

Surface Analysis of Sheet Molded Composite (SMC)
Material as Related to Adhesion

by

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(ABSTRACT)

The surface chemical properties of Sheet Molded Composite (SMC) materials, formulated to contain polyester binder, calcium carbonate filler, and glass fibers, have been investigated with emphasis on how the surface properties are related to adhesion. These surface properties, relative elemental concentrations and their chemical states, were studied using x-ray photoelectron spectroscopy (XPS) before and after a series of surface treatments as well as after mechanical lap shear fracture tests for SMCs bonded with urethane adhesive. Surface chemical functionalities, including $-C-O-R(X)$ / $-NCO_2R$ and $-C=O$ (ester carbonyl) groups, were found to promote good adhesion using urethane adhesives. These chemical functionalities were particularly enhanced after treating the SMC surface with an isocyanate primer as well as after a solvent/abrasive surface pretreatment done with a Scotch Brite abrasive pad soaked in methylene chloride and after washing the SMC surfaces with hot aqueous chemicals at high pressures.

To those who choose to BE

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I. Introduction

Molded composite materials are becoming more prevalent in applications where once only metal components were utilized. The auto industry is especially interested in these materials due to their advantages over metal, namely: reduced weight, reduced cost, anti-corrosive properties, and ease of fabrication. The joining of the composites is accomplished using a variety of adhesives after one of several surface preparations is performed on the material. The concern of this study is to analyze the surfaces of SMC, using x-ray photoelectron spectroscopy (XPS or ESCA), before and after a series of surface treatments as well as after mechanical lap shear fracture tests for Sheet Molded Composite (SMC) materials bonded with urethane adhesive. By correlating the XPS data; the elements present, the relative concentrations, and the chemical states, with the mechanical fracture tests, it was hoped to determine what chemical and/or mechanical factors are favorable for bonding.

This thesis is divided into five sections. The Historical/Background (1) section discusses some of the bulk properties of SMC: its composition, general properties, and the way it is made. This section also gives a brief theory of adhesion as well as discussing the modes of fracture resulting from the lap shear mechanical testing. A brief discussion of XPS as a surface analytical tool for the study of polymers and inorganics is also given.

The Experimental (2) section gives the details of the surface pretreatments, how the materials were bonded and how they were lap shear fractured. The lap shear fracture tests were carried out under three conditions to examine the strength of the SMC/urethane bond. This section also gives the quantitative details of the XPS surface analysis as well as the analysis procedure undertaken to account for the initial heterogeneous nature of the surfaces.

The Results and Discussion (3) section presents the XPS results for the individual components which comprise the SMC/adhesive system as well as the standards used to provide the necessary information needed in the curve resolution procedure. The information obtained in this section enables the identification of the constituents present on the SMC or adhesive surfaces.

The Pretreatment results (4) section discusses the XPS results of untreated and treated SMC. It is shown in a latter section, as determined by lap shear fracture tests, that some pretreatments enhance bonding better than others. The objective here was to correlate surface features, i.e., the elements present, the relative concentration, and the chemical states, which are indicative of the various pretreatments, in the hope of pinpointing which feature(s) promote good adhesive bonding as well as discerning any surface chemical features among seven different SMC materials.

The next section (5) presents the complete results of the lap shear tests for various combinations of urethane adhesive, SMC substrate, surface pretreatments, and lap shear conditions. It shows that several

surface pretreatments enhance bonding under all the lap shear conditions studied as compared to no pretreatment.

It is hoped that the information contained in this study can be used further to help develop new adhesives or pretreatments that give the desired surface properties which promote good bonding.

II. History/Background

SMC: Composition/Manufacture

The term sheet molded composite (SMC) comprises a wide range of polyester resin, thermosetting, molded materials usually reinforced with short glass fibers randomly arranged in the resin. There are two primary reasons for using glass fibers in SMC. The fibers improve the mechanical/physical properties of the materials, e.g., tensile modulus, dimensional stability, fatigue endurance, deformation under load, and hardness. They also reduce the cost of production by replacing expensive resins with relatively inexpensive glass fibers. The SMC composite system is based on styrene monomer as a crosslinking agent and unsaturated polyester resin. It is both a fibrous and particulate reinforced system. A typical composition is shown in Table 1 [1].

SMC is usually fabricated by compression molding but with the necessary equipment injection molding is also possible. The molding of the fiber reinforced thermoset components is a very complex process involving a strongly exothermic chemical reaction which takes place in the presence of flow and thermal gradients [2,3]. The flow itself is complicated by time and temperature dependent rheological characteristics [4]. Many researchers are currently investigating the mechanisms of SMC manufacturing especially in terms of the basic kinematic mechanisms present in the flow of SMC under manufacturing conditions [5]. These studies are particularly relevant in understanding the general inhomogeneous characteristics of SMC.

Table 1
Typical SMC Composition

| <u>Resin:</u> | <u>% by Wt</u> |
|----------------------------|----------------|
| unsaturated polyester | 10.5 |
| low shrink additive | 3.45 |
| styrene monomer | 13.4 |
| CaCO ₃ (filler) | 40.7 |
| MgO (thickener) | 0.70 |
| Initiator | 0.25 |
| Zinc stearate (lubricant) | 1.0 |
| Glass Fibers (12-50 mm) | 30.0 |

Lap Shear Test [6]

The tensile lap shear tests undertaken in this study measure the failure loads (strength of the bond) and the failure modes. There are three types of failure modes: adhesive failure, cohesive failure, and substrate (delamination) failure. They are shown schematically in Figure 1. It can be seen from Figure 1 that adhesive failure occurs at the adhesive-substrate interface, whereas a cohesive failure occurs within the adhesive itself, and substrate failure occurs within the substrate (SMC). The tensile lap shear test is a quick and convenient way to test the failure loads and failure modes of adhesive/adherend systems.

General Principles of Adhesion

The basic thermodynamic theory of adhesion states that substrates with higher surface energies will tend to attract materials of lesser surface energies in order to lower the net energy of the system. This implies that substrates with low surface energies will not attract adhesive as well as materials with high surface energies as they are already at a low energy state (e.g., Teflon and SMC with low energy organic components at the surface). Substrates with high surface energies are preferred [7].

Surface roughness also increases adhesive strength by enhancing the mechanical properties of the bond as well as by increasing the surface area [8]. Primers applied to surfaces before bonding can also markedly increase the adhesive properties of the system as they react with the

FAILURE MODES

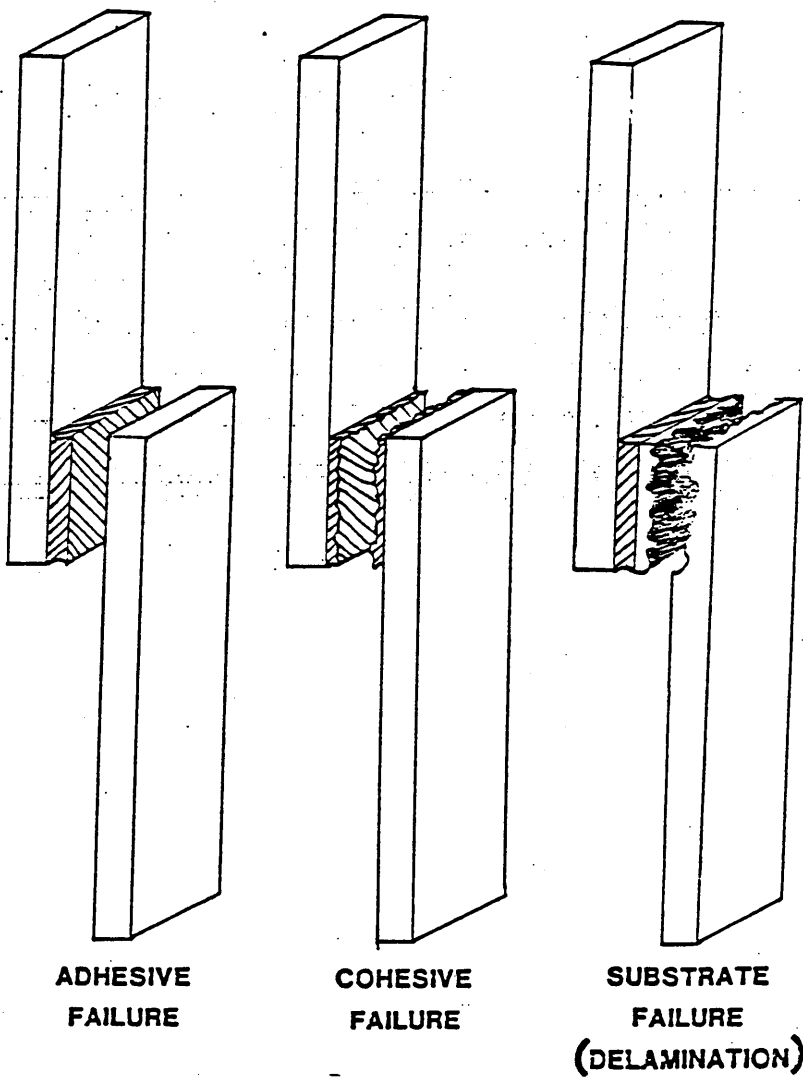


Figure 1. Lap Shear Failure Modes

adherend to give a product which subsequently reacts with the adhesive forming a tight bond.

Bond failures can be the result of many factors. Three basic scientific explanations for bond failure would be: 1) the inability of the adhesive to wet the substrate adequately (if at all), 2) the presence of surface impurities that inhibit bonding, or 3) surface pretreatments that alter the surface chemical functions responsible for adhesive bonding.

General Principles of XPS

The major analytical tool used in this study, x-ray photoelectron spectroscopy involves precise measurement of the kinetic energy of photoelectrons emitted from a sample which is irradiated with x-rays. The measured kinetic energy is related to the binding energy of the electron in the sample and is a function of the element irradiated and its chemical environment. The binding energy of the electron from a particular orbital is determined from the following equation:

$$E_{\text{binding}} = h\nu - E_{\text{k.e.}} - \phi$$

where $h\nu$ is the energy of incident x-ray (e.g., 1254 eV for Mg $K\alpha$), $E_{\text{k.e.}}$ is the kinetic energy of the emitted electrons, and ϕ is the spectrometer work function. The work function also takes into account any charging that occurs on the sample.

XPS is an extremely sensitive surface technique. The depth in a sample from which electrons originate is very limited as the electrons cannot experience any inelastic collisions prior to being analyzed.

Typically, the sampling depth is not more than 50 Å but can be limited further by varying the angle the sample makes with analyzer (angle resolved XPS) [9].

Characterization of Polymers

XPS is becoming increasingly more prevalent as an analytical technique in the analysis of polymeric materials. Numerous fundamental studies on well-characterized polymers give results which correlate well with molecular orbital calculations [10]. These results established that with absolute and relative binding energies and relative peak areas (intensities) the elucidation of many important aspects of polymer surface chemistry is possible. Table 2 summarizes the information available from the XPS technique. All of the features present in Table 2 apply to inorganics as well except that satellites are not

$\pi \rightarrow \pi^*$.

Numerous precautions must be considered when dealing with XPS as the bombarding of the sample with x-rays in a high vacuum environment can alter the sample and result in erroneous data, especially with polymeric materials. Volatility and thermal decomposition can be minimized by cooling the sample with liquid nitrogen, but when photodecomposition is indicated, it may be necessary to extrapolate binding energies and peak shapes to zero exposure time [11]. The effects of charging of insulating samples (e.g., SMC) and contamination on the surface layer can sometimes be difficult to take into account as the binding energies will be altered. However, with good

Table 2Principal Features in the XPS Spectra of Polymers

| <u>Spectral Feature</u> | <u>Information</u> |
|-----------------------------|-------------------------------------|
| Main Peak Position | Atom identification |
| Peak-area ratios | Stoichiometry |
| Shake-up satellites | $\pi \rightarrow \pi^*$ transitions |
| Chemical shift ¹ | Oxidation state |

¹ the slight perturbation in binding energy relative to the element in its zero oxidation state resulting from an element's oxidation state.

standards the experimental parameters in XPS such as binding energies can be adjusted to provide useful data. This adjustment often involves referencing all the binding energies in the spectra to one well-defined peak which is always present, often the hydrocarbon photoelectron peak. Much more information can be obtained by curve fitting the various photoelectron peaks according to the oxidation states present. For instance, the carbon 1s photoelectron peak of polymethylmethacrylate (PMMA) can be resolved into its three distinguishable carbons, namely; hydrocarbon (CH_n), ether carbon (C-O-R), and ester carbonyl (C=O). From the area ratio calculations of each resolved peak, the stoichiometry can be elucidated.

III. Experimental

Sources of SMC

The sheet molded composite (SMC) samples used in this study were supplied as specimens cut from auto deck lids. Four different manufactures supplied SMC coupons and were designed by the code numbers listed in parenthesis: SMC-1, SMC-2, SMC-3, and SMC-4. All SMC samples were formulated with 4.5% zinc stearate mold release agent. These SMC materials contained low profile additives such as polymethylmethacrylate, polyvinyl acetate, or polystyrene in various proportions that enhance the surface smoothness. In addition to these, samples were also supplied differing in the amount of zinc stearate. They are referred to as "old" SMC with zinc stearate amounts of 3.0, 4.5, and 6.0%. All specimens received had dimensions of 1"x4" with a thickness of approximately 1/4". All samples were further cut using a low speed diamond impregnated saw while the region to be analyzed was wrapped in aluminum foil. The aluminum foil is necessary to prevent SMC dust created during the cutting process from settling on, and thus contaminating the surface to be analyzed. The cut samples had areas varying from approximately 15x17 mm to 12x12 mm. The XPS photon beam covers this whole sample area but only a 10 mm x 2 mm area is actually sampled by the analyzer electron optics. All samples were degassed for 10 hours or more on a diffusion pumped vacuum line trapped with liquid nitrogen before introduction into the XPS analysis chamber.

Surface Pretreatments

One of the following pretreatments was applied to the SMC surface:

- A: No treatment: bonded or XPS analyzed as received, after dusting with a Kim-wipe tissue.
- B: Methylene chloride wipe: a light hand wipe (3 times) with a Kim-wipe soaked in CH_2Cl_2 .
- C: Solvent/Abrasive wipe: a light hand wipe (3 times) with a Scotch Brite abrasive pad soaked in CH_2Cl_2 followed by a CH_2Cl_2 wipe.
- D: Primer wipe: a light hand wipe (3 times) with Kim-wipe soaked in an isocyanate primer (solvent is CH_2Cl_2).
- E: Flame Treatment: SMC (old) was passed through a reducing flame generated using a Meeker burner; the approximate velocity of the SMC through the burner flame was 30 ft/min.
- F: Power Wash: SMC sample coupons (1"x4") were treated by the respective vendors at the vendor sites using vendor procedures, wash solutions, and conditions. Information on the content of the wash solutions is given in Appendix I.

The resulting pretreated samples were either surface analyzed or bonded using urethane adhesive.

In addition to these treatments a thermal treatment of as received SMC was done with the objective of discerning whether surface concentrations of SMC components or additives were altered. This treatment was carried out by placing specimens in a glass tube furnace maintained at 177°C (350°F) under a 70 cc/min flow of "breathing air" (compressed air). This thermal treatment was conducted for 50 minutes. No adhesive bonding of these specimens was carried out. After the thermal pretreatment Ar⁺ ion sputtering at 4 KeV was done for intervals of 0, 10, 20, 30, 60, and 120 minutes. After each sputtering interval an XPS analysis was conducted. These two surface treatments, i.e., thermal and Ar⁺ sputtering, were used on selected "old" SMC samples.

Nomenclature

Two groups of adhesively bonded specimens were prepared. The first group consisted of "old" SMC samples containing 3.0 and 6.0% zinc stearate mold release agent. They were bonded with one of three urethane adhesives designated 6-, 7-, or 8-adhesive following one of four surface pretreatments. These four pretreatments were: A) no treatment, B) wiping with CH₂Cl₂, C) wiping with a CH₂Cl₂ soaked Scotch Brite abrasive pad, and; D) passing the SMC through a reducing flame at approximately 30 ft/min. Nomenclature of the following form: 6B6, is used throughout for these samples. The first digit refers to the adhesive used, the second digit refers to the mode of pretreatment, and the third digit refers to the zinc stearate level. The complete set of designations for these samples is:

| | | | |
|-----|-----|-----|-----|
| 6A3 | 7A3 | 6A6 | 7A6 |
| 6B3 | 7B3 | 6B6 | 7B6 |
| 6C3 | 7C3 | 6C6 | 7C6 |
| 6D3 | 7D3 | 6D6 | 7D6 |

The second group of bonded specimens was prepared using one of four vendor supplied SMC materials i.e., SMC-1, SMC-2, SMC-3, and SMC-4. All contain 4.5% zinc stearate and were adhesively bonded using either 6- or 8-adhesive. These SMC materials were bonded following pretreatment procedures designated as:

- A: No treatment; bonded as received after dusting with a Kim-wipe tissue
- B: Scotch Brite/ CH_2Cl_2 abrasion followed by methylene chloride wipe
- C: Application of isocyanate primer

The sample nomenclature is illustrated:

61A: 6 - adhesive-6

61A: 1 - SMC-1

61A: A - no chemical surface pretreatment

The complete set of sample designations for this series is:

| | | | | | |
|-----|-----|-----|-----|-----|-----|
| 61A | 81A | 61B | 81B | 61C | 81C |
| 62A | 82A | 62B | 82B | 62C | 82C |
| 63A | 83A | 63B | 83B | 63C | 83C |
| 64A | 84A | 64B | 84B | 64C | 84C |

A series of SMC materials was bonded together using SMC-1 which had been power washed. The wash pretreatment designations are:

| <u>Treatment</u> | <u>Code</u> |
|------------------|-------------|
| Oakite 07 | 007 |
| Oakite 08 | 008 |
| Parker 3B | P3B |
| Chemfil C3 | CC3 |
| Chemfil C23 | CC23 |
| Chemfil C24 | CC24 |
| Chemfil C31 | CC31 |

These samples were adhesively bonded using either adhesive-6 or -8 before any surface pretreatment (designated A) or after the application of isocyanate primer to the surfaces (designated C). An illustration is shown below:

8C008: 8-adhesive-8

8C008: C-bonded after primer treatment

8C008: 008-Oakite 08 power washed

The complete sample nomenclature is:

| | | | |
|--------|--------|--------|--------|
| 6A007 | 8A007 | 6C007 | 8C007 |
| 6A008 | 8A008 | 6C008 | 8C008 |
| 6AP3B | 8AP3B | 6CP3B | 8CP3B |
| 6ACC3 | 8ACC3 | 6CCC3 | 8CCC3 |
| 6ACC23 | 8ACC23 | 6CCC23 | 8CCC23 |
| 6ACC24 | 8ACC24 | 6CCC24 | 8CCC24 |
| 6ACC31 | 8ACC31 | 6CCC31 | 8CCC31 |

Adhesive Bonding

Appropriate pretreated samples were bonded with one of three urethane adhesives: 6-, 7-, or 8-adhesive. Glass spacers of 30 mil were used to provide uniform separation between the bonded pieces. All bonds were cured at 275°C (135°F) for 30 minutes after they remained at room temperature for 30-45 min. In addition the 7- and 8-adhesives were cured under pressure in a double heated fixture.

Lap Shear Tests

Adhesively bonded SMC samples were tested as noted: a) tested at room temperature 72°F (22°C), b) soaked in distilled water maintained at 130°F (54°C) for one week and then tested at 130°F (54°C) immediately after removal from the water bath, and c) maintained at 180°F (82°C) for 1 hour in air in an oven, and then tested at 180°F (82°C) immediately after removal from the oven. Lap shear specimens were tested using an Instron Model 1125 instrument with a cross head speed of 0.1 in/min and a constant grip area.

XPS Sample Introduction

The pretreated samples were placed onto stainless steel sample mounts (1" diameter) which had groves of approximately 1/4" thickness to compensate for the SMC thickness. The SMC was held onto these mounts using double-stick tape. Samples were introduced into the XPS

sample introduction vacuum system where they were initially pumped by a turbomolecular pump. After about 5 min. samples were admitted to the main analysis chamber where they were pumped by an ion pump (360 l/sec) and titanium sublimation pump during the XPS analysis (usually 30-60 min.). The chamber pressure during analysis was between 2×10^{-7} and 5×10^{-8} torr or lower.

Quantitative XPS Information

The XPS spectra of all samples (SMC, components, and standards) were measured using a Perkin-Elmer PHI model 5300 XPS system. This spectrometer uses a hemispherical energy analyzer and a position sensitive detector. The system was run with a Perkin-Elmer PHI 7500 computer system and operated using PHI software. An analyzer pass energy of 44.74 eV was used for wide scans (~1000 eV range) while an analyzer pass energy of 17.89 eV was used for narrow scans (~20 eV range). Photoionization was initiated using Mg K α radiation of energy 1253.6 eV. All XPS results presented here are the result of at least two separate measurements on different samples. The precision of the binding energy measurements is about ± 0.1 eV while that of the relative percent concentrations (including curve fits) is approximately $\pm 10\%$. All spectra were measured with the sample surface at an angle of 53.7° with respect to the x-ray source and 90° with respect to the analyzer.

XPS Analysis Procedure

Following early findings regarding the inhomogeneity of the SMC samples, a procedure was followed to permit a direct comparison of analysis results before and after surface treatment for the SMC-1, SMC-2, SMC-3 and SMC-4 series samples. The adopted procedure was to cut samples from the same and different 1"x4" SMC coupons. These samples were then attached to stainless steel mounts and characterized via XPS. Next the surface was pretreated by either a methylene chloride, methylene chloride/Scotch Brite abrasion, or primer wipe as described earlier. The samples were then reintroduced into the XPS instrument for characterization. Using this procedure a more direct and accurate evaluation of chemical surface changes could be obtained. The nature and logistic arrangements for the flame and power wash treatments did not permit surface analysis of the exact same SMC sample before and after treatment. Instead for the later case, pieces were cut from the same 1"x4" coupon one of which was analyzed without any pretreatment and the other analyzed after the surface pretreatment. No surface analysis of flame treated SMC was done as they were immediately bonded.

Direct comparisons were not performed on the initial "old" SMC materials. Instead of first analyzing the untreated SMC material and then reanalyzing it after the appropriate surface treatment, average values of at least four measurements were obtained from different pieces of SMC before and following surface treatment.

XPS of Components

Urethane 6- and 7-adhesive films of 30 mil thickness and about 24 mm² area were analyzed on flat stainless steel mounts. These films were prepared by placing a shot of adhesive on "waxed" paper and rolling it through a roller set to give a 30 mil thick film. Adhesive-8 was prepared and analyzed. The viscous uncured 8-adhesive resulting from the hand mix was deposited into a groove (14 mm x 10mm x 4mm) cut in a stainless steel sample mount, leveled out, and left to cure. In addition to these studies, urethane 6- and 8-adhesive samples were taken from adhesive that had been cured in a plastic hypodermic syringe tube. The adhesive was removed from the tube after making a small cut at the surface of the cylinder and perpendicular to the longitudinal axis. The adhesive was fractured after being immersed in liquid nitrogen for 5 minutes and one of the fractured surfaces was used to obtain XPS results for the cured adhesive.

SMC resin components containing polyester and polystyrene were analyzed by depositing the resins (resin A and resin B) onto stainless steel probes and waiting until solvent evaporation before analyzes. Glass fibers were mounted on the circular probes using silver print paint on the probe's outer circumferences to hold to fibers in place. No silver was detected in the XPS wide scan survey assuring that the area analyzed was indeed glass fiber and not glass fiber/silver print paint. Isocyanate primer was also analyzed on flat stainless steel and gold coated sample mounts. The primer was applied with a pipette until a sufficient layer remained after solvent evaporation.

Thin films of polymethylmethacrylate (PMMA) and polypropylene standards were XPS analyzed. The PMMA film was cast from acetone. Calcium carbonate and zinc stearate standards were also analyzed by XPS. They were held onto the XPS probe using double stick tape. A comparison of the XPS analysis for the tape alone and for samples on the tape indicated that contributions to the sample spectra from exposed tape components were not significant and did not affect the results for the test materials of interest.

Curve Fitting

For all curve resolution results reported, standard photopeak parameters were evaluated by measuring spectra for polypropylene (C 1s) and polymethylmethacrylate (PMMA) (C 1s and O 1s) films. From these spectra C 1s and O 1s photopeak full width at half maxima (FWHM) values were obtained. Curve resolution techniques and procedures were developed to permit obtaining stoichiometric relationships among carbon and among other elements from photopeak area measurements. Polypropylene was used as a standard to establish the FWHM for the C 1s level. Spectra for PMMA were analyzed to develop the procedures for extracting chemical speciation information from photopeaks containing multiple components. PMMA is a particularly suitable material since it contains $-CH_n$, $-C-O-R$, and $-C=O$ (ester carbonyl) functional groups; groups which are of importance in this study. The curve fitting procedure assumed peaks of Gaussian shape, FWHM values of 1.55 ± 0.1 eV for carbon and 1.8 ± 0.1 eV for oxygen, and that values for components in SMC and in the adhesives

were equivalent to those found for the PMMA and polypropylene standards, i.e., 1.55 ± 0.1 eV for C 1s and 1.8 ± 0.1 eV for O 1s.

Data Calculations

All binding energies were referenced to the hydrocarbon (CH_n) portion of the C 1s peak taken as 284.6 eV. This is natural consequence of the fact that the CH_n peak is usually the most well defined and discernable peak for all the samples studied. The accuracy for the binding energies of each peak is about 0.1 eV or better. Peak areas were calculated using PHI software by first smoothing all peaks and then inputting the integration limits as determined precisely by a computer cursor. The areas were not necessarily taken between the same energy limits (B.E.) as the FWHM varied slightly as a function of surface pretreatment. The resulting areas obtained were then corrected for their photoionization probabilities by dividing each by its photoionization cross section. These cross section values for C 1s, O 1s, Zn 2p, Si 2p, Ca 2p, and N 1s are 1.0, 2.85, 18.0, 0.855, 3.08, and 1.77 respectively [12]. The relative percents were then calculated by dividing the corrected area of each element by the corrected area of carbon and then multiplying by 100%. The expected precision for these areas is judged to be within 10%.

SEM Photomicrographs

To obtain information on the topographical nature of fractured/unfractured SMC surfaces SEM photomicrographs were taken using a

Perkin-Elmer/PHI Model 610 AES/SIMS instrument. The SMC material was lightly sputter coated with gold and clamped to a stainless steel mount with aluminum conducting strips to help minimize charging. The gold sputtering lasted for 30 seconds at 1 kV and 5mPa pressure and was on an Edwards model S150E sputter coater. The remainder of the mounting procedure was identical to that described for the XPS system except that the sample was analyzed (photographed) at 90° with respect to the electron gun and at 15° with respect to the secondary electron detector. The electron gun parameters were: beam voltage = 4 kV, filament current = 2 amps, and an emission current of 0.05 mAmps. Photomicrographs of magnification 200x and 800x were taken. A cursory attempt was made to obtain elemental maps of the fractured surfaces, but these attempts were frustrated by sample charging. To obtain such maps newer experimental procedures must be employed.

IV. Results and Discussion

To help in the understanding of what materials comprise the SMC surface, individual pure components of the SMC matrix were analyzed via XPS. Pure isocyanate primer which was used in one of the surface pretreatments was also XPS analyzed.

XPS Results of Isocyanate Primer

Table 3 shows XPS data for isocyanate primer deposited on stainless steel mounts and gold coated stainless steel mounts. Also shown in Table 3 are the carbon 1s curve resolution results. Peaks C_1 , C_2 , and C_3 are indicative of CH_n , $-C-O-R/-NCO$, and $-C=O$ (ester carbonyl) moieties, respectively. The primer contains only oxygen, nitrogen, and carbon in detectable amounts (>0.1 atomic percent). From the results of Table 3 it appears that the primer has reacted slightly on either the stainless steel surface or on the gold coated surface. That a reaction of some sort has occurred is best evidenced by the differences in $C-O-R/NCO$ concentration, i.e., 14.7 and 20.1 percent for primer on the stainless steel versus primer on the gold surface. The exact nature of this apparent reaction is not known however oxidation of Au^0 to $Au(I)$ might be possible by an isocyanate. Figure 2 shows the unresolved C 1s spectra for the primer on each surface indicating the presence of at least three different carbon species for each. The nitrogen binding energies (400.2 and 400.0 eV for primer on stainless steel and on Au, respectively) are in the range for $-C-N$ or $-C=O$ groups [13].

