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Issues and Effects of Atomic Oxygen Interactions With Silicone Contamination on Spacecraft in Low Earth Orbit

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ISSUES AND EFFECTS OF ATOMIC OXYGEN INTERACTIONS WITH SILICONE CONTAMINATION ON SPACECRAFT IN LOW EARTH ORBIT

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***ABSTRACT** - The continued presence and use of silicones on spacecraft in low Earth orbit (LEO) has been found to cause the deposition of contaminant films on surfaces which are also exposed to atomic oxygen. The composition and optical properties of the resulting SiO_x -based (where x is near 2) contaminant films may be dependent upon the relative rates of arrival of atomic oxygen, silicone contaminant and hydrocarbons. This paper presents results of in-space silicone contamination tests, ground laboratory simulation tests and analytical modeling to identify controlling processes that affect contaminant characteristics.*

1 – INTRODUCTION

Silicones have been widely used on spacecraft as potting compounds, adhesives, seals, gaskets, hydrophobic surfaces and atomic oxygen protective coatings. Contamination of optical and thermal control surfaces on spacecraft in LEO has been an ever-present problem as a result of atomic oxygen interaction volatile species from silicones and hydrocarbons onboard spacecraft [Bank 91, Crut 91, Blak 92, and Harv 93]. The deposited contaminant films typically appear to be oxidation products resulting from the interaction of atomic oxygen with arriving silicone and hydrocarbon (if present) volatiles. The depositing contaminant is a risk to spacecraft performance because it can form an

optically absorbing film on the surfaces of sun sensors, star trackers, optical components or increase the solar absorptance of thermal control surfaces. The transmittance, absorptance and reflectance of such contaminant films seem to vary widely from very transparent SiO_x films to much more absorbing SiO_x -based films which contain hydrocarbons. The intent of this paper is to examine contamination observed on LEO spacecraft, in ground laboratory LEO simulations and propose some models that may assist in explaining the underlying issues and effects.

2 – APPARATUS AND PROCEDURE

Selected in-space results of silicone contamination will be presented from two spacecraft: the Long Duration Exposure Facility (LDEF) and the Russian Mir Space Station. The LDEF was deployed in LEO on April 7, 1984 and retrieved 5.75 years later on January 12, 1990. Eight panels of the non-articulating photovoltaic array on the Mir core module, which was deployed in LEO on June 16, 1987, were removed 10.4 years later, on November 3, 1997, then retrieved in January of 1998. Measurements of the efficiency of a retrieved solar cell were made using a Spectrolab Large Area Pulsed Solar Simulator.

Ground laboratory contamination test results will be presented from contamination tests involving thermal energy atomic oxygen interactions with volatiles from silicones and hydrocarbons. The contaminants chosen were RTV-560 silicone and Tygon[®] type R-3603 polyvinylchloride tubing (which served as the hydrocarbon contaminant by evolving a phthalate contaminant). The contaminants were either in the form of a solid piece or tubing segment or chopped into many small pieces 2-3 mm in diameter. Contamination tests were conducted at NASA Glenn Research Center in both an RF plasma asher [Rutl 94] which was operated on air and in a thermal energy microwave powered directed atomic oxygen beam facility [Stid 93] which was operated on pure oxygen. Both facilities used fused silica windows that were simultaneously exposed to atomic oxygen (Kapton[®] effective flux of 1×10^{16} atoms/($\text{cm}^2 \text{ sec}$)) and a flux of contaminants to allow the accumulation of contamination. The geometrical configurations for both types of contamination exposures were similar in that they allowed the contaminant flux to arrive at grazing incidence on the fused silica windows that also had atomic oxygen impingement. Both facilities were tested to verify that no contaminant deposited if no source of contaminant was present. The geometrical configuration was chosen to replicate sun sensors on the Ofeq-3 spacecraft (launched into LEO in 1996) which exhibited evidence of transmittance degradation due to contamination and exposure to atomic oxygen [Note 1996]. The RF plasma asher contamination experiment configuration (Fig. 1) was performed with the window and all the contaminants at the same temperature ($\sim 50^\circ\text{C}$).

