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SOURCES AND TRANSPORT OF SILICONE NVR

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SUMMARY

The retrieved LDEF had varying amounts of visible contamination films (brown stains) at many locations. FTIR spectra of heavy film deposits at vents and of optical windows from tray E5 indicated methyl silicone and silica in the contaminant films. Two possible sources of the methyl silicone are DC-710 phenyl methyl silicone in the shuttle-bay-liner beta cloth, and the shuttle tile waterproofing silane. It is concluded that much of the silicone and silica contamination came from ground operations and the orbiter.

INTRODUCTION

A brown stain of varying thickness was present on most of the retrieved LDEF (ref. 1). Several analyses have indicated significant silicone and silica in these stains (ref. 2). The source of the silicon, silica, or precursor silicones is not understood since most of the exposed surfaces of LDEF were anodized aluminum of urethane based paints. Organic silicones have strong absorptions in the 10 micrometer region of the spectrum. FTIR spectroscopy has been applied to LDEF samples, suspected silicones, and spacecraft facility witness plates at KSC in order to better understand the silicone contamination of LDEF.

MEASUREMENT TECHNIQUE

Fourier transform infrared spectroscopy (FTIR) was used for the identification of silicones and silica. The spectra are 4 cm^{-1} resolution and the spectrometer was optimized for the 5 to 10 micrometer region. The sample spectra are ratioed to a background spectrum to give transmission spectra. Sample residues are placed on IR transmitting windows (i. e., CaF_2, MgF_2, NaCl) and centered in the IR beam at the beam focus in the sample compartment. Additional information regarding FTIR spectroscopy for contamination analysis is in reference 3.

Solvent-wash plates are used in aerospace cleanrooms to measure accumulation of organic films. These witness plates are typically syringed with an aggressive solvent such as freon, chloroform, or methylene chloride. This solvent is allowed to evaporate in a fume hood and the residue is transferred to a weighing pan for mass measurement.

Organic films can also be removed from hardware or facility surfaces by wetting the surfaces with a solvent and then wiping the surface with an extracted cleanroom wipe (refs. 4, 5). The wipes are then extracted again by soaking for 30 minutes in spectroscopic grade isopropyl alcohol (IPA), the alcohol is evaporated, and the organic residue transferred to an IR window for measurement and analysis.

LDEF DATA

Some of the heaviest organic film deposits were on the ram direction edge of the 1/4 inch thick aluminum end plates (Figure 1). These end plates were at vent openings to the interior of LDEF and hence the organic films result primarily from outgassing from the interior. FTIR spectra of a scraping of film from an end plate is presented in figure 2. The absorption at 1260 cm^{-1} is identified as resulting from methyl silicone (SiCH3). This absorption is normally spectral sharp and stable in frequency, and hence is a convenient and reliable indicator of a methy silicone group in a molecule.

Calcium fluoride and magnesium fluoride windows were flown in tray E5 of LDEF. An IR spectrum of the calcium fluoride window is presented as figure 3. The 1260 cm^{-1} methyl silicone absorption is more pronounced here than in the vent scraping. The optical windows in tray E5 were mounted with Chorlastic R500 silicon rubber gaskets on the back side. Microscope examination revealed the windows had thin, brittle contamination films on both sides. However, the film on the center of the back surface of the magnesium fluoride window (figure 4) adhered to the gasket. The IR spectrum of only the front surface film is presented in figure 5. Again the 1260 cm^{-1} methyl silicone absorption is present. The broad absorption at 1050 cm^{-1} suggests silica. The 1260 cm^{-1} absorption in the front surface film suggests an external source rather than an interior source for much of the silicone.

The IR spectra of contamination on LDEF can be compared to spectra of typical spacecraft and cleanroom organic films. Figure 6 is the IR spectra of residue from Kapton multi-layer insulation which was used as a witness plate. Figure 7 is the IR spectra of residue from the cleanroom wipes used during integration and processing of the Upper Atmosphere Research Satellite (UARS). These spectra are dominated by strong carbonyl absorption at 1750 cm^{-1} and are not similar to spectra of contamination on LDEF.

Brown stains, similar to those on LDEF, have been reported in orbiter bays and on flight hardware. Such a stain in the Columbia bay after the LDEF retrieval is reported in reference 6. Photographs of faint brown stains in the Discovery bay after STS-48 were taken October 9, 1991, and are presented as figures 8 and 9. These stains suggest a possible nonpayload source of contamination.

BETA CLOTH OIL

Beta cloth is a woven fabric used for thermal control of spacecraft and is used to line much of the orbiters' bays. The fibers are about 10 micron diameter glass fibers coated with about a 10 micron layer of Teflon. Silicone oil is usually added to the fabric during manufacturing to enhance the mechanical properties (increase flexibility and reduce particle shedding) of the fabric. The DC-704 and DC-710 have vapor pressures of about 10^{-7} Torr at room temperature (ref. 7 and 8). Although the vapor pressure is low, all of this material is expected to outgas during long-term vacuum exposure. The expected mode of contamination at standard temperature and pressure is by contact transfer. The molecular structure for DC-704 (ref. 9) is presented as figure 10. Some beta cloths have as much as 100 mg/ft^2 of DC-710 extractable by soaking the cloth for 30 minutes in IPA. The beta cloth used in the Discovery bay for STS-48 had 10 mg/ft^2 of extractable silicone residue. The IR spectra of the residue from the Discovery bay liner beta cloth is presented in figure 11. The SiCH3 absorption as well as the SiO absorptions are characteristically sharp and well defined in figure 11.

