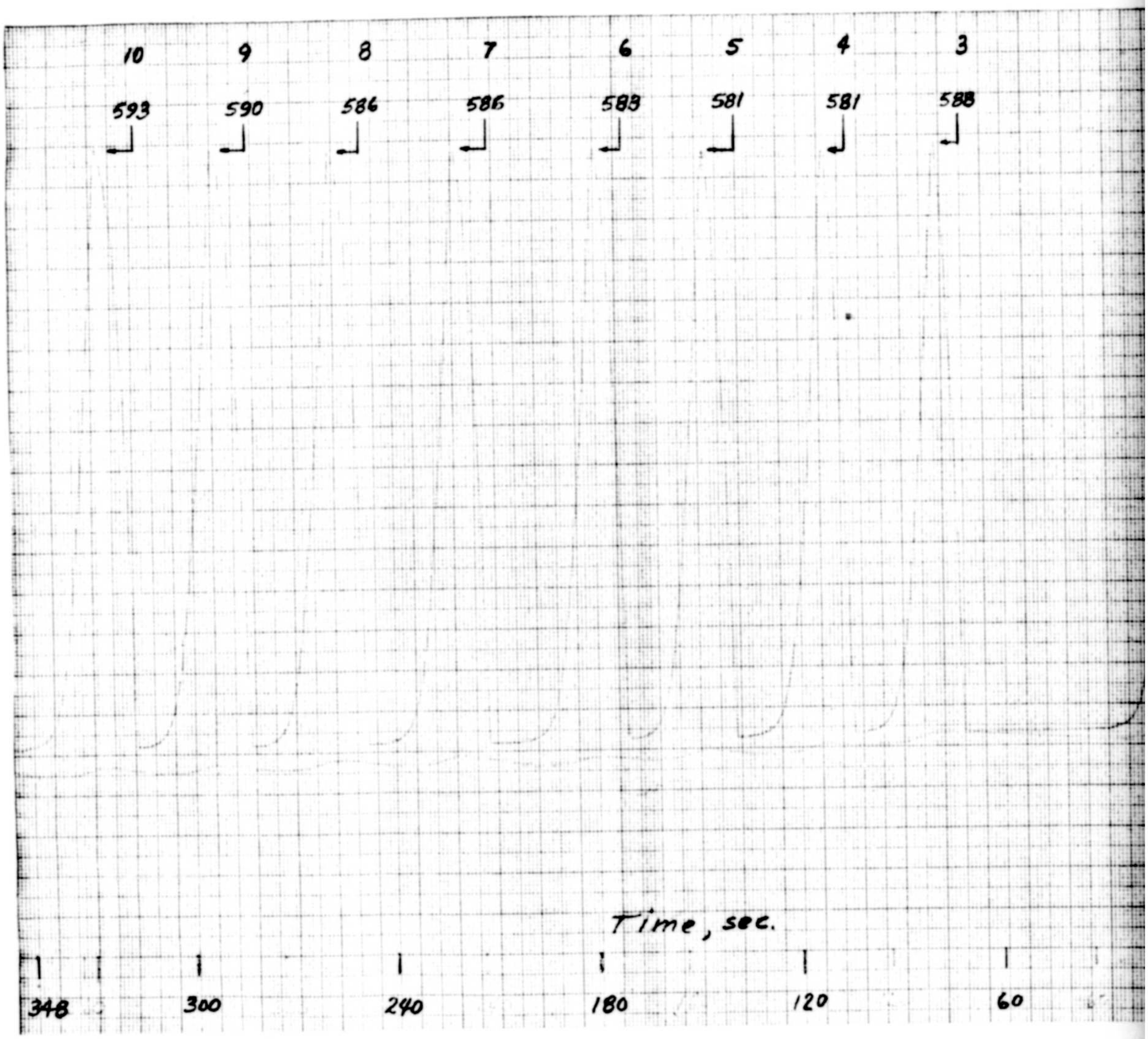
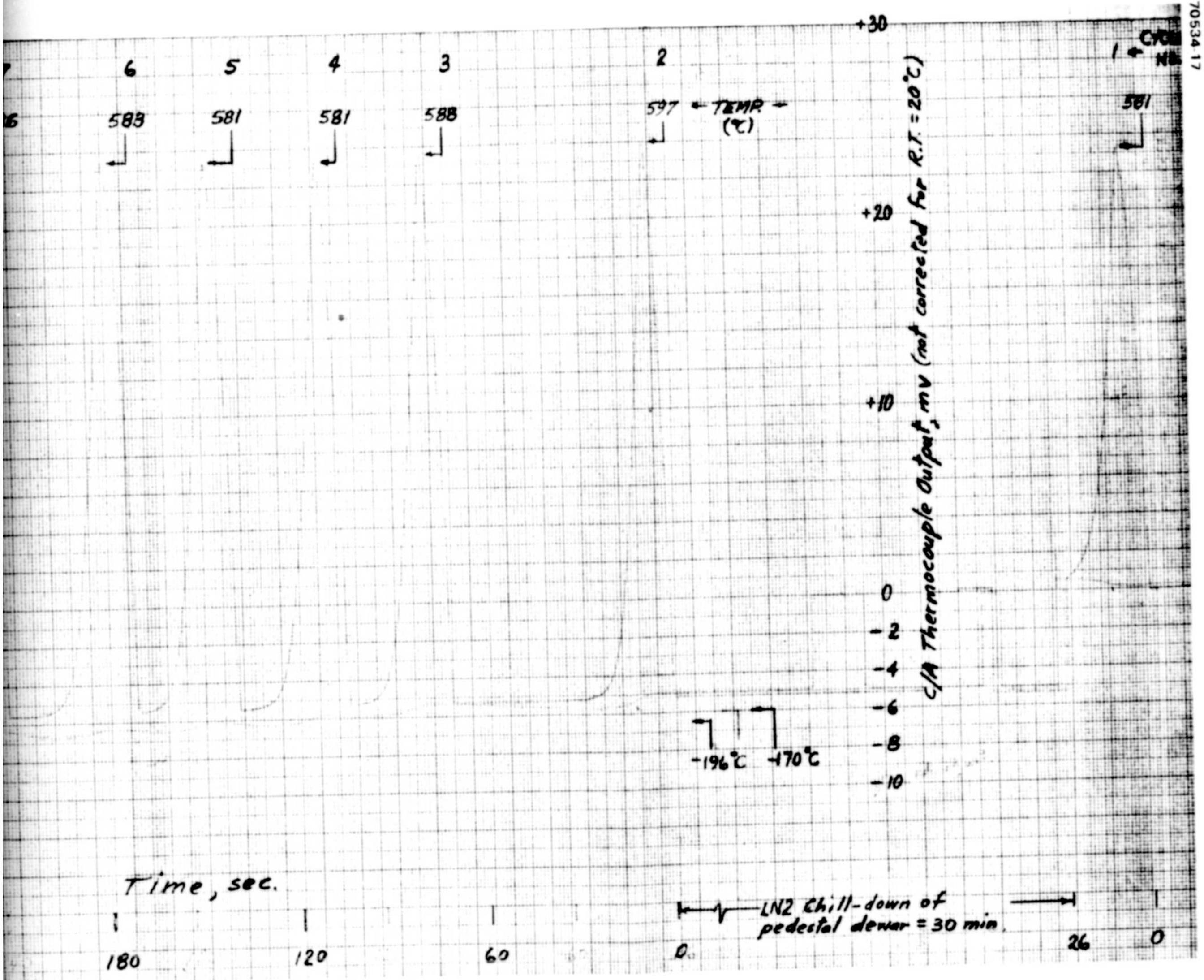