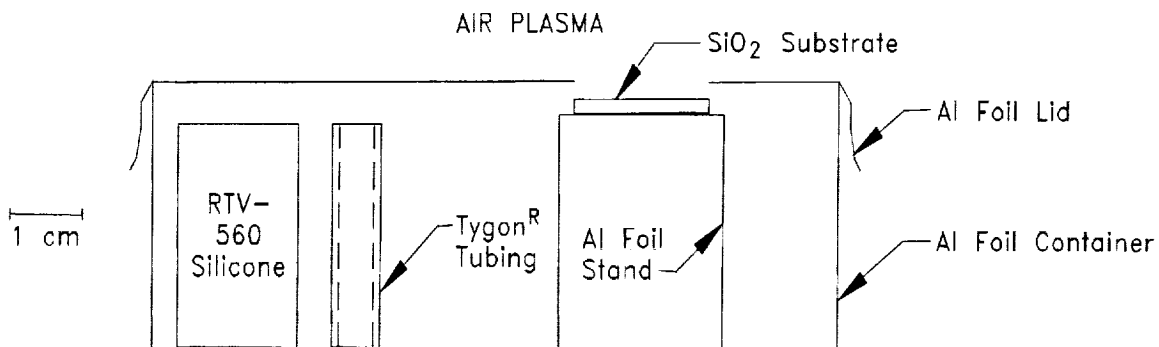


Fig. 1 - Experiment configuration for contamination tests in RF plasma asher.

The directed atomic oxygen beam contamination experiment configuration used two effusion cells (one for silicone and one for hydrocarbon) (Fig. 2).

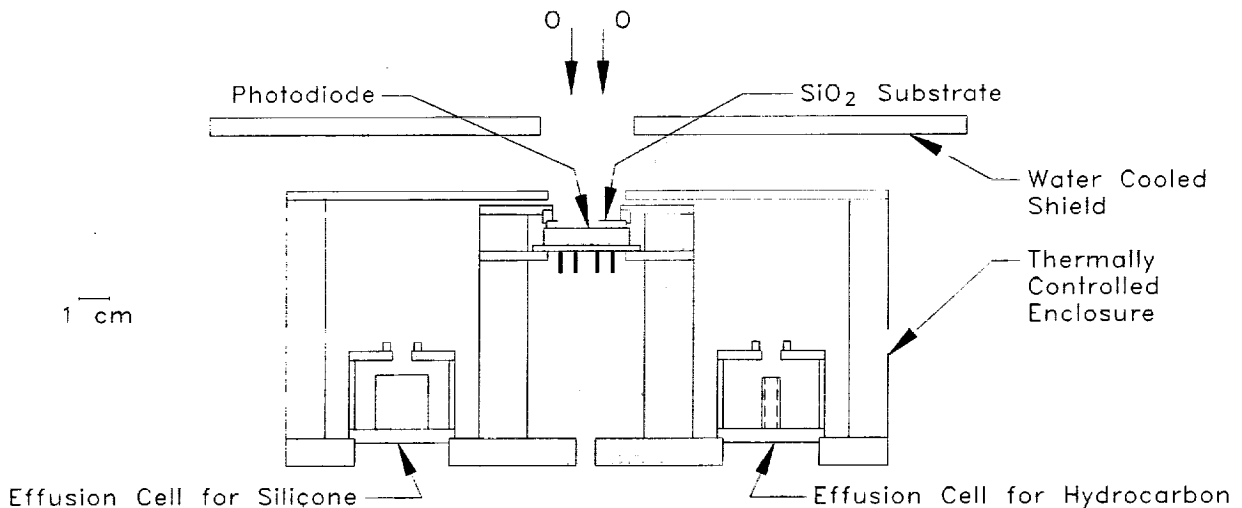


Fig. 2 - Experiment configuration for contamination tests in atomic oxygen beam facility.

The directed atomic oxygen beam facility produced a Kapton[®] effective flux of 3.3×10^{15} atoms/(cm² sec). In this facility the transmittance of the fused silica was periodically and automatically measured in vacuum using an incandescent lamp that was moved over the silica window which covered a photodiode detector. The short circuit current was used to measure contamination-caused changes in transmittance during the testing. Before and after exposure transmittance measurements of the fused silica window were made in air using a Perkin-Elmer λ -19 spectrophotometer to calculate air mass zero solar transmittance values reported in this paper. The temperature of each effusion cell, the fused silica window and the photodiode could be independently controlled. Contaminant thickness measurements were made using Dektak IIA Profilometer measuring at a location near the outside edge of the fused silica windows where a step was formed by a protective ring that held the windows.

Mathematical modeling of atomic oxygen interaction with silicon volatiles was performed by making assumptions on the time variation of the flux of arriving silicones and a reaction rate based on the fractional coverage of the surface with arriving silicones and atomic oxygen. These assumptions were then used to predict the rate of growth of the resulting SiO_x.

3 – RESULTS AND DISCUSSION

3.1-In-Space Silicone Contamination

On the LDEF spacecraft, atomic oxygen was able to impinge on the interior sides of several uniquely located experiment trays by passing through the holes in nut plates that were used to fasten protective covers for experiments during ground handling of the LDEF. As a consequence of presence of silicone volatiles within the interior of the LDEF, a flux of both silicone and atomic

oxygen was able to impinge on the aluminum tray sides at a few properly oriented locations below nut plate holes (Fig. 3). The geometry was such that negligible UV radiation exposure occurred