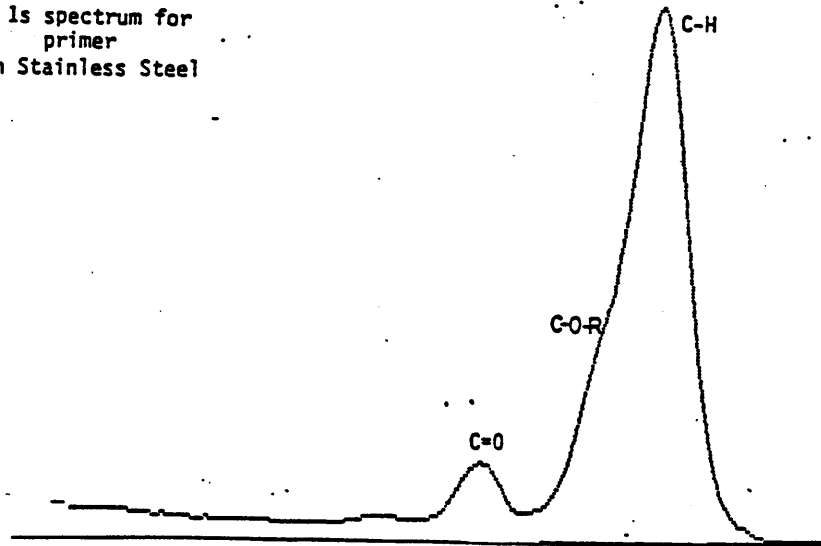
Table 3XPS Analysis Results for SMC ComponentsIsocyanate Primer on Stainless Steel/and on Au Coated Stainless Steel

| <u>Element</u> | <u>Relative Concentration</u> | <u>B.E.(eV)</u> |
|---------------------------------|-------------------------------|-----------------|
| $C_1=CH_n$ | 77.6/74.1 | 284.6/284.6 |
| $C_2=-C-O-R/-NCO$ | 14.7/20.1 | 286.0/286.1 |
| $C_3= -C=O$ (ester carbonyl) | 7.8/5.8 | 288.8/288.9 |
| C_t (total) | 100/100 | ---/--- |
| O | 16.3/14.7 | 532.6/532.5 |
| N | 10.6/7.7 | 400.2/400.0 |

Zinc Stearate

| <u>Element</u> | <u>Relative Concentration Experimental/Calcuated</u> | <u>B.E.(eV)</u> |
|----------------|--|-----------------|
| $C_1=CH_n$ | 94.0/94.4 | 284.6 |
| $C_2=-CO_2^-$ | 6.0/5.6 | 288.8 |
| C_t (total) | 100/100 | --- |
| Zn | 2.6/2.8 | 1022.6 |
| O | 10.6/11.1 | 531.9 |

C 1s spectrum for
primer
on Stainless Steel



C 1s spectrum for
primer on Au

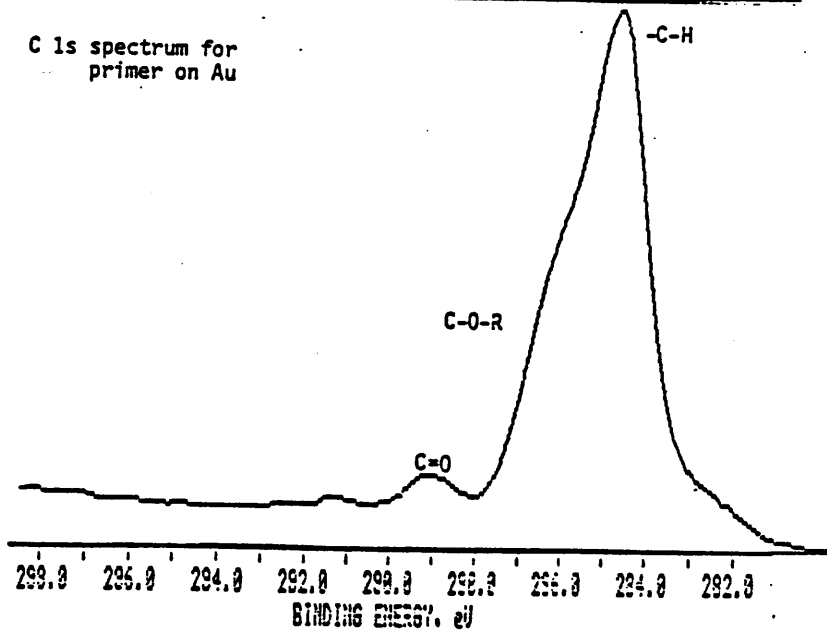


Figure 2. Carbon 1s Spectra for Primer on Stainless Steel and on Au Coated Stainless Steel

XPS Results of Zinc-Stearate Powder

The zinc stearate powder (Table 3) gave relative concentrations of carbon, zinc, and oxygen in accord with its chemical formula. The C 1s spectrum exhibits evidence for carboxyl carbon (B.E. = 288.8 eV) of a level of 6.0% as determined from curve resolution results. This is in accord with the formulation of zinc-stearate, $Zn(CH_3(CH_2)_{16}COO)_2$.

XPS of Urethane Adhesives: Thin Films and Bulk

XPS analysis results for the adhesive films are shown in Table 4. The films were prepared as described in the experimental section. Especially interesting is the appearance of silicon in significant quantities. Figure 3 shows unresolved C 1s spectra for the three adhesive films of Table 4. The spectra indicate the presence of two major carbon functionalities, C-O-R/-NCO₂R and CH_n. A third component appears at 288.9 eV which could be attributed to ester carbonyl carbon or to a carbon shake-up satellite feature. For each adhesive film the C-O-R/-NCO₂R carbon content is slightly greater than that for CH_n-type carbon. Binding energies for silicon (-102.2 eV) are typical of those for organosilicon polymers/compounds (R₂SiO)_n [14]. The nitrogen 1s binding energy results are indicative of -C-N or -NCO₂R groups. For nitrogen and silicon the peak width at half maximum (FWHM) is indicative of the presence of only one type of nitrogen or silicon (Figure 4).

Table 4

XPS Results for 6-, 7- and 8-Adhesive Films and Fractured Cylinders
(Relative Atomic Percent)

| Element | <u>Films</u> | | | <u>Fractured</u> | |
|------------------------|--------------|------|------|------------------|------|
| | 6 | 7 | 8 | 6 | 8 |
| $C_1 = CH_n$ | 46.5 | 47.2 | 46.2 | 50.1 | 53.6 |
| $C_2 = -C-O-R/-NCO_2R$ | 51.0 | 50.6 | 50.8 | 45.9 | 43.4 |
| $C_3 = -C=O$ | 2.5 | 2.2 | 3.0 | 4.0 | 3.0 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 |
| O | 30.3 | 30.8 | 30.2 | 67.9 | 35.7 |
| N | 3.3 | 3.7 | 3.0 | 3.2 | 4.0 |
| Si | 0.6 | 1.6 | 0.17 | 37.9 | 10.0 |
| Mg | 0.1 | 0.1 | 0.1 | 15.4 | 0.1 |
| Al | 0.1 | 0.1 | 0.1 | 15.0 | 2.5 |

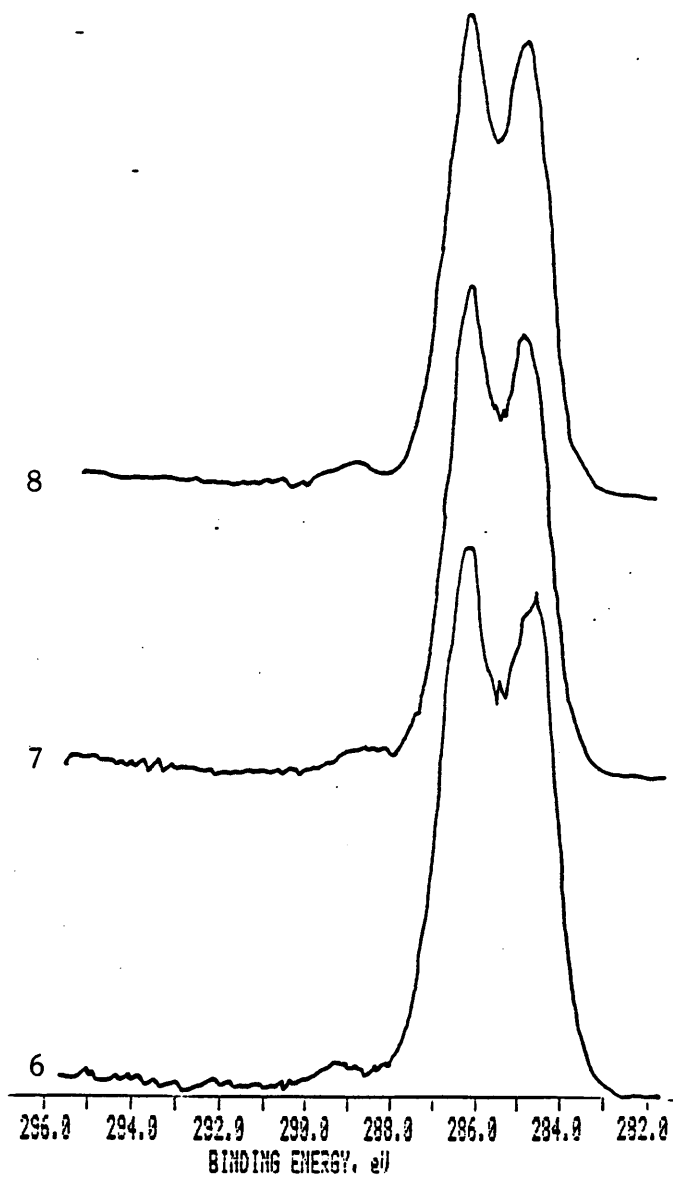


Figure 3. C 1s Spectra for Urethane Films 8, 7, and 6.

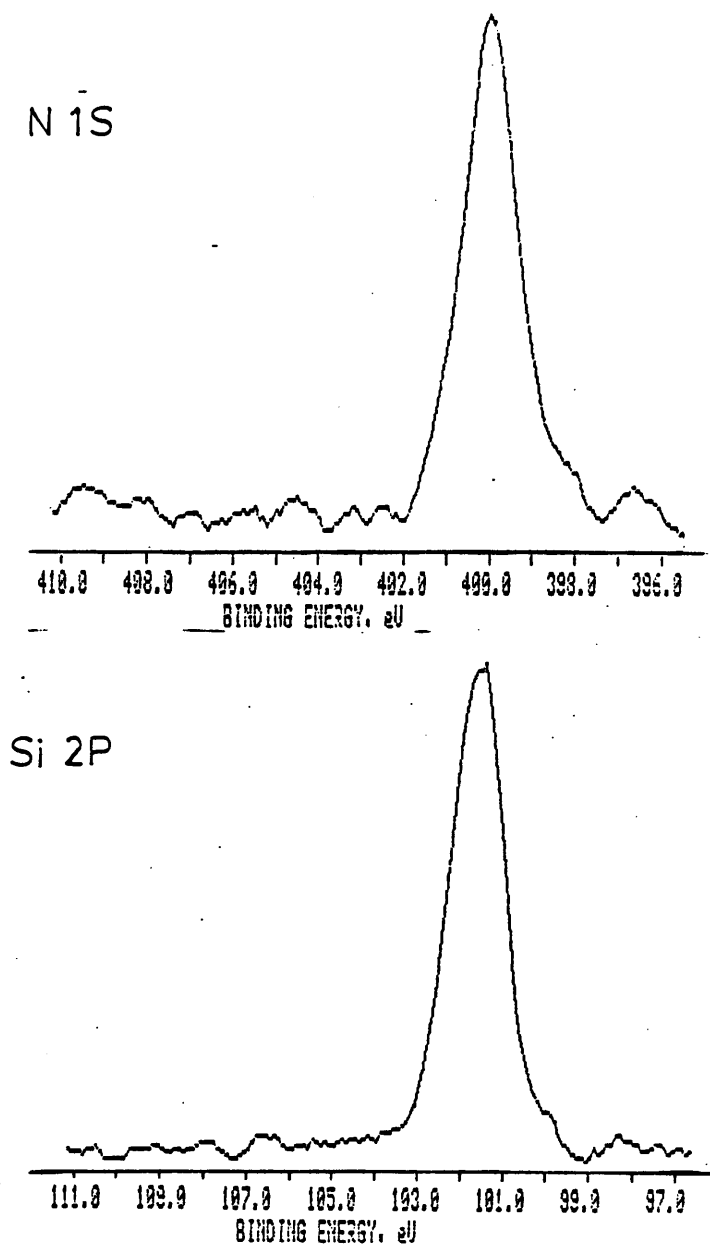


Figure 4. N 1s and Si 2p Spectra for a Urethane Adhesive Film

These characteristic binding energies and spectral peak shapes will be particularly useful in the determination of the chemical nature of the fractured samples.

In addition to studying the films of the 6-, 7- and 8-adhesives, XPS analysis of 6- and 8-adhesive surfaces provided by fracturing cured adhesive from cylinders of one inch diameter was performed. The measurements are also presented in Table 4. A cursory examination of the results in Table 4 and the spectra in Figure 5, which compares wide scan spectra of 6-adhesive film and fracture specimens, reveal significant differences in the XPS results obtained for the 6-adhesive film and fractured specimens. Specifically the fractured adhesive shows significant amounts of silicon, magnesium, and aluminum in relative concentrations of 37.9, 15.4, and 15.0 percent, respectively. The corresponding film shows only a slight amount of silicon (0.6 relative percent.) The 8-adhesive film and fractured samples show similar differences as seen from Table 4. The reasons for these differences are not known at this time but a likely answer could be that fracture after $N_2(l)$ immersion occurs along a weak interphase consisting of a high concentration of inorganic substituents. The reported results are reproducible for each sample so it can only be concluded that the surface properties obtained in preparing the samples are different. As will be discussed in the section on fractured materials, the analysis of fractured (lap shear) SMC surfaces containing residual adhesive films yields results similar to those obtained for prepared film samples. For lap shear specimens high concentrations of silicon, magnesium or

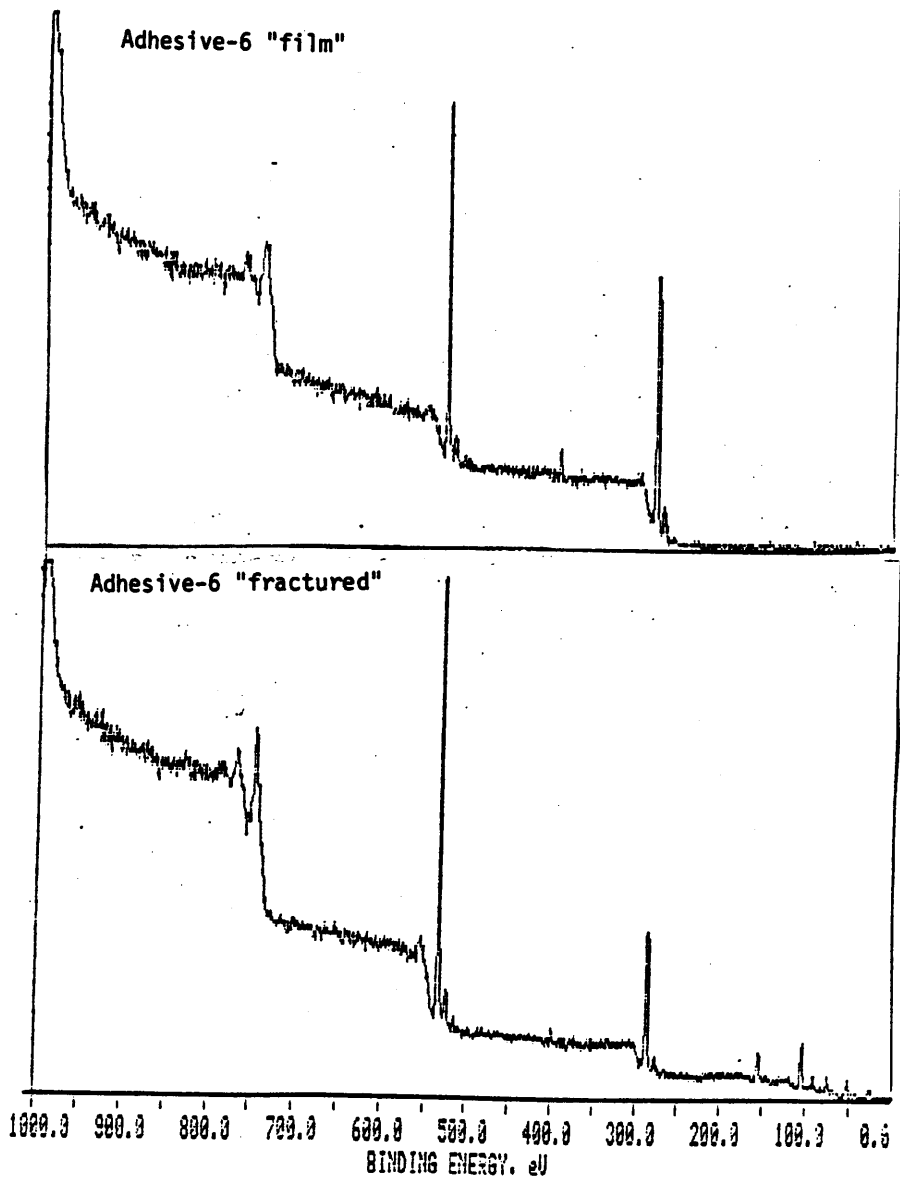


Figure 5. XPS Wide Scan Surveys Comparing Film/Fracture Adhesive

aluminum are not detected. Thus at this point one can only suggest that the internal surfaces on the adhesive cured cylinder do not represent the chemical nature of adhesive at the fractured surface.

XPS of Polypropylene and Polymethylmethacrylate Standards

For the curve resolution procedures reported here, standard photopeak parameters were evaluated using polypropylene and polymethylmethacrylate (PMMA) (C 1s and O 1s) films (Figure 6). From the PMMA the C 1s FWHM and binding energies for the CH_n , -C-O-R and -C=O (ester carbonyl) carbon moieties were deduced; the values are: 1.60 and 284.6, 1.55 and 286.2, and 1.55 eV and 288.8 eV, respectively. Table 5 shows a summary of the C 1s and O 1s curve resolved data for PMMA comparing the experimental with calculated values.

XPS of Split SMC and Glass Fiber Component

As mentioned earlier 1"x4" SMC coupons with a thickness of approximately 1/4" were pried apart lengthwise and analyzed. This provided reference data about bulk SMC. As noted in Table 6 split samples only show C, O, and Ca in detectable amounts. That the glass fibers (composed primarily of silicon) are not detected suggests that they are covered by a layer of other SMC components. From the analysis of the pure glass fiber SMC component it was found that the binding energy of the Si 2p photoelectron peak was 102.7 eV.

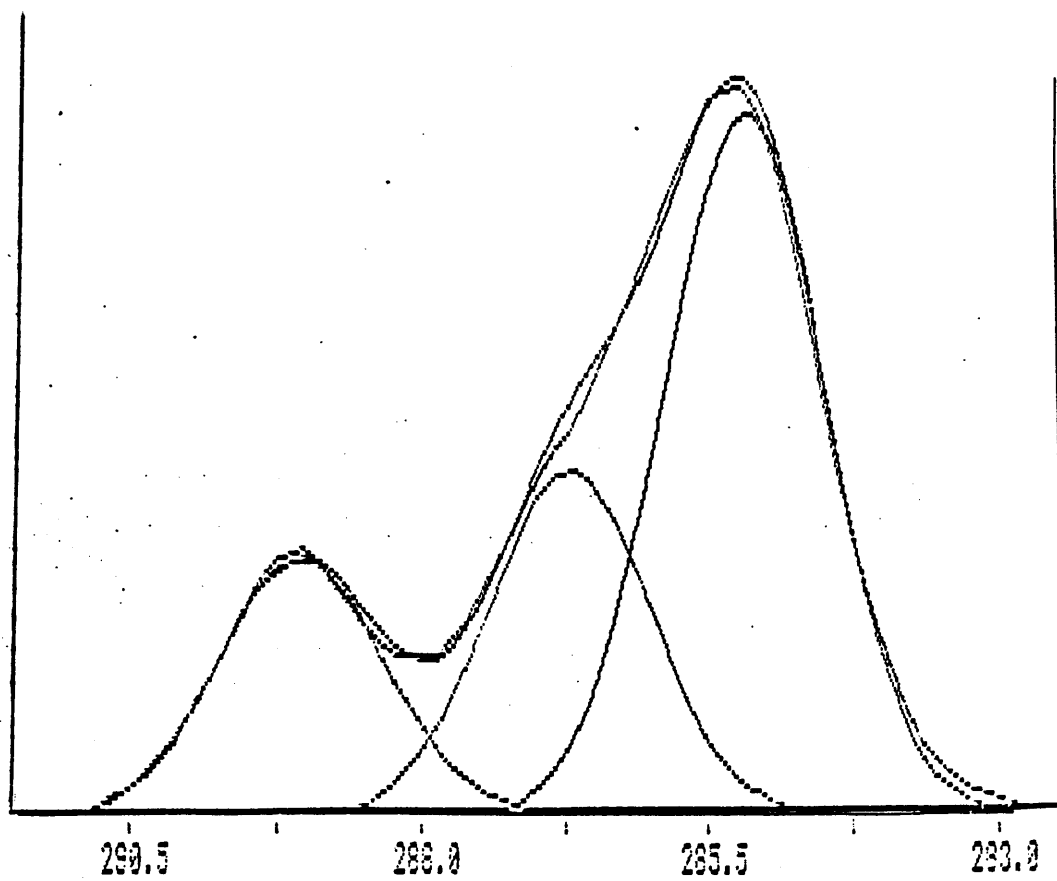


Figure 6. Carbon 1s Curve Resolved Spectrum for Polymethylmethacrylate (PMMA)

Table 5XPS Curve Resolved Data for
Polymethylmethacrylate (PMMA)

| <u>Element</u> | <u>Relative Concentration Experimental/Calculated</u> | <u>B.E. (eV)</u> |
|-------------------------------|---|------------------|
| $C_1 = \underline{C}H_n$ | 2.89/3 | 284.6 |
| $C_2 = -\underline{C}-O-R$ | 1.18/1 | 286.1 |
| $C_3 = -C=O$ (ester carbonyl) | 1.00/1 | 288.8 |
| $O_1 = -C=\underline{O}$ | 1.02/1 | 532.1 |
| $O_2 = -C-\underline{O}-R$ | 0.99/1 | 534.5 |

Table 6XPS Data of Four Vendor SMC Samples Split Down the Middle(Rel. % Composition/B.E.(eV))

| | <u>SMC-1</u> | <u>SMC-2</u> | <u>SMC-3</u> | <u>SMC-4</u> |
|---------------|--------------|--------------|--------------|--------------|
| $C_1 = CH_n$ | 68.7/284.6 | 69.3/284.6 | 67.8/284.6 | 68.1/284.6 |
| $C_2 = C-O-R$ | 25.1/286.2 | 25.1/286.1 | 25.6/286.1 | 25.5/286.1 |
| $C_3 = C=O$ | 6.2/288.8 | 5.6/288.7 | 6.6/288.7 | 6.4/288.8 |
| C_4 (total) | 100/- | 100/- | 100/- | 100/- |
| O | 26.8/532.2 | 22.8/532.4 | 24.6/532.5 | 23.8/532.2 |
| Ca | 1.7/348.5 | 1.3/347.9 | 1.9/347.9 | 1.5/348.0 |

XPS of SMC Resin Components

SMC resin components A and B were each applied onto XPS sample probes and upon evaporation of solvent were analyzed. The results are shown in Table 7. Only carbon and oxygen are detected in significant amounts. From the binding energy values of component A, the results are not significantly different than those determined for polymethylmethacrylate. However component B gives binding energies significantly higher than that of previously analyzed materials for the -COR and -C=O carbon functionalities. Resin B binding energy values, 287.9 and 289.1 eV, respectively, are about 1.7 and 0.5 eV higher than the binding energies previously assigned to the -COR(X) and -C=O (ester carbonyl) groups. This result suggests a higher concentration of ester (-OC-) functionality in Resin B.

XPS of Pretreated SMC: Old and New SMC

Samples of "old" SMC n% zinc stearate (n = 3, 4.5, and 6) following pretreatments including 1) no pretreatment (as received), 2) methylene chloride wipe with a Kim-wipe tissue, 3) abrasion using a Scotch-Brite pad soaked with methylene chloride, and 4) following the application of isocyanate primer on the surface with a Kim-wipe have been analyzed using XPS. The principal objective of this work was to identify surface chemical alterations that occur in the pretreatment before adhesive bonding. Average relative concentration values are displayed in column 1 of Table 8 for the three original "old" SMC materials. Each value is an average of at least four individual measurements on different pieces

Table 7

XPS of SMC Resin Components:
Relative Atomic Concentrations/B.E.(eV)

| <u>Element</u> | <u>Component A</u> | <u>Component B</u> |
|-----------------------------------|--------------------|--------------------|
| C ₁ = -CH _n | 52.5/284.6 | 43.0/284.6 |
| C ₂ = -COR | 29.9/286.2 | 38.0/287.9 |
| C ₃ = -C=O | 17.6/288.6 | 19.0/289.1 |
| C _t (total) | 100/--- | 100/--- |
| O | 35.2/532.5 | 45.8/532.0 |

Table 8

Average Relative Concentrations for "old"
SMC Samples: as received and following surface treatments

| <u>Element</u> | AR | CH ₂ Cl ₂ <u>SMC: 3.0%</u> | CH ₂ Cl ₂ /SB | Primer |
|--|------|---|-------------------------------------|--------|
| C ₁ = -CH _n | 77.6 | 72.5 | 63.0 | 63.8 |
| C ₂ = -C-O-R | 14.7 | 18.5 | 27.3 | 31.8 |
| C ₃ = -C=O | 7.7 | 9.0 | 7.4 | 4.4 |
| C ₄ = CO ₃ ²⁻ | -- | -- | 2.3 | -- |
| C _t (total) | 100 | 100 | 100 | 100 |
| Zn | 0.30 | 0.27 | 0.21 | -- |
| O | 20.6 | 25.9 | 26.4 | 20.0 |
| Si | -- | trace | -- | -- |
| Ca | 0.7 | 0.6 | 1.1 | -- |
| N | -- | -- | -- | 7.4 |
| | | <u>SMC: 4.5%</u> | | |
| C ₁ = -CH _n | 77.9 | 70.6 | 61.7 | 64.9 |
| C ₂ = -C-O-R | 16.3 | 19.4 | 28.5 | 30.5 |
| C ₃ = -C=O | 5.8 | 10.0 | 7.8 | 4.6 |
| C ₄ = CO ₃ ²⁻ | -- | -- | 2.0 | -- |
| C _t (total) | 100 | 100 | 100 | 100 |
| Zn | 0.36 | 0.25 | 0.27 | -- |
| O | 20.6 | 27.1 | 25.2 | 21.0 |
| Si | -- | -- | -- | -- |
| Ca | 0.7 | 0.5 | 1.4 | -- |
| N | -- | -- | -- | 5.6 |

Table 8
(Continued)

| <u>Element</u> | | <u>SMC: 6.0%</u> | | |
|-------------------|------|------------------|------|------|
| $C_1 = -CH_n$ | 78.3 | 67.4 | 65.4 | 64.2 |
| $C_2 = -C-O-R$ | 16.0 | 20.6 | 24.9 | 31.0 |
| $C_3 = -C=O$ | 5.7 | 12.0 | 7.2 | 4.8 |
| $C_4 = CO_3^{2-}$ | -- | -- | 2.5 | -- |
| C_t (total) | 100 | 100 | 100 | 100 |
| Zn | 0.60 | 0.46 | 0.53 | -- |
| O | 21.0 | 32.3 | 28.3 | 19.5 |
| Si | -- | -- | -- | -- |
| Ca | 1.0 | 0.4 | 2.8 | -- |
| N | -- | -- | -- | 8.0 |

of the same 1"x4" SMC specimen and are indicative of the top 50Å of each sample. Different specimens were prepared and analyzed as "as received" material and as pretreated samples. This procedure does not allow for a direct comparison of before and after results on the exact same specimen but reasonable comparisons are possible since all samples for a particular treatment were cut from the same 1"x4" coupon.

The principal elements detected via the XPS surface characterization measurements of untreated SMC are C, O, Zn, and Ca. Other elements that could likely be present are Mg, Si, and Na. This is because magnesium oxide thickener is often added to SMC. Sodium, usually from fingerprints is a likely contaminant. Since these elements are not detected it is reasoned that their surface concentrations must be less than about 0.1 atomic percent. Although silicon-containing glass fibers are present in the SMC, such fibers are not present in the outer surface region (50Å) of these materials. This finding is not surprising when it is realized that this outer surface is probably composed primarily of low profile additives (often polymethylmethacrylate (PMMA) or polyvinyl acetate) in various ratios and small amounts of mold release agent.