FIGURE 15. COUPON CYCLING TEST CT-4: QUARTZ FABRIC (HASPS)/ V6018A ADHESIVE/SILVER



CLING TEST CT-4: QUARTZ FABRIC (HASPS)/
ER

2

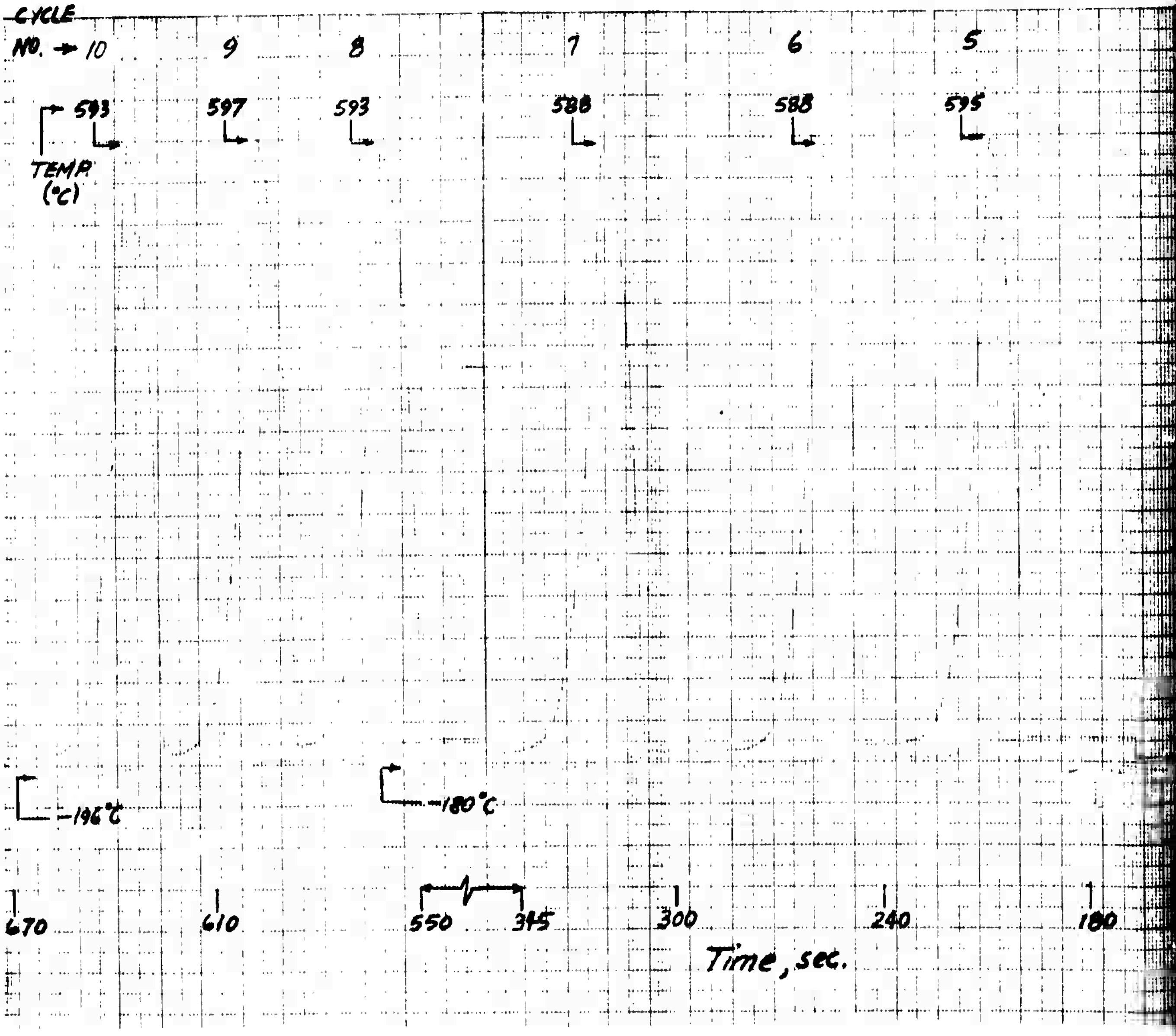
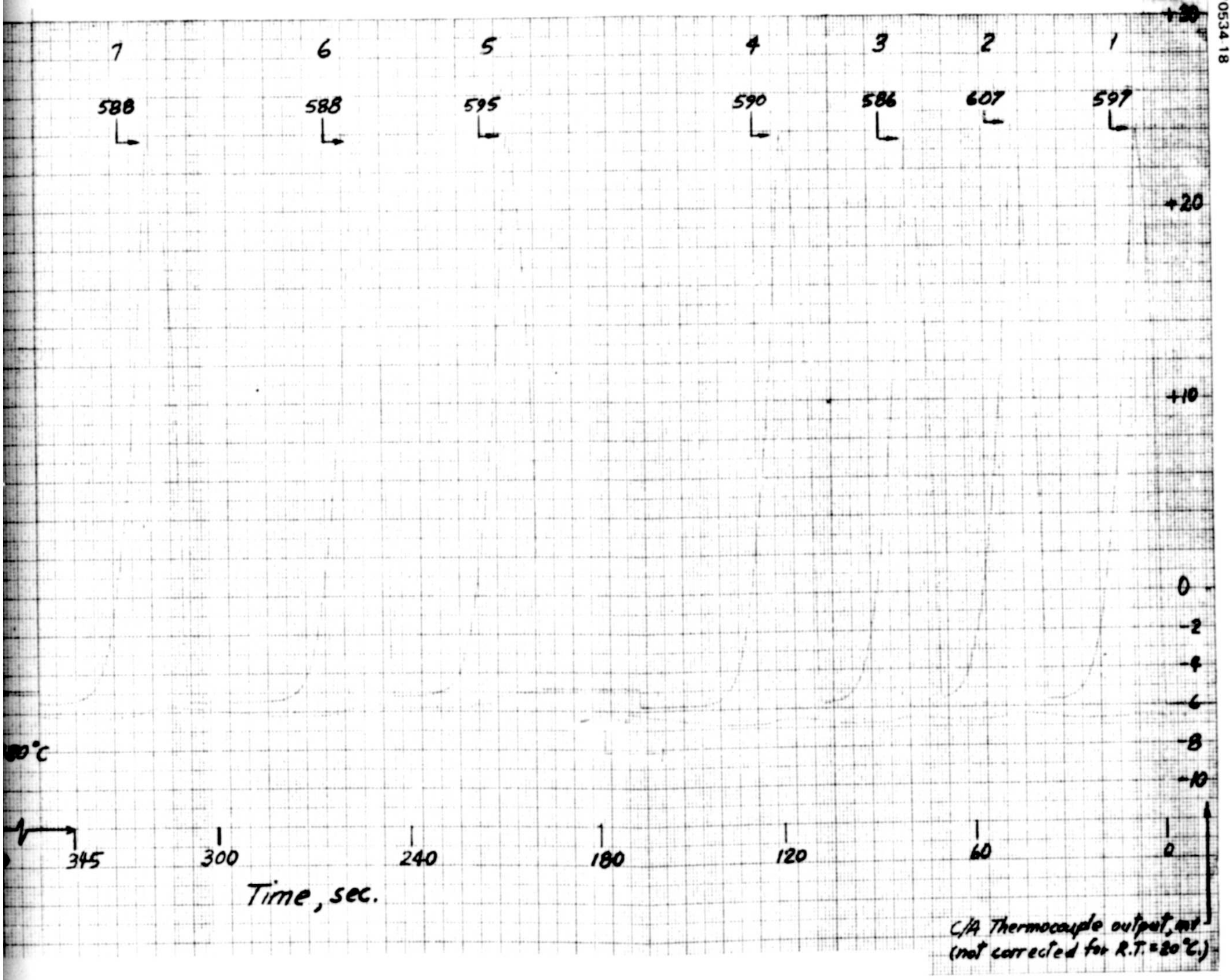