RTV-142 RESIDUE

RTV-142 is a silicone potting compound that was used on the UARS spacecraft and is believed to be representative of silicone potting compounds used sparingly on LDEF. Four measurements of NVR from RTV-142 were made. The four independent measurements are mass loss during vacuum bake, residue from 30 minute soak in IPA, mass spectroscopy via residual gas analyser, and baking in a vacuum gas cell.

The mass loss during a 24 hour bake at 70°C was ≈0.08 percent. The mass loss during a 24 hour bake at 160°C was ≈0.23 percent. The recovered NVR from a 30 minute soak in IPA was ≈0.5 percent. The IR spectra from the IPA soak is presented as figure 12. These spectra and 3.4 micrometer spectra indicate the residue is a phenyl methyl silicone. The RGA gives principal mass fragments of 15 (CH3), 29 (CHO & C2H5), 31, and 43. Spectra of residue in the heated gas cell were similar to those from the IPA soak.

All of these tests indicated small mass loss of RTV-142 under vacuum. The higher mass recovered from IPA soaking compared to a 24 hour bake indicates slow outgassing.

PAYLOAD CHANGEOUT ROOM WASH PLATES

One foot square aluminum wash plates were exposed in the Payload Changeout Room (launch complex 39 PCR) during processing of the UARS spacecraft. Two wash plates were exposed during the period July 23 to August 13, 1991, near station 900 of the orbiter in the PCR. The plates were syringed with CH2Cl2 and the residues weighed. The residues were analyzed by the KSC Microchemical Analysis Branch (ref. 10). IR spectra of a transfer of residue with hexane is presented as figures 13 and 14. The spectra clearly show silicones, primarily dimethyl silicones. IR spectra of transfers of residue with CH2Cl2, a more aggressive solvent, show primarily carbonyl and C-O absorption. The hexane transferred residues indicate a light or volatile silicone.

STS-48 RESIDUES

A 14-inch by 14-inch square of 5 mil Kapton multi-layer insulation was attached to the UARS airborne support equipment (UASE) module during the STS-48 mission. The IR spectra of residue from an IPA syringe of this witness plate is presented as figure 15. Although only 0.01 mg of residue was recovered from this witness plate, SiCH3 and SiO absorptions are strongly indicated. This witness plate was covered until August 13, 1991, and was retrieved from the shuttle bay October 9, 1991. The delay in retrieving this witness plate was due to the orbiter landing at Dryden rather than at KSC as planned, and conflicts in orbiter operations in the orbiter processing facilities.

Four dry wipes of the UARS Airborne Support Equipment (UASE) tool box, using extracted polyester wipes (ref. 4), were taken. IR spectra of a UASE dry wipe is presented as figure 16. Silicone absorption is indicated in the residue. However, some silicone is also indicated in residual residue of the control wipe (fig. 17) so caution should be exercised in interpretation of the UASE wipe data.

ORBITER TILE WATERPROOFING

The heat protective tile and upper surface external blankets of the orbiter are waterproofed to avoid unnecessary water absorption prior to launch. The waterproofing compound used for the STS-48 mission was dimethylethoxy silane (DMES). A diagram of the molecular structure of this material is presented as figure 18, and an IR spectrum is presented as figure 19. A strong SiH absorption is present at 2200 cm^{-1} and methyl and methylene absorptions are also present at 2900 cm^{-1}.

This silane compound is used because it chemically reacts with the silica in the tiles to bond methyl silicones to the silica (ref. 11). About 200 pounds of DMES were used to waterproof the orbiter for STS-48*. DMES is extremely volatile; i. e., its vapor pressure is about 230 mm Hg at 20°C (ref. 12). The PCR wash plates suggest transfer of waterproofing compound in orbiter processing facilities.

A few drops of DMES were transferred to CaF2 and NaCl windows placed on a deuterium lamp. A thin SiO2 film (figure 20) was left on both of these windows. Therefore, DMES is a precursor to both methyl silicones (ref. 11) and silica.

DMES is not the silane used to rewaterproof the Challenger for the LDEF deployment. Hexamethyldisilizane (HMDS) was used to rewaterproof the Challenger for mission 41C.

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* Palou, J., private comm., December 1991.

CONCLUSIONS

Several potential sources of silicone contamination from orbiter and spacecraft processing at KSC have been identified. The most suspect source is the orbiter tile waterproofing compound, a volatile silane. Further work is needed in order to better understand the role of the waterproofing compound in the production of the silicones and silica detected on LDEF.

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12. Anon., "Material Safety Data Sheet for Dimethylethoxysilane," HULS America Inc., 1992.

ACKNOWLEDGMENTS

Phil Klich (LaRC) and Sharon Straka (GSFC) assisted in obtaining HALOE and UARS witness plates at KSC. Barbara Lambert (GSFC) provided photographs of the Discovery bay. Jaime Palou (KSC) implemented the IR analysis of witness from the PCR. Bill Carman (KSC) performed the IR analysis of the PCR residues and reviewed the analysis in detail with the author. Tommy Leiffel (LaRC) provided samples of tile waterproofing compound (DMES).