The XPS results in Table 9 indicate some heterogeneity among the samples. SMC samples A, B, and C for the 6% zinc stearate SMC are taken from different 1"x4" untreated specimen coupons, whereas samples C, D, and E are different portions of the same 1" x 4" specimen. The respective concentrations of zinc and oxygen for samples A and C are

Table 9

Elemental Composition of Old SMC Samples
(3.0, 4.5, 6.0 % Zn Stearate)

| Atom | 3% | | | 4.5% | | | 6.0% | | | | | | | |
|------|------|-----------------|------|------|------|------|------|------|----------------|----------------|------------------|----------------|------|------|
| | I | J | K | Avg. | F | G | H | Avg. | A ¹ | B ¹ | C ^{1,2} | D ² | E | Avg. |
| C | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | 0.32 | 0.21 | 0.26 | 0.26 | 0.44 | 0.81 | 0.17 | 0.47 | 0.56 | 0.63 | 0.52 | 0.39 | 0.41 | 0.50 |
| O | 22.1 | 20.6 | 18.2 | 20.3 | 20.7 | 23.1 | 18.1 | 20.6 | 20.5 | 21.0 | 19.2 | 19.0 | 17.4 | 19.4 |
| Ca | 1.3 | ND ³ | 0.35 | 0.55 | 1.1 | 1.6 | 0.40 | 1.0 | 0.61 | 0.89 | 0.47 | 0.87 | 0.47 | 0.66 |

1: different 1 x 4 specimens

2: the same 1 x 4 specimen

3: ND - not detected: < 0.1%

very similar and near the precision of the measurements and suggests similar surface compositions. However, the variation of zinc among samples B, D, and E is outside the expected precision. Further it is found that differences in calcium concentrations for the samples are well beyond the limits of precision. Such results could be due to larger precision errors at these low concentrations, bulk SMC dust rich in calcium, contaminating the sample during the cutting process, or to real variations in calcium content in the samples investigated. For samples of 4.5% Zn stearate SMC, F, G, H, a wide variation in calcium (1.6 to 0.4) and zinc (0.81 to 0.17) surface content is noted. On the other hand for the 3% Zn stearate SMC materials a wide variation is found only for the calcium content. Clearly if such wide variations in surface concentrations are related to heterogeneity in component concentration, then some solvent precleaning or other surface pretreatment of the samples is necessary to insure formation of more homogeneous and reproducible SMC surface.

XPS binding energy for untreated "old" SMC are shown in Table 10. Shown in Table 8 are the relative atomic concentration curve resolved data for the carbon 1s spectra which are resolved into four components, CH_n , -C-O-R, -C=O (ester carbonyl), and CO_3^{2-} designated as C_1 , C_2 , C_3 and C_4 , respectively. Treatment with methylene chloride (CH_2Cl_2 wipe) is shown from Table 8 to decrease hydrocarbon surface concentration while exposing more carbonyl and -C-O-R moieties. The carbonate carbon (C_4) was only detected in samples where abrasive treatment (Scotch Brite/ CH_2Cl_2) was used. This is probably due to exposure of CaCO_3 from the

Table 10

Binding Energy Results (eV) for SMC Samples
("O1d" 6.0, 4.5, 3.0 % Zn Stearate)

| <u>Element</u> | <u>Core Level</u> | <u>3.0%</u> | | <u>4.5%</u> | | <u>6.0%</u> | |
|----------------|-------------------|-------------|----------------------|-------------|----------------------|-------------|----------------------|
| | | <u>B.E.</u> | <u>Functionality</u> | <u>B.E.</u> | <u>Functionality</u> | <u>B.E.</u> | <u>Functionality</u> |
| C | 1s | 284.6 | CH _n | 284.6 | CH _n | 284.6 | CH _n |
| | | 286.2 | COR | 286.2 | COR | 286.1 | COR |
| | | 288.8 | C=O | 288.8 | C=O | 288.8 | C=O |
| Zn | 2P _{3/2} | 1022.8 | Zn ²⁺ | 1022.7 | Zn ²⁺ | 1022.8 | Zn ²⁺ |
| | | 532.8 | R-COO-R | 532.7 | R-COO-R | 532.4 | R-COO-R |
| 0 | 1s | 348.1 | Ca ²⁺ | 348.2 | Ca ²⁺ | 348.1 | Ca ²⁺ |
| Ca | 2P _{3/2} | | | | | | |

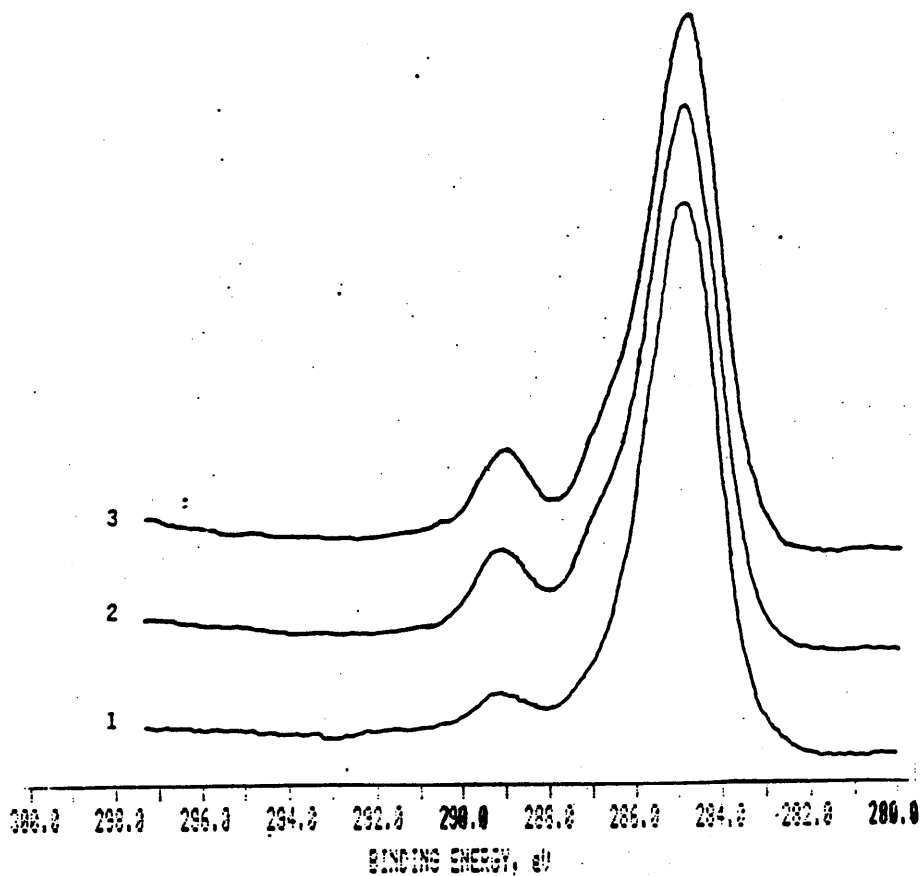
bulk SMC as a corresponding increase in Ca is also observed. Application of primer results in an increase in $-C-O-R/-NCO_2R$ (C_2) carbon at the expense of hydrocarbon (C_1). This coupled with the detection of nitrogen in significant concentrations (e.g., 8.0% for SMC 6%) indicate that derivatization of the surface or a surface film is formed in the application of primer.

Treatment of "old" SMC with CH_2Cl_2 and with Scotch Brite/ CH_2Cl_2 (Table 8) alters the chemical nature of the surface as noted by a slight decrease in the zinc content, an increase in oxygen content, and changes in the distribution of carbon species. The calcium concentration for all three samples following the CH_2Cl_2 wipe is about 0.5%. A calcium binding energy of about 348.0 eV suggests Ca^{2+} as the calcium species, most probably from $CaCO_3$. For the 3% and 4.5% SMC samples this represents little or no change. However, this value corresponds to a reduction from 1.0% to 0.4% for the 6.0% SMC. Whether this large change is due to the inhomogeneous nature of the SMCs or to sampling irregularities is not known. The greatest change in calcium occurs following abrasion in the Scotch-Brite/ CH_2Cl_2 treatment. The calcium content increases by a factor of 1.6, 2.0, and 2.8 for the 3, 4.5, and 6% SMCs, respectively. This finding when compared to the results for CH_2Cl_2 cleaning alone, indicates that abrasion either removes organic material, mobilizes calcium so that it appears in greater concentrations on the surface, or begins to expose the bulk SMC which contains $CaCO_3$.

The C 1s spectra for SMC containing 4.5% zinc stearate before and following treatments of the SMC with CH_2Cl_2 and with Scotch-Brite/

CH_2Cl_2 are shown in Figure 7. The most striking result is that the spectra following a methylene chloride wipe and a methylene chloride/Scotch-Brite abrasive wipe respectively, are not significantly altered. However, when these spectra are compared with that for no treatment, it is noted that the intensity increases for carbons with binding energies in the 286.2 and 288.8 eV regions corresponding to C-O-R and -C=O type species, respectively. The increase in these carbon-oxygen species is accompanied by a relative decrease in the CH_n carbon content (B.E. = 284.6 eV). This increase in the 288.8 eV carbon signal could be attributed to carbon from carbonate (CaCO_3); however, the quantity of calcium is not sufficient even after the Scotch Brite/ CH_2Cl_2 treatment to account for the increase in the oxygen percentage that occurs for the 4.5% zinc stearate SMC following treatments 2 and 3. This result is consistent with an increase in carbon-oxygen species noted above. Similar changes in the C 1s spectra were observed following treatments 2 and 3 for 3% and 6% samples as shown in Table 8.

The application of isocyanate primer to the surface of all three samples eliminates XPS evidence for zinc and calcium. In addition the carbon and oxygen photopeaks are altered compared to as received SMC and a photopeak attributable to nitrogen appears. This result is more easily visualized by examining Figure 8, where the C 1s spectrum for primer on 4.5% SMC ("old") is compared to untreated SMC. The carbon photopeaks can be attributed to CH_n , -C-O-R/- NCO_2R , and C=O type carbons, where the relative concentration percent of each type varies in the manner $\text{CH}_n = 64.9$, -COR/- $\text{NCO}_2\text{R} = 30.5$, -C=O = 4.6%. The nitrogen 1s



Treatment 1: no treatment
Treatment 2: CH_2Cl_2 wipe
Treatment 3: Scotch Brite/ CH_2Cl_2 wipe

Figure 7. C 1s Spectra for a 4.5% Zn Stearate α -SMC Sample Following Surface Treatment

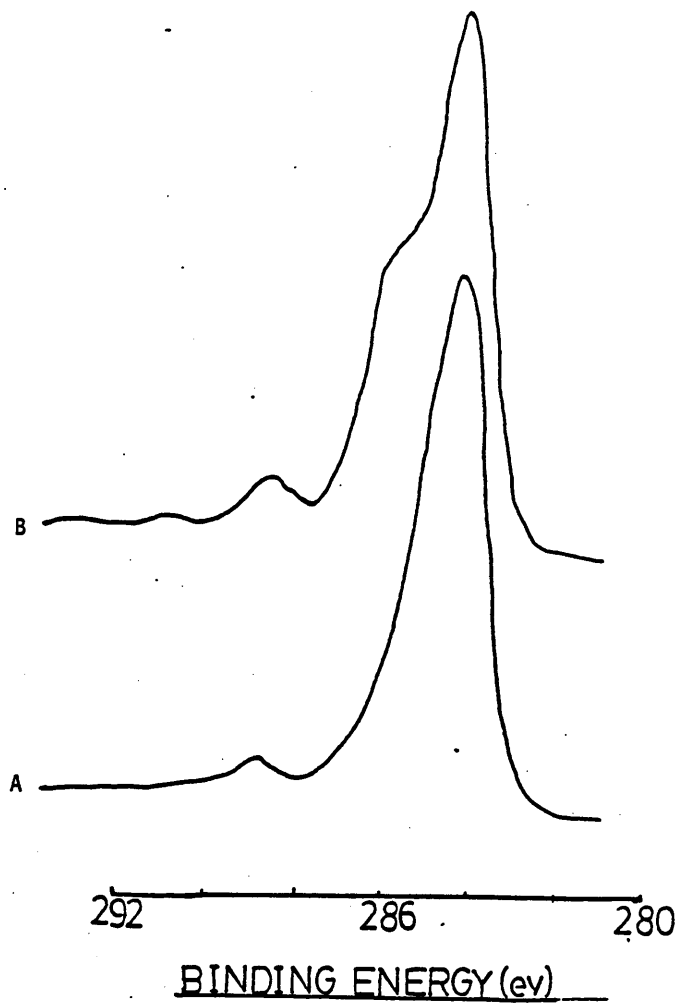


Figure 8. C 1s for "old" SMC Untreated (A) and Primer Wiped Treated (B) Samples

binding energy at 400.0 eV is characteristic of R_3-N , NCO_2R , or $-C\equiv N$ functionality. The oxygen 1s FWHM (1.8 eV) (Figure 9) is reduced from a value of about 2.8 eV in the untreated SMC. This result indicates that some of the oxygen-containing components in the original SMC are removed, reacted, or covered by a thin film of the isocyanate primer components. The FWHM for the O 1s level (1.8 eV) is equal to that noted for simple oxygen-containing components. The oxygen 1s binding energy is suggestive of carbonyl (C=O) type oxygen.

There is an apparent difference in the percent oxygen and nitrogen in the measurements on "pure" primer (cast on a stainless steel sample probe coated with gold) and primer applied to the SMC material. The percent compositions are: percent oxygen: 16.3, 20.0; and percent nitrogen 10.6, 7.4 for "pure" and primer applied/SMC, (3.0%), respectively. It is not apparent what physical or chemical processes could account for these differences. Clearly specific chemical reactions of primer with SMC could alter the nitrogen and oxygen surface content or a specific physical orientation or diffusion of primer components into the SMC surface could yield surface compositions unlike "pure" primer. The important finding following primer treatment of SMC is that the surface chemical properties are altered either by the formation of a thin film of primer components or by reaction of primer components with SMC surface species. Clearly application of primer masks or removes the inorganic components, calcium and zinc.

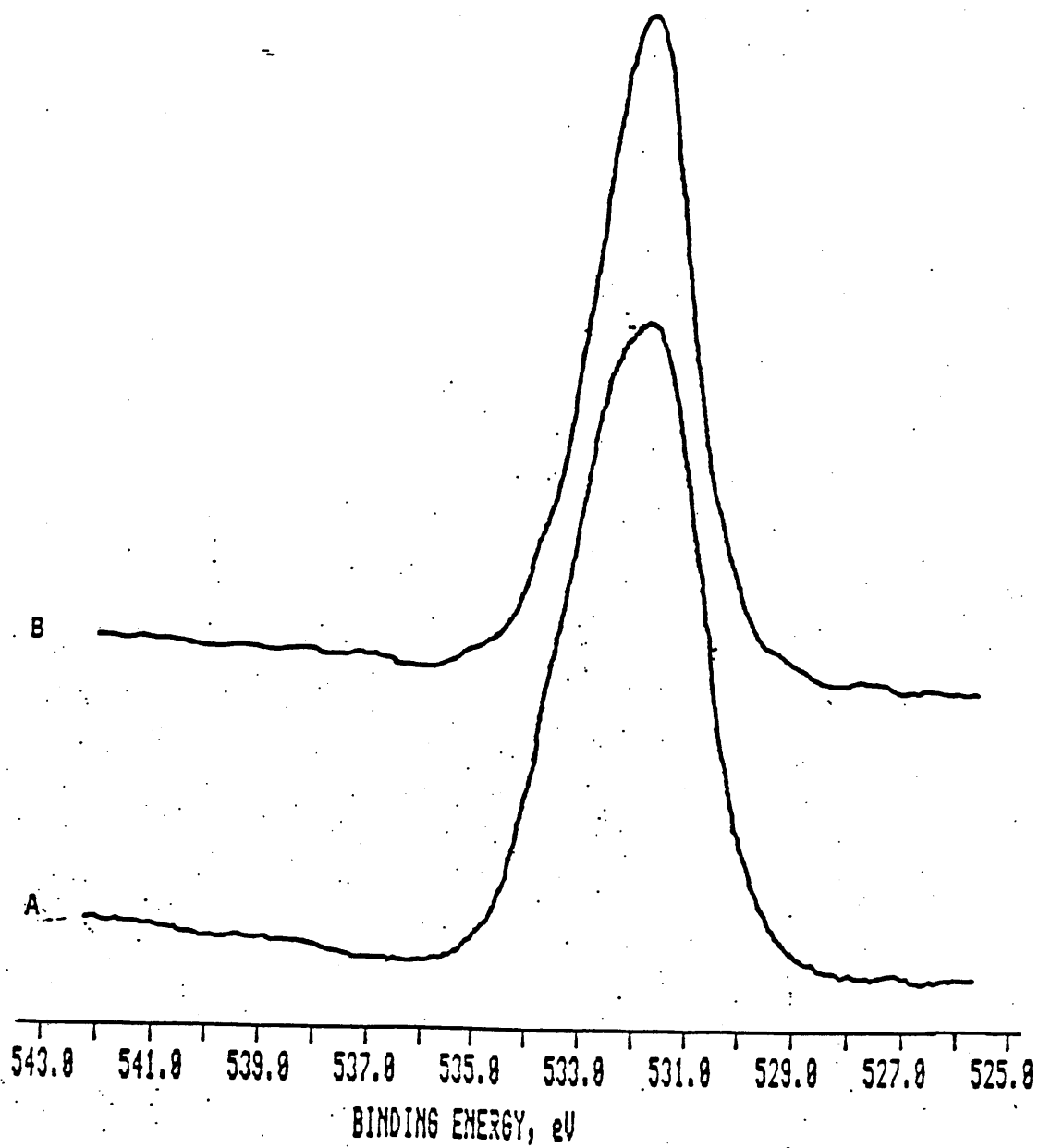


Figure 9. O 1s Spectra for "old" SMC Untreated (A) and Primer Wiped Treated (B) Samples

Thermally Treated "Old" SMC (3.0, 4.5, 6.0% Zn Stearate)

"Old" SMC differing in the amount of zinc stearate mold release agent was thermally treated at 177°C for 50 minutes. The results are shown in Table 11. The objective of this treatment was to discern whether surface concentrations of SMC components or additives are altered. These data represent the average of at least two replicate measurements on thermally treated specimens. It should be noted that samples used for the thermal treatment were not taken from the exact same 1"x4" specimen coupons that were used for the analyses of untreated SMC. Clearly interpretations and conclusions noted could be compromised by the heterogeneous surface nature of the material. The principal differences in the surface following thermal treatment are the decrease in the oxygen content for the 6.0% and the 4.5% Zn stearate SMCs, and the decrease in -C=O functionality for all three SMCs. Depletion of oxygen could arise from the loss of resin components, processing compounds, or chemisorbed water. It is not apparent why a significant oxygen decrease should be noted for only the 6.0% and 4.5% zinc stearate SMC specimens and not for the 3.0% specimen. The change in calcium concentration is erratic and no clear pattern to the alterations emerges. Perhaps this occurs as a result of contamination of SMC dust filler materials deposited onto the SMC surface during the cutting operation.

The depth profile results for thermally treated samples are given in Table 12. The change in concentrations parallels that found for the untreated samples. Carbon remains as the most abundant surface element,

Table 11

XPS Results (Relative Concentrations/B.E.(eV)) Before and After Thermal Treatment at 350°F (177°C) for 50 min. for SMC Samples (Old 3.0, 4.5 and 6.0% zinc stearate)

| <u>Element</u> | <u>3.0%</u> | | <u>4.5%</u> | | <u>6.0%</u> | |
|-----------------------------------|------------------|----------------|------------------|----------------|------------------|----------------|
| | <u>Untreated</u> | <u>Treated</u> | <u>Untreated</u> | <u>Treated</u> | <u>Untreated</u> | <u>Treated</u> |
| C ₁ = -CH _n | 77.6/284.6 | 82.0/284.6 | 78.9/284.6 | 79.9/284.6 | 78.3/284.6 | 83.4/284.6 |
| C ₂ = -C-O-R | 14.6/286.2 | 16.6/286.1 | 19.1/286.2 | 20.1/286.2 | 16.0/286.1 | 14.5/286.2 |
| C ₃ = -C=O | 7.8/288.8 | 1.4/288.8 | 5.8/288.8 | 2.0/288.9 | 5.7/288.8 | 2.1/288.9 |
| C _t (total) | 100/---- | 100/---- | 100/---- | 100/---- | 100/---- | 100/---- |
| Zn ²⁺ | 0.30/1022.8 | 0.31/1022.7 | 0.36/1022.7 | 0.41/1022.7 | 0.60/1022.8 | 0.75/1022.5 |
| O | 20.6/532.8 | 23.2/532.2 | 20.6/532.7 | 16.8/532.5 | 21.0/532.4 | 13.8/532.2 |
| Ca ²⁺ | 0.7/348.1 | 1.1/347.9 | 0.7/348.2 | 0.86/347.8 | 1.0/348.1 | 0.47/348.1 |

Table 12
Depth Profile Results SMC Samples as a Function of
Sputter Time

| a) untreated | | b) following thermal treatment (50 min. @ 177°C) | | | | |
|------------------------|------|--|------|------|------|------|
| Time (min) | 0 | 10 | 20 | 30 | 60 | 120 |
| 6.0% Zn St. SMC | | | | | | |
| C a | 100 | 100 | 100 | 100 | 100 | 100 |
| b | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn a | 0.63 | 0.60 | 0.50 | 0.23 | 0.12 | 0.15 |
| b | 0.75 | 0.52 | 0.48 | 0.27 | 0.20 | 0.19 |
| O a | 21.0 | 18.9 | 16.2 | 7.1 | 5.9 | 7.0 |
| b | 13.8 | 10.4 | 7.1 | 6.7 | 5.9 | 10.2 |
| Ca a | 0.89 | ND* | 0.70 | 1.1 | 1.3 | 2.0 |
| b | 0.47 | 0.60 | 1.2 | ND* | ND* | 1.9 |
| 4.5% Zn St. SMC | | | | | | |
| C a | 100 | 100 | 100 | 100 | 100 | 100 |
| b | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn a | 0.44 | 0.27 | 0.21 | 0.11 | ND* | ND* |
| b | 0.41 | 0.27 | 0.22 | 0.13 | 0.16 | 0.10 |
| O a | 20.6 | 16.6 | 13.8 | 8.1 | 7.1 | 6.2 |
| b | 16.8 | 5.7 | 5.5 | 5.1 | 4.7 | 4.5 |
| Ca a | 1.1 | 1.3 | 1.0 | 1.2 | 1.3 | 1.1 |
| b | 0.86 | 1.3 | ND | ND | 0.7 | 1.1 |
| 3.0% Zn St. SMC | | | | | | |
| C a | 100 | 100 | 100 | 100 | 100 | 100 |
| b | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn a | 0.32 | 0.25 | 0.17 | 0.14 | 0.09 | 0.08 |
| b | 0.31 | 0.26 | 0.25 | 0.25 | 0.20 | 0.18 |
| O a | 22.1 | 18.7 | 14.9 | 14.1 | 5.7 | 5.9 |
| b | 23.2 | 15.9 | 14.6 | 14.0 | 13.0 | 11.1 |
| Ca a | 1.3 | 0.49 | 0.54 | 0.31 | 0.81 | 0.56 |
| b | 1.1 | 1.1 | 1.0 | 1.4 | 1.3 | 1.2 |

*ND - Not detected; < 0.1%

a decrease in the zinc and surface oxygen content is found, and the variation in the calcium percentage is either erratic or unchanged. The zinc content decreases to a more or less constant level for the 6% zinc stearate SMC material upon sputtering and virtually disappears for the remaining two specimens. This reduction could indicate that the sputtering may have exposed a region low in zinc. The similarity of results for zinc in untreated and treated samples indicates that no significant migration of zinc occurs during the thermal treatment. The data for oxygen do not provide any additional information regarding the chemical changes that are associated with or are responsible for loss of oxygen upon thermal treatment for the 6.0% and 4.5% zinc stearate SMC samples.

XPS of Vendor SMC

The elemental characterization results for the four vendor SMC materials all containing 4.5% zinc stearate mold release agent are summarized in Table 13. Shown in Table 13 are the measured relative atomic percent concentrations and an average value for each of six (6) measurements on the four as received SMC samples. In all four samples the prominent surface elements are carbon, zinc, oxygen, and calcium. Neither silicon nor nitrogen is detected ($< 0.1\%$) in these four samples. It should be noted that the variability in the measured zinc concentrations among different pieces of the same SMC (but from different 1"x4" coupons) is small for SMC-3 (0.24-0.30) and somewhat more variable for the other vendor's samples: SMC-1 (0.19-0.34);

Table 13

XPS Characterization of "as received" SMC (4.5% Zn-stearate)
 Coupons from selected vendors: SMC-1, SMC-2, SMC-3, SMC-4
 Atomic % relative to carbon

| | SMC-1 | | | | SMC-2 | | | | SMC-3 | | | | SMC-4 | | | | Ave. |
|-------|-------|------|------|------|-------|------|-------|------|-------|------|------|------|-------|------|------|------|-------|
| | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | |
| C | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | .31 | .25 | .34 | .30 | .19 | 0.28 | .30 | .30 | .24 | .45 | .18 | .25 | .18 | .25 | .18 | .25 | 0.29 |
| O | 20.4 | 18.4 | 19.3 | 18.1 | 16.0 | 17.1 | 18.2 | 15.3 | 17.0 | 15.6 | 16.3 | 18.5 | 16.8 | 16.8 | 16.1 | 17.8 | 16.6 |
| Si | ND* | ND* | ND* | ND* | ND* | ND* | < 0.1 | ND | ND | ND | ND | ND | ND | ND | ND | ND | < 0:1 |
| Ca | 0.4 | tr* | 0.8 | 0.5 | tr | 0.3 | 0.50 | tr | tr | tr | tr | tr | tr | tr | tr | tr | tr |
| SMC-3 | | | | | | | | | | | | | | | | | |
| | SMC-3 | | | | SMC-4 | | | | SMC-4 | | | | Ave. | | | | |
| | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | | 100 | 100 | 100 | 100 |
| C | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | .30 | .28 | .24 | .25 | .30 | .24 | 0.27 | .24 | .13 | .51 | .18 | .21 | .18 | .21 | .18 | .18 | 0.24 |
| O | 18.8 | 17.4 | 19.2 | 14.4 | 18.5 | 16.8 | 17.5 | 19.2 | 17.6 | 25.0 | 16.4 | 16.1 | 17.8 | 16.1 | 17.8 | 17.8 | 18.7 |
| Si | ND | ND | ND | ND | ND | ND | < 0.1 | ND | ND | ND | ND | ND | ND | ND | ND | ND | < 0.1 |
| Ca | 0.5 | 0.2 | 0.7 | 0.2 | tr | tr | 0.30 | 0.7 | tr | 0.3 | 0.4 | tr | 0.4 | tr | 0.4 | 0.4 | 0.30 |

ND = not detected (< 0.1%)
 tr = trace ≈ 0.1%

SMC-2 (0.18-0.45) and SMC-4 (0.13-0.51). The variation in oxygen content is relatively small for the SMC-1, SMC-2, and SMC-3 materials, average standard deviations being: SMC-1, 1.2; SMC-2, 0.9; and SMC-3, 1.3, while for SMC-4 samples a greater deviation is found: SMC-4, 2.3. The calcium content is above the trace level in most of the SMC-1, SMC-3, and SMC-4 samples tested but was not above the trace level for SMC-2 coupons. The magnitude of the average calcium content is 0.5 to 0.4% in the SMC-1, SMC-3 and SMC-4 series coupons. In general the surfaces of these four SMC materials seem to be significantly less heterogeneous than the corresponding "old" SMC samples. This is probably due to better experimental techniques: namely covering the sample with Al foil during cutting preparation and taking care to align each sample the same way during the XPS data acquisition.

Photoelectron peak shapes and binding energies for carbon, zinc, oxygen, and calcium are similar for all four groups of materials. The carbon spectra are all characterized by an intense (CH_n) peak. Evidence in the form of a shoulder on the high binding energy side of the C 1s peak (-286.2 eV) is recorded for -C-O-R functionality and a small peak at about 288.8 eV is indicative of C=O moieties. The photopeaks for the remaining elements are typical of those recorded for zinc and calcium as a single component element composition. The oxygen 1s photopeaks (Figure 10) are broader than those determined for simple organic and inorganic oxygen-containing compounds (FWHM ~1.8 eV). The breadth (~2.7 eV) is indicative of at least two different oxygen components in the SMC materials corresponding to carbonyl and ether oxygen.