FIGURE 16. COUPON CYCLING TEST CT-5: QUARTZ FABRIC (HASPS)/ V6018A ADHESIVE/ALUMINUM FOIL (5 MIL)



CYCLING TEST CT-5: QUARTZ FABRIC (HASPS)/
LUMINUM FOIL (5 MIL)

2

quartz fabric peel member may also be noted, as discussed earlier, as a complicating factor. Although 600°C cycling for aluminum was intended to assess compatibility only, aluminum distortion was minimal.

The magnitude of 45° peel strengths between various adherend combinations of interest is estimated to fall in the range 450 to 900 g/cm after ten thermo-vacuum cycles, well above the goal value of 200 g/cm. The peel force — vertical displacement records are presented in Figure 26, with the derived peel strength values shown in Table 9.

Demonstrated adhesive compatibility with various adherends and retention of bond strength after cycling from cryogenic to 600°C temperatures provide additional support for continued interest in these poly (carborane siloxane) polymer blends.

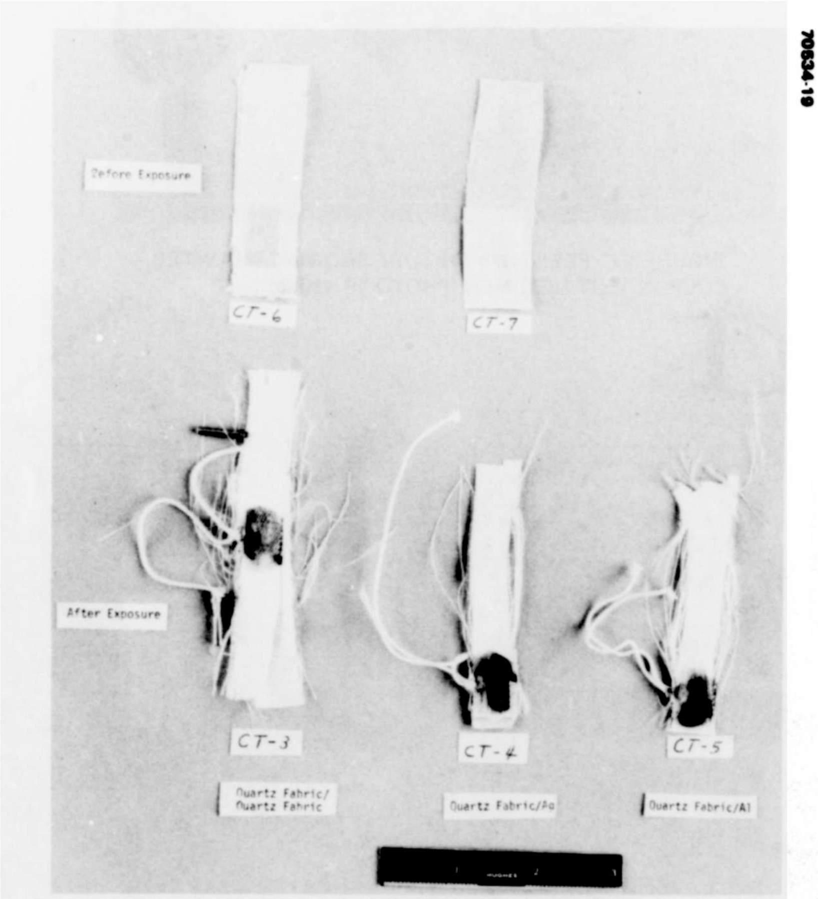


FIGURE 17. COUPON TEST SPECIMENS BEFORE AND AFTER CYCLE EXPOSURE, PRIOR TO PEEL (PHOTO 77-56302)

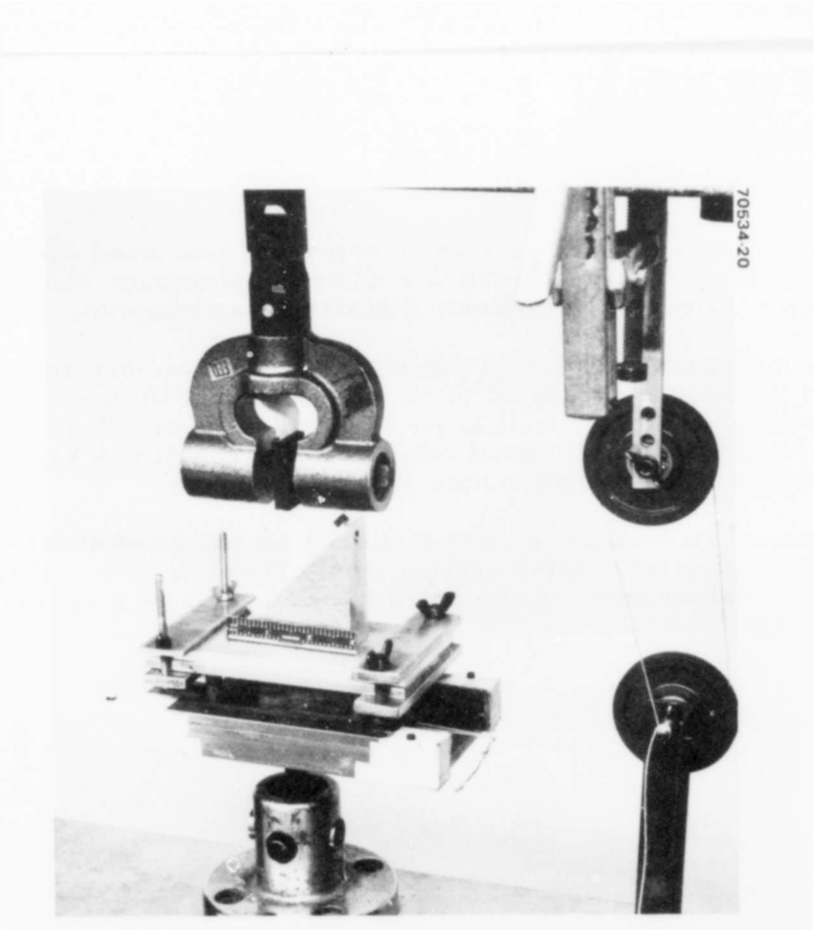


FIGURE 18. PEEL (45°) FIXTURE SHOWING MOUNTED COUPON TEST SPECIMEN (PHOTO 4R 48038)

