

SILAZANE TO SILICA

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ABSTRACT

Thin film silica and/or methyl silicone have been detected on most external surfaces of the retrieved LDEF. Both solar ultraviolet radiation and atomic oxygen can convert silicones to silica. Known sources of silicone in or on the LDEF appear inadequate to explain the ubiquitous presence of the silica and silicone films. Hexamethyldisilazane (HMDS) was used as the Challenger tile waterproofing compound for the Challenger/LDEF deployment mission. HMDS is both volatile and chemically reactive at STP. In addition, HMDS releases NH_3 which depolymerizes silicone RTV's. Polyurethanes are also depolymerized. Experiments are reported that indicate much of the silicone and silica contamination of LDEF resulted directly or indirectly from HMDS.

INTRODUCTION

A brown stain of varying thickness was present on much of the external surfaces of LDEF (ref. 1). This visible contamination resulted primarily from outgassing of the thermal-control paints and will not be discussed in this paper. However, mixed in with the visible contamination and on visually clean surfaces are films of methyl silicones and silica (refs: 2-4). Organic film cleanliness measurements of facility wash plates during processing of the Upper Atmosphere Research Satellite (UARS) suggested silicone contamination of payloads from orbiter rewaterproofing compounds (ref. 2).

The orbiters are protected from heating during reentry by the thermal protection system (TPS) of reusable surface insulation tiles and fibrous insulation blankets. The tiles and blankets are waterproofed prior to installation on the orbiters by treatment in an oven that contains methyltrimethoxysilane (MTMS) vapor (ref. 5). This initial waterproofing is burned off by high-temperatures during reentry. Scotchguard was used early in the shuttle flight program to rewaterproof the orbiters at KSC, but was ineffective (ref. 5). Hexamethyldisilazane (HMDS) was used for rewaterproofing of the orbiters starting with the Challenger in 1983. This continued, including LDEF/Challenger (April 1984), until the sixth flight of the Challenger (October 1984) when a tile was lost during reentry. Widespread degradation (depolymerization) of the silicone adhesives used to attach the tiles, RTV-560 and 577, was traced to reaction products from HMDS, particularly ammonia (ref. 5). Subsequently, the chemistry of HMDS and silicones was studied extensively by Rockwell International (ref. 6). Additional information regarding silane surface chemistry is in reference 7. Since 1988 (STS-26) dimethylethoxyxilane (DMES) has been used to rewaterproof the tiles and external blankets. The chemistry of DMES and other silanes for waterproofing of silica surfaces has been studied by Johnson et. al. (refs. 8 and 9). Table 1 lists the schedule for the shuttle flights and the associated rewaterproofing agents. Two cc/6"x 6" tile of waterproofing compound are injected into each of approximately 25,000 tiles. About 200 pounds of waterproofing compound, DMES, was applied to the orbiter for mission STS-48.

TABLE 1
SHUTTLE SCHEDULE

<u>Flight</u>		<u>Date</u>	<u>Waterproofing</u>	<u>Comments</u>
STS-1	Columbia	4/12/81	MTMS	
STS-2	Columbia	11/12/81	SG (Scotchguard)	
STS-3	Columbia	3/22/82	SG	
STS-4	Columbia	6/27/82	SG	
STS-5	Columbia	11/11/82	SG	
STS-6	Challenger	4/4/83	MTMS	
STS-7	Challenger	6/18/83	HMDS	
STS-8	Challenger	8/30/83	HMDS	
STS-9	Columbia	11/28/83	HMDS	
STS-41B	Challenger	2/3/84	HMDS	
STS-41C	Challenger	4/6/84	HMDS	LDEF Deployed
STS-41D	Discovery	8/30/84	MTMS	
STS-41G	Challenger	10/5/84	HMDS	Tiles Off
STS-51A	Discovery	11/8/84	HMDS	Brown Stain
STS-51C	Discovery	1/24/85	SG	
STS-51D	Discovery	4/12/85	SG	
STS-51B	Challenger	4/29/85	SG	Challenger Return to Flight
STS-51G	Discovery	6/17/85	SG	
STS-51F	Challenger	7/29/85	SG	
STS-51I	Discovery	8/27/85	SG	
STS-51J	Atlantis	10/3/85	MTMS	
STS-61A	Challenger	10/30/85	SG	
STS-61B	Atlantis	11/26/85	SG	
STS-61C	Columbia	1/12/86	SG	
STS-51L	Challenger	1/28/86	SG	In-Flight Explosion
STS-26	Discovery	9/29/88	DMES	Return to Flight
STS-27	Atlantis	12/2/88	DMES	
STS-29	Discovery	3/13/89	DMES	
STS-30	Atlantis	5/4/89	DMES	
STS-28	Columbia	8/8/89	DMES	
STS-34	Atlantis	10/18/89	DMES	
STS-33	Discovery	11/22/89	DMES	
STS-32	Columbia	1/9/90	DMES	LDEF Retrieval
STS-36	Atlantis	2/28/90	DMES	
STS-31	Discovery	4/24/90	DMES	HST
STS-41	Discovery	10/6/90	DMES	
STS-38	Atlantis	11/15/90	DMES	
STS-35	Columbia	12/2/90	DMES	
STS-39	Discovery	3/ /91	DMES	
STS-37	Atlantis	4 / /91	DMES	
STS-40	Columbia	5/ /91	DMES	
STS-43	Discovery	7/ /91	DMES	
STS-44	Atlantis	8/ /91	DMES	
STS-48	Discovery	9/13/91	DMES	UARS
STS-42	Atlantis	1/ /92	DMES	Brown Stain
STS-46	Discovery	2/ /92	DMES	
STS-45	Atlantis	4/ /92	DMES	