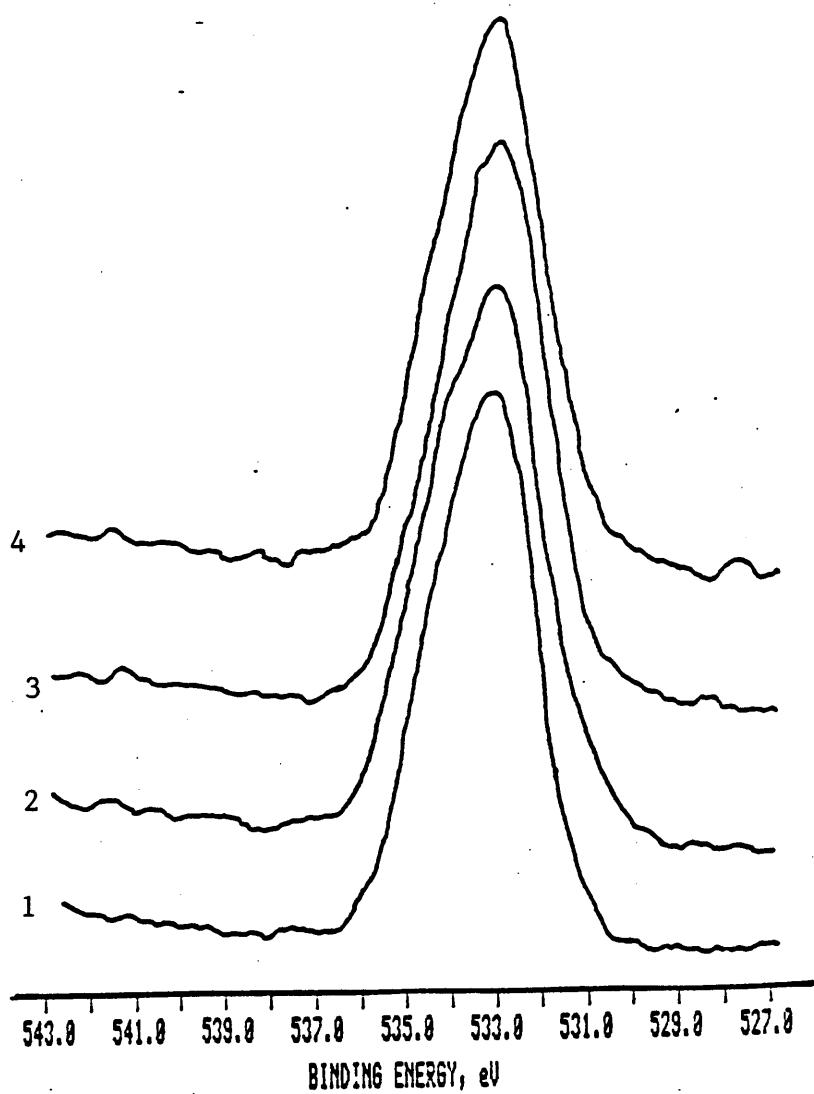


Figure 10. O 1s As Received: SMC-1, SMC-2, SMC-3, SMC-4

Surface Analysis of Treated Vendor SMC Materials

Surface analysis data for the four SMC materials before and after treatment involving a CH_2Cl_2 wipe, after abrasion with a Scotch Brite/ CH_2Cl_2 pad, and after application of isocyanate primer are presented in Tables 14, 15, and 16, respectively. Table 17 shows the curve resolved C 1s spectral data for all vendor samples as a function of pretreatment and Figure 11 shows the corresponding spectra. Recall that for these measurements, an SMC specimen was mounted on a sample probe, XPS surface characterization was carried out, this same sample was treated with CH_2Cl_2 , etc., and then characterized again using XPS. In the tables the results are presented as A/B where A refers to the before (as received) treatment result and B corresponds to the after treatment data.

The findings following CH_2Cl_2 wipe (Table 14) are that the zinc content remains relatively unchanged or decreases slightly. A very slight increase is noted for one of the SMC-1 and SMC-3 samples but this change is within the experimental error of the determinations ($\pm 10\%$). Changes in the oxygen content do not follow any well identified pattern. For samples SMC-2 and SMC-3 there is no significant change in the surface oxygen content, whereas for the SMC-4 series a decrease in oxygen is noted on the two samples studied. For the SMC-1 samples one shows a marked decrease (20.4 to 16.5%) whereas the other piece (# 2) exhibits a modest increase in oxygen content. Following treatment, the calcium content for all samples was either at trace levels ($\sim 0.1\%$) or not detectable. This result was found also for samples that contained

Table 14

Comparison of Relative Concentrations for Untreated Sample and
Methylene Chloride wiped sample: A/B
 (A = as received; B = after treatment)

"----" = no detectable amount; < 0.1%
 trace = relative concentration; ~ 0.1%

| | <u>Piece #1</u> | | <u>Piece #2</u> |
|----|-----------------|--------------|-----------------|
| | | <u>SMC-1</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.34/0.37 | | 0.34/0.25 |
| O | 20.4/16.5 | | 18.4/19.1 |
| Si | ----/---- | | ----/---- |
| Ca | 0.40/trace | | trace/trace |
| | | <u>SMC-2</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.30/0.23 | | 0.30/0.27 |
| O | 15.3/17.1 | | 17.0/17.1 |
| Si | ----/---- | | ----/---- |
| Ca | trace/---- | | trace/trace |
| | | <u>SMC-3</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.30/0.37 | | 0.28/0.26 |
| O | 18.8/19.4 | | 17.4/18.0 |
| Si | ----/trace | | ----/---- |
| Ca | 0.50/trace | | 0.20/trace |
| | | <u>SMC-4</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.24/0.10 | | 0.13/0.15 |
| O | 19.2/15.1 | | 17.6/14.2 |
| Si | trace/---- | | ----/trace |
| Ca | 0.70/trace | | trace/---- |

Table 15

Comparison of Relative Concentrations for Untreated Sample and
Methylene Chloride/Scotch Brite Wiped Sample: A/B
 (A = as received; B = after treatment)

"----" = no detectable amount; < 0.1%
 trace = relative concentration; ~ 0.1%

| | <u>Piece #1</u> | | <u>Piece #2</u> |
|----|-----------------|--------------|-----------------|
| | | <u>SMC-1</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.31/0.39 | | 0.25/0.24 |
| O | 19.3/25.3 | | 18.1/24.8 |
| Si | ----/---- | | ----/trace |
| Ca | 0.80/2.0 | | 0.50/1.7 |
| | | <u>SMC-2</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.24/0.37 | | 0.45/0.37 |
| O | 15.6/30.5 | | 16.3/22.8 |
| Si | ----/---- | | ----/---- |
| Ca | trace/3.4 | | trace/1.3 |
| | | <u>SMC-3</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.24/0.33 | | 0.25/0.24 |
| O | 19.2/19.7 | | 14.4/20.0 |
| Si | 0.50/trace | | 0.20/trace |
| Ca | 0.70/1.3 | | ----/1.0 |
| | | <u>SMC-4</u> | |
| C | 100/100 | | 100/100 |
| Zn | 0.51/0.24 | | 0.18/0.27 |
| O | 25.0/31.6 | | 16.4/21.5 |
| Si | ----/---- | | ----/---- |
| Ca | 0.30/2.3 | | 0.4/2.2 |

Table 16

Comparison of Relative Concentrations for Untreated Sample and
Isocyanate Primer Wiped Sample: A/B
(A = as received; B = after treatment)

"----" = no detectable amount; < 0.1%
trace = relative concentration; ~ 0.1%

| | <u>Piece #1</u> | <u>Piece #2</u> |
|----|-----------------|-----------------|
| | <u>SMC-1</u> | |
| C | 100/100 | 100/100 |
| Zn | 0.30/---- | 0.19/---- |
| O | 16.0/21.5 | 17.1/22.0 |
| Si | trace/---- | ----/---- |
| Ca | trace/---- | 0.3/0.2 |
| N | ----/5.5 | ----/6.5 |
| | <u>SMC-2</u> | |
| C | 100/100 | 100/100 |
| Zn | 0.18/---- | 0.25/---- |
| O | 18.5/23.7 | 16.8/23.0 |
| Si | 0.20/---- | ----/---- |
| Ca | trace/---- | ----/---- |
| N | ----/6.1 | ----/6.0 |
| | <u>SMC-3</u> | |
| C | 100/100 | 100/100 |
| Zn | 0.30/---- | 0.24/---- |
| O | 17.3/23.1 | 17.7/23.6 |
| Si | 0.2/---- | ----/---- |
| Ca | trace/---- | trace/---- |
| N | ----/6.0 | ----/6.6 |
| | <u>SMC-4</u> | |
| C | 100/100 | 100/100 |
| Zn | 0.21/---- | 0.18/---- |
| O | 16.1/25.6 | 17.8/24.6 |
| Si | trace/---- | trace/---- |
| Ca | ----/---- | 0.4/---- |
| N | ----/6.3 | ----/6.3 |

Table 17

Carbon 1s Curve Resolved Data for SMC (4.5% Zinc Stearate) From Selected Vendors: SMC-1, SMC-2, SMC-3, SMC-4

| SMC | photo-peak | Treatment 1 | Treatment 2 | Treatment 3 | Treatment 4 |
|-------|---------------------|-------------|-------------|-------------|-------------|
| SMC-1 | $C_1=CH_n$ | 80.1 | 79.8 | 63.0 | 69.3 |
| | $C_2=C-O-R/-NCO_2R$ | 14.7 | 16.0 | 26.6 | 27.9 |
| | $C_3=-C=O$ | 5.2 | 4.2 | 8.4 | 2.8 |
| | $C_4=CO_3^{2-}$ | -- | -- | 2.0 | -- |
| SMC-2 | $C_1=CH_n$ | 82.6 | 78.4 | 62.1 | 58.0 |
| | $C_2=C-O-R/-NCO_2R$ | 11.8 | 15.3 | 27.1 | 38.3 |
| | $C_3=-C=O$ | 5.6 | 6.3 | 8.5 | 3.7 |
| | $C_4=CO_3^{2-}$ | -- | -- | 2.3 | -- |
| SMC-3 | $C_1=CH_n$ | 85.6 | 82.5 | 60.5 | 60.1 |
| | $C_2=C-O-R/-NCO_2R$ | 11.6 | 14.0 | 27.9 | 36.3 |
| | $C_3=-C=O$ | 2.8 | 3.5 | 9.0 | 3.6 |
| | $C_4=CO_3^{2-}$ | -- | -- | 2.6 | -- |

Table 17
(Continued)

| SMC | photo-peak | Treatment 1 | Treatment 2 | Treatment 3 | Treatment 4 |
|-------|---------------------|-------------|-------------|-------------|-------------|
| SMC-4 | $C_1=CH_n$ | 84.8 | 84.0 | 61.7 | 55.3 |
| | $C_2=C-O-R/-NCO_2R$ | 12.5 | 12.9 | 28.5 | 41.2 |
| | $C_3=-C=O$ | 2.7 | 3.1 | 7.8 | 3.5 |
| | $C_4=CO_3^{2-}$ | -- | -- | 2.0 | -- |

--: not detected (< 0.1%)

Treatment 1: no treatment (as received)

Treatment 2: CH_2Cl_2 wipe

Treatment 3: SB/ CH_2Cl_2 wipe; CH_2Cl_2 wipe

Treatment 4: isocyanate primer application

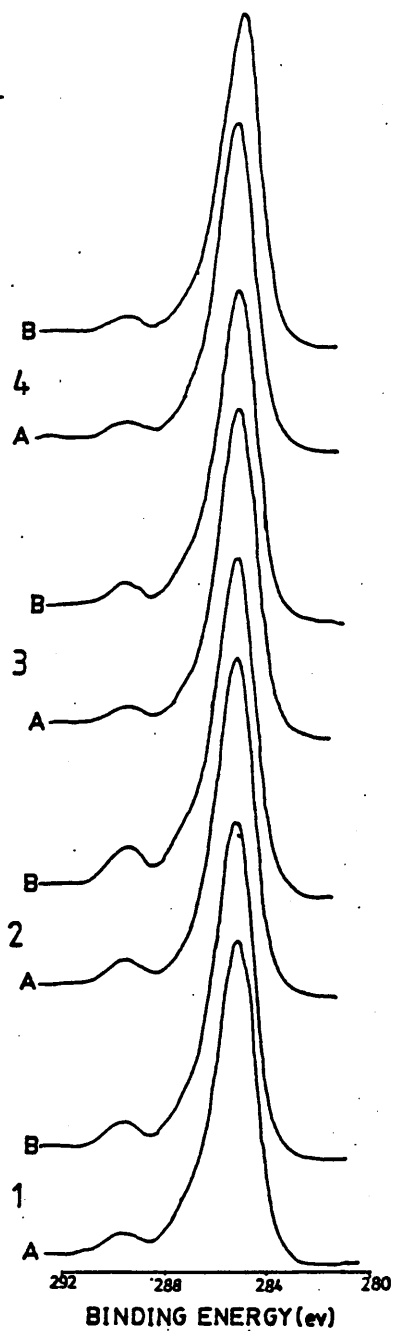


Figure 11. C 1s Spectra Pairs of SMC-1, SMC-2, SMC-3, SMC-4. SMC Before (A) and After (B) a CH_2Cl_2 Treatment

reasonable levels of calcium in the as received materials. Thus the CH_2Cl_2 wipe reduces the calcium content to values at the detection level in these samples.

Examination of the photoelectron spectra reveal modest changes in the chemical nature of the SMC surfaces following CH_2Cl_2 treatment. The C 1s curve resolved data (Table 17) show a decrease in $-\text{CH}_n$ concentration at the expense of $-\text{C}-\text{O}-\text{R}$ moiety in the case of SMC-1, SMC-2 and SMC-3. The C 1s curve resolved data for SMC-4 shows no significant change upon treatment with CH_2Cl_2 . Little or no change was found in the intensity for the $\text{C}=\text{O}$ group. Among the four samples the shapes of the photoelectron peaks for oxygen (O 1s) are also unchanged following CH_2Cl_2 treatment.

These results are in contrast to the observations discussed above for CH_2Cl_2 treatment of the "old" SMC materials. For the new series of samples no significant increase in the oxygen content is found and the marked increase in the C 1s peaks associated with carbon-oxygen groups (i.e., $-\text{C}-\text{O}-\text{R}$, $-\text{C}=\text{O}$) is not observed. At the moment no explanation for differences in the behavior of the original and new SMC materials can be offered.

Analysis results following Scotch Brite/ CH_2Cl_2 surface treatment are summarized in Table 15. Carbon is the dominant element and silicon is not detected or is found at trace levels ($\sim 0.1\%$). Zinc is detectable in all samples and the variations noted between untreated and treated specimens are irregular. For some specimens there is virtually

no change in the zinc content, SMC-1; while for some samples of the other materials studied, increases, decreases and no change in the zinc content are found. The important point is that this pretreatment has no significant effect on the zinc content. Following Scotch Brite/ CH_2Cl_2 treatment the oxygen surface concentration increases for all samples. Samples in the SMC-1 and SMC-4 series show an increase in oxygen content in the range of about 30% while for the SMC-2 series the percent changes are 95 to 40% and for the SMC-3 series the increases are about 3 and 40%. It is not apparent whether the variations in percentage increases are due to inhomogeneities in the samples or are due to a combination of unidentified factors. The most significant change in elemental surface concentrations occurs for calcium. For all samples the calcium content increases to a level of 1-3%. For samples in the SMC-1, SMC-2, and SMC-4 series, the calcium levels after the treatment are approximately equal for pairs of specimens in each series i.e., SMC-1, 2.0 and 1.7%; SMC-3, 1.3 and 1.0%; and SMC-4, 2.3 and 2.2%. The calcium levels for the two SMC-200 samples are 3.4 and 1.3%. The changes in the surface chemical nature of the elements are evident from the C 1s, O 1s, and Ca 2p XPS spectra, shown in Figures 12-14 respectively, for the before and after Scotch Brite/ CH_2Cl_2 treatment. Spectra for an SMC-3 sample were selected as representative of those where changes in chemical nature were discerned. The principal change in the C 1s spectrum is the increase in signals due to oxygen-containing components. Portions of the spectra where these increases occur are identified with an arrow (\downarrow) in the figures. The increase in oxygen content does not

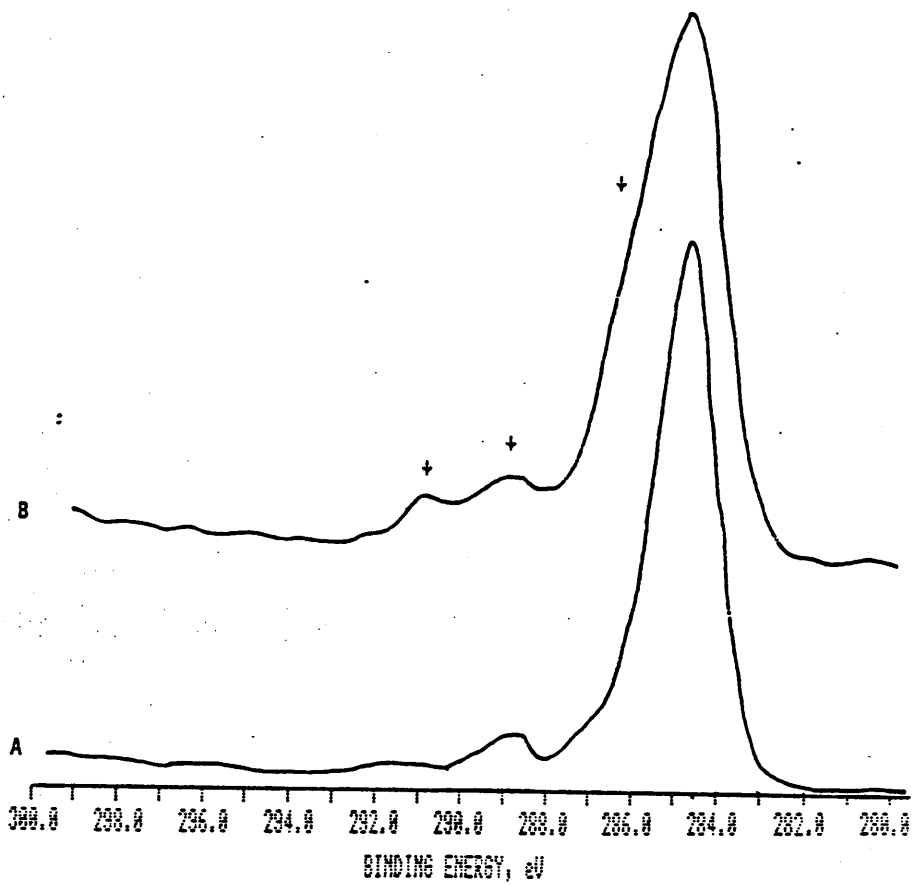


Figure 12. C 1s Spectra for a 4.5% Zn Stearate SMC Before (A) and After (B) a CH_2Cl_2 S.B. Treatment (SMC-3)

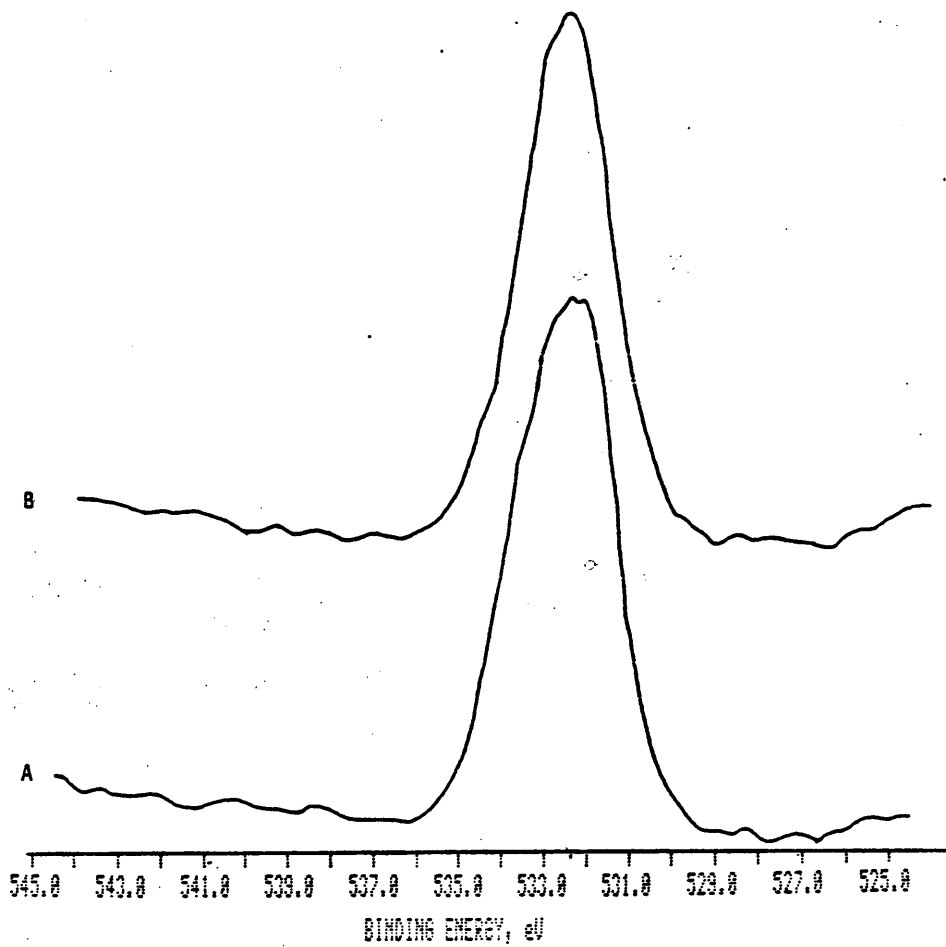


Figure 13. O 1s Spectra for a 4.5% Zn Stearate SMC Before (A) and After CH_2Cl_2 /S.B. Treatment (SMC-3)

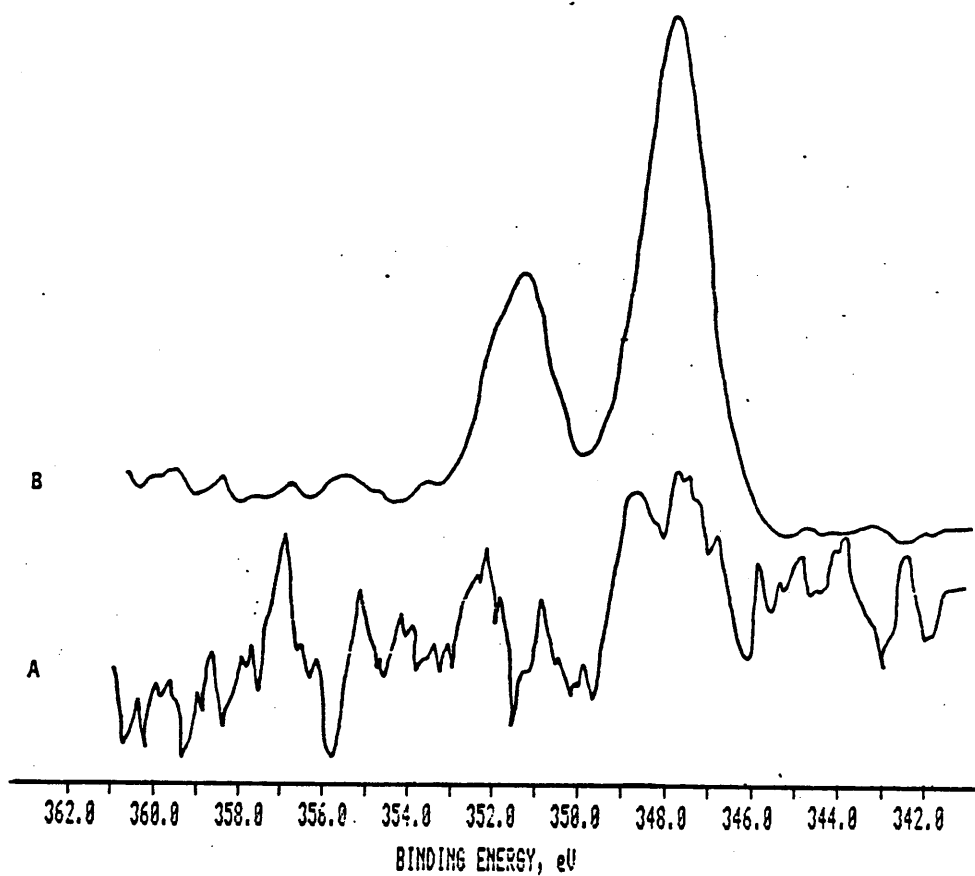


Figure 14. Ca 2p Spectra for a 4.5% Zn Stearate SMC Before (A) and After (B) a $\text{CH}_2\text{Cl}_2/\text{S.B.}$ Treatment (SMC-3)

result in any appreciable alteration in the O 1s spectra (Figure 13). The vivid change in the calcium content before and after treatment (Figure 14) illustrates the increase in calcium content on the SMC surface. The binding energy results for the Ca $2p_{3/2}$ level are consistent with the presence of calcium as Ca^{2+} , an expected result.

Treatment of SMC samples with isocyanate primer renders the surfaces of all samples virtually identical (Table 16). For all samples following treatment, no zinc, calcium or silicon is detected with the exception of one SMC-1 specimen where the calcium content is reduced only slightly. In addition a significant nitrogen photopeak is recorded which corresponds to approximately the same percent nitrogen content ($\sim 6\%$) on each specimen. After primer application the surface oxygen content is also similar for all samples ($\sim 23\%$).