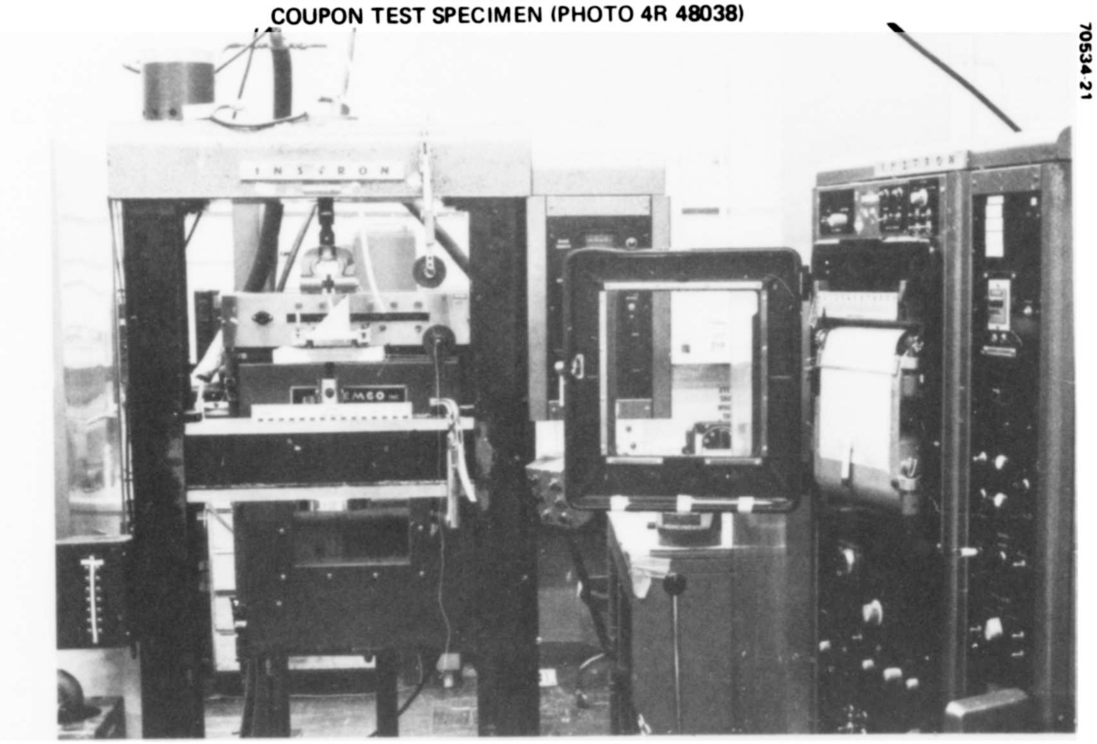


FIGURE 19. PEEL APPARATUS (PHOTO 4R 48037)