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 $900\text{-}1800\text{ cm}^{-1}$ spectral region. The sample spectra are generally ratioed to equivalent background spectra to give transmission spectra. Sample residues and films 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 measurement and analysis is in reference 10.

Absorption bands resulting from chemical bonds in molecules are useful in identifying classes of chemical compounds. For example, the sharp absorption at 1260 cm^{-1} results from the silicon-methyl bond and indicates SiCH_3 in the compound. The absorption bands of major interest in this paper are: 940 cm^{-1} (SiN), $1000\text{-}1100\text{ cm}^{-1}$ (O-Si-O), $1050\text{-}1200\text{ cm}^{-1}$ (O-C-O), 1185 cm^{-1} (SiNH), 1260 cm^{-1} (SiCH_3) and 1730 cm^{-1} (O=C-O). A broad single peak near 1050 cm^{-1} is indicative of silica (SiO_2). Most contamination films are mixtures of compounds, and discretion should be used in the interpretation of IR spectra of residues.

HMDS CHEMICAL PATHWAYS

Hexamethyldisilazane [$(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$] is a clear liquid at STP with a molecular weight of 161.4 Daltons and a vapor pressure of 1.04 mm at 20°C (ref. 11). The chemical structure is shown in figure 1. An IR spectrum of HMDS is presented as figure 2. The SiCH_3 absorption at 1260 cm^{-1} is very strong, but the SiO at $1000\text{-}1100\text{ cm}^{-1}$ (strong in silicones and silica) and the SiH absorption at 2200 cm^{-1} (strong in DMES) are absent. The strong, sharp absorption at 1180 cm^{-1} (NH) serves as a convenient identifier for HMDS.

There are several chemical pathways by which HMDS can produce a silicone residue, or a thin film of SiO_2 on a surface. A silicone residue is left in a vessel after evaporation of HMDS. Commercial HMDS is generally specified as 98% pure. The residue may be impurities in delivered HMDS. An IR spectrum of current production (HULS America CH7300, January 1992) HMDS residue is presented as figure 3. The residue has the visual appearance of clear oil. A few small, translucent particles ≈ 10 microns diameter are imbedded in the residue. An IR spectrum of residue from aged HMDS (Pfaltz and Bauer, Inc. ≈ 1983) is presented as figure 4. More, and larger gel-like particles are imbedded in the residue (figure 5).

A pathway by which HMDS can be converted directly to thin film silica is by exposure to ultraviolet radiation. A few drops of HMDS were transferred to CaF_2 and NaCl windows placed on a deuterium lamp and exposed for 5 minutes to the ultraviolet radiation. The IR spectra of the residue films are shown in figures 6 and 7. A silica film is present on the CaF_2 window. No silica film is present on the NaCl window. This indicates that HMDS surface chemistry is substrate dependent.

A third chemical pathway in which HMDS can produce silicone residue is by the depolymerization of silicone sealants and potting compounds (ref. 6, 7). A film of RTV-142 (which had been previously cleaned by soaking for 30 minutes in IPA, ref. 2) was placed in a sealed glass vessel with HMDS vapor for 7 days. The film of RTV was then soaked again in IPA for 30 minutes and the IPA allowed to evaporate. The IR spectra of residue from the RTV is presented in figure 8. The molecular weight distribution of the residue is presented as figure 9. The residue mass from the HMDS-vapor-exposed RTV was 6 percent. The residue mass from a film of RTV-560 exposed to HMDS vapor for 7 days was 0.1 percent. A silicone adhesive, DC6-1104, was used to attach velcro strips to the LDEF experiment

trays (≈ 17) with silvered teflon blankets. The LDEF materials handbook lists 7.5 grams of DC6-1104 for each tray. That is, only a small amount of silicone material is listed on the LDEF manifest. The total mass loss (ASTM E-595) for DC6-1104 is about 0.2% (ref. 12).