The presence of isocyanate primer on the surfaces alters the peak shape for the carbon and oxygen photopeaks as shown in Figures 15 and 16, respectively, for a SMC-3 series sample. The appearance of C 1s peaks attributable to $-C-O-R/-NCO_2R$ groups is evident (see arrow). Further the FWHM of the O 1s peak is reduced from about 2.8 eV in the untreated SMC to about 1.8 eV for treated SMC. This result indicates that some of the oxygen-containing components in the original SMC are removed, reacted or covered by a thin film of isocyanate primer components. The FWHM for the oxygen 1s level is equal to that noted for simple oxygen containing components. Clearly some SMC components could have FWHM values and binding energy values equal to those measured for primer treated SMC. However comparison of these results with those for "pure"

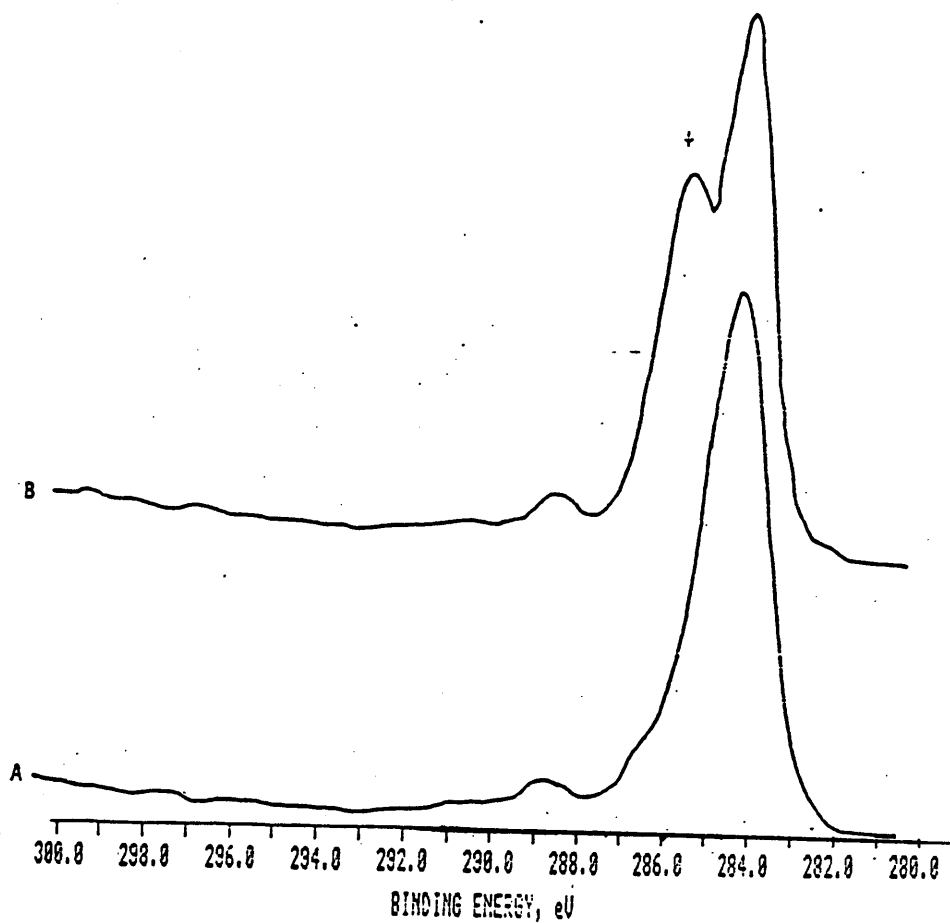


Figure 15. C 1s Spectra for a 4.5% Zn Stearate SMC Before (A) and After (B) a Primer Treatment (SMC-3)

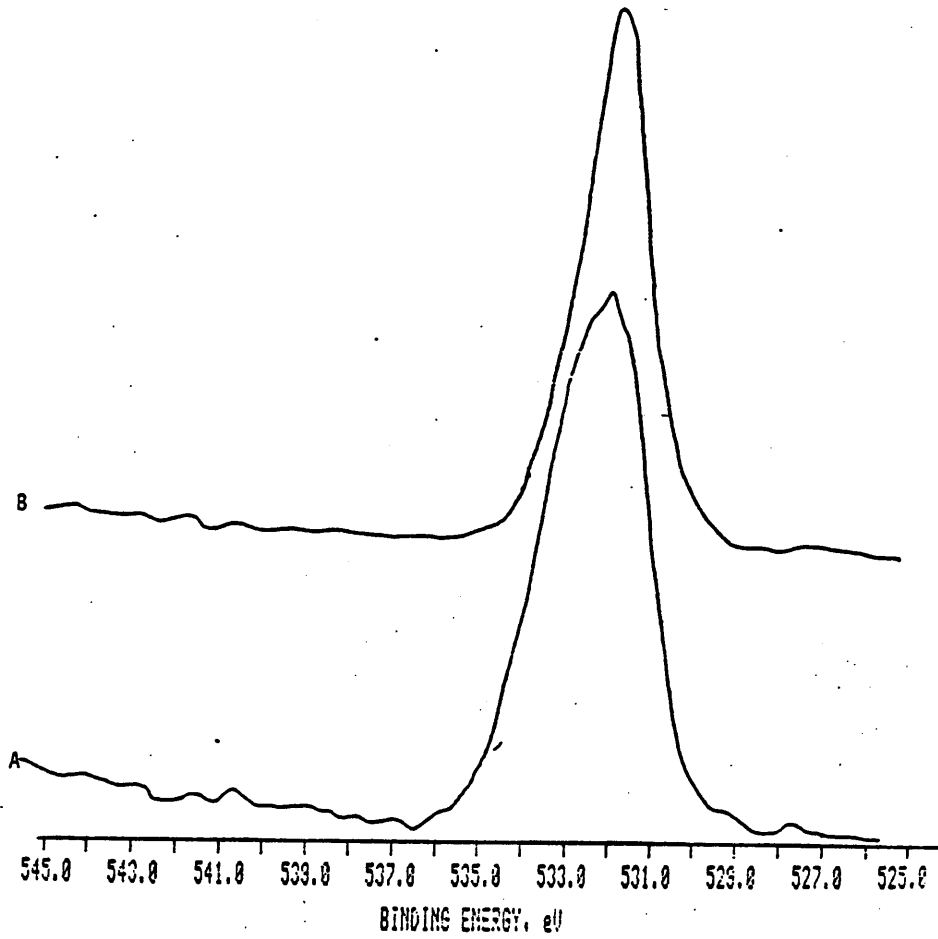


Figure 16. O 1s Spectra for a 4.5% SMC Before (A) and After (B) a Primer Treatment (SMC-3)

primer suggests that application of primer to the SMC surface produces a thin film of primer and/or primer/SMC reaction products and that the components present are simple, carbon-, oxygen-, and nitrogen-containing species. Table 17 gives summary of the effect, each pretreatment has on each of the four vendor SMC materials as noted in the C 1s spectra. In the table are the carbon 1s curve resolved results in terms of their relative atomic concentrations. Shown is the decrease in hydrocarbon (C_1) at the expense of the ether carbon (C_2) after CH_2Cl_2 wiping for all specimens except SMC-1 (treatment 2) and the large increase in ether carbon at the expense of hydrocarbon after the Scotch Brite/ CH_2Cl_2 wipe (treatment 3). Also shown is the exposure of CO_3^{2-} (C_4) and a large increase in carbonyl concentration after treatment 3. The application of isocyanate primer (treatment 4) is shown to increase the $-C-O-R/-NCO_2R$ (C_2) functionality at the expense of hydrocarbon.

XPS of Power-Washed SMC: As Received

Six SMC-1 samples which were power washed, i.e., sprayed with chemicals at high pressure, were XPS analyzed before (as received) and after isocyanate primer application. Appendix I gives the details of each of six power-wash pretreatments. These six different power washes are referred to as: Parker 3B (P3B), Oakite 07 (007), Oakite 08 (008), Chemfil C3 (CC3), Chemfil C24 (CC24), and Chemfil C31 (CC31). Table 18 gives relative atomic percent concentrations for each of the six power washed materials as well as carbon 1s curve resolved results for the as received samples.

Table 18

XPS Results for Power Washed SMC-1 Specimens
Before Primer Application (As Received)*
Relative Atomic Percent

| Element | <u>Sample</u> | | | | | |
|----------------|---------------|--------------|--------------|---------------|----------------|----------------|
| | Parker 3B | Oakite 07 | Oakite 08 | Chemfil C3 | Chemfil C24 | Chemfil C31 |
| $C_1 = CH_n$ | 83.2 | 81.4 | 83.1 | 82.1 | 83.0 | 81.9 |
| $C_2 = -C-O-R$ | 13.6 | 14.7 | 13.0 | 12.9 | 14.0 | 13.9 |
| $C_3 = C=O$ | 3.2 | 3.9 | 3.9 | 5.0 | 3.0 | 4.2 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| O | 20.6 | 19.7 | 18.9 | 18.8 | 19.2 | 20.0 |
| Si | 2.7 | < 0.1 | 2.4 | < 0.1 | < 0.1 | < 0.1 |
| Ca | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| N | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |

* NOTE: All Chemfil samples were actually wiped with CH_2Cl_2 first to remove contaminants as no untouched Chemfil specimens were available.

Typical curve resolved carbon 1s spectra are collected in Figures 17 and 18 for selected unwashed SMC-1 and SMC-4 (primed/unprimed) and power washed SMC-1, P3B and 007 (primed/unprimed), respectively. Similar curve resolved results were obtained for the other samples. The quantitative XPS data for the six power washed as received SMC samples (Table 18) indicate that the surfaces of the Parker and Oakite samples (P3B, 007, and 008) as a group are similar to the Chemfil samples (CC3, CC24, and CC31). All three Chemfil samples show a zinc content of less than 0.1 atomic percent. The Oakite and the Parker power washed samples also show no zinc (~0.1%). Somewhat surprisingly, the similarity in the C 1s curve resolved spectra for the Oakite and Parker power washed SMC-1 samples is very similar to the non-power washed SMC-1 samples (Table 17), where it is noted that little or no change in the distribution of carbon species is found compared to the starting material SMC-1. However other elemental concentrations change at the SMC-1 surface following power washing. The most notable alterations are the increase in surface silicon following Parker 3B and Oakite 08 treatment (Table 18) and the disappearance of detectable surface concentrations of zinc and calcium (see Tables 14-16 for untreated SMC-1). Loss of calcium and zinc could potentially occur in the wash, since hot aqueous solutions are sprayed on the SMC thus removing the low surface concentrations of these two components. With no knowledge of the specific chemical components in the power wash solutions, it is virtually impossible to account reasonably for calcium and zinc removal. Similarly the appearance of silicon in the Parker 3B and Oakite 08

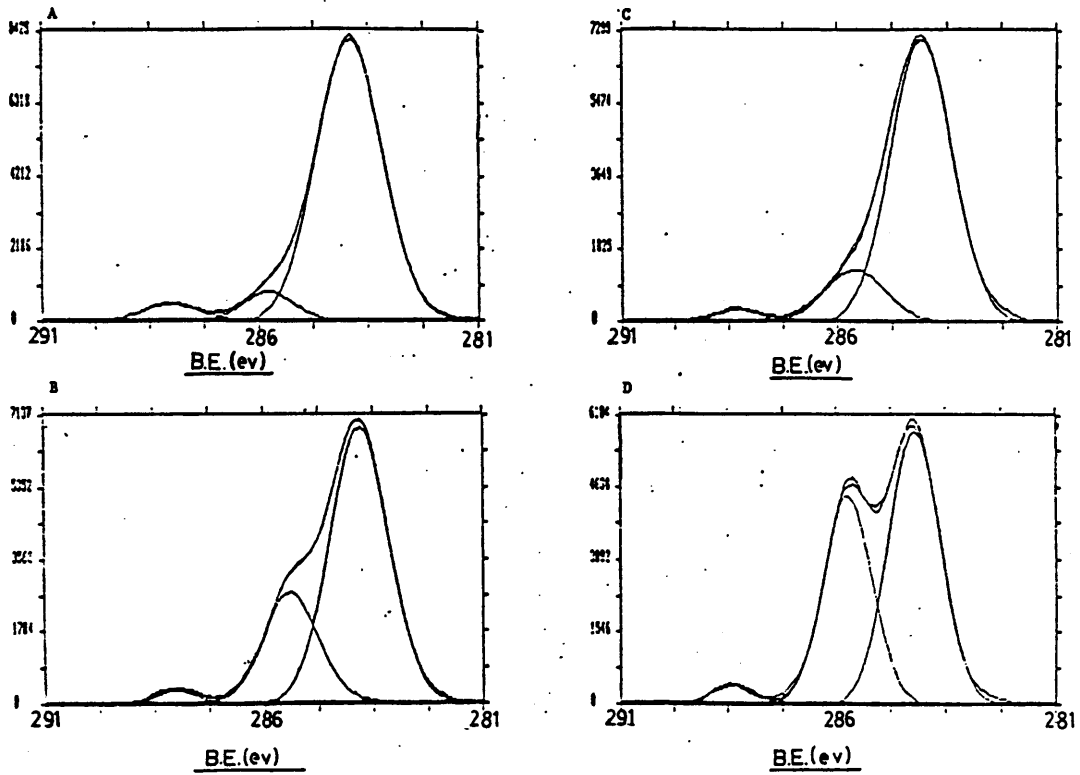


Figure 17. C 1s Spectra of SMC-1 and SMC-4 Before and After Primer Treatment

| | | |
|----|-------|-------------|
| A: | SMC-1 | As Received |
| B: | SMC-1 | Primed |
| C: | SMC-4 | As Received |
| D: | SMC-4 | Primed |

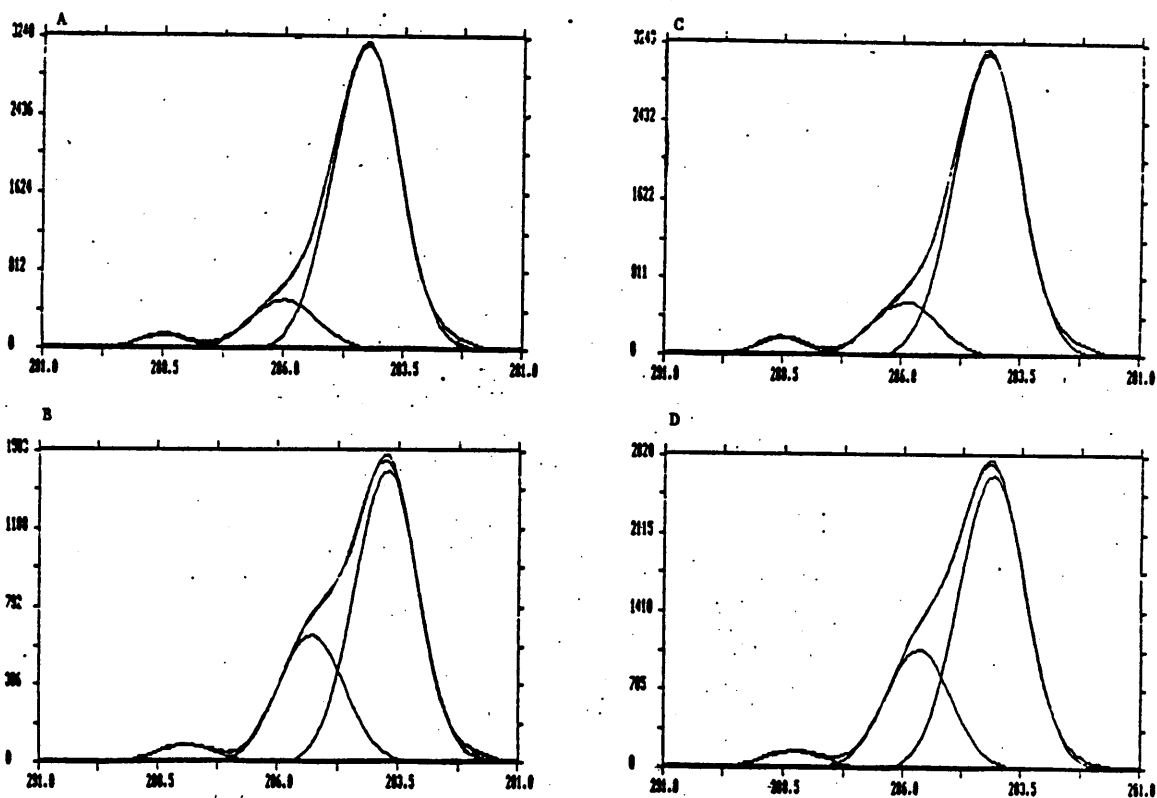


Figure 18. C 1s Spectra of P3B and 007 Before and After Primer Treatment

| | | |
|----|-----------|-------------|
| A: | Parker 3B | As Received |
| B: | Parker 3B | Primed |
| C: | Oakite 07 | As Received |
| D: | Oakite 07 | Primed |

treated samples could arise by removal of surface additives from SMC materials and exposure of silicon, or could be an ingredient in the power wash solutions. Thus except for the changes in the inorganic constituent surface concentrations, the power wash treatment has little or no significant effect on the carbon and oxygen surface chemistry of the Parker and Oakite treatments, but may alter the carbon chemistry after each of the three Chemfil treatments as each was first wiped with methylene chloride.

XPS of Power Washed SMC: After Isocyanate Primer Application

The XPS analysis results for SMC materials following the application of isocyanate primer are summarized in Table 19 and representative spectra are given in Figure 18. Two significant points can be noted from the data in Table 19: 1) the inorganic sample constituents are masked by the application of primer, and 2) all samples regardless of the particular power wash treatment give similar elemental results after the application of primer. The masking effect due to primer application was noted in the case of the four vendor SMCs as well as with the "old" SMCs discussed previously. Similar observations here indicate that derivatization of the surface or a surface film is formed in the application of primer.

It is also noted that the power washed SMC-1 samples exhibit results similar to those found for unwashed SMC-1 samples (Table 17 treatment 4) after each has been wiped with primer. The C₂ carbon content is around 26-29% for the primed power washed SMC-1 materials and

Table 19

XPS Results for Power Washed SMC-1 Specimens
Following Primer Application
Relative Atomic Percent

| Element | <u>Sample</u> | | | | | |
|------------------------|---------------|--------------|--------------|---------------|----------------|----------------|
| | Parker 3B | Oakite 07 | Oakite 08 | Chemfil C3 | Chemfil C24 | Chemfil C31 |
| $C_1 = -CH_n$ | 66.3 | 68.5 | 66.0 | 67.8 | 68.6 | 70.7 |
| $C_2 = -C-O-R/-NCO_2R$ | 29.8 | 27.6 | 29.7 | 27.6 | 28.1 | 25.9 |
| $C_3 = -C=O$ | 3.9 | 3.9 | 4.3 | 4.6 | 3.3 | 3.4 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| O | 18.1 | 17.4 | 19.5 | 18.8 | 19.1 | 16.6 |
| Si | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Ca | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| N | 7.4 | 6.9 | 7.9 | 7.2 | 8.3 | 8.0 |
| N/C_2 | 0.25 | 0.25 | 0.27 | 0.26 | 0.30 | 0.30 |

the N/C_2 ratio is relatively constant and only slightly greater than that found for untreated SMC-1. Thus from a surface chemical reference, power washing does not appear to alter significantly the extent or nature of the reaction with primer as interpreted from the results for SMC-1 and SMC-1/P3B, SMC-1/Oakite 07, SMC-1/Oakite 08, and SMC-1/Chemfil C3, C24, and C31 SMC materials.

Lap Shear Test Results

Room Temperature Lap Shear Results

Appendix II shows lap shear data for room temperature measurements for "old" SMC after one of four surface pretreatments. All bonds were bonded with either urethane 6- or 7-adhesive. For all the lap shear tests the Scotch Brite/ CH_2Cl_2 and the CH_2Cl_2 wipe pretreatments gave the highest percentage of substrate failure. It should be noted that substrate failure is the desired mode of failure as it indicates that the adhesive bond was sufficiently strong. These two treatments also gave the highest force needed to induce failure.

Appendix III shows the results recorded at room temperature for the SMC-1, SMC-2, SMC-3 and SMC-4 series SMC samples bonded using urethane 6- and 8-adhesive with selected pretreatments. Although there are many results in Appendix III, it is apparent that no pretreatment (A) leads to mixed substrate adhesive failure for all samples except SMC-2 coupons bonded with the 8-adhesive (82A) and SMC-3 samples bonded with the 6-adhesive (63A). For the SMC-1 materials a significant number of non-bonded SMC failures were obtained. This result limits severely any

statistical evaluation of the results for the SMC-1 series coupons. For the SMC-1 materials where 100% substrate failure occurred, the greatest fracture force was recorded for bonds prepared using isocyanate primer and 8-adhesive, i.e., samples 81C. Samples bonded following the Scotch-Brite/methylene chloride treatment using 8-adhesive (series 81B) also yielded 100% substrate failure and an average failure force of 590 lbs/in².

Observation of 100% substrate failure for the SMC-2 series samples occurred for samples 82A, 62B, 82B, with 62C at 95% substrate failure. Where comparisons can be made, the average fracture force was greater for samples bonded with the 8-adhesive. There is not a significant difference in the fracture force results when comparing the Scotch-Brite/CH₂Cl₂ or primer pretreatments for either 6- or 8-adhesive, e.g., 62B (501) vs. 62C (509), and 82B (581) vs 82C (561).

For the SMC-3 materials, both the Scotch-Brite/CH₂Cl₂ and primer pretreatments yield almost complete 100% substrate failure for 6- and 8-adhesives, the exception is one sample (83C) which gave 75% substrate failure. These two pretreatments have little or no effect on the failure force for 83B and 83C but the force for the 6-adhesive varies 63B > 63C. For all the SMC-3 samples the fracture force is greater than that for any of the other SMC materials.

The fracture behavior for the SMC-4 series coupons is most similar to that for the SMC-2 materials. Only for samples 64C and 84C is the average fracture force significantly greater than that for SMC-2.

The lap shear results for chemically washed SMC samples fractured at room temperature are given in Appendix IV. In this series the samples treated via the Oakite 07 and 08 and by the Parker 3B procedure, primed with isocyanate primer, and bonded with 6- or 8-adhesive yielded 100% substrate failure. Oakite pretreated (07 and 08) samples bonded without primer showed mixed failure mode while Parker (P3B) treated and bonded materials (no primer) showed 100% substrate failure. All of the Chemfil samples (C3, C24, and C31), primed and unprimed gave 100% substrate failure at room temperature.

In summary the room temperature lap shear results indicate that 1) the greatest occurrence of substrate failure is for Scotch Brite/ CH_2Cl_2 and primer pretreatments, 2) the average fracture force for the SMC series corresponding to 100% substrate failure varies in the order SMC-3 > SMC-4 > SMC-1 > SMC-2 (although more non-bonded failures resulted with the SMC-1 series).

Lap Shear Results after 7 day 130°F (54°C) water soak

In Appendices V and VI lap shear results are presented for specimens following soaking of samples in distilled water at 130°F (54°C) for one week and tested at 130°F (54°C) immediately after removal from the bath. Appendix V shows lap shear data for the SMC-1, SMC-2, SMC-3 and SMC-4 series SMC and Appendix VI shows data for the power washed SMC-1. The findings in this test indicate that all specimens yielded 100% substrate failure where the Scotch Brite/ CH_2Cl_2 pretreatment was used (Appendix V) and samples were bonded with 6- or

8-adhesive. Specimens pretreated with isocyanate primer and bonded with 6-adhesive exhibited 100% substrate failure, however use of the primer with the 8-adhesive gave 100% substrate failure only for the SMC-3 series. For the other SMC materials using primer and bonded with 8-adhesive the average failure mode was SMC-1; 50S/50A; SMC-2, 95S/5A; SMC-4, 80S/20A. When no pretreatment was used only the SMC-4 samples failed 100% in the substrate, for both 6- and 8-adhesives. For SMC-1, SMC-2 and SMC-3 specimens the procedure with no pretreatment and bonding with 6-adhesive gave mixed adhesive and substrate failure, while the no pretreatment 8-adhesive bonding procedure yielded 100% adhesive failure. For the latter case it is likely that a thin film of adhesive remains on the SMC portion of the failed specimen.

The order of average failure force for the different SMCs is equivalent to that noted for the room temperature tests. The average order is SMC-3 > SMC-4 > SMC-1 > SMC-2. Clearly for some results the order is not exactly SMC-3 > SMC-4 > SMC-1 > SMC-2, but this order is altered only for the nonpretreated materials where the SMC-4 series is slightly better than the SMC-3 specimens.

The lap shear test results for chemically washed SMC samples (SMC-1) obtained following the 130°F (54°C) water bath treatment are shown in Appendix VI. In this series the samples treated via the Oakite 08 and 07 and by the Parker 3B procedure, primed, and bonded using 6- or 8-adhesive yielded 100% substrate failure when tested following the 130°F (54°C) water bath soak. Pull tests for materials bonded as received (6AX and 8AX series) exhibited 100% substrate failure mode for

Oakite 08, mixed mode for Oakite 07: 100%S, 6A007; 100%A, 8A007; and for Parker P3B: 100%S, 6AP3B; and 50S/50A, 8AP3B. Pull test following the 130°F (54°C) water soak for the three Chemfil samples (primed and unprimed) showed mixed mode failure. Only two samples, 8CCC24 and 8CCC3 showed 100% substrate failure. The others showed substrate failure ranging from 25%S to 88%S with 8ACC23 showing the former value and 8CCC23 showing the later.

Examination of the average fracture force data in Appendices IV and VI do not reveal any chemical wash pretreatment that is clearly superior to another. However treatment with Oakite 08 does result in 100% substrate failure for unprimed SMC bonded with either 6- or 8-adhesive (6A008 and 8A008) after the 130°F (54°C) water bath soak. In addition the Oakite 07 treatment results in 100%S when bonded with 6-adhesive after tests done at room temperature and after the water bath soak. It is also apparent that the application of isocyanate primer before bonding with 6- or 8-adhesive yields favorable fracture results in terms of substrate failure and fracture force.

Lap Shear Results after 180°F (82°C) Heating for One Hour

In Appendix VII and VIII lap shear results are presented for specimens following heating at 180°F (82°C) in air for 1 hour and then testing at 180°F (82°C) immediately after removal from the oven. The most favorable adhesive bond occurs for the abrasion Scotch-Brite/methylene chloride pretreatment and for the isocyanate primer treated SMC materials. The failure force is significantly less than that for

Lap shear measurements conducted at room temperature and at 130°F (54°C) after soaking in water at 130°F (54°C) for 7 days. The failure force as a function of SMC material varies approximately in the manner SMC-3 > SMC-4 > SMC-2 = SMC-1.

XPS Analysis of Fractured (Lap Shear) Specimens

Surface analysis was carried out for fractured SMC material surfaces where non-substrate failure occurred. A uniform series of samples amenable to surface analysis was obtained from lap shear tests carried out at room temperature, following a 7 day 130°F (54°C) water bath treatment, and testing at 180°F (82°C) following treatment at 180°F (82°C) for one hour.

Surface Analysis Results for Fractured Samples from the Series 62A and 81A (Lap shear test at room temperature)

Two samples each prepared with no pretreatment using 6-adhesive to bond SMC-2 and using 8-adhesive to bond SMC-1 are discussed in detail and then the results are compared with other specimens in the series. The atomic percent concentration results are summarized in Table 20 and representative XPS spectra are shown in Figures 19-22, for the adhesive and SMC sides of the fractured specimens, along with spectra for as received materials. In the figures, ad refers to the adhesive side of the fractured specimen, SMC denotes spectra for the SMC side, and AR represents spectra for as received materials (i.e., no treatment). Analysis of the adhesive side of the fractured specimen yields atomic