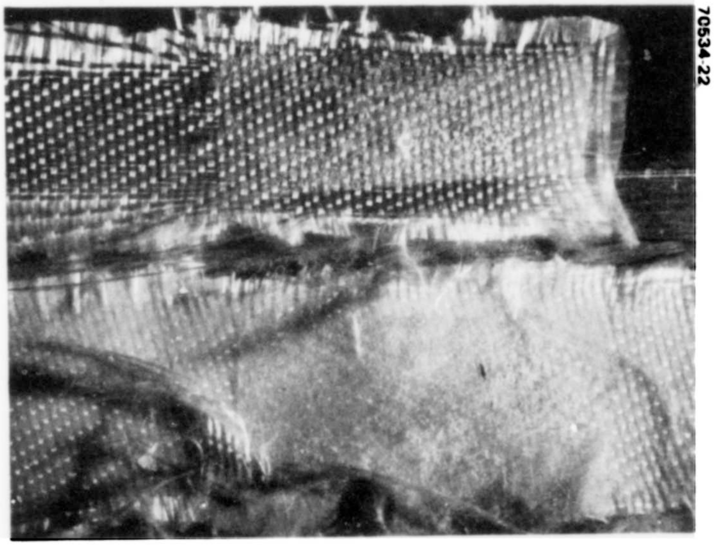


FIGURE 20. CT-2 AFTER 45° PEEL (EXPOSED QUARTZ/QUARTZ)
MAGNIFICATION: 3X; ETCH: NONE

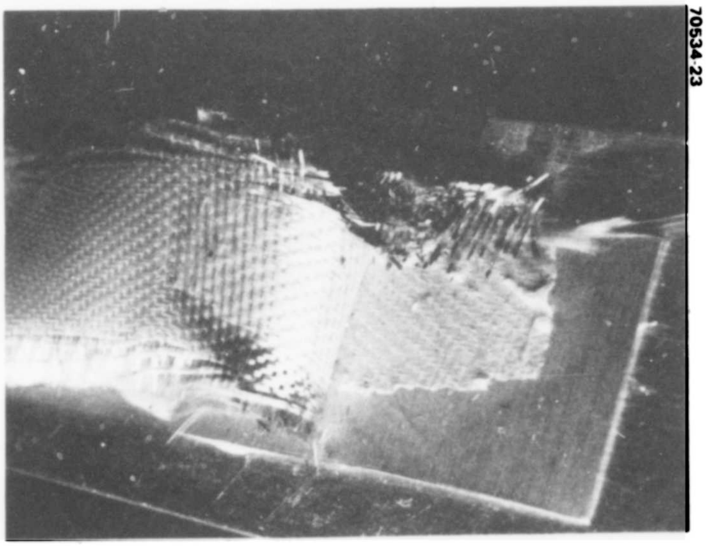


FIGURE 21. CT-5 AFTER 45° PEEL (EXPOSED QUARTZ/ALUMINUM)
MAGNIFICATION: 3X; ETCH: NONE

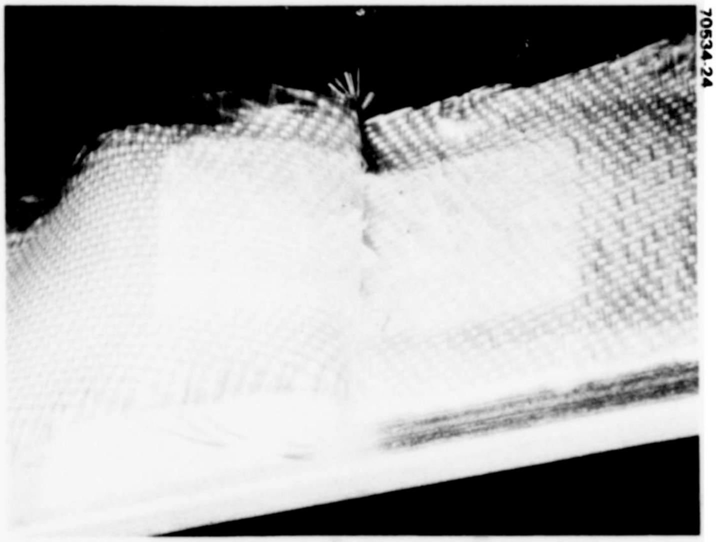


FIGURE 22. CT-6 AFTER 45° PEEL (UNEXPOSED QUARTZ/QUARTZ)
MAGNIFICATION: 2.5X; ETCH: NONE

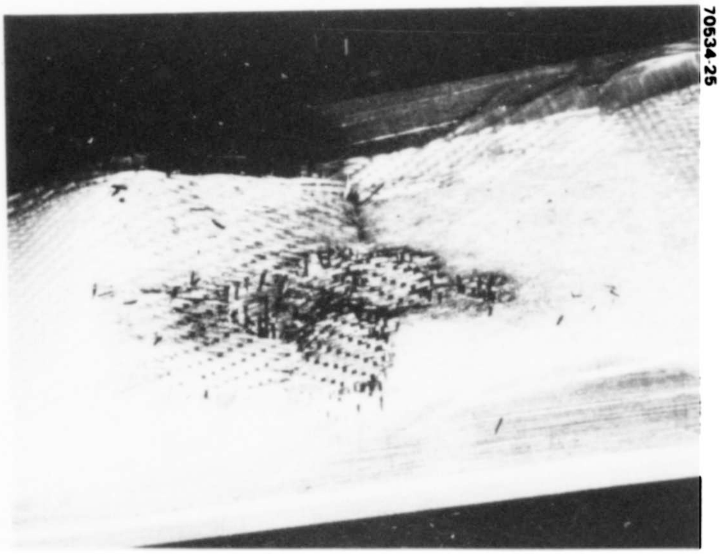


FIGURE 23. CT-3 AFTER 45° PEEL (EXPOSED QUARTZ/QUARTZ)
MAGNIFICATION: 3X; ETCH: NONE

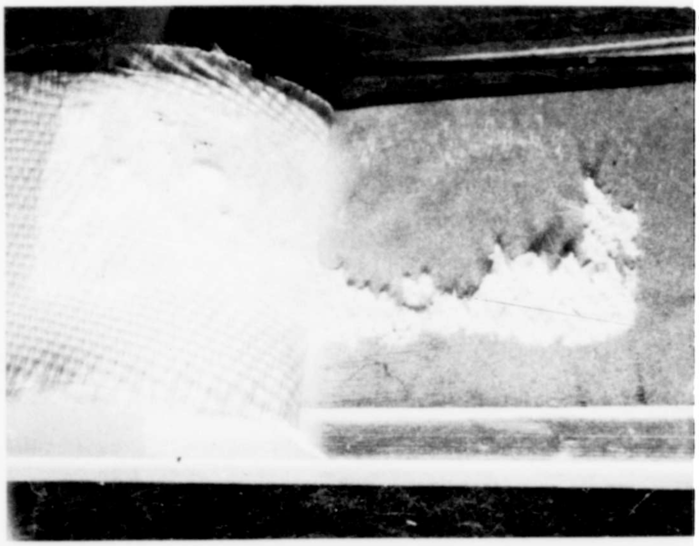


FIGURE 24. CT-7 AFTER 45° PEEL (UNEXPOSED QUARTZ/SILVER)
MAGNIFICATION: 3X; ETCH: NONE

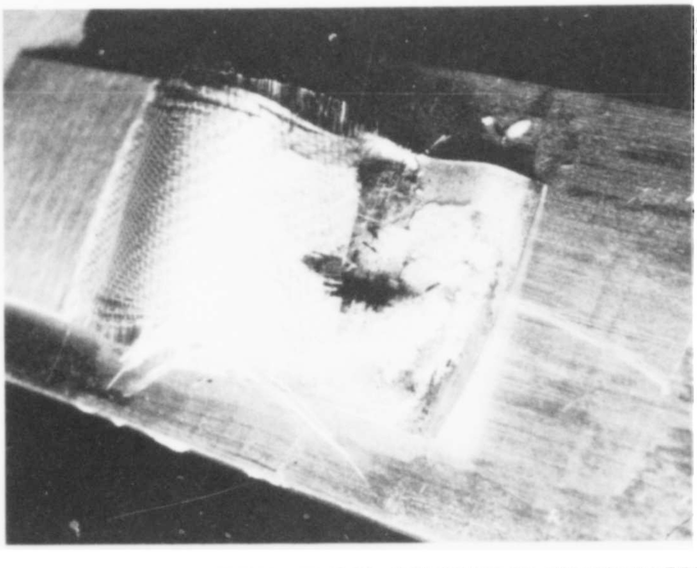
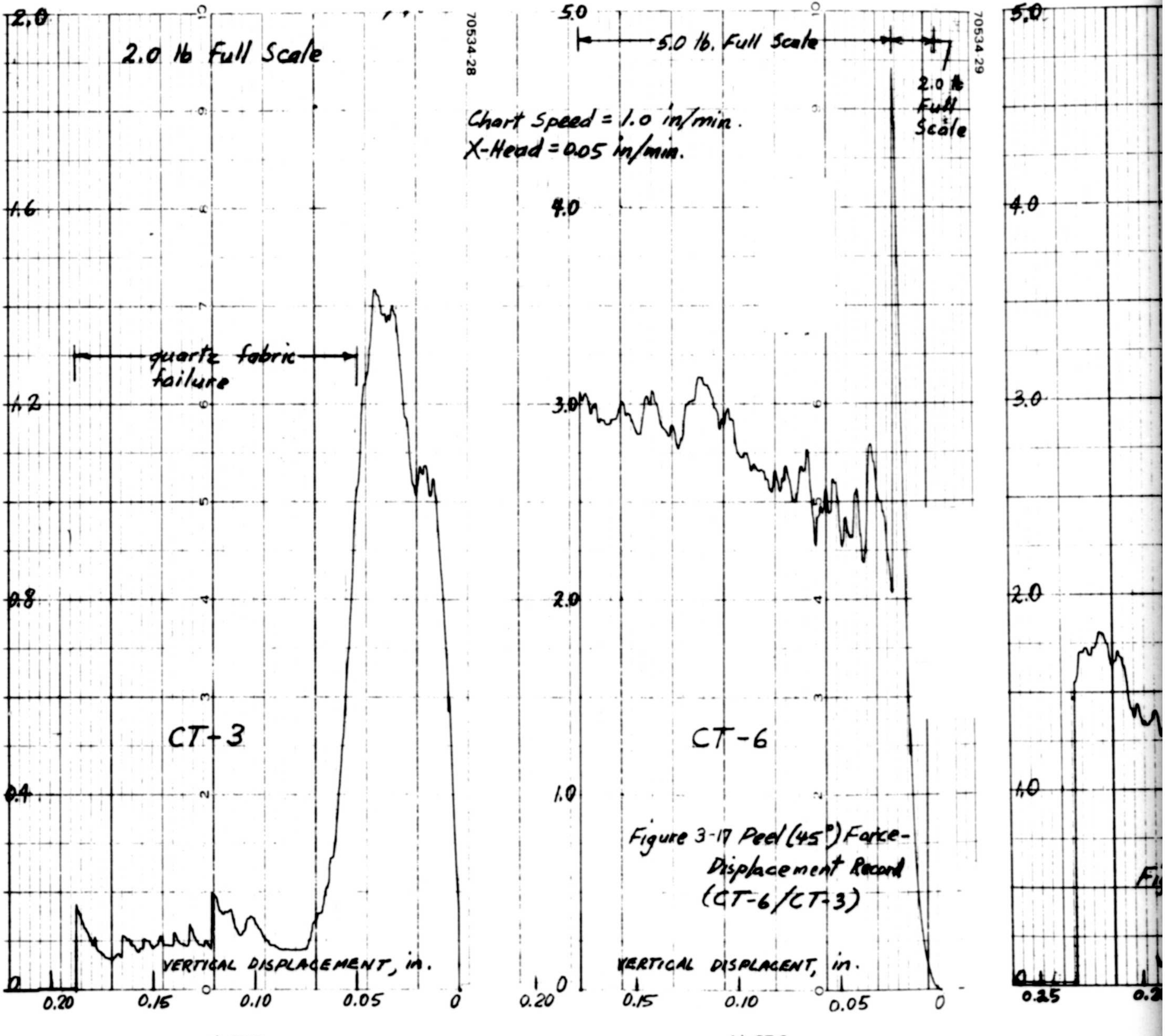