A previously cleaned film of Chemglaze Z306 (ref. 2), the polyurethane based thermal control paint used on LDEF, was also placed in a sealed glass vessel with HMDS vapor for 8 days. The film of Z306 was soaked in IPA for 30 minutes and the IPA allowed to evaporate. The spectra of residue from the Z306 is presented in figure 10. The residue mass from the HMDS-vapor-exposed Z306 was 1%. Thus, HMDS vapor depolymerizes Z306 as well as RTV's.

A fourth chemical pathway for HMDS to produce silicone films is the polymerization of products of reaction of HMDS with moisture. HMDS reacts with water to form ammonia (NH_3) and trimethylsilanol ($(\text{CH}_3)_3\text{SiOH}$) (ref. 5). But trimethylsilanol is very reactive and quickly polymerizes to hexamethyldisiloxane ($(\text{CH}_3)_6\text{Si}_2\text{O}$) and water. Hexamethyldisiloxane is relatively stable, but has a high vapor pressure (201 mbar/122°F) and hence will be transported by convection at standard temperature and pressure. The silicone compounds trimethylsilanol, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane were detected in the Challenger crew compartments during the LDEF deployment mission (Table 2, ref. 13). Trimethylsilanol is an immediate reaction product of HMDS and H_2O . It is not clear if the crew compartment siloxanes are related to HMDS.

TABLE 2
STS-13 (41-C) INFLIGHT ATMOSPHERIC ANALYSIS

Compound	SAMPLE			
	S/N-1016	S/N-1013	S/N-1014	S/N-1015
Carbon Monoxide	<0.500(<0.572)	<0.500(<0.572)	<0.500(<0.572)	<0.500(<0.572)
Methane	3.360(2.198)	19.240(12.588)	57.219(37.435)	80.904(52.931)
Bromotrifluoromethane	1.054(6.422)	1.073(6/537)	1.323(8.060)	0.707(4.307)
1,1,2-Trichloro-1,2,2-Trifluoroethane	0.001(6.422)	0.011(0.084)	0.008(0.061)	0.008(0.061)
Ethanal	0.002(0.004)	0.008(0.015)	0.011(0.019)	0.022(0.040)
2-Propanone	0.002(0.004)	0.049(0.115)	0.054(0.129)	0.037(0.088)
Dichloromethane	nd	0.006(0.022)	0.010(0.034)	0.015(0.051)
2-Propanol	nd	0.019(0.040)	0.015(0.036)	0.018(0.044)
Ethanol	nd	1.335(2.510)	0.586(1.102)	1.551(2.917)
Hexamethylcyclotrisiloxane	nd	0.004(0.037)	0.002(0.020)	0.010(0.092)
Trimethylsilanol	nd	0.003(0.011)	0.003(0.012)	0.009(0.032)
Toluene	nd	0.002(0.006)	0.001(0.003)	0.001(0.005)
Octamethylcyclotetrasiloxane	nd	0.004(0.040)	0.003(0.033)	0.013(0.158)
Silicone, M.W. = 452	nd	0.032(0.595)	0.021(0.393)	0.067(1.232)

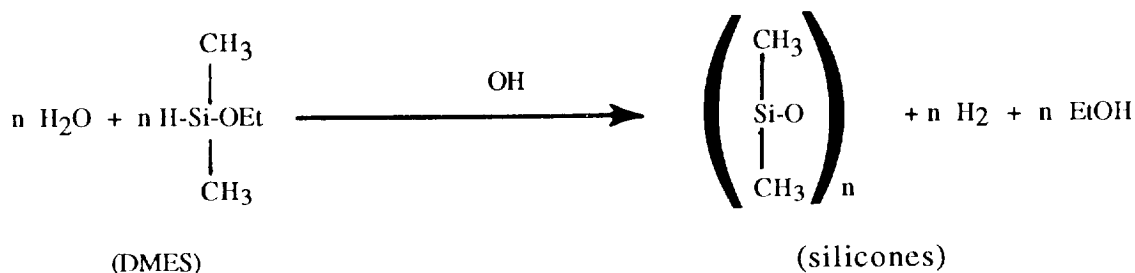
^aConcentrations not in parenthesis are ppm; in parenthesis are mg/m³.

ORBITER FACILITIES DATA

Silicone residues were obtained from the Payload Changeout Room (PCR Pad A) during processing of STS-48 (Upper Atmosphere Research Satellite, 8/92) (ref. 2). Additional NVR measurements of orbiter processing facilities have subsequently been made in order to confirm and better understand these residues.

Four NVR wash plates were exposed in the PCR (3/12 to 4/5/84) during processing of STS-41C. Two NVR wash plates were exposed (12/18/91 to 1/21/92) in the PCR during processing of STS-42. Two other NVR wash plates were exposed (1/15 to 1/29/92) in the Orbiter Processing Facility (OPF) where the rewaterproofing agent DMES was applied. The residue masses from these wash plates are listed in Table 3. A different gravimetric procedure is used for the OPF wash plates than is used for the PCR wash plates. The residue transfer is with dimethyl chloride for the PCR plates and with carbon tetrachloride for the OPF plates. Significant residue masses were measured from PCR wash plates.