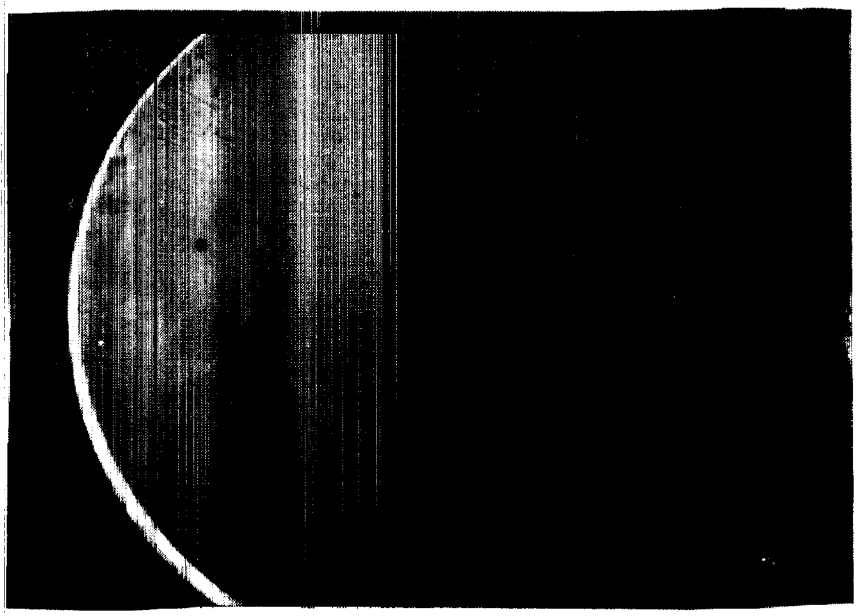

Figure 1. - Photograph of peeling contamination film near vent.

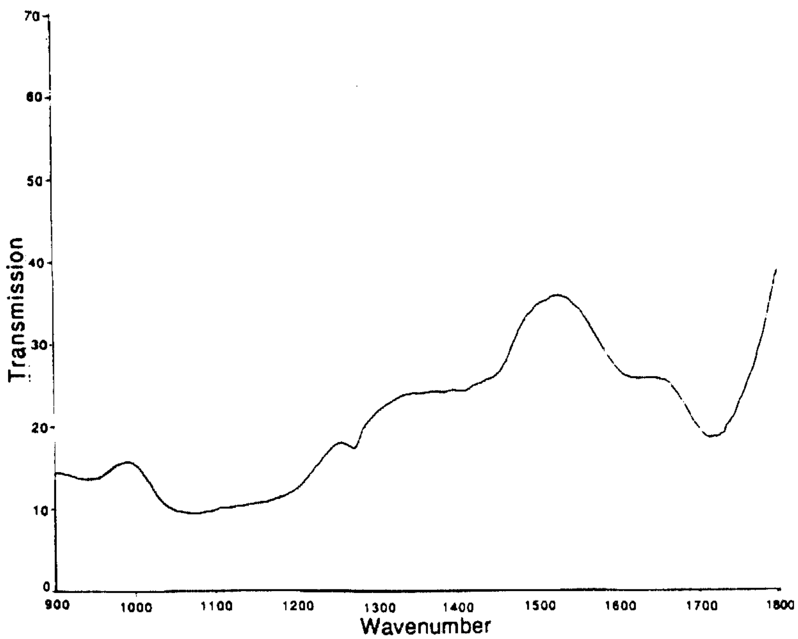

Figure 2. - IR spectrum of contamination film.

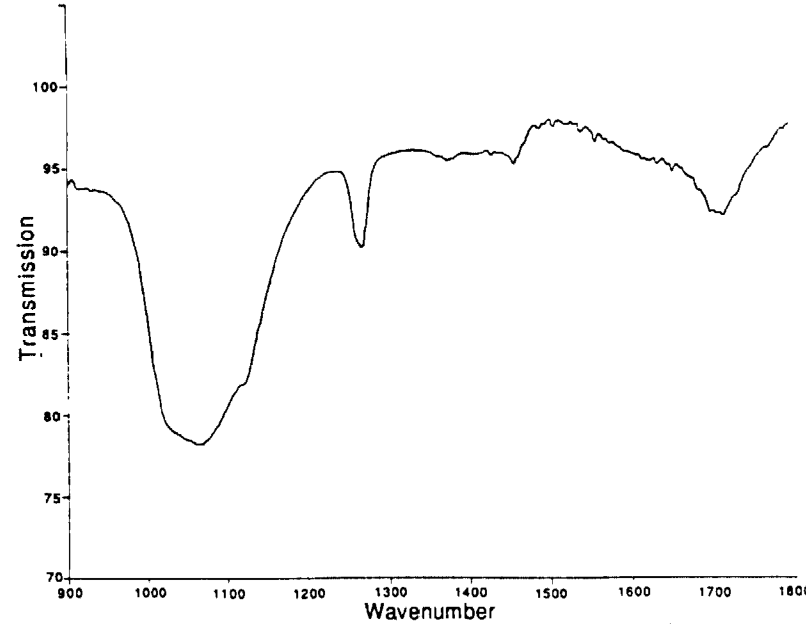

Figure 3. - IR spectrum of films on CaF2 optical window.