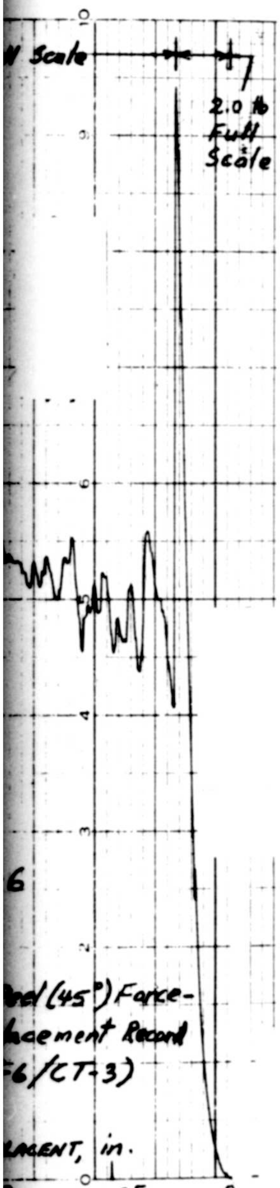
FIGURE 25. CT-4 AFTER 45° PEEL (EXPOSED QUARTZ/SILVER)
MAGNIFICATION: 3X; ETCH: NONE



a) CT-3

b) CT-6

FIGURE 26. PEEL (45°) FORCE-DISPLACEMENT RECORD



eel (45°) Force-
lacement Record
-6/CT-3)

CT-6

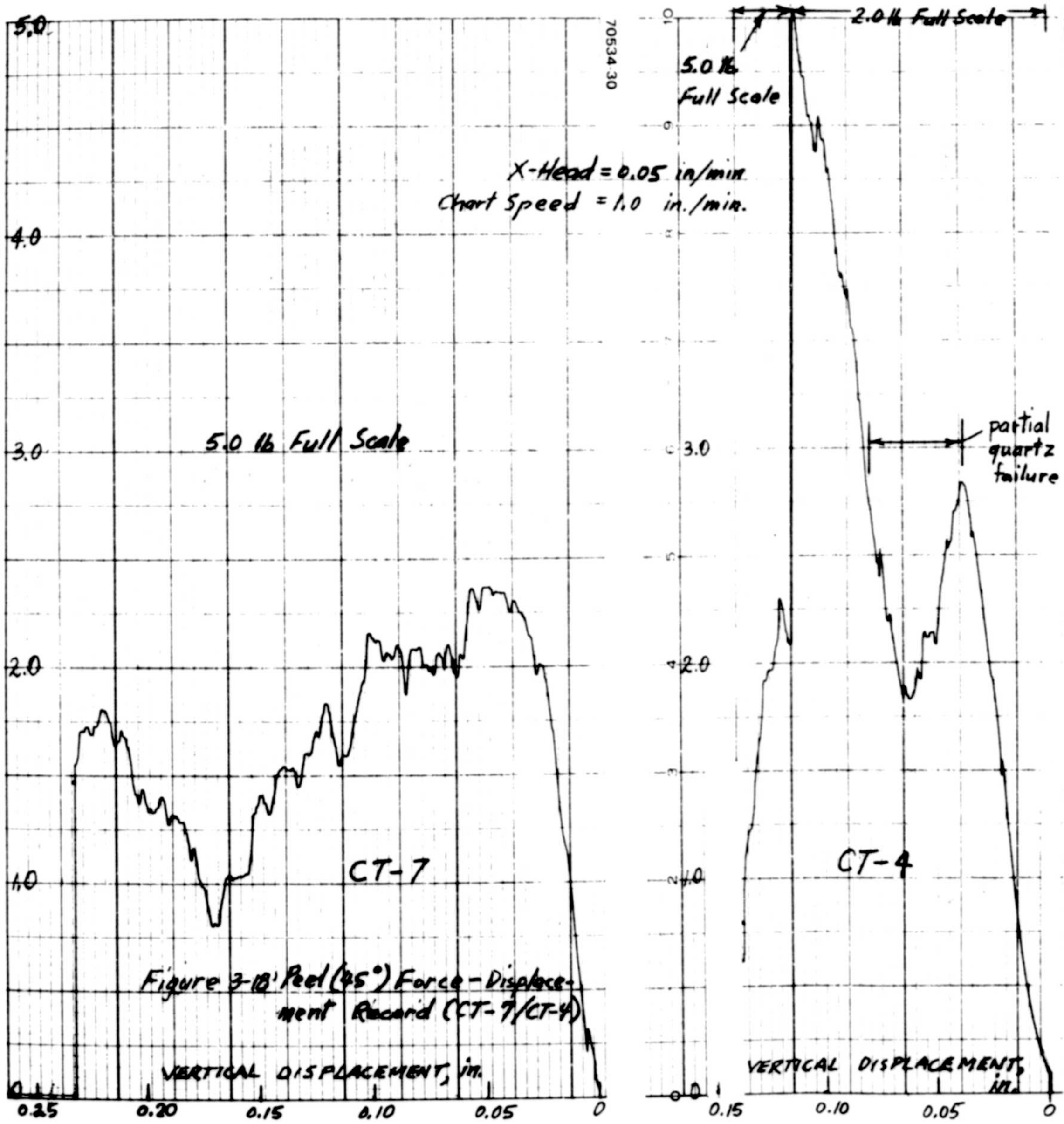
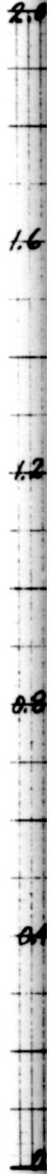
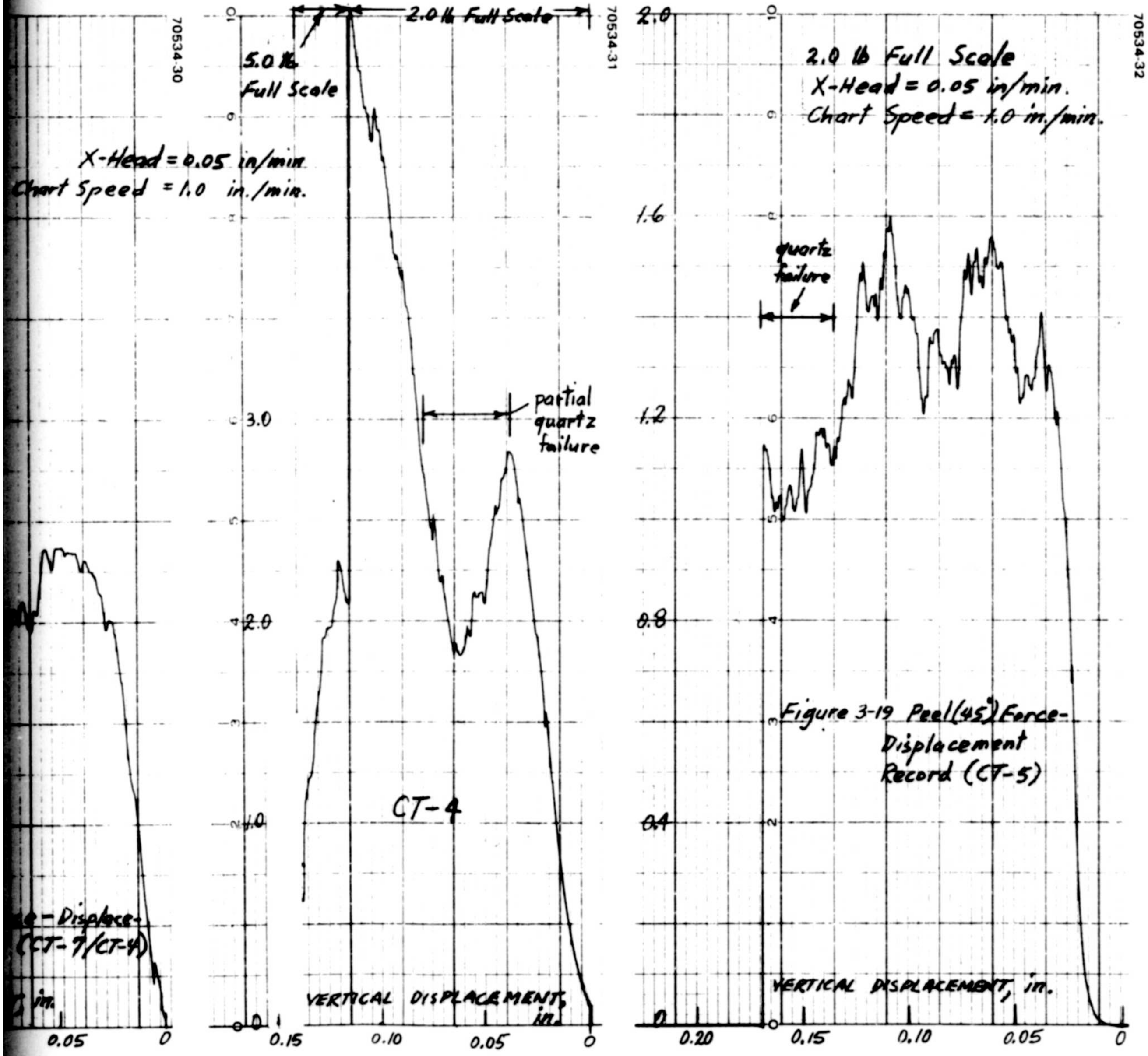