An IR spectrum of hexane-transferred residue from the STS-48 processing in the PCR is presented as figure 11. The strongest absorption is from the silicone band (1000 cm^{-1} to 1100 cm^{-1}). Alkaline water reacts with both the hydrogen and ethoxy groups to give DMES bifunctionality and results in the formation of silicone polymers (ref.8).



Thus, figure 11 is compatible with expected reaction product of DMES. The 1730 cm^{-1} carbonyl absorption indicates other compounds are also present in the PCR residue.

An IR spectrum, of methylene chloride-transferred residue from the STS-42 processing in the PCR, is presented as figure 12. The strongest absorptions are carboxyl (1100 cm^{-1}) and carbonyl (1730 cm^{-1}) and obscure any silicone absorption. Some type of chromatography (i.e. hexane transfer for silicones followed by methylene chloride transfer for phthalates) is needed to clearly identify silicones in residues.

TABLE 3 - ORBITER FACILITY RESIDUE MASSES

Wash Plate	Facility	Date	NVR Mass (mg)
2 Side 2	PCR	3/12-4/5/84	.94
3 Side 4	PCR	"	.64
4 Side 2	PCR	"	.42
5 Side 4	PCR	"	.30
6	PCR	7/23-8/13/91	.27
7	PCR	8/13-9/9/91	.35
8	PCR	12/18-1/21/92	.40
9	PCR	"	.22
7W-X	OPF	1/15-1/29/92	.027
7E-V	OPF	"	.031

CONCLUSIONS

HMDS is capable of producing silicone and silica films by both direct and indirect pathways. Direct pathways include the absorption of HMDS vapor on surfaces with subsequent reactions and polymerization, and absorption of reaction products, such as hexamethyldisiloxane, and subsequent polymerization. Outgassing of polymerized residues in HMDS is also likely. Indirect pathways are: depolymerization of silicone materials such as RTV's which subsequently outgas and produce silicone films on surfaces. Subsequent exposure to solar UV and or atomic oxygen could convert the silicones to silica. Depolymerization of other plastics such as urethanes can increase the total organic film on some surfaces. The surface chemistry of HMDS is dependent on surface material. Much of the silicone and silica contamination on LDEF resulted from several chemical processes in which HMDS, its reaction products, or depolymerized organic materials are deposited on surfaces during payload processing and in orbit.

CONCLUDING REMARKS

During the 1970's the space shuttle program was in its development stage; LaRC was conceiving a proposed first shuttle payload that was to become LDEF, and the Viking Project was the largest program at LaRC. The Viking Project expended much effort to insure that the Viking Mars Landers were biologically sterile and would not biologically contaminate Mars with viable organisms from Earth. A general concern at LaRC was that payloads from manned launch vehicles would not be as clean as those from unmanned launch vehicles. Fifteen years later, this early concern has largely been forgotten.

The NASA space-flight centers, LaRC and GSFC, generally go to great efforts to insure flight instrument cleanliness. Assembly, testing, and integration of flight hardware are typically performed in class 100 clean rooms and organic films are restricted to budgets of 1 milligram per 0.1 square meter of surface area. Rigorous material selection criteria are imposed. Beta cloth, which sometimes has a phenylmethyl silicone oil with a vapor pressure about 1×10^{-7} Torr at room temperature, is a borderline material for space flight qualification. The silanes used to rewaterproof the shuttle tiles and blankets have vapor pressure almost a billion times higher, and hence are subject to transport on the ground as well as in space.

The STS-48 launch of HALOE/UARS was possibly the first mission in which a payload program requested IR analyses of wash plate residues from orbiter processing facilities. Evidently, payload programs have relied on early cleanliness assessments from STS-2, 3, and 4 which did not indicate contamination (at 1970's cleanliness levels) during launch and short term on-orbit operations. Needless to say, the flight instrument centers have been remiss in not following through on their cleanliness programs to include the orbiter processing, and launch and deployment phases of launch operations.

In addition to silicone residues, orbiter tile and beta cloth fibers (ref. 14), and shuttle waste dump residues (ref. 3) are present on the LDEF and indicate cross-contamination from shuttle operations. Even though both HMDS and Chemglaze Z306 are no longer widely used in the space program, a sustained, broadly based measurement and analysis program for residues from all flight-hardware-flow facilities is still needed.

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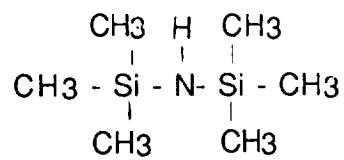


Figure 1. Molecular structure of hexamethyldisilazane (HMDS).