Table 20XPS Results for Fractured SMC Specimens: 62A and 81A

(concentrations in relative atomic %; room temperature tests)

| <u>62A</u> | <u>#1</u> | | <u>#2</u> | |
|------------|------------|-------------|------------|-------------|
| | <u>SMC</u> | <u>Adh.</u> | <u>SMC</u> | <u>Adh.</u> |
| C | 100 | 100 | 100 | 100 |
| Zn | 0.1 | 0.1 | 0.15 | ND |
| O | 26.7 | 30.1 | 18.8 | 28.6 |
| Si | ND | 0.1 | ND | 0.36 |
| Ca | 0.5 | ND | 0.23 | 0.1 |
| N | 0.8 | 1.8 | 0.89 | 3.8 |
| Mg | ND | ND | ND | ND |
| Al | ND | ND | ND | ND |
| | | | | |
| <u>81A</u> | <u>#3</u> | | <u>#4</u> | |
| | <u>SMC</u> | <u>Adh.</u> | <u>SMC</u> | <u>Adh.</u> |
| C | 100 | 100 | 100 | 100 |
| Zn | tr | tr | tr | tr |
| O | 25.1 | 28.9 | 28.8 | 29.3 |
| Si | 0.20 | 0.5 | ND | ND |
| Ca | 1.1 | 0.35 | ND | 0.9 |
| N | 2.2 | 3.2 | 1.3 | 2.5 |
| Mg | ND | ND | ND | ND |
| Al | ND | ND | ND | ND |

tr = ~0.1%

ND = not detected < 0.1%

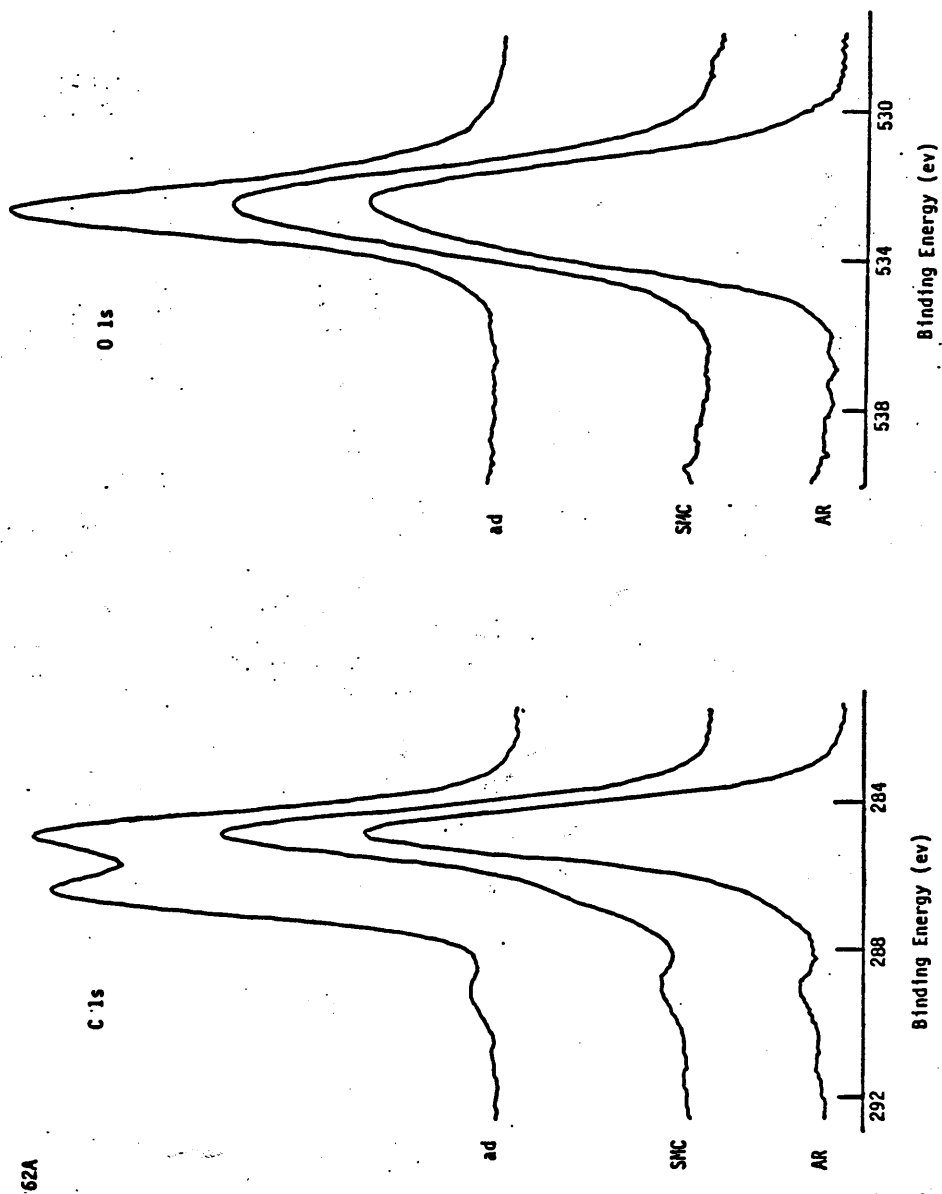


Figure 19. C 1s and O 1s XPS Spectra of 62A Fractured SMC

62A

62A

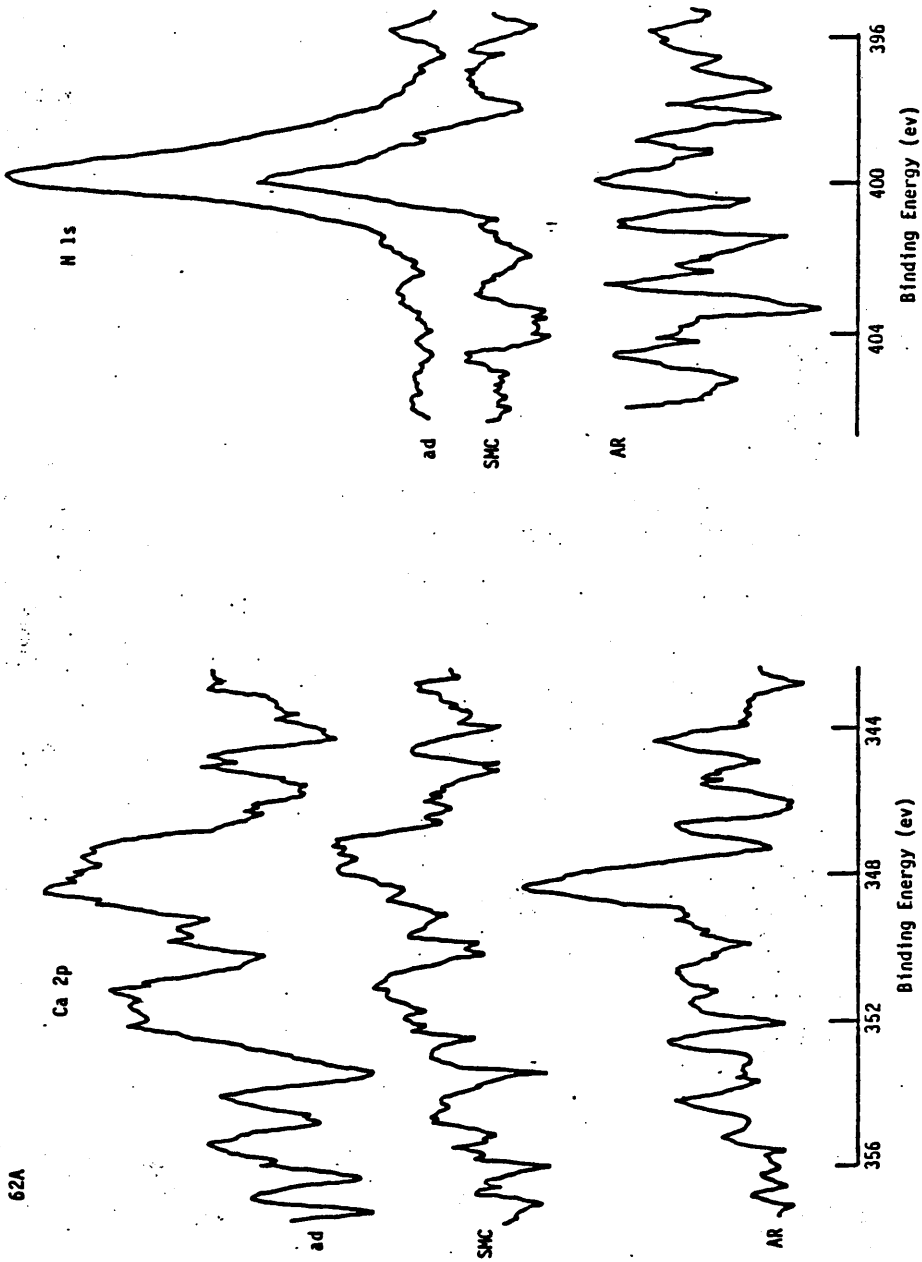


Figure 20. N 1s and Ca 2p XPS Spectra of 62A Fractured SMC

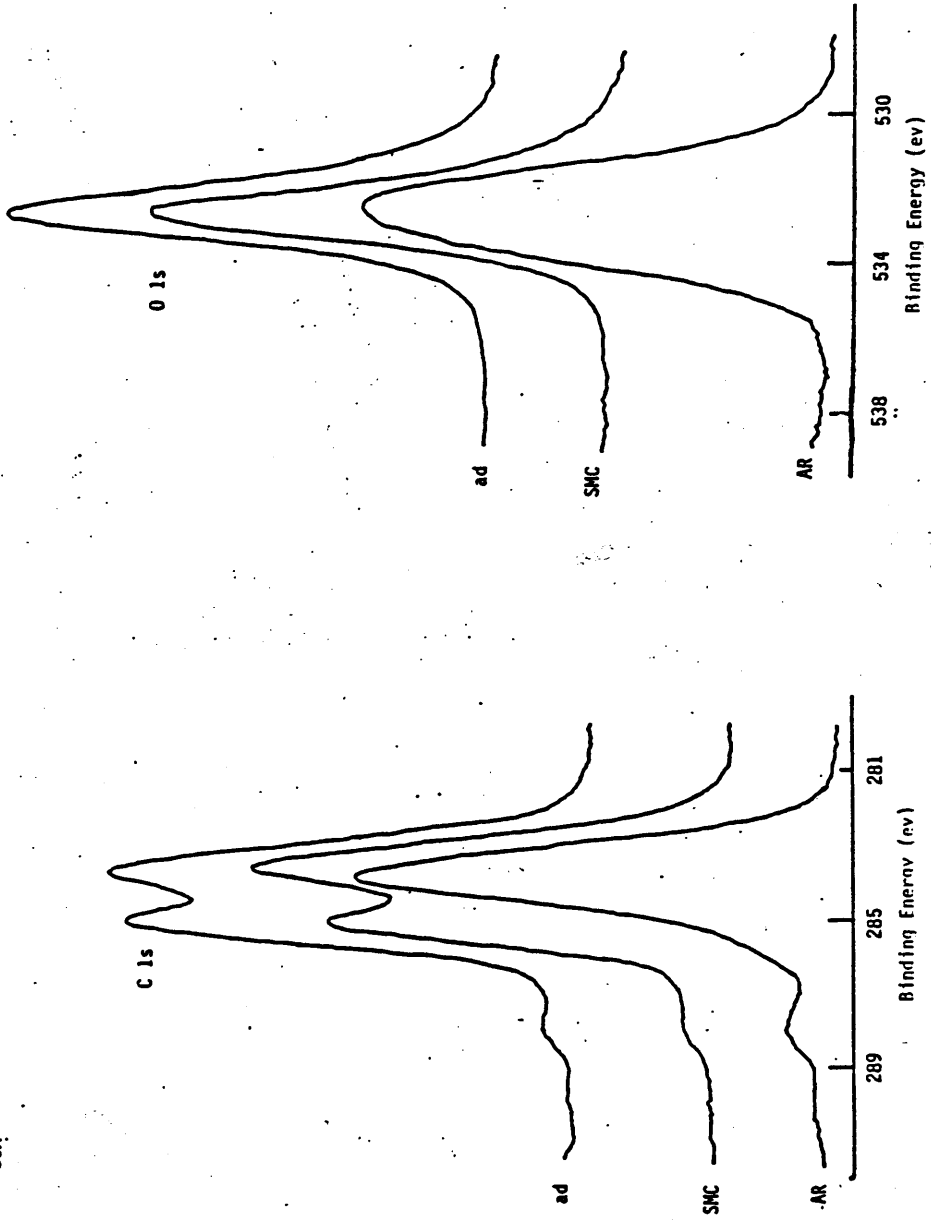


Figure 21. C 1s and O 1s XPS Spectra of 81A Fractured SMC

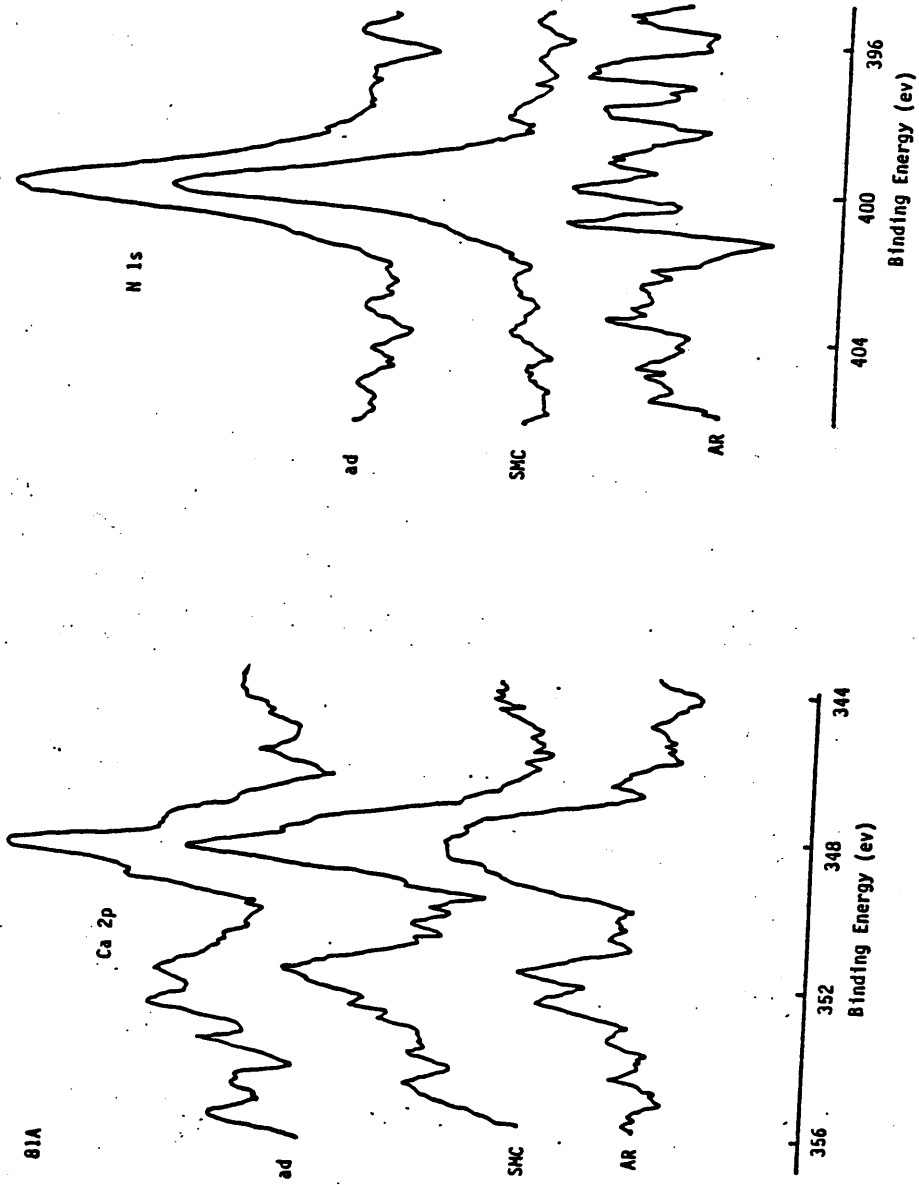


Figure 22. N 1s and Ca 2p XPS Spectra of 81A Fractured SMC

percentages that are similar to those determined previously for films of 6- and 8-adhesive. The oxygen content for the two samples bonded with 6-adhesive, i.e., -29%, compares with 30.3% measured for the 6-adhesive film. The oxygen content for the two films bonded with 8-adhesive, i.e., -29% compares with a value of 30.2% for the 8-adhesive film (Table 4). The nitrogen content for the samples with the exception of 62A (#3) is in a reasonable range compared to the 3.3% N found for the 6-adhesive film and the 3.0% N found for the 8-adhesive film. Additional components that appear on the adhesive side which are not components of the adhesive are silicon and calcium, with zinc appearing at trace levels in some samples.

XPS as a Function of Lap Shear Test Conditions

In Table 21 results are summarized for samples 62A, 81A and 8A007 tested at room temperature; 130°F (54°C) H₂O bath; and 180°F (82°C). These samples were prepared from as received (no pretreatment) SMC-2 bonded with 6-adhesive (62A); SMC-1 bonded with 8-adhesive (81A); and power-washed SMC-1 (Oakite 07 process) bonded with 8-adhesive (8A007). A number of observations and trends are evident in the results:

- 1.) The appearance of a nitrogen 1s photopeak and an increase in the -COR/-NCO₂R C 1s peak intensity for the SMC side of the fractured samples indicate that an adhesive film is present on the SMC surface. These features in the spectra are found for all three samples for all three test conditions. It should be noted that no N 1s signal was detected for sample 81A following the test at room temperature however

Table 21
XPS Surface Analysis of Fractured (Lap Shear)
SMC Specimens
Relative Atomic Percent

62A (RT, 130°, 180° fracture results)

| | <u>RT</u> | | <u>130°F</u> | | <u>180°F</u> | |
|---|-----------|------|--------------|------|--------------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad |
| C ₁ = -CH _n | 66.6 | 55.6 | 67.8 | 48.2 | 77.6 | 54.0 |
| C ₂ = -C-O-R/ -NCO ₂ R | 24.1 | 37.4 | 25.9 | 47.5 | 18.5 | 41.7 |
| C ₃ = -C=O | 9.3 | 7.0 | 6.3 | 4.3 | 3.9 | 4.3 |
| C _t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | 0.12 | 0.12 | --- | --- | --- | --- |
| O | 26.7 | 30.1 | 27.1 | 28.9 | 19.2 | 26.6 |
| Si | --- | tr | --- | 1.2 | --- | 1.8 |
| Ca | 0.5 | --- | --- | --- | --- | --- |
| N | 0.8 | 1.8 | 0.8 | 3.8 | 0.7 | 3.6 |
| Mg | --- | --- | --- | --- | --- | --- |
| Al | --- | --- | --- | --- | --- | --- |

--- = < 0.1%; tr ≡ 0.1%

Table 21
(Continued)

| <u>81A</u> | <u>RT</u> | | <u>130°F</u> | | <u>180°F</u> | |
|------------------------|-----------|------|--------------|------|--------------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad |
| $C_1 = -CH_n$ | 71.2 | 53.8 | 58.5 | 50.6 | 66.3 | 52.2 |
| $C_2 = -C-O-R/-NCO_2R$ | 25.0 | 42.0 | 35.4 | 45.5 | 29.5 | 43.5 |
| $C_3 = -C=O$ | 3.8 | 4.2 | 6.1 | 3.9 | 4.2 | 4.3 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | 0.3 | --- | --- | --- | --- | --- |
| O | 13.6 | 27.0 | 28.8 | 29.3 | 24.0 | 29.7 |
| Si | --- | --- | --- | --- | --- | tr |
| Ca | --- | 0.9 | 0.4 | 0.8 | 0.5 | --- |
| N | --- | 2.5 | 1.4 | 3.4 | 1.1 | 3.2 |
| Mg | --- | --- | --- | --- | --- | --- |
| Al | --- | --- | --- | --- | --- | --- |

--- = < 0.1%; tr ≡ 0.1%

Table 21
(Continued)

| <u>8A-007</u> | <u>RT</u> | | <u>130°F</u> | | <u>180°F</u> | |
|------------------------|-----------|------|--------------|------|--------------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad |
| $C_1 = -CH_n$ | 67.9 | 53.2 | 65.8 | 61.5 | 66.8 | 51.7 |
| $C_2 = -C-O-R/-NCO_2R$ | 27.1 | 41.5 | 29.3 | 35.1 | 29.4 | 43.3 |
| $C_3 = -C=O$ | 5.0 | 5.3 | 5.0 | 3.4 | 3.8 | 4.9 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | 0.3 | --- | tr | --- | --- | --- |
| O | 26.6 | 30.5 | 27.4 | 26.1 | 25.9 | 31.2 |
| Si | --- | --- | 1.3 | 1.0 | 1.4 | 1.1 |
| Ca | tr | 0.1 | 1.8 | 0.6 | --- | --- |
| N | 0.5 | 2.8 | 1.4 | 2.1 | 1.1 | 2.7 |
| Mg | --- | --- | --- | --- | --- | --- |
| Al | --- | --- | --- | --- | --- | --- |

--- = < 0.1%; tr ≡ 0.1%

the C 1s photopeak intensity for the $-C-O-R/-NCO_2R$ functional group is greater than the corresponding intensity for as received SMC. The increase in the C_2 carbon signal is an indication that an adhesive film is present on the SMC side of sample 81A but the concentration of the film is insufficient to permit the detection of nitrogen.

2.) The relative concentrations for C_1 , C_2 and nitrogen are similar on all adhesive sides of the samples and the elemental ratios are in the range of concentrations found for adhesive films. For samples with concentrations of nitrogen near that for pure adhesive and yet which show calcium or zinc it is possible that voids in the adhesive film are exposing underlying SMC or these elements have been transported to the fracture interface. Elements detected on the SMC side of the fracture include carbon, oxygen, calcium and sometimes traces of silicon and zinc. Significant nitrogen photopeaks are recorded when analyzing the SMC surfaces. For sample 81A (#1) the nitrogen content is equal to that found on the adhesive side while for the other SMC-side samples the nitrogen percentage is less than that for the adhesive side. The detection of nitrogen and also SMC components, namely Si, Ca and Zn, on the SMC portion of the fracture suggests that either a very thin film (< 50Å) of adhesive remains on the SMC surface or that a thin film of adhesive of undefined thickness and tears or holes in the adhesive film are present.

SEM Photomicrographs of Fractured Bonds

SEM photomicrographs were taken of the adhesive and SMC sides of the fractured bond. Shown in Figure 23 are representative adhesive sides of two fractured bonds, 81A tested at 180°F and 8A007 tested at 130°F. These photos demonstrate the existence of voids or tears in the adhesive film. While these voids appear to be deep, they do not appear to extend down to the SMC substrate surface. Figure 24 shows a comparison of untreated SMC-1 and 81A (SMC side) tested at 180°F (82°C). The relative smoothness on the left half side of the latter surface is indicative of a thin adhesive film. These films which remain on the SMC side of the fractured bond are clearly not homogeneous over the fractured surface but are rather quite discontinuous. Figure 25 further demonstrates this. Shown is sample 8A007 (SMC side) tested at room temperature. The majority of the surface, as indicated by its CH_n to $-C-O-R/-NCO_2R$ carbon ratio is approximately equal to that for the pure adhesive film. The carbon component distribution on the adhesive side for a few samples 62A (RT and 180°F) and 8A007 (130°F) is unlike that for other samples and for the adhesive films. The principal difference is that the CH_n carbon is more intense for these samples. Such a result suggests that the adhesive film on the adhesive side of the fracture may not be uniform and that tears or voids exist, exposing substrate SMC.

3. The oxygen content for room temperature and 180°F tested samples is greater for the adhesive side of the fracture. This result is expected since the adhesive side contains a urethane film which



Figure 23 SEM Photomicrographs of 81A (Ad.) (top) and 8A007 (Ad.) (bottom) tested at 180°F (82°F) and 130°F (54°C), respectively

Relative Magnification: 200x

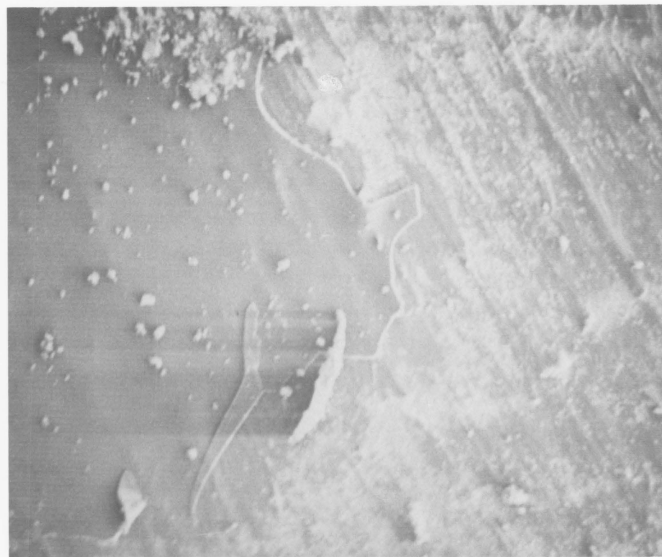
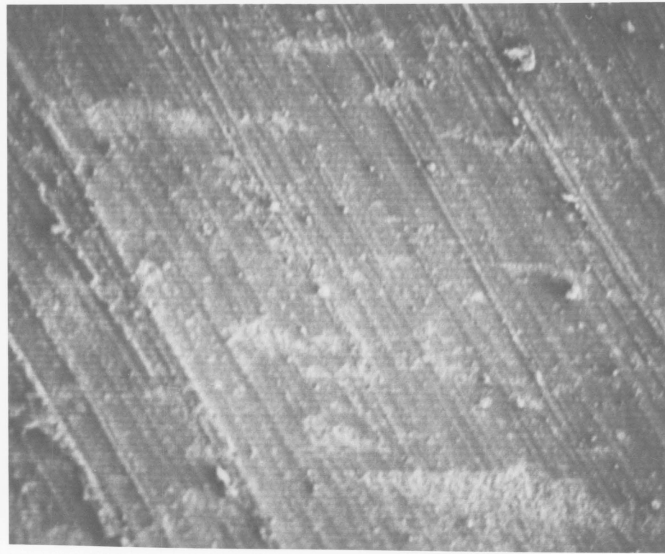


Figure 24 SEM Photomicrographs of SMC-1 (top) and 81A SMC (bottom) tested at 180°F (82°C)

Relative Magnification: 200x

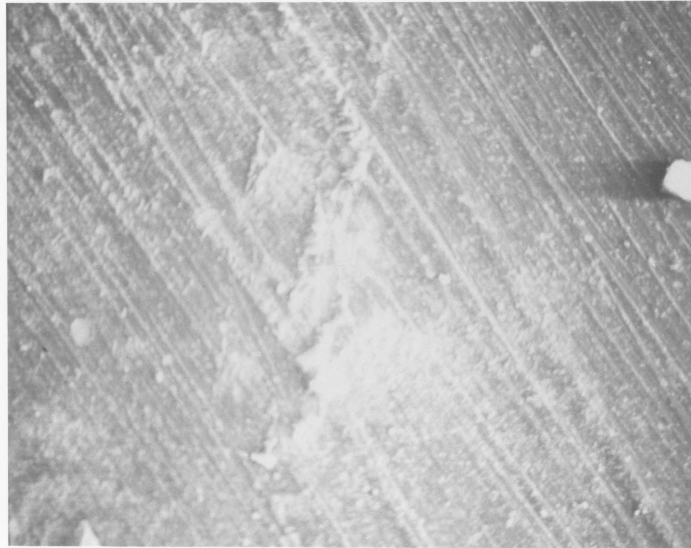


Figure 25 SEM Photomicrograph 8A007 (SMC side) tested at 72°F (22°C)

Relative Magnification: 200x

should exhibit greater oxygen content relative to the SMC side. The oxygen 1s photopeak full width at half maximum (FWHM) for the adhesive side of fractured SMCs is indicative of only one type of oxygen. For the 130°F water soaked samples, the surface oxygen content is approximately equal for SMC and adhesive sides of the fractured specimen. In addition the O 1s peak FWHM is smaller for the SMC side of the 130°F samples compared to RT and 180°F materials. The RT and 180°F SMC surfaces have oxygen photopeaks indicative of oxide and hydroxide functional groups. On the other hand the O 1s FWHM for the 130°F water treated SMC samples is consistent with only one oxygen type, and the FWHM for SMC and adhesive sides are equal. These findings indicate that the aqueous treatment alters the surface oxygen concentration and chemistry. To account for such a change it is likely that water penetrates the SMC material and reacts in some undetermined fashion.

4. Significant calcium concentrations are apparent for the fractured 130°F water treated SMC samples using 8-adhesive while no calcium is detectable for similar tests of the SMC sample bonded with 6-urethane adhesive. It could be imagined that water penetration at the SMC surface occurs in regions near calcium sites and that some hydrolysis reaction occurs facilitating fracture at this site.

5. Silicon is also detected at significant levels in the 8A007 samples tested at 130°F (water bath) and at 180°F. No silicon was detected in the as received power-washed material. The source of this silicon is unknown, although it could arise from the adhesive or SMC. The present experimental results do not permit a definitive answer.

The 180°F lap shear tests provided a suite of samples so that the effect of the SMC substrate on adhesion could be evaluated; series 61A, 62A, 63A, 64A; and a series so that the effect of the pretreatment could be probed, 81A, 81B, 81C, and 82A, 82C. The XPS results for this group of samples are presented in Tables 22 and 23, respectively for samples bonded with 6- and 8-adhesive.

The XPS results presented in Table 22 indicate that the surfaces for fractured samples are similar. For the SMC side, the CH_n , $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$, and $-\text{C}=\text{O}$ relative percentages are only slightly less than the values measured for as received samples. The oxygen content is also increased only slightly, while no zinc or calcium is detected on the fractured SMC surface. The nitrogen content, while low, is indicative of adhesive on the surface. The presence of an adhesive film would be consistent with the levels of carbon; CH_n , $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$ oxygen and nitrogen detected. The significant point of these results is that bonding to the untreated (as received) surfaces is similar. All samples fail leaving a thin film of adhesive on the SMC surface.

Surface analysis results for the adhesive side of the fractured samples (Table 22) indicate too, that the different SMC samples behave similarly. The carbon, oxygen, and nitrogen concentrations are all similar and are approximately equal to the values determined for the pure adhesive film. The absence of significant quantities of zinc and calcium on these adhesive side samples could suggest that the films are more uniform and that little or no tearing or transfer of SMC components has occurred. The presence of silicon on the adhesive surface, could

Table 22

XPS Results for SMC-1, SMC-2, SMC-3, SMC-4
As Received, SMCs Bonded with 6-Adhesive
(Lap Shear Tests at 180°F (82°C))
Relative Atomic Percent

| Element | 61A | | 62A | | 63A | | 64A | |
|------------------------|------|------|------|------|------|------|------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad | SMC | Ad |
| $C_1 = -CH_n$ | 75.0 | 52.6 | 77.6 | 54.0 | 76.2 | 51.9 | 72.4 | 50.8 |
| $C_2 = -C-O-R/-NCO_2R$ | 20.8 | 44.6 | 18.5 | 41.7 | 20.9 | 44.3 | 22.0 | 43.4 |
| $C_3 = -C=O$ | 4.2 | 2.8 | 3.9 | 4.3 | 2.9 | 3.8 | 5.6 | 5.8 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | --- | --- | --- | --- | --- | --- | --- | --- |
| O | 21.8 | 27.3 | 19.2 | 26.6 | 20.9 | 28.8 | 23.0 | 29.5 |
| Si | --- | 1.0 | --- | 1.8 | 1.0 | tr | --- | 1.2 |
| Ca | --- | tr | --- | --- | --- | --- | tr | --- |
| N | 0.5 | 3.4 | 0.7 | 3.6 | tr | 3.7 | 1.2 | 3.0 |

--- = < 0.1%; tr ≡ 0.1%

Table 23

XPS Results for SMC-1 and SMC-2 Bonded with 8-Adhesive Following No Pretreatment,
 $\text{CH}_2\text{Cl}_2/\text{SB}$, and Isocyanate Primer Pretreatment (Lap Shear Tests
 at 180°F (82°C)) Relative Atomic Percent

| Element | 81A | | 81B | | 81C | | 82A | | 82C | |
|--|------|------|------|------|------|------|------|------|------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad | SMC | Ad | SMC | Ad |
| $\text{C}_1 = -\text{CH}_n$ | 66.3 | 52.2 | 40.9 | 53.8 | 74.5 | 59.1 | 73.3 | 50.1 | 59.7 | 56.7 |
| $\text{C}_2 = -\text{C}-\text{O}-\text{R}/$ $-\text{NCO}_2\text{R}$ | 29.5 | 43.5 | 44.3 | 38.6 | 21.5 | 36.7 | 20.2 | 44.1 | 33.3 | 38.2 |
| $\text{C}_3 = -\text{C}=\text{O}$ | 4.2 | 4.3 | 6.4 | 6.4 | 4.0 | 4.2 | 6.5 | 5.8 | 7.0 | 5.1 |
| $\text{C}_4 = \text{CO}_3^{2-}$ | --- | --- | 8.4 | 1.2 | --- | --- | --- | --- | --- | --- |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| O | 24.0 | 29.7 | 38.2 | 30.9 | 20.7 | 26.5 | 23.5 | 30.9 | 28.0 | 29.0 |
| Si | --- | tr | --- | --- | --- | tr | --- | 1.1 | --- | --- |
| Ca | 0.5 | --- | 0.7 | 2.1 | --- | --- | --- | --- | 1.9 | --- |
| N | 1.1 | 3.2 | 1.6 | 2.3 | 1.1 | 4.9 | 2.2 | 2.4 | 1.8 | 3.0 |

---- = < 0.1%; tr \approx 0.1%

arise from adhesive components or SMC additives. The present measurements do not permit one to identify the source.

The analysis results in Table 23 permit a comparison of the three pretreatments for SMC-1 bonded with 8-adhesive and for two pretreatments of SMC-2 bonded with 8-adhesive. The data for the 81X series indicate an adhesive film on the SMC surface. The relative atomic concentrations for 81A are similar to other samples pretreated in the same manner. There are however significant differences in the results for other elements in this series. For the 81B sample (Scotch Brite/ CH_2Cl_2 pretreatment) the SMC and adhesive sides show carbonate carbon ($\text{C}_4 = \text{CO}_3^{2-}$) and significant calcium. The calcium content on the SMC side is significantly greater than the level found for pretreated, but non-bonded samples, i.e., 2.0%, while the concentration on the adhesive side is only slightly less than that on the pretreated, non-bonded surface. That carbonate and calcium are detected at such high levels indicates significant areas on the surface where filler material is present. The presence of such areas could be responsible for failure of this specimen. The relative oxygen concentrations for SMC and adhesive sides are reversed from what is usually observed. For this sample the oxygen content on the SMC side is significantly greater than that on the adhesive portion. This finding is also consistent with the presence of carbonate on the surface. A similar result was found for fractured samples bonded with 6- and 7-adhesive using SMC ("old") with 3 and 6% zinc stearate levels.

The XPS analysis for sample 81C yields results indicating significant CH_n carbon and a usual concentration of nitrogen. The carbon content distribution gives a higher CH_n and a lower $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$ concentration than on primed non-bonded samples. The carbon content results are more like the results obtained for bonded as received samples. This fact suggests that the primer application for this sample was ineffective and thus the failure could be due to the absence of proper priming. For the adhesive side the analysis results are similar to those obtained for other adhesive side samples and are consistent with the presence of adhesive on the SMC surface. That inorganics at reasonable concentration levels were not detected, suggests that the adhesive film is uniform with few or no voids or tears.

The pretreatments for SMC-2 samples, 82A and 82C, Table 23, exhibit a different behavior compared to the 81X counter parts. For 82A SMC side the CH_n to $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$ concentration ratio is greater than for the 82C material and very near that found for the 6XA samples (Table 22). This finding suggests that the bonding of 8-adhesive with SMC-2 samples is similar to 6-adhesive bonding with other SMCs. The results for the SMC side of 82C show a lower CH_n and a greater $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$ concentration compared to 82A. The result is consistent with the idea that the application of primer alters the surface chemistry to increase the $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$ concentration thereby enhancing bonding.

The adhesive side results for carbon, oxygen and nitrogen for 82A and 82C compare favorably with each other and with other adhesive side

specimens. This comparison indicates that the thick adhesive film is similar for all substrates and for the two adhesives.

An interesting comparison of the effectiveness of primer pretreatment related to SMC materials is evident by comparing the XPS results for 81C and 82C. The XPS data for the adhesive sides are equivalent and the absence of significant inorganic components indicates a uniform film of adhesive. A comparison of the SMC-side results for 81C and 82C shows that the CH_n content on 81C is high compared to 82C. In fact the CH_n and $-\text{C}-\text{O}-\text{R}/-\text{NCO}_2\text{R}$ concentrations on 81C are similar to those measured for non-treated as received samples (see discussion above), while the corresponding concentrations for 82C-SMC are near the values for primed SMC-2. In the discussion of results for primed samples it was noted that the SMC-1 series materials appeared not to react as effectively with primer as the other SMC samples. The results presented here for fractured samples seem to be a direct reflection of that finding: that isocyanate primer is not as effective for SMC-1 and that failure occurs to yield an SMC-1 surface equivalent to that of an unprimed as received sample. Clearly, such conclusions are being generalized from data on only two samples and confirmation and support of this suggestion would require analysis of additional similar specimens.

An additional point regarding the relationship of adhesive and SMC substrate can be obtained by comparing the results for the SMC side of samples 61A, 81A, 82A, and 62A all tested at 180°F (82°C). The carbon content distribution for 61A, 62A and 82A are approximately

equal, $CH_n = 75\%$ and $-C-O-R/-NCO_2R = 20\%$ while the corresponding values for 81A are approximately 66% and 80%. These values for 81A, showing greater $-C-O-R/-NCO_2R$ and decreased CH_n concentrations, are in the range found for primer treated bonded and non-bonded samples. One interpretation of these results could be that 8-adhesive is more effective for bonding to SMC-1 than to other SMCs or that 8-adhesive is a better adhesive for SMC-1 than the 6-adhesive. This particular behavior for untreated samples was found only for the SMC-1, 8-adhesive combination. Whether this result is significant, reproducible, or interpretable as indicated above, would require further comparative measurements.

Surface analysis findings for power-washed SMC samples bonded with 6- and 8-adhesive are summarized in Table 24. Carbon 1s XPS spectra for 6A008 and 6C008 fractured samples are shown in Figure 26. Results are given for five specimens that were bonded as received and one that was bonded after the application of isocyanate primer, 6C008. The results for the adhesive side of the SMCs for the carbon component distribution are similar to those found earlier. However for all samples, except 6A008, significant calcium and/or silicon concentrations are found suggesting the migration of SMC components to the adhesive film surface or voids/tears in the adhesive. Silicon was detected on as received Parker 3B and Oakite 08 treated samples, so the presence of calcium suggests voids on the adhesive surface.

The analysis data for the SMC sides indicate 1-2% concentration levels of nitrogen, a result consistent with a thin film of adhesive on

Table 24

XPS Results for 6A008, 6C008, 8A007, 8AP3B, 8ACC23 and
8ACC24 Samples Following Lap Shear Tests
(Lap Shear Tests at 180°F (82°C))
Relative Atomic Percent

| Element | 6A 008 | | 6C 008 | | 8A 007 | |
|------------------------|--------|------|--------|------|--------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad |
| $C_1 = -CH_n$ | 71.5 | 61.9 | 75.1 | 52.6 | 66.8 | 51.7 |
| $C_2 = -C-O-R/-NCO_2R$ | 23.3 | 34.3 | 19.3 | 41.7 | 29.4 | 43.4 |
| $C_3 = -C=O$ | 5.2 | 3.8 | 5.6 | 5.7 | 3.8 | 4.9 |
| C_t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | --- | --- | --- | --- | --- | --- |
| O | 23.3 | 24.9 | 20.0 | 31.1 | 25.9 | 31.2 |
| Si | --- | --- | 1.3 | 0.9 | 1.4 | 1.1 |
| Ca | 1.1 | --- | 0.3 | 0.6 | --- | --- |
| N | 1.3 | 3.0 | 1.2 | 4.9 | 1.1 | 2.7 |

--- = < 0.1%; tr ≡ 0.1%

Table 24
(Continued)

XPS Results for 6A008, 6C008, 8A007, 8AP3B, 8ACC23 and
8ACC24 Samples Following Lap Shear Tests
(Lap Shear Tests at 180°F (82°C))
Relative Atomic Percent

| Element | 8A P3B | | 8A CC23 | | 8A CC24 | |
|---|--------|------|---------|------|---------|------|
| | SMC | Ad | SMC | Ad | SMC | Ad |
| C ₁ = -CH _n | 71.9 | 62.6 | 74.1 | 56.6 | 67.6 | 60.3 |
| C ₂ = -C-O-R/ -NCO ₂ R | 22.2 | 32.4 | 20.7 | 39.0 | 27.3 | 34.1 |
| C ₃ = -C=O | 5.9 | 5.0 | 5.2 | 4.4 | 5.1 | 5.6 |
| C _t (total) | 100 | 100 | 100 | 100 | 100 | 100 |
| Zn | 0.3 | --- | --- | --- | tr | --- |
| O | 28.0 | 26.5 | 25.7 | 29.8 | 26.0 | 30.9 |
| Si | --- | --- | --- | --- | 1.1 | 2.2 |
| Ca | 1.9 | 0.6 | 1.6 | 0.9 | 1.3 | 0.9 |
| N | 1.8 | 2.6 | 1.8 | 3.2 | 1.2 | 1.8 |

--- = < 0.1%; tr ≡ 0.1%

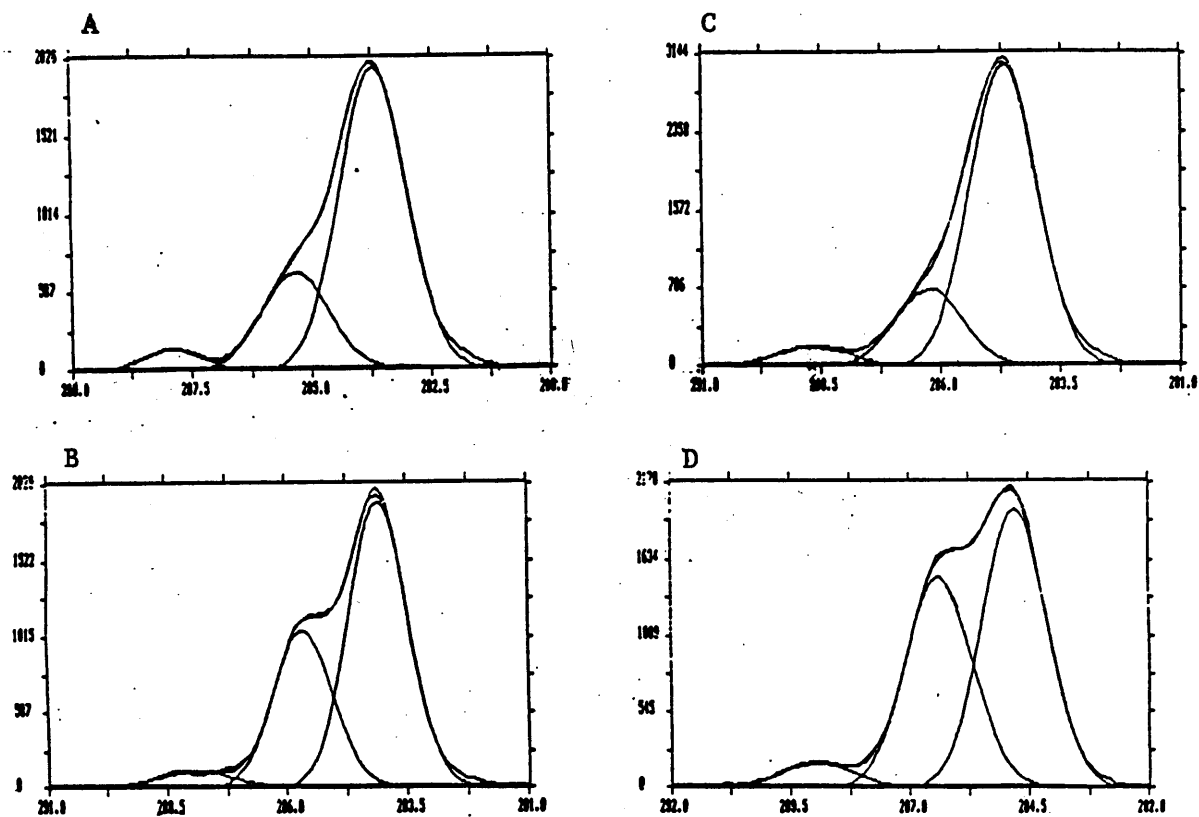


Figure 26. C 1s XPS Spectra for Samples 6A008 and 6C008 Tested at 180°F (82°C)

| | | |
|----|-----|--------|
| A: | SMC | 6A-008 |
| B: | Ad | 6A-008 |
| C: | SMC | 6C-008 |
| D: | Ad | 6C-008 |

the surface. On the other hand the carbon component distributions are approximately equal to those found for as received non-bonded samples. That the SMC surface appears to be similar to the as received surface indicates that the adhesive film must be quite thin or inhomogeneous. The calcium that remains on the adhesive side of the fracture for samples 6C008, 8AP3B, 8ACC23, and 8ACC24, is indicative of either SMC substrate remnants from the SMC side, element migration, or contamination from the sample preparation cutting process. Why sample 8A007 shows no calcium on either the adhesive or SMC side of the fracture is not clear. It is also interesting to note that both samples 8A007 and 8ACC24 show silicon on both sides of the fracture. They both also have the largest -C-O-R/-NCO₂R concentration (and the lowest CH_n concentration) on the SMC side of fractured samples. In addition the fracture force for these two samples (240 and 260 lbs/in², respectively) is slightly lower than for other power washed samples tested under similar conditions. Samples 8AP3B and 8ACC23 show similar XPS results for both sides of fracture with the exception that the relative oxygen concentration is less on the adhesive side of fracture than on the SMC side of 8AP3B. The reason for this is not known at present. Examination of the data for the primed sample, 6C008, shows that the effectiveness of the primer for this sample was not significant. The relative carbon component and oxygen concentrations are approximately equal to those for the corresponding unprimed sample (6A008), but different than values for a primed surface or the pure adhesive film.

This comparison suggests that for this sample the primer is ineffective and fracture occurs in a manner like that for unprimed samples.

CONCLUSIONS

The principal findings from this study are summarized below:

A: SMC Materials

1) Surface characterization of SMC materials containing 3, 4.5, and 6% zinc stearate and materials containing 4.5% zinc stearate indicated that the surfaces were heterogeneous with respect to the distribution of inorganic constituents.

B: Pretreatments

2) The most favorable surface pretreatments that yield good adhesive bonds are abrasive Scotch Brite/ CH_2Cl_2 treatment, application of primer (isocyanate), and power wash treatments (Parker and Oakite).

3) These pretreatments alter the surface chemistry of SMC to enhance principally the $-\text{C}-\text{O}-\text{R}(\text{X})/-\text{NCO}_2\text{R}$ functionality and to a lesser extent the $-\text{C}=\text{O}$ group.

4) The pretreatments also lower the hydrocarbon content at the surface, and it appears that at least one factor that contributes favorably to good adhesion is the presence of $-\text{C}-\text{O}-\text{R}(\text{X})/-\text{NCO}_2\text{R}$ functionality.

5) The calcium content increases dramatically following the abrasive pretreatment.

6) Pretreatment with primer yields a surface film including -C-O-R(X)/-NCO₂R and nitrogen species that mask the SMC substrate components.

C. Fractured Adhesive/SMC Specimens

7) For samples that do not fail via substrate failure/fiber tear, a thin film of adhesive remains on the SMC surface.

8) The SMC surfaces do not appear to have a continuous adhesive film in that elements of the SMC substrate are detected in the surface analysis measurements.

9) The fracture forces and the uniformity of lap shear results vary among SMCs and the variation is related to the source (formulator/manufacturer) of SMC.

10) Secondary electron photomicrographs reveal areas of SMC where the adhesive film appears to be torn from substrate SMC leaving voids at the surface.

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APPENDIX I

CHEMICALLY CLEANED SMC-1

| nomenclature | treatment | reference |
|-----------------------|--|--|
| Oakite 08 (008) | 1 oz/gal., 104-B-350 1 min. @ 130°F | Mike Kovacs phone: 201-464-6900 |
| Oakite 07 (007) | 2 oz/gal., 104-B-352 1 min @ 130°F follow by 3% 75-G-2S, 1 min. @ 130°F | same as above |
| Parker 3B (P3B) | -PPCL 2978 (Aq. oxygenated glycol) 100% mist-1 min -PPST 2183 (Caustic) 10% by vol. 150°F spray-1 min -W.W.R. - 1 min (warm water rinse -W.W.R. - 1 min -D.I. - 0.5 min | Dr. Gary Kent phone: 313-583-9300 |
| Chemfil C3 (CC3) | Chemkleen 45 (NaOH) 1 oz./ gal. @ Ambient Temp | Dr. Harry Charles phone: 313-689-0720 |
| Chemfil C23 (CC23) | -Chemkleen 338 (mild alkaline) 5% by vol. -rinse -Chemfog 107 FA (high fluorinating-2N Phosphate) -rinse D.I. | same as above |
| Chemfil C24 (CC24) | -Chemkleen 49 (mild alkaline with silicates) 1 oz/gal. -rinse Chemfog 168 (modified 107) -rinse D.I. | same as above |
| Chemfil C31 (CC31) | -Chemkleen 49 -rinse D.I. | same as above |

APPENDIX II

Lap Shear Results - Room Temperature 72°F (22°C)

Samples: "original" SMC; 3.0, 4.5, or 6.0%

Zinc-stearate; 6 or 7-Adhesive

Treatment: A = bonded as received

B = wiping with CH₂Cl₂

C = wiping with CH₂Cl₂ soaked Scotch Brite abrasive pad

D = passing the SMC through a reducing flame at ~30
ft/min

NB SMC = non-bonded SMC failure

| Sample | Failure Force (lbs/in ²) | Average Failure Force (lbs/in ²) | % Substrate Failure |
|--------|--------------------------------------|--|---------------------|
| 6A3 | 130 | 140 | 0 |
| 6A3 | 150 | | 0 |
| 6B3 | 131 | 163 | 0 |
| 6B3 | 195 | | 0 |
| 6C3 | 230 | 240 | 0 |
| 6C3 | 250 | | 25 |
| 6D3 | 138 | 151 | 0 |
| 6D3 | 163 | | 10 |
| 6A4 | 120 | 135 | 0 |
| 6A4 | 150 | | 0 |
| 6B4 | 205 | 228 | 0 |
| 6B4 | 251 | | 25 |
| 6C4 | 237 | 244 | 25 |
| 6C4 | 251 | | 100 |
| 6D4 | 120 | 130 | 0 |
| 6D4 | 140 | | 0 |
| 6A6 | 105 | 120 | 0 |
| 6A6 | 135 | | 0 |
| 6B6 | 260 | 243 | 50 |
| 6B6 | 225 | | 0 |
| 6C6 | 219 | 216 | 50 |
| 6C6 | 213 | | 100 |
| 6D6 | 150 | 128 | 0 |
| 6D6 | 105 | | 0 |
| 7A3 | 108 | 136 | 0 |
| 7A3 | 163 | | 0 |
| 7B3 | 250 | 300 | 50 |
| 7B3 | 349 | | 75 |
| 7C3 | 245 | 233 | 100 |
| 7C3 | 221 | | 100 |
| 7D3 | 210 | 195 | 0 |
| 7D3 | 180 | | 0 |
| 7A4 | 152 | 161 | 0 |
| 7A4 | 170 | | 0 |

APPENDIX II Continued

| Sample | Failure Force (lbs/in ²) | Average Failure Force (lbs/in ²) | % Substrate Failure |
|--------|--------------------------------------|--|---------------------|
| 7B4 | 190 | 183 | 0 |
| 7B4 | 175 | | NB SMC |
| 7C4 | 252 | 259 | 25 |
| 7C4 | 265 | | 75 |
| 7D4 | 138 | 156 | 0 |
| 7D4 | 169 | | 0 |
| 7A6 | 193 | 177 | 0 |
| 7A6 | 161 | | 0 |
| 7B6 | 200 | 208 | 0 |
| 7B6 | 215 | | 25 |
| 7C6 | 302 | 314 | 50 |
| 7C6 | 325 | | 75 |
| 7D6 | 130 | 156 | 0 |
| 7D6 | 182 | | 0 |

APPENDIX III

Lap Shear Results - Room Temperature

Pulled on an Instron at room temperature, 72°F (22°C)

Samples - SMC-1, SMC-2, SMC-3, SMC-4; 4.5% Zn-stearate;
SMC coupons, 6- and 8-adhesives

Treatment - A = bonded as received

B = Scotch Brite/methylene chloride abrasion, then
methylene chloride wipe

C = isocyanate primer

NBSMC = non-bonded SMC failure

| Sample | Force (lbs/in ²) | Failure | Ave. Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--------------------------------------|--------------|
| 1. 61A | 578 | 75%S/25%A | 410 | 50%S/50%A |
| 2. 61A | 270 | 25%S/75%A | | |
| 3. 61A | 310 | NBSMC | | |
| 4. 61A | 440 | NBSMC | | |
| 5. 61A | 382 | 25%S/75%A | | |
| 1. 81A | 605 | 25%S/75%A | 599 | 67%S/33%A |
| 2. 81A | 572 | 100%S | | |
| 3. 81A | 620 | 75%S/25%A | | |
| 4. 81A | 580 | NBSMC | | |
| 5. 81A | 490 | NBSMC | | |
| 1. 61B | 215 | 100%S | 190 | 100%S |
| 2. 61B | 85 | NBSMC | | |
| 3. 61B | 165 | 100%S | | |
| 4. 61B | 180 | NBSMC | | |
| 5. 61B | 201 | NBSMC | | |
| 1. 81B | 610 | 100%S | 590 | 100%S |
| 2. 81B | 611 | NBSMC | | |
| 3. 81B | 583 | NBSMC | | |
| 4. 81B | 650 | 100%S | | |
| 5. 81B | 510 | 100%S | | |
| 1. 61C | 750 | 100%S | 610 | 100%S |
| 2. 61C | 637 | NBSMC | | |
| 3. 61C | 583 | NBSMC | | |
| 4. 61C | 630 | 100%S | | |
| 5. 61C | 450 | 100%S | | |
| 1. 81C | 765 | 100%S | 735 | 100%S |
| 2. 81C | 700 | 100%S | | |
| 3. 81C | 855 | 100%S | | |
| 4. 81C | 519 | NBSMC | | |
| 5. 81C | 620 | 100%S | | |

APPENDIX III (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--|--------------|
| 1. 62A | 421 | 50%S/50%A | 509 | 60%S/40%A |
| 2. 62A | 590 | 100%S | | |
| 3. 62A | 470 | 25%S/75%A | | |
| 4. 62A | 610 | 75%S/25%A | | |
| 5. 62A | 455 | 50%S/50%A | | |
| 1. 82A | 525 | 100%S | 537 | 100%S |
| 2. 82A | 415 | 100%S | | |
| 3. 82A | 585 | 100%S | | |
| 4. 82A | 560 | 100%S | | |
| 5. 82A | 600 | 100%S | | |
| 1. 62B | 475 | 100%S | 501 | 100%S |
| 2. 62B | 549 | 100%S | | |
| 3. 62B | 461 | 100%S | | |
| 4. 62B | 420 | 100%S | | |
| 5. 62B | 600 | 100%S | | |
| 1. 82B | 473 | 100%S | 581 | 100%S |
| 2. 82B | 630 | 100%S | | |
| 3. 82B | 538 | 100%S | | |
| 4. 82B | 550 | 100%S | | |
| 5. 82B | 712 | 100%S | | |
| 1. 62C | 557 | 100%S | 509 | 100%S |
| 2. 62C | 414 | 100%S | | |
| 3. 62C | 590 | 100%S | | |
| 4. 62C | 395 | 100%S | | |
| 5. 62C | 588 | 100%S | | |
| 1. 82C | 535 | 100%S | 561 | 95%S/5%A |
| 2. 82C | 502 | 100%S | | |
| 3. 82C | 572 | 100%S | | |
| 4. 82C | 670 | 100%S | | |
| 5. 82C | 525 | 75%S/25%A | | |

APPENDIX III (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--|--------------|
| 1. 63A | 710 | 100%S | 635 | 100%S |
| 2. 63A | 775 | 100%S | | |
| 3. 63A | 410 | 100%S | | |
| 4. 63A | 668 | 100%S | | |
| 5. 63A | 613 | 100%S | | |
| 1. 83A | 575 | 25%S/75%A | 664 | 70%S/30%A |
| 2. 83A | 640 | 100%S | | |
| 3. 83A | 670 | 50%S/50%A | | |
| 4. 83A | 815 | 75%S/25%A | | |
| 5. 83A | 520 | 100%S | | |
| 1. 63B | 879 | 100%S | 827 | 100%S |
| 2. 63B | 670 | 100%S | | |
| 3. 63B | 900 | 100%S | | |
| 4. 63B | 763 | 100%S | | |
| 5. 63B | 925 | 100%S | | |
| 1. 83B | 675 | 100%S | 705 | 100%S |
| 2. 83B | 580 | 100%S | | |
| 3. 83B | 685 | 100%S | | |
| 4. 83B | 795 | 100%S | | |
| 5. 83B | 788 | 100%S | | |
| 1. 63C | 780 | 100%S | 725 | 100%S |
| 2. 63C | 795 | 100%S | | |
| 3. 63C | 710 | 100%S | | |
| 4. 63C | 780 | 100%S | | |
| 5. 63C | 560 | 100%S | | |
| 1. 83C | 640 | 100%S | 708 | 95%S/5%A |
| 2. 83C | 659 | 100%S | | |
| 3. 83C | 678 | 100%S | | |
| 4. 83C | 865 | 100%S | | |
| 5. 83C | 700 | 75%S/25%A | | |

APPENDIX III (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--|--------------|
| 1. 64A | 560 | 100%S | | |
| 2. 64A | 565 | 100%S | 548 | 94%S/6%A |
| 3. 64A | 605 | 100%S | | |
| 4. 64A | 452 | NBSMC | | |
| 5. 64A | 458 | 75%S/25%A | | |
| 1. 84A | 625 | 75%S/25%A | 520 | 75%S/25%A |
| 2. 84A | 555 | 50%S/50%A | | |
| 3. 84A | 575 | 50%S/50%A | | |
| 4. 84A | 365 | 100%A | | |
| 5. 84A | 480 | 100%S | | |
| 1. 64B | 620 | 100%S | 562 | 100%S |
| 2. 64B | 603 | 100%S | | |
| 3. 64B | 619 | 100%S | | |
| 4. 64B | 320 | 100%S | | |
| 5. 64B | 650 | 100%S | | |
| 1. 84B | 615 | 100%S | 645 | 100%S |
| 2. 84B | 668 | 100%S | | |
| 3. 84B | 440 | NBSMC | | |
| 4. 84B | 642 | 100%S | | |
| 5. 84B | 655 | 100%S | | |
| 1. 64C | 840 | 100%S | 680 | 100%S |
| 2. 64C | 717 | NBSMC | | |
| 3. 64C | 640 | NBSMC | | |
| 4. 64C | 610 | 100%S | | |
| 5. 64C | 590 | 100%S | | |
| 1. 84C | 707 | NBSMC | | |
| 2. 84C | 770 | 100%S | 695 | 100%S |
| 3. 84C | 730 | 100%S | | |
| 4. 84C | 671 | NBSMC | | |
| 5. 84C | 585 | 100%S | | |

*NOTE: Ave. Failure Force does not take into account the NBSMC failures

APPENDIX IV

Chemical Wash Pretreatment

Lap Shear Results - Room Temperature

Chemically treated SMC

Samples were bonded with 6- and 8-adhesives and pulled on an Instron at room temperature

Instron crosshead speed - 0.1 in./min

Coupon pretreatments

A - bonded as received (chemical pretreatment)

C - isocyanate primer

NBSMC = non-bonded SMC failure

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|----------|------------------------------|-----------|---|---------------|
| 1. 6A008 | 575 | 100%S | 403 | 62.5%S/37.5%S |
| 2. 6A008 | 230 | 25%S/75%A | | |
| 3. 6A008 | 410 | NBSMC | | |
| 4. 6A008 | 201 | NBSMC | | |
| 1. 8A008 | 550 | 50%S/50%A | 595 | 69%S/31%A |
| 2. 8A008 | 525 | 100%S | | |
| 3. 8A008 | 740 | 100%S | | |
| 4. 8A008 | 565 | 25%S/75%A | | |
| 1. 6C008 | 479 | NBSMC | 680 | 100%S |
| 2. 6C008 | 360 | NBSMC | | |
| 3. 6C008 | 680 | 100%S | | |
| 4. 6C008 | 431 | NBSMC | | |
| 1. 8C008 | 529 | 100%S | 536 | 100%S |
| 2. 8C008 | 510 | 100%S | | |
| 3. 8C008 | 570 | 100%S | | |
| 4. 8C008 | 431 | 100%S | | |
| 1. 6A007 | 129 | NBSMC | 645 | 100%S |
| 2. 6A007 | 598 | 100%S | | |
| 3. 6A007 | 692 | 100%S | | |
| 4. 6A007 | 501 | NBSMC | | |
| 1. 8A007 | 88 | NBSMC | 637 | 92%S/8%A |
| 2. 8A007 | 700 | 100%S | | |
| 3. 8A007 | 660 | 75%S/25%A | | |
| 4. 8A007 | 550 | 100%S | | |

APPENDIX IV (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|----------|---------------------------------|---------|--|--------------|
| 1. 6C007 | 222 | NBSMC | | |
| 2. 6C007 | 590 | 100%S | 635 | 100%S |
| 3. 6C007 | 680 | 100%S | | |
| 4. 6C007 | 238 | NBSMC | | |
| 1. 8C007 | 169 | NBSMC | | |
| 2. 8C007 | 430 | NBSMC | | |
| 3. 8C007 | 489 | NBSMC | | |
| 4. 8C007 | 283 | NBSMC | | |
| 1. 6AP3B | 511 | NBSMC | 640 | 100%S |
| 2. 6AP3B | 266 | NBSMC | | |
| 3. 6AP3B | 640 | 100%S | | |
| 4. 6AP3B | 349 | NBSMC | | |
| 5. 6AP3B | 418 | NBSMC | | |
| 1. 8AP3B | 636 | 100%S | 564 | 100%S |
| 2. 8AP3B | 510 | 100%S | | |
| 3. 8AP3B | 547 | 100%S | | |
| 4. 8AP3B | 102 | NBSMC | | |
| 5. 8AP3B | 417 | NBSMC | | |
| 1. 6CP3B | 613 | NBSMC | 645 | 100%S |
| 2. 6CP3B | 589 | 100%S | | |
| 3. 6CP3B | 701 | 100%S | | |
| 4. 6CP3B | 414 | NBSMC | | |
| 5. 6CP3B | 419 | NBSMC | | |
| 1. 8CP3B | 562 | 100%S | 617 | 100%S |
| 2. 8CP3B | 671 | 100%S | | |
| 3. 8CP3B | 510 | NBSMC | | |
| 4. 8CP3B | 198 | NBSMC | | |
| 5. 8CP3B | 317 | NBSMC | | |

APPENDIX IV (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure ₂ Force (lbs/in ²) | Ave. Failure |
|-----------|---------------------------------|---------|---|--------------|
| 1. 8ACC24 | 410 | NBSMC | | |
| 2. 8ACC24 | 318 | NBSMC | 511 | 100%S |
| 3. 8ACC24 | 511 | 100%S | | |
| 1. 8CCC23 | 504 | NBSMC | | |
| 2. 8CCC23 | 605 | 100%S | 605 | 100%S |
| 3. 8CCC23 | 490 | NBSMC | | |
| 4. 8CCC23 | 391 | NBSMC | | |
| 1. 8ACC3 | 575 | 50%S | | |
| 2. 8ACC3 | 405 | NBSMC | 582 | 37.5%S |
| 3. 8ACC3 | 157 | NBSMC | | |
| 4. 8ACC3 | 588 | 25%A | | |
| 1. 8CCC24 | 415 | NBSMC | | |
| 2. 8CCC24 | 712 | 100%S | 712 | 100%S |
| 3. 8CCC24 | 405 | NBSMC | | |
| 4. 8CCC24 | 318 | NBSMC | | |
| 1. 8CCC31 | 483 | NBSMC | | |
| 2. 8CCC31 | 728 | NBSMC | -- | -- |
| 3. 8CCC31 | 625 | NBSMC | | |
| 4. 8CCC31 | 543 | NBSMC | | |
| 1. 8ACC31 | 451 | NBSMC | | |
| 2. 8ACC31 | 778 | 100%S | 785 | 100%S |
| 3. 8ACC31 | 792 | 100%S | | |
| 1. 8ACC23 | 491 | NBSMC | | |
| 2. 8ACC23 | 442 | NBSMC | 638 | 100%S |
| 3. 8ACC23 | 638 | 100%S | | |
| 4. 8ACC23 | 500 | NBSMC | | |
| 1. 8CCC3 | 255 | NBSMC | | |
| 2. 8CCC3 | 235 | NBSMC | 720 | 100%S |
| 3. 8CCC3 | 720 | 100%S | | |
| 4. 8CCC3 | 241 | NBSMC | | |

*NOTE: does not include NBSMC failure

APPENDIX V

Lap Shear Results: 130°F (54°C) water bath, 1 week;
pulled at 130°F (54°C) immediately
after removal from water bath.

Pulled on an Instron: sample at 130°F (54°C)

Instron crosshead speed - 0.1 in./min

Samples - SMC-1, SMC-2, SMC-3, SMC-4; 4.5% Zn-stearate;

SMC coupons, 6- and 8-adhesives

Treatment - A = bonded as received

B = Scotch Brite/methylene chloride abrasion, then methylene
chloride wipe

C = isocyanate primer

NBSMC = non-bonded SMC failure

| Sample | Force (lbs/in ²) | Failure | Ave. Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--------------------------------------|--------------|
| 1. 61A | 205 | 100%A | 230 | 95%S/5%A |
| 2. | 200 | 100%A | | |
| 3. | 210 | 100%A | | |
| 4. | 280 | 100%A | | |
| 5. | 255 | 25%S/75%A | | |
| 1. 81A | 214 | NBSMC | 223 | 100%A |
| 2. | 177 | 100%A | | |
| 3. | 273 | 100%A | | |
| 4. | 250 | 100%A | | |
| 5. | 190 | 100%A | | |
| 1. 61B | 465 | 100%S | 465 | 100%S |
| 2. | 441 | NBSMC | | |
| 3. | 318 | NBSMC | | |
| 4. | 427 | NBSMC | | |
| 5. | 207 | NBSMC | | |
| 1. 81B | 331 | NBSMC | 374 | 100%S |
| 2. | 299 | NBSMC | | |
| 3. | 440 | 100%S | | |
| 4. | 360 | 100%S | | |
| 5. | 322 | 100%S | | |
| 1. 61C | 441 | NBSMC | 531 | 100%S |
| 2. | 485 | 100%S | | |
| 3. | 455 | 100%S | | |
| 4. | 585 | 100%S | | |
| 5. | 600 | 100%S | | |

APPENDIX V (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--|--------------|
| 1. 81C | 310 | 25%S/75%A | 322 | 50%S/50%A |
| 2. | 325 | 100%A | | |
| 3. | 200 | NBSMC | | |
| 4. | 314 | NBSMC | | |
| 5. | 361 | 25%S/75%A | | |
| 1. 62A | 330 | 25%S/75%A | 329 | 30%S/70%A |
| 2. | 280 | 100%A | | |
| 3. | 271 | NBSMC | | |
| 4. | 350 | 50%S/50%A | | |
| 5. | 356 | 50%S/50%A | | |
| 1. 82A | 215 | 100%A | 196 | 100%A |
| 2. | 100 | 100%A | | |
| 3. | 232 | 100%A | | |
| 4. | 200 | 100%A | | |
| 5. | 235 | 100%A | | |
| 1. 62B | 410 | 100%S | 388 | 100%S |
| 2. | 350 | 100%S | | |
| 3. | 375 | 100%S | | |
| 4. | 323 | 100%S | | |
| 5. | 480 | 100%S | | |
| 1. 82B | 317 | 100%S | 367 | 100%S |
| 2. | 410 | 100%S | | |
| 3. | 387 | 100%S | | |
| 4. | 305 | 100%S | | |
| 5. | 415 | 100%S | | |
| 1. 62C | 510 | 100%S | 455 | 100%S |
| 2. | 440 | 100%S | | |
| 3. | 460 | 100%S | | |
| 4. | 410 | 100%S | | |
| 5. | NBSMC | | | |
| 1. 82C | 313 | 100%S | 351 | 90%S/10%A |
| 2. | 387 | 100%S | | |
| 3. | 362 | 100%S | | |
| 4. | 390 | 100%S | | |
| 5. | 305 | 50%S/50%A | | |

APPENDIX V (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--|--------------|
| 1. 63A | 470 | 75%S/25%A | 407 | 80%A/20%S |
| 2. | 442 | 66%S/33%A | | |
| 3. | 565 | 100%S | | |
| 4. | 320 | 100%A | | |
| 5. | 240 | 100%A | | |
| 1. 83A | 450 | 100%A | 403 | 100%A |
| 2. | 362 | 100%A | | |
| 3. | 425 | 100%A | | |
| 4. | 400 | 100%A | | |
| 5. | 379 | 100%A | | |
| 1. 63B | 440 | 100%S | 545 | 100%S |
| 2. | 695 | 100%S | | |
| 3. | 555 | 100%S | | |
| 4. | 580 | 100%S | | |
| 5. | 453 | 100%S | | |
| 1. 83B | 591 | 100%S | 567 | 100%S |
| 2. | 562 | 100%S | | |
| 3. | 230 | NBSMC | | |
| 4. | 547 | 100%S | | |
| 5. | 514 | NBSMC | | |
| 1. 63C | 581 | 100%S | 562 | 100%S |
| 2. | 521 | NBSMC | | |
| 3. | 671 | 100%S | | |
| 4. | 495 | 100%S | | |
| 5. | 500 | 100%S | | |
| 1. 83C | 565 | 100%S | 569 | 100%S |
| 2. | 605 | 100%S | | |
| 3. | 641 | 100%S | | |
| 4. | 545 | 100%S | | |
| 5. | 488 | 100%S | | |

APPENDIX V (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|-----------|--|--------------|
| 1. 64A | 438 | NBSMC | | |
| 2. | 374 | NBSMC | | |
| 3. | 505 | 100%S | 463 | 100%S |
| 4. | 448 | 100%S | | |
| 5. | 435 | 100%S | | |
| 1. 84A | 351 | NBSMC | | |
| 2. | 372 | 100%S | 408 | 100%S |
| 3. | 480 | 100%S | | |
| 4. | 373 | 100%S | | |
| 5. | 27 | NBSMC | | |
| 1. 64B | 390 | 100%S | 427 | 100%S |
| 2. | 362 | NBSMC | | |
| 3. | 520 | 100%S | | |
| 4. | 372 | 100%S | | |
| 5. | 368 | NBSMC | | |
| 1. 84B | 529 | 100%S | 523 | 100%S |
| 2. | 510 | 100%S | | |
| 3. | 440 | NBSMC | | |
| 4. | 433 | 100%S | | |
| 5. | 619 | 100%S | | |
| 1. 64C | 588 | 100%S | 552 | 100%S |
| 2. | 515 | 100%S | | |
| 3. | 541 | NBSMC | | |
| 4. | 531 | NBSMC | | |
| 5. | 388 | NBSMC | | |
| 1. 84C | 515 | 100%S | 455 | 87%S/13%A |
| 2. | 442 | 50%S/50%A | | |
| 3. | 532 | 100%S | | |
| 4. | 330 | 100%S | | |
| 5. | 322 | NBSMC | | |

* NOTE: Does not include NBSMC failures

APPENDIX VI

Chemical Wash Pretreatment

Lap Shear Results: 130°F (54°C) water bath, 1 week; pulled at 130°F (54°C) and performed immediately after removal from water bath.

Chemically Treated SMC (SMC-1 samples)

Pulled on an Instron at 130°F (54°C)

Crosshead speed - 0.1 in./min

Samples - Oakite Parker Chemfil chemically washed SMC-1 samples, 6- and 8-adhesives

Treatment - A = bonded as received (chemical pretreatment)

C = isocyanate primer

NBSMC = non-bonded SMC failure

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|----------|------------------------------|---------|---|--------------|
| 1. 6A008 | 275 | NBSMC | 400 | 100%S |
| 2. | 400 | 100%S | | |
| 3. | 312 | NBSMC | | |
| 4. | 295 | NBSMC | | |
| 1. 8A008 | 361 | NBSMC | 562 | 100%S |
| 2. | 448 | NBSMC | | |
| 3. | 562 | 100%S | | |
| 4. | 335 | NBSMC | | |
| 1. 6C008 | 221 | NBSMC | | |
| 2. | 458 | NBSMC | | |
| 3. | 416 | NBSMC | | |
| 4. | 161 | NBSMC | | |
| 1. 8C008 | 414 | NBSMC | 524 | 100%S |
| 2. | 530 | 100%S | | |
| 3. | 262 | NBSMC | | |
| 4. | 518 | 100%S | | |
| 1. 6A007 | 292 | NBSMC | 520 | 100%S |
| 2. | 520 | 100%S | | |
| 3. | 405 | NBSMC | | |
| 4. | 446 | NBSMC | | |
| 1. 8A007 | 395 | NBSMC | 448 | 100%A |
| 2. | 422 | NBSMC | | |
| 3. | 477 | 100%A | | |
| 4. | 418 | 100%A | | |

APPENDIX VI (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|----------|---------------------------------|-----------|--|--------------|
| 1. 6C007 | 523 | NBSMC | 585 | 100%S |
| 2. | 433 | NBSMC | | |
| 3. | 585 | 100%S | | |
| 4. | 345 | NBSMC | | |
| 1. 8C007 | 95 | NBSMC | 530 | 100%S |
| 2. | 315 | NBSMC | | |
| 3. | 530 | NBSMC | | |
| 4. | 530 | 100%S | | |
| 1. 6AP3B | 490 | 100%S | 475 | 100%S |
| 2. | 344 | NBSMC | | |
| 3. | 460 | 100%S | | |
| 4. | 217 | NBSMC | | |
| 5. | 310 | NBSMC | | |
| 1. 8AP3B | 417 | NBSMC | 499 | 50%S/50%A |
| 2. | 511 | NBSMC | | |
| 3. | 499 | 50%S/50%A | | |
| 4. | 381 | NBSMC | | |
| 5. | 394 | NBSMC | | |
| 1. 6CP3B | 390 | 100%S | 390 | 100%S |
| 2. | 281 | NBSMC | | |
| 3. | 245 | NBSMC | | |
| 4. | 225 | NBSMC | | |
| 5. | 280 | NBSMC | | |
| 1. 8CP3B | 550 | 100%S | 618 | 100%S |
| 2. | 740 | 100%S | | |
| 3. | 565 | 100%S | | |
| 4. | 410 | NBSMC | | |
| 5. | 485 | NBSMC | | |
| 1. 8ACC3 | 494 | 25%S/75%A | 426 | 60%S/40%A |
| 2. | 370 | 75%S/25%A | | |
| 3. | 450 | 100%S | | |
| 4. | 389 | 50%S/50%A | | |
| 1. 8CCC3 | 305 | NBSMC | 436 | 100%S |
| 2. | 440 | 100%S | | |
| 3. | 432 | 100%S | | |
| 4. | 285 | NBSMC | | |

APPENDIX VI (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|-----------|---------------------------------|---------|--|--------------|
| 1. 8ACC23 | 510 | 50S/50A | 403 | 25S/75A |
| 2. | 430 | 50S/50A | | |
| 3. | 330 | 100A | | |
| 4. | 340 | 100A | | |
| 1. 8CCC23 | 281 | NBSMC | 405 | 88S/12A |
| 2. | 312 | NBSMC | | |
| 3. | 275 | 75S/25A | | |
| 4. | 535 | 100S | | |
| 1. 8ACC24 | 440 | 25S/75A | 513 | 75S/25A |
| 2. | 512 | 75S/25A | | |
| 3. | 620 | 100S | | |
| 4. | 480 | 100S | | |
| 1. 8CCC24 | 600 | 100S | 577 | 100S |
| 2. | 580 | 100S | | |
| 3. | 550 | 100S | | |
| 4. | 208 | NBSMC | | |
| 1. 8ACC31 | 281 | NBSMC | | |
| 2. | 391 | NBSMC | | |
| 3. | 312 | NBSMC | | |
| 4. | 370 | NBSMC | | |
| 1. 8CCC31 | 520 | NBSMC | 599 | 50S/50A |
| 2. | 599 | 50S/50A | | |
| 3. | 403 | NBSMC | | |
| 4. | 412 | NBSMC | | |

APPENDIX VII

Lap Shear Results - 180°F(82°C)

Pulled on an Instron at 180°F after 1 hr preheat at 180°F

Samples- SMC-1, SMC-2, SMC-3, SMC-4; 4.5% Zn-stearate; SMC coupons
6- and 8-adhesives

Treatment A: bonded as received

B: Scotch-Brite/methylene chloride abrasion, then methylene
chloride wipe

C: isocyanate primer application

NBSMC = non-bonded SMC failure

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|---------|--|--------------|
| 1. 61A | 270 | 0%S | 230 | 0%S |
| 2. 61A | 225 | 0%S | | |
| 3. 61A | 197 | 0%S | | |
| 4. 61A | 310 | NBSMC | | |
| 5. 61A | 210 | NBSMC | | |
| 1. 61B | 391 | NBSMC | 532 | 100%S |
| 2. 61B | 362 | NBSMC | | |
| 3. 61B | 560 | 100%S | | |
| 4. 61B | 280 | NBSMC | | |
| 5. 61B | 505 | 100%S | | |
| 1. 61C | 276 | NBSMC | 608 | 100%S |
| 2. 61C | 425 | NBSMC | | |
| 3. 61C | 221 | NBSMC | | |
| 4. 61C | 608 | 100%S | | |
| 5. 61C | 440 | NBSMC | | |
| 1. 62A | 335 | 0%S | 276 | 0%S |
| 2. 62A | 205 | 0%S | | |
| 3. 62A | 241 | 0%S | | |
| 4. 62A | 274 | 0%S | | |
| 5. 62A | 325 | 0%S | | |
| 1. 62B | 349 | 100%S | 355 | 100%S |
| 2. 62B | 431 | 100%S | | |
| 3. 62B | 325 | 100%S | | |
| 4. 62B | 363 | 100%S | | |
| 5. 62B | 310 | 100%S | | |
| 1. 62C | 350 | 100%S | 334 | 60%S |
| 2. 62C | 328 | 100%S | | |
| 3. 62C | 370 | 100%S | | |
| 4. 62C | 308 | NBSMC | | |
| 5. 62C | 315 | 0%S | | |

APPENDIX VII (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure 0%S |
|--------|---------------------------------|---------|--|---------------------|
| 1. 63A | 245 | 0%S | 300 | 0%S |
| 2. 63A | 243 | 0%S | | |
| 3. 63A | 312 | 0%S | | |
| 4. 63A | 391 | 0%S | | |
| 5. 63A | 281 | 0%S | | |
| 1. 63B | 503 | 60%S | 500 | 92%S |
| 2. 63B | 548 | 100%S | | |
| 3. 63B | 570 | 100%S | | |
| 4. 63B | 449 | 100%S | | |
| 5. 63B | 415 | 100%S | | |
| 1. 63C | 428 | 20%S | 390 | 2%S |
| 2. 63C | 342 | 0%S | | |
| 3. 63C | 381 | 0%S | | |
| 4. 63C | 344 | 0%S | | |
| 5. 63C | 397 | 0%S | | |
| 1. 64A | 200 | 0%S | 255 | 33%S |
| 2. 64A | 170 | NBSMC | | |
| 3. 64A | 371 | 100%S | | |
| 4. 64A | 395 | 0%S | | |
| 5. 64A | 384 | NBSMC | | |
| 1. 64B | 470 | 100%S | 450 | 100%S |
| 2. 64B | 412 | 100%S | | |
| 3. 64B | 505 | 100%S | | |
| 4. 64B | 391 | 100%S | | |
| 5. 64B | 473 | 100%S | | |
| 1. 64C | 415 | 35%S | 428 | 75%S |
| 2. 64C | 460 | 100%S | | |
| 3. 64C | 411 | 100%S | | |
| 4. 64C | 301 | NBSMC | | |
| 1. 81A | 145 | 0%S | 190 | 0%S |
| 2. 81A | 140 | 0%S | | |
| 3. 81A | 253 | 0%S | | |
| 4. 81A | 167 | 0%S | | |
| 5. 81A | 195 | 0%S | | |
| 1. 81B | 455 | 100%S | 401 | 66%S |
| 2. 81B | 75 | NBSMC | | |
| 3. 81B | 350 | 100%S | | |
| 4. 81B | 400 | 0%S | | |
| 5. 81B | 522 | NBSMC | | |

APPENDIX VII (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|---------|--|--------------|
| 1. 81C | 442 | 0%S | | |
| 2. 81C | 301 | NBSMC | 404 | 31%S |
| 3. 81C | 340 | 0%S | | |
| 4. 81C | 550 | 100%S | | |
| 5. 81C | 285 | 25%S | | |
| 1. 82A | 244 | 0%S | | |
| 2. 82A | 231 | 0%S | 250 | 0%S |
| 3. 82A | 253 | 0%S | | |
| 4. 82A | 263 | 0%S | | |
| 5. 82A | 255 | 0%S | | |
| 1. 82B | 396 | 100%S | | |
| 2. 82B | 374 | 100%S | 390 | 100%S |
| 3. 82B | 447 | 100%S | | |
| 4. 82B | 354 | 100%S | | |
| 5. 82B | 380 | 100%S | | |
| 1. 82C | 231 | 0%S | | |
| 2. 82C | 291 | 0%S | 306 | 15%S |
| 3. 82C | 345 | 20%S | | |
| 4. 82C | 250 | NBSMC | | |
| 5. 82C | 360 | 40%S | | |
| 1. 83A | 292 | 0%S | | |
| 2. 83A | 304 | 0%S | 310 | 0%S |
| 3. 83A | 318 | 0%S | | |
| 4. 83A | 310 | 0%S | | |
| 5. 83A | 325 | 0%S | | |
| 1. 83B | 530 | 100%S | | |
| 2. 83B | 520 | 100%S | 532 | 100%S |
| 3. 83B | 480 | 100%S | | |
| 4. 83B | 585 | 100%S | | |
| 5. 83B | 500 | 100%S | | |
| 1. 83C | 410 | 0%S | | |
| 2. 83C | 325 | 0%S | 407 | 20%S |
| 3. 83C | 329 | 0%S | | |
| 4. 83C | 470 | 100%S | | |
| 5. 83C | 500 | 0%S | | |

APPENDIX VII (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure ₂ Force (lbs/in ²) | Ave. Failure |
|--------|---------------------------------|---------|---|--------------|
| 1. 84A | 350 | 0%S | | |
| 2. 84A | 280 | 0%S | 288 | 0%S |
| 3. 84A | 250 | 0%S | | |
| 4. 84A | 285 | 0%S | | |
| 5. 84A | 270 | 0%S | | |
| 1. 84B | 405 | 100%S | | |
| 2. 84B | 452 | 100%S | 404 | 100%S |
| 3. 84B | 355 | 100%S | | |
| 4. 84B | 308 | NBSMC | | |
| 5. 84B | 352 | NBSMC | | |
| 1. 84C | 410 | 0%S | | |
| 2. 84C | 391 | 0%S | 373 | 0%S |
| 3. 84C | 338 | 0%S | | |
| 4. 84C | 325 | NBSMC | | |
| 5. 84C | 355 | 0%S | | |

APPENDIX VIII

Chemical Wash Pretreatment

Lap Shear Results - 180°F (82°C)
 Pulled on an Instron at 180°F after a preheat at 180°F for 1 hr
 Chemically treated SMC (SMC-1 samples)
 Crosshead speed 0.1 in /min
 6- and 8-adhesives

Treatment A: bonded as received (Chemical pretreatment)
 C: isocyanate primer application

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|----------|---------------------------------|---------|--|--------------|
| 1. 6A008 | 273 | 0%S | | |
| 2. 6A008 | 471 | 0%S | 372 | 0%S |
| 3. 6A008 | 165 | NBSMC | | |
| 4. 6A008 | 304 | NBSMC | | |
| 1. 6C008 | 495 | 100%S | | |
| 2. 6C008 | 507 | 0%S | 461 | 33%S |
| 3. 6C008 | 465 | NBSMC | | |
| 4. 6C008 | 382 | 0%S | | |
| 1. 6A007 | 55 | NBSMC | | |
| 2. 6A007 | 308 | NBSMC | -- | -- |
| 3. 6A007 | 648 | NBSMC | | |
| 4. 6A007 | 388 | NBSMC | | |
| 1. 6C007 | 440 | 100%S | | |
| 2. 6C007 | 592 | 100%S | 516 | 100%S |
| 3. 6C007 | 322 | NBSMC | | |
| 4. 6C007 | 340 | NBSMC | | |
| 1. 6AP3B | 550 | 100%S | | |
| 2. 6AP3B | 505 | NBSMC | 456 | 50%S |
| 3. 6AP3B | 472 | NBSMC | | |
| 4. 6AP3B | 320 | NBSMC | | |
| 5. 6AP3B | 362 | NBSMC | | |
| 1. 6CP3B | 408 | NBSMC | | |
| 2. 6CP3B | 515 | 100%S | 598 | 100%S |
| 3. 6CP3B | 620 | 100%S | | |
| 4. 6CP3B | 450 | NBSMC | | |
| 5. 6CP3B | 660 | 100%S | | |

APPENDIX VIII (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure ₂ Force (lbs/in ²) | Ave. Failure |
|-----------|---------------------------------|---------|---|--------------|
| 1. 8AP3B | 265 | 0%S | | |
| 2. 8AP3B | 265 | 0%S | 301 | 0%S |
| 3. 8AP3B | 300 | 0% | | |
| 4. 8AP3B | 385 | 0%S | | |
| 5. 8AP3B | 292 | 0%S | | |
| 1. 8CP3B | 290 | NBSMC | | |
| 2. 8CP3B | 345 | 0%S | 378 | 50%S |
| 3. 8CP3B | 315 | NBSMC | | |
| 4. 8CP3B | 398 | NBSMC | | |
| 5. 8CP3B | 411 | 100%S | | |
| 1. 8ACC3 | 198 | 0%S | | |
| 2. 8ACC3 | 265 | 0%S | 227 | 0%S |
| 3. 8ACC3 | 218 | 0%S | | |
| 4. 8ACC3 | 230 | 0%S | | |
| 1. 8ACC23 | 369 | 0%S | | |
| 2. 8ACC23 | 304 | 0%S | 255 | 0%S |
| 3. 8ACC23 | 288 | 0%S | | |
| 1. 8ACC24 | 270 | 0%S | | |
| 2. 8ACC24 | 168 | NBSMC | 248 | 0%S |
| 3. 8ACC24 | 342 | 0%S | | |
| 4. 8ACC24 | 282 | 0%S | | |
| 1. 8ACC31 | 321 | 0%S | | |
| 2. 8ACC31 | 310 | 0%S | 307 | 0%S |
| 3. 8ACC31 | 265 | NBSMC | | |
| 4. 8ACC31 | 290 | 0%S | | |
| 1. 8CCC3 | 381 | 0%S | | |
| 2. 8CCC3 | 355 | 0%S | 350 | 35%S |
| 3. 8CCC3 | 350 | 100%S | | |
| 4. 8CCC3 | 315 | 50%S | | |
| 1. 8CCC23 | 592 | 100%S | | |
| 2. 8CCC23 | 440 | 40%S | 516 | 70%S |
| 3. 8CCC23 | 402 | NBSMC | | |
| 4. 8CCC23 | 235 | NBSMC | | |
| 1. 8CCC24 | 520 | 40%S | | |
| 2. 8CCC24 | 304 | 0%S | 347 | 35%S |
| 3. 8CCC24 | 298 | 0%S | | |
| 4. 8CCC24 | 468 | 100%S | | |

APPENDIX VIII (continued)

| Sample | Force (lbs/in ²) | Failure | Ave. Failure Force (lbs/in ²) | Ave. Failure |
|-----------|---------------------------------|---------|--|--------------|
| 1. 8CCC31 | 403 | 50%S | 386 | 25%S |
| 2. 8CCC31 | 370 | 0%S | | |
| 3. 8CCC31 | 390 | NBSMC | | |
| 4. 8CCC31 | 300 | NBSMC | | |
| 1. 8A007 | 231 | 0%S | 239 | 0%S |
| 2. 8A007 | 270 | 0%S | | |
| 3. 8A007 | 225 | 0%S | | |
| 4. 8A007 | 230 | 0%S | | |
| 1. 8A008 | 248 | 0%S | 277 | 12.5% |
| 2. 8A008 | 295 | 0%S | | |
| 3. 8A008 | 272 | 50%S | | |
| 4. 8A008 | 291 | 0%S | | |
| 1. 8C007 | 468 | NBSMC | 605 | |
| 2. 8C007 | 432 | NBSMC | | |
| 3. 8C007 | 516 | NBSMC | | |
| 4. 8C007 | 605 | 100%S | | |
| 1. 8C008 | 421 | NBSMC | 394 | |
| 2. 8C008 | 190 | NBSMC | | |
| 3. 8C008 | 502 | NBSMC | | |
| 4. 8C008 | 394 | 0%S | | |

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