Figure 3-18 Peel (45°) Force-Displacement Record (CT-7/CT-4)

c) CT-7

d) CT-4





d) CT-4

e) CT-5

Figure 3-19 Peel(45°) Force-Displacement Record (CT-5)

ATTACHMENT I. UV SPECTROPHOTOMETRIC ANALYSIS FOR "SUBSTITUTED UREA" COPRODUCT IN UNFORMULATED UCARSIL POLYMERS

Revision A,
1/10/77

1. INTRODUCTION

UV analysis for the "substituted urea", N-phenyl-1-pyrrolidinecarboxamide (also termed N-pyrrolidino-N'-phenylurea), is based on detection of the UV absorption band associated with the phenyl-N< entity. As dissolved in the recommended solvent, 1,2-dichloroethane ($ClCH_2CH_2Cl$), the band peak is displayed at a wavelength of 245 nm (millimicrons) for the pure "urea". This band location is shown in Figure 27 for the case of "urea" contamination of an all-methyl carborane siloxane polymer (10615-104), where curves A and B are differing concentrations of the as-received condition, and curve C represents "urea" additions to the curve B polymer solution. Similarly, curve 1 in Figure 28 displays the as-received condition for a methyl phenyl polymer (10615-98), and curves 2-4 represent "urea" additions to the as-received polymer. Data analysis indicates no interference at 245 nm (the "urea" band) from the band structure located at wavelengths greater than 250 nm associated with the phenyl constituent in the methyl phenyl polymer. The proviso is that the concentration of methyl phenyl polymer be kept relatively low, e.g., an order of ≤ 5 mg per 10 ml of solution.

2. PROCEDURE

A Model 202 Perkin Elmer UV/VIS spectrophotometer has been used. Specimen solution is contained in a 1.0 cm path length, fused silica, optical transmission cell; 1,2-dichloroethane (spectroscopic grade only) is the recommended solvent. Chloroform and methylene chloride should not be used because their low wavelength cutoff is unacceptable. The procedure is as follows:

1) Turn on UV lamp. Allow to warmup for approximately 10 minutes.

2) Set gain and balance controls in accordance with manufacturer's specifications.