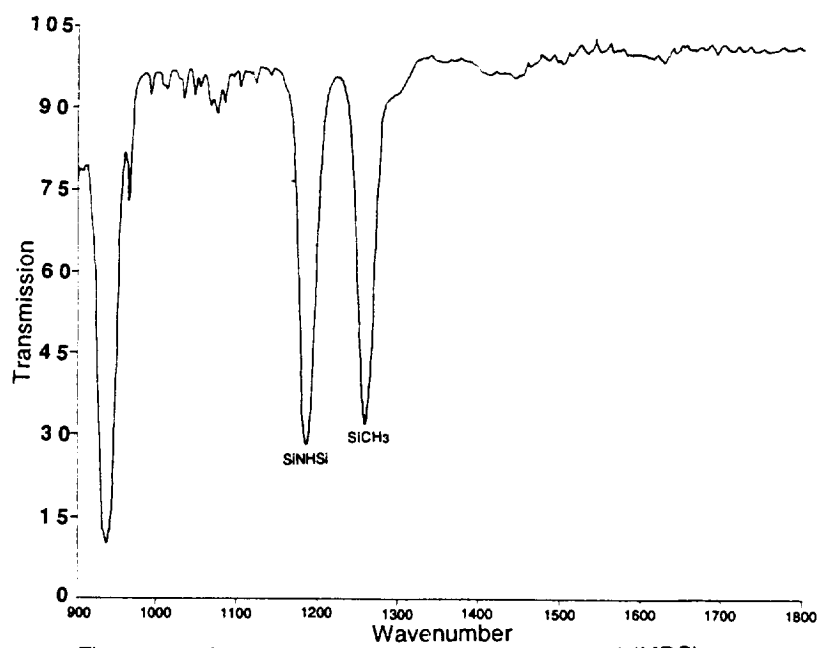


Figure 2. IR spectrum of hexamethyldisilazane (HMDS).

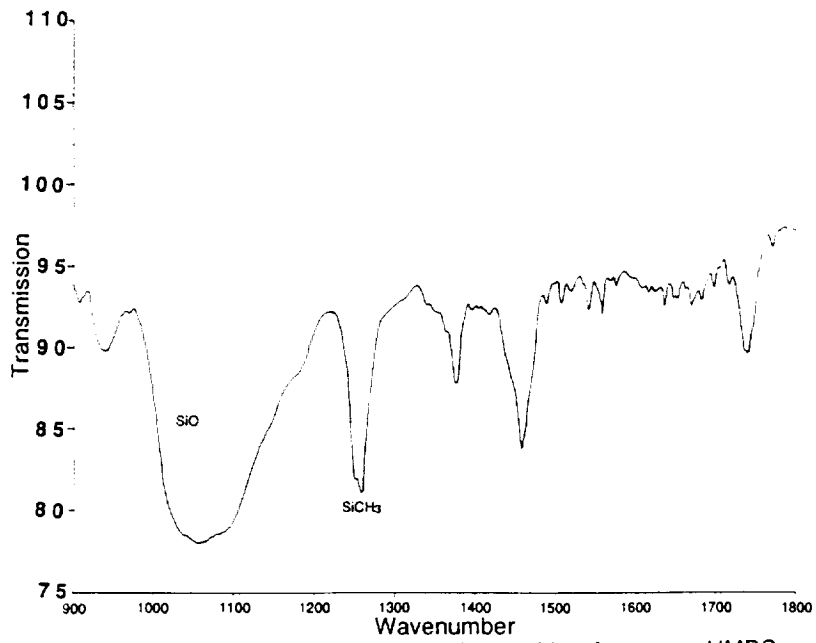


Figure 3. IR spectrum of evaporation residue from new HMDS.

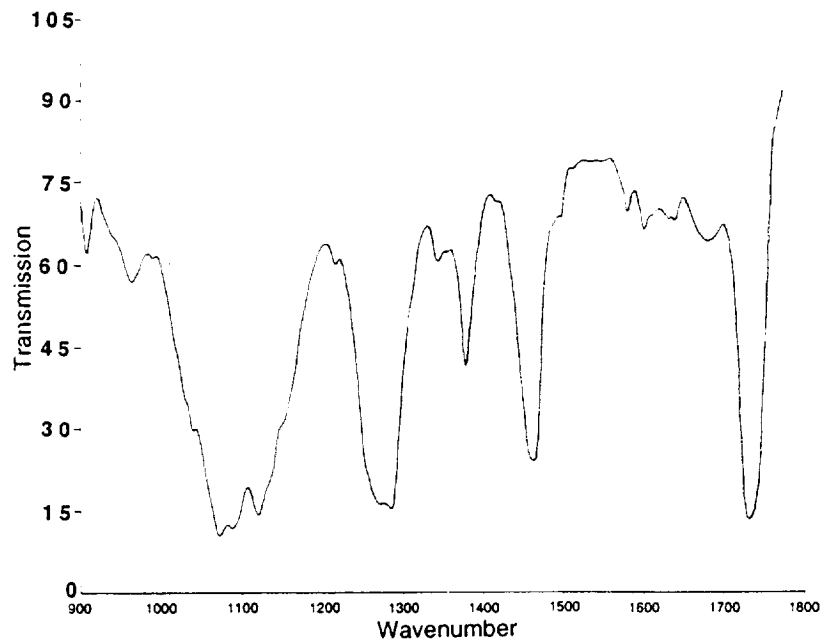


Figure 4. IR spectrum of evaporation residue from aged HMDS.

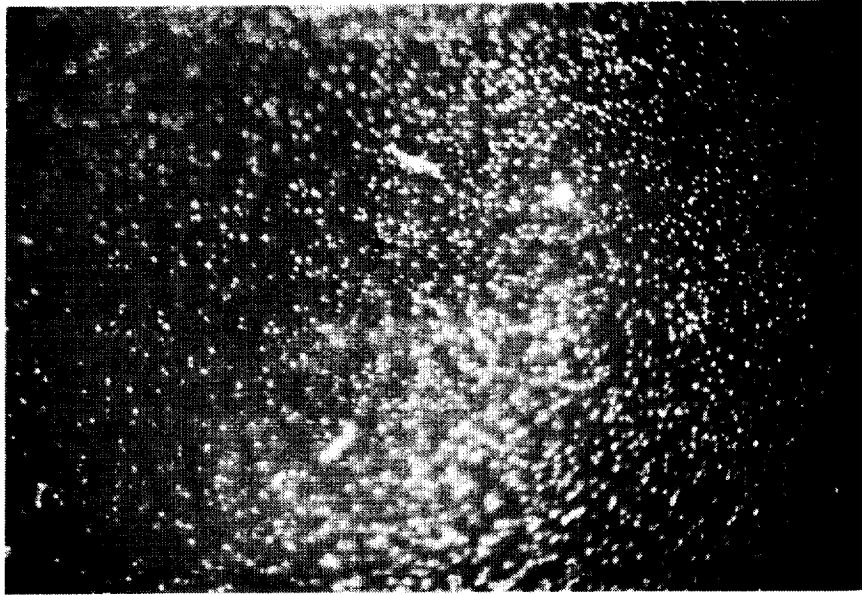


Figure 5. Photograph of evaporation residue from aged HMDS.

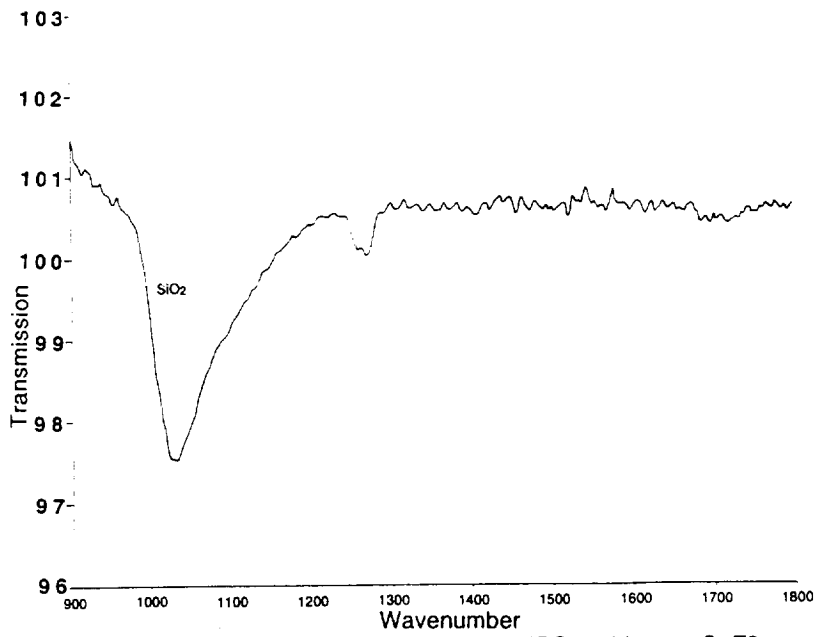


Figure 6. IR spectrum of UV exposed HMDS residue on CaF₂.

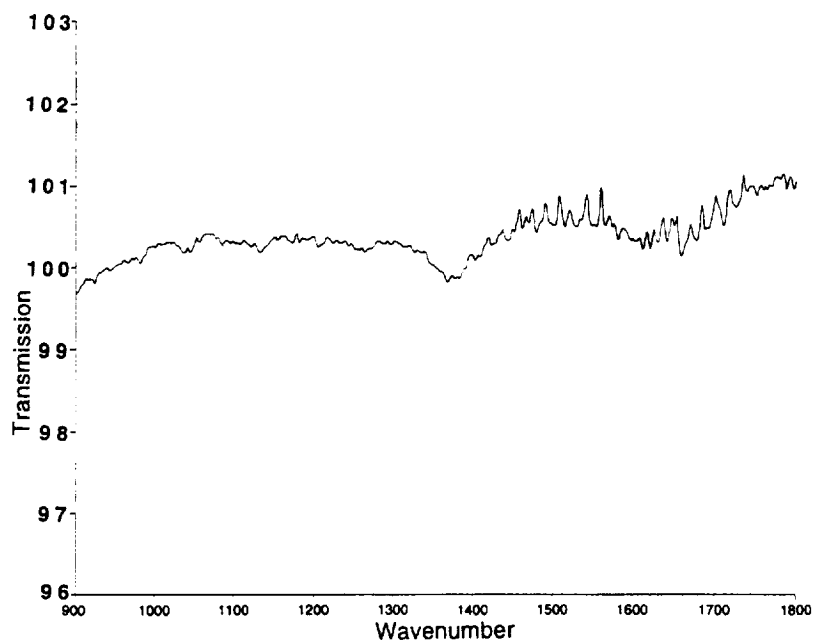


Figure 7. IR spectrum of UV exposed HMDS residue on NaCl.

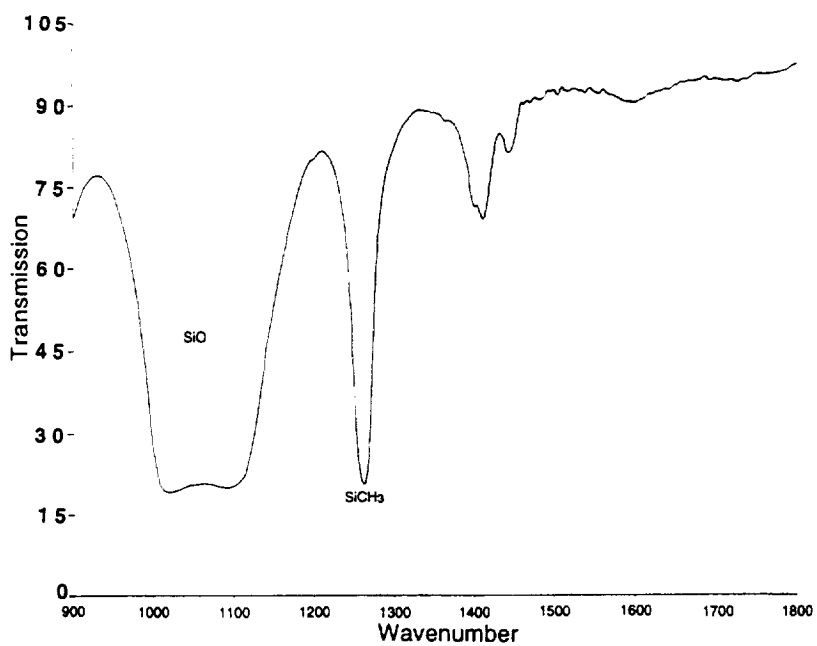


Figure 8. IR spectrum of residue from HMDS-vapor-exposed RTV-142.

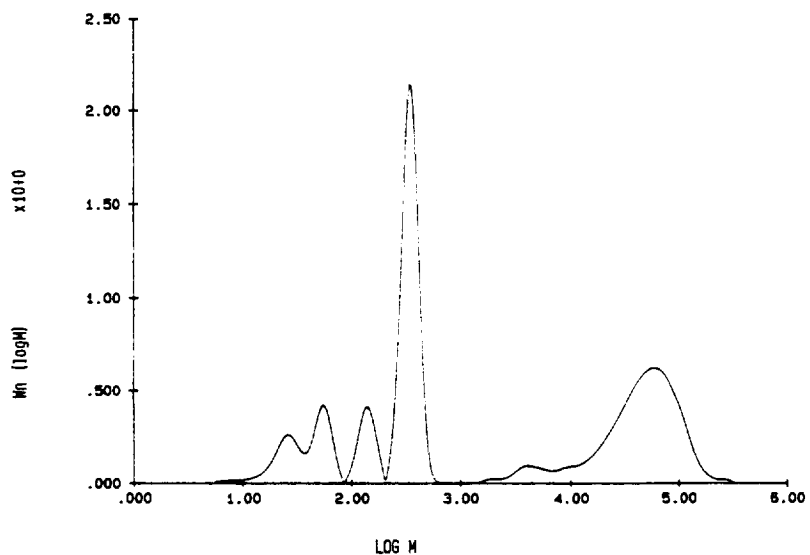


Figure 9. Molecular weight distribution of HMDS-vapor-exposed RTV residue.

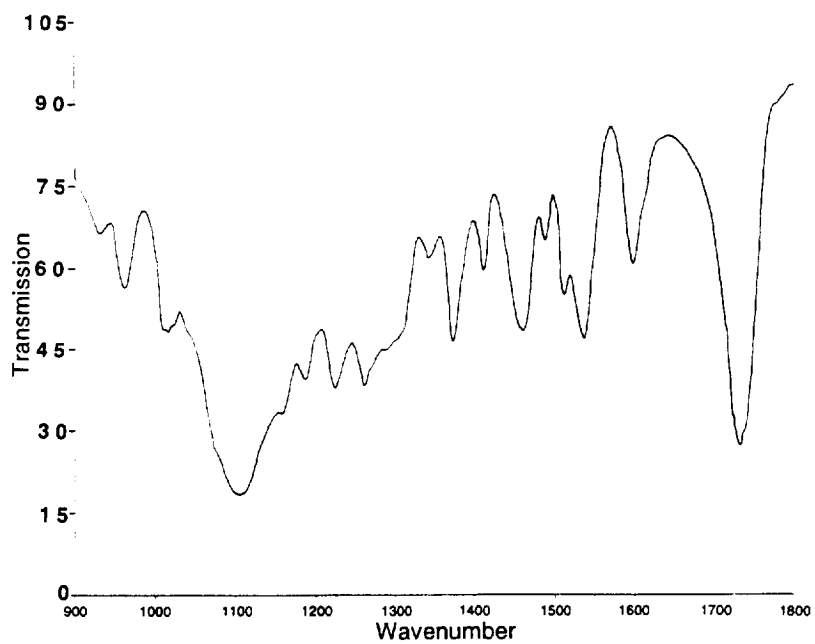


Figure 10. IR spectrum of HMDS-vapor-exposed Chemglaz Z306 residue.

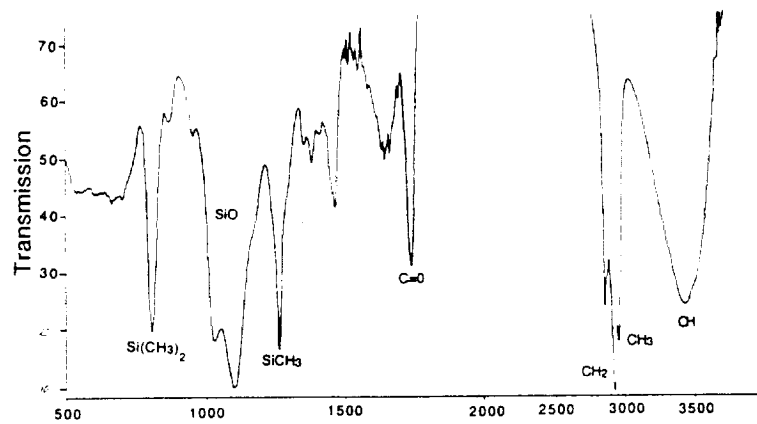


Figure 11. IR spectrum of hexane-transferred residue from the PCR (STS-48).

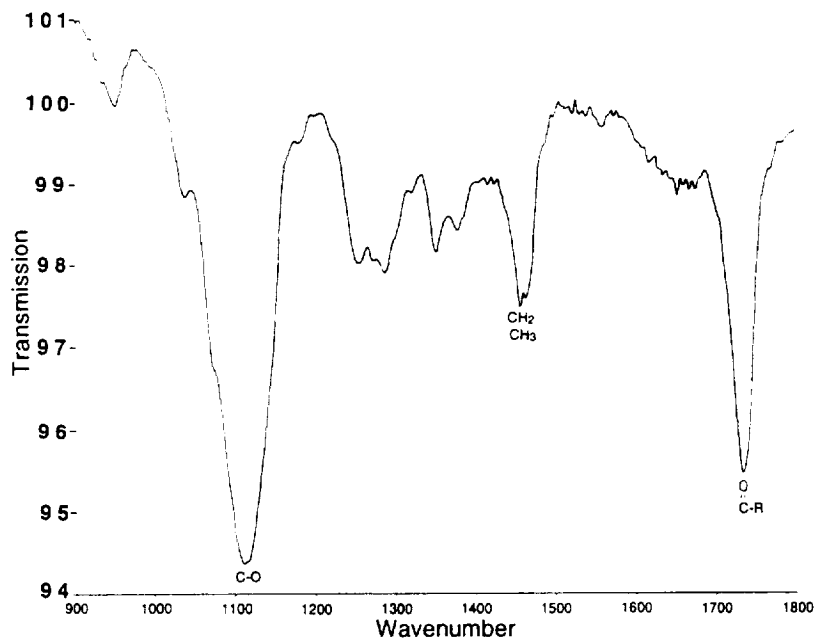


Figure 12. IR spectrum of CH₂Cl₂-transferred residue from the PCR (STS-42).