Figure 4. - Photograph of MgF2 optical window from tray E5.

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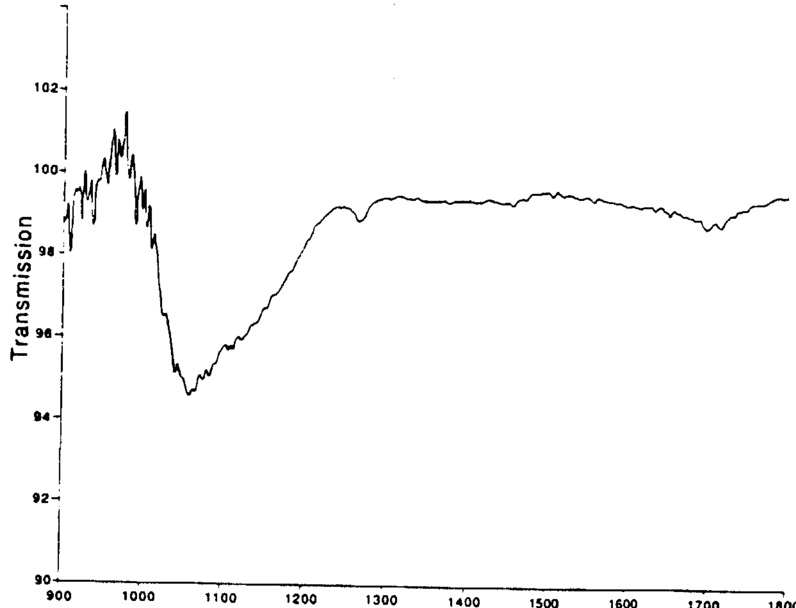

Figure 5. - IR spectrum of front surface on MgF2 optical window.

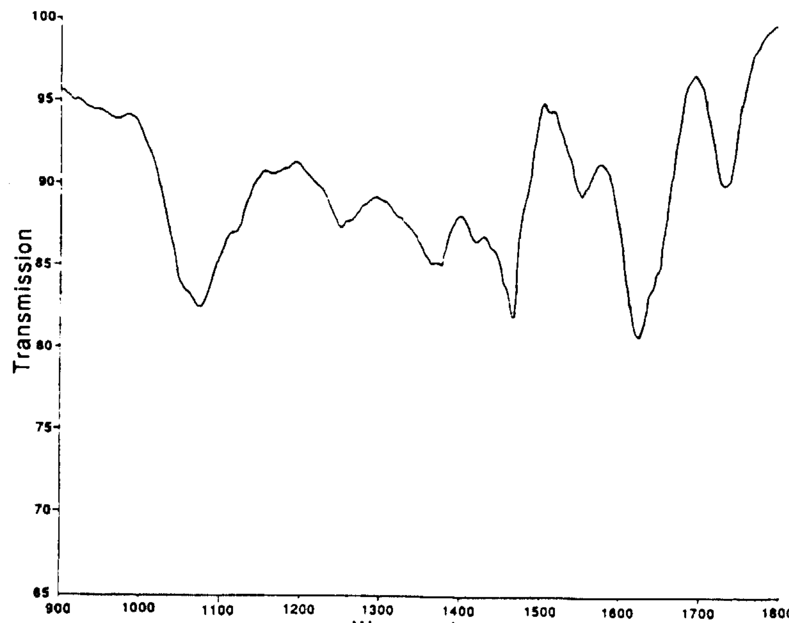

Figure 6. - IR spectrum of residue on ground control MLI witness.

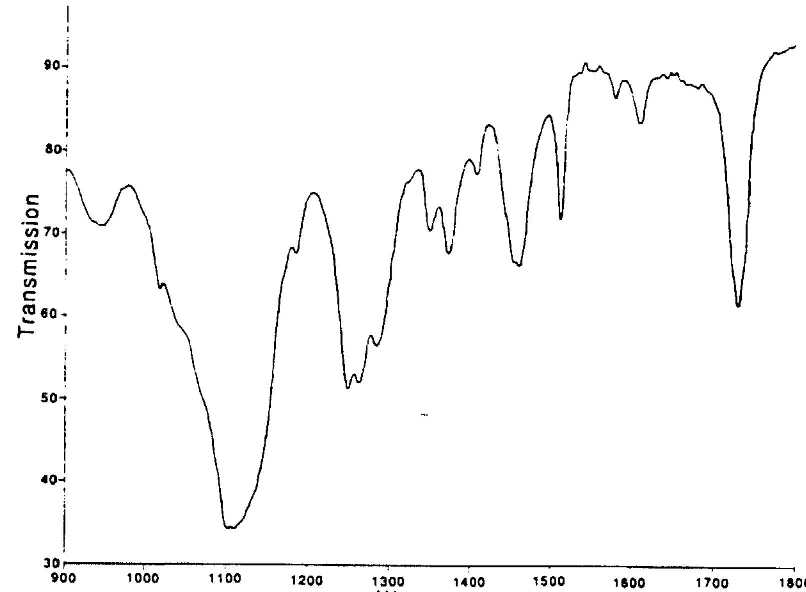

Figure 7. - IR spectrum of wipe residue.

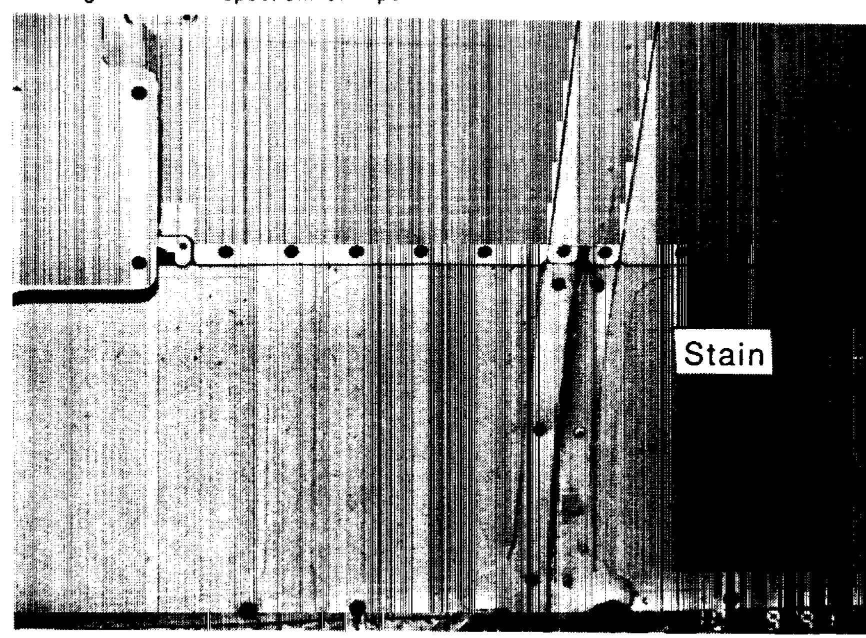

Figure 8. - Photograph of faint brown stain in postflight STS-48 bay.

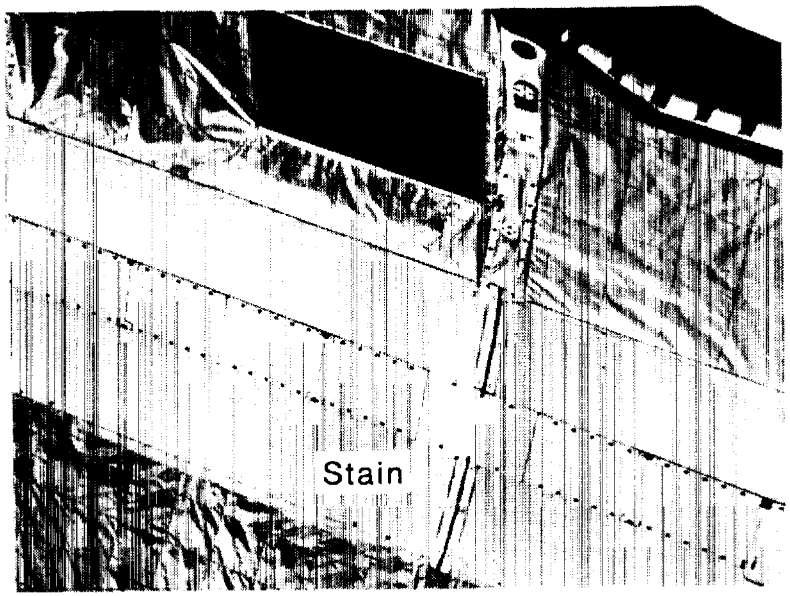

Figure 9. - Photograph of faint brown stain in postflight STS-48 bay.

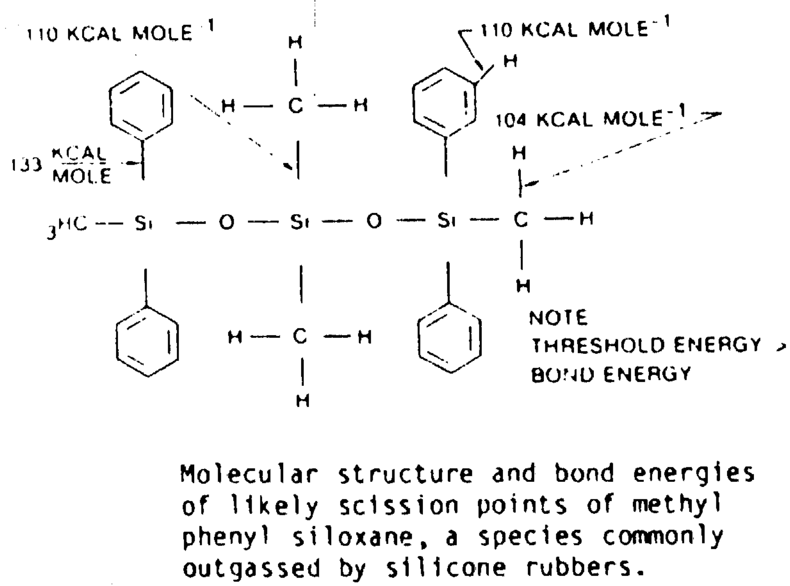

Figure 10. - Molecular structure of DC-704 oil.

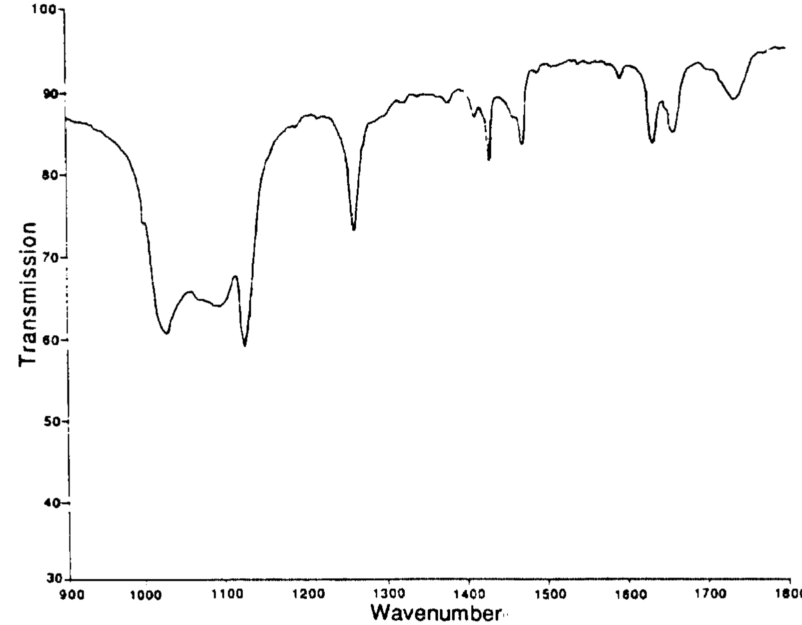

Figure 11. - IR spectrum of residue from STS-48 (Discovery) beta cloth.

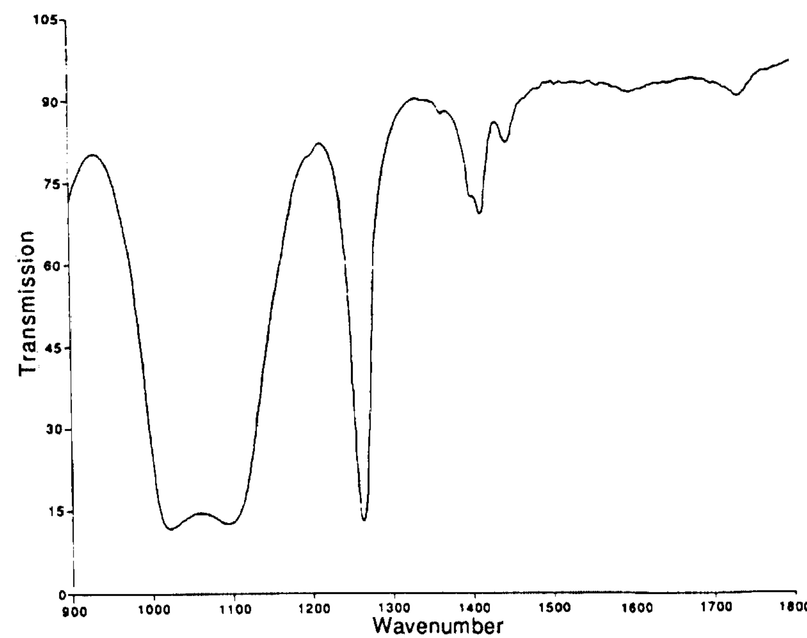

Figure 12. - IR spectrum of residue from RTV-142.

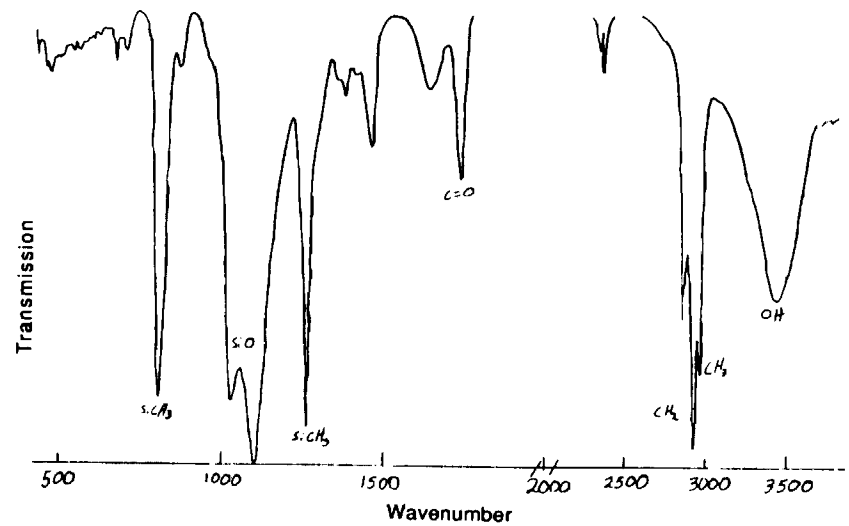

Figure 13. - IR spectrum of wash plate #056 residue from the PCR.

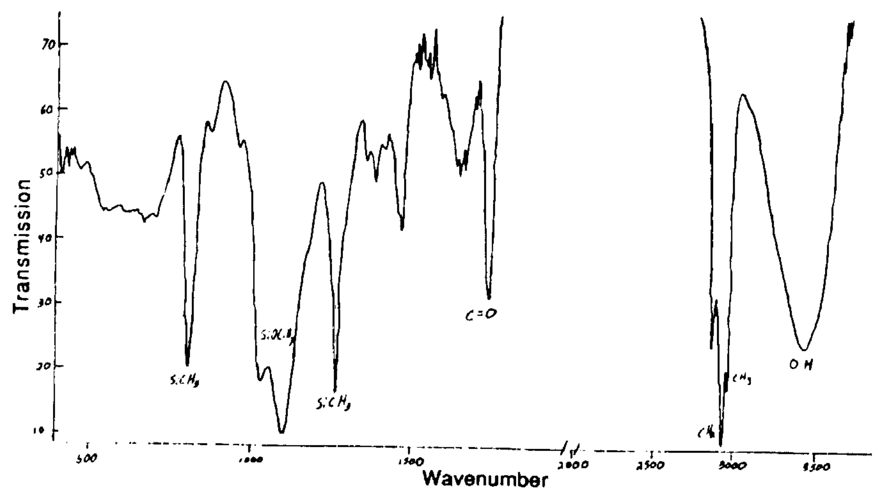

Figure 14. - IR spectrum of wash plate #047 residue from the PCR.

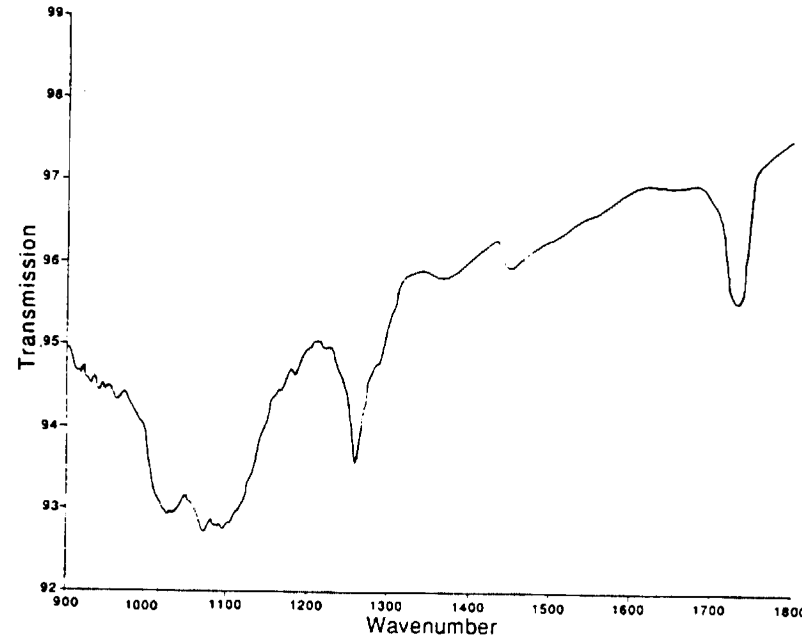

Figure 15. - IR spectrum of UARS/UASE flight MLI witness.

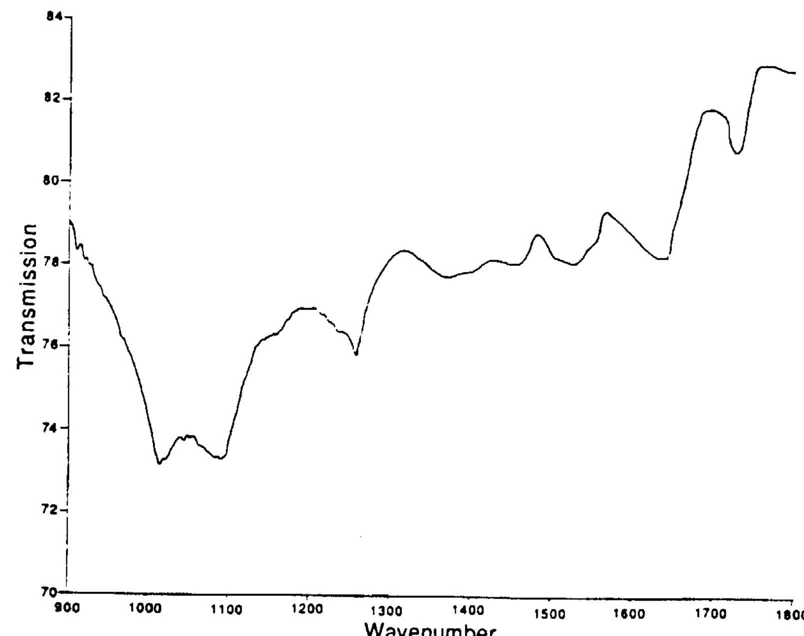

Figure 16. - IR spectrum of dry wipe UARS/UASE toolbox.

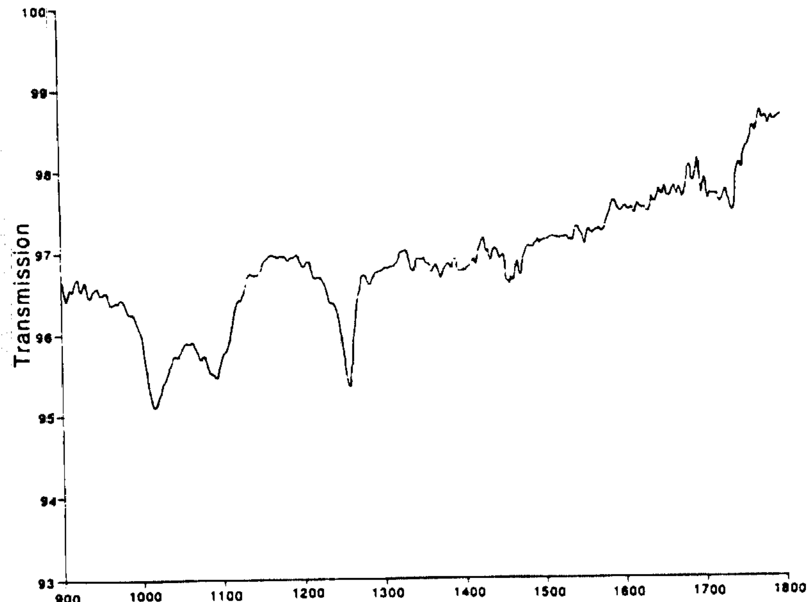

Figure 17. - IR spectrum of control wipe.

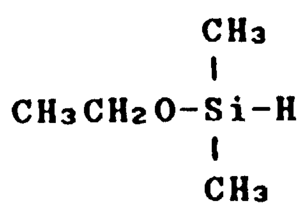

Figure 18. - Molecular structure of STS-48 rewaterproofing compound (DMES).

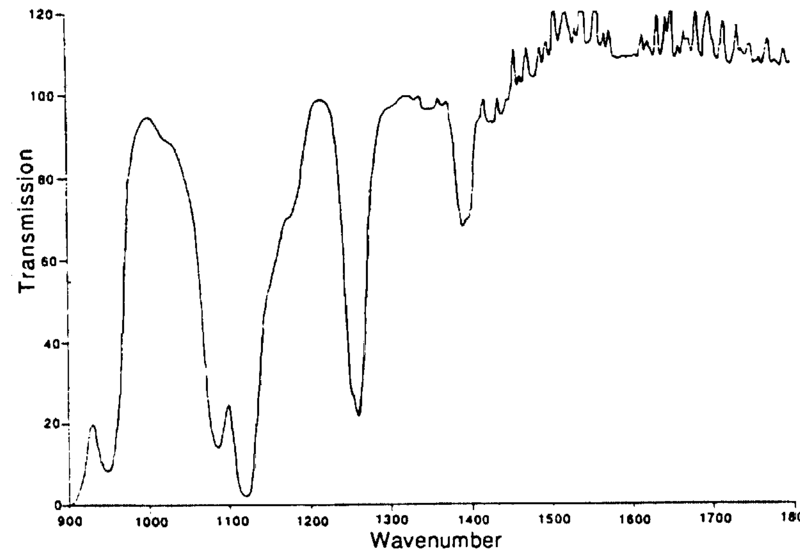

Figure 19. - IR spectrum of DMES rewaterproofing compound.

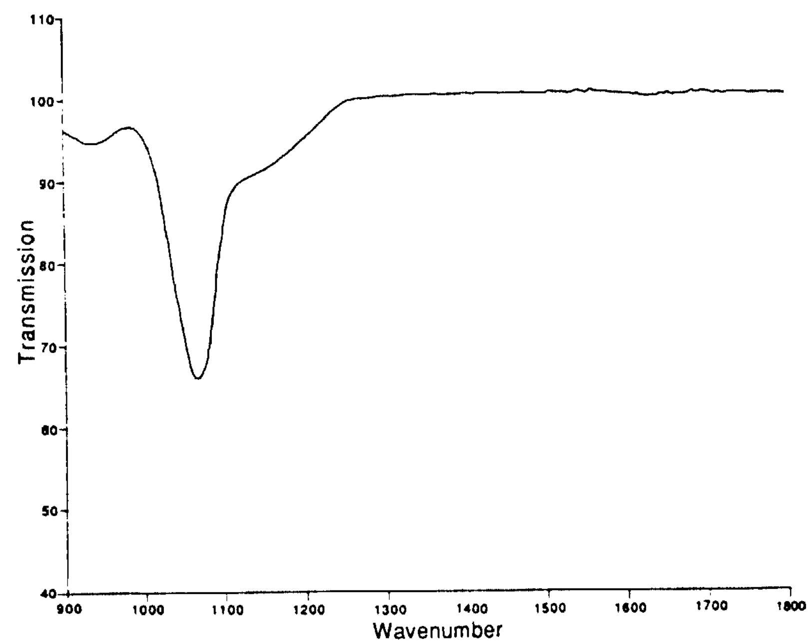

Figure 20. - IR spectrum of UV exposed DMES.

Thermal Control Coatings, Protective Coatings, and Surface Treatments

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