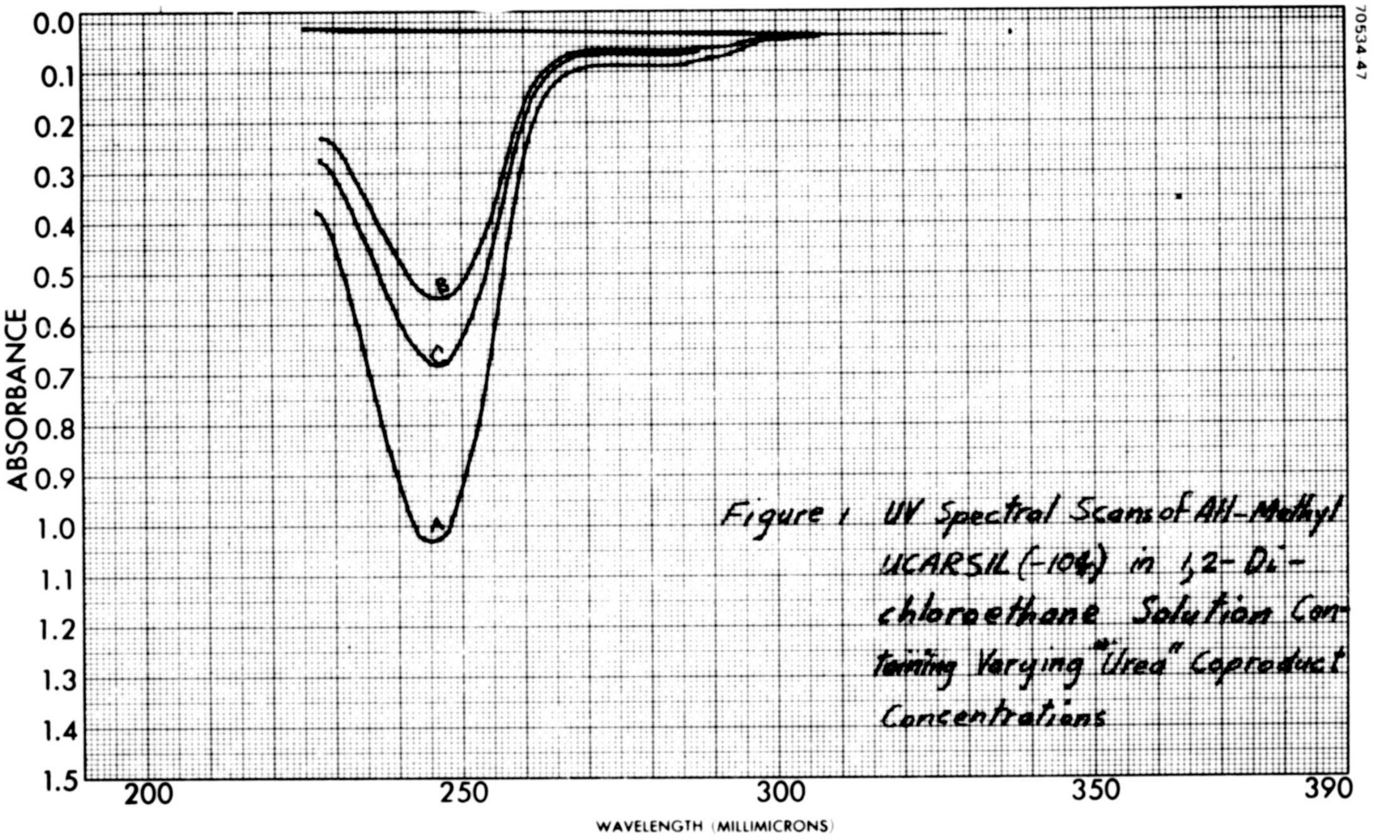


FIGURE 27. UV SPECTRAL SCANS OF ALL-METHYL UCARSIL (-104) IN 1,2-DICHLOROETHANE SOLUTION CONTAINING VARYING "UREA" COPRODUCT CONCENTRATIONS

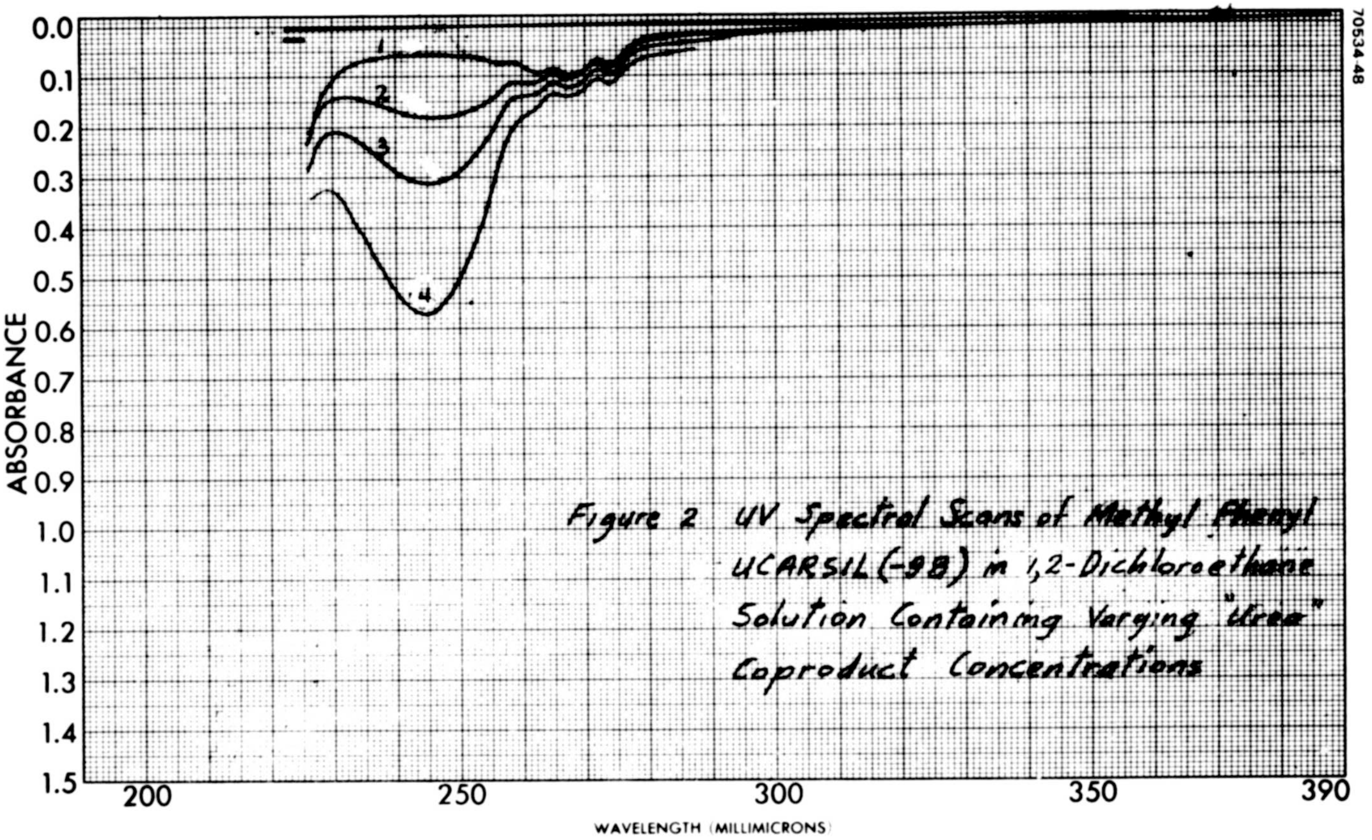


FIGURE 28. UV SPECTRAL SCANS OF METHYL PHENYL UCARSIL (-98) IN 1,2-DICHLOROETHANE SOLUTION CONTAINING VARYING "UREA" COPRODUCT CONCENTRATIONS

3) Place spectroquality 1,2-dichloroethane in the 1 cm silica cells in both the sample and the reference beam. Run a baseline between 225 nm and 310 nm.

4) Carefully weigh out an amount of polymer in the range 2-5 mg into a 10 ml volumetric flask. Add approximately 8 ml of 1,2-dichloroethane and swirl carefully until polymer specimen is dissolved. Add 1,2-dichloroethane until solution volume is exactly 10.0 ml.

5) Place a portionof this solution (in a cell) in the sample beam, leaving the pure 1,2-dichloroethane in the reference beam. Scan between 225 nm and 310 nm.

3. "UREA" DETERMINATION

The estimate of the "urea" content is made from the measured band peak absorbance A as follows:

$$\ell n\, I_o/I = A = \varepsilon bC = \varepsilon b\,(c/190)$$

where

ε = molar absorptivity, cm^2/g-mole

ℓ = 1.9×10^4 cm^2/g-mole

b = path length = 1 cm

C = "urea" concentration, g-mole/ℓ solution

c = "urea" concentration, g/ℓ solution

Thus, $c = A/[1.9 \times 10^4/190] = 0.01A$ g "urea"/ℓ. Concentration of "urea" in polymer = c/polymer concentration in solution. Example (see Figure 1, curve B):

$$A = 0.531;\ c = (0.01)\ 0.531 = 5.31 \times 10^{-3}$$

$$\text{"Urea" concentration} = \frac{5.31 \times 10^{-3}}{(0.00275)(1000/10)} \times 100 = 1.9\% \text{ by wt.}$$

	UCARSIL		"Urea" Content, % by vt.	
No.	RV	$\overline{M}_w$	All-Methyl	Methylphenyl
-104	0.2	5.0×10^4	1.93	--
-104-1	0.2	5.0×10^4	0.039	—
-104-2	0.2	5.0×10^4	0.029	—
-128	0.17	—	0.01	—
-111	0.48	1.4×10^5	—	0.21
-126	0.33	—	—	0.10
-110	2.34	4.0×10^6	—	0.11
-80	3.6	10.0×10^6	—	0.14
-98	3.87	10.0×10^6	—	0.23
-117	3.59	10.0×10^6	—	0.16
-81		$\sim 3.0 \times 10^6$	—	?

*U.S.Government Printing Office: 1978 — 757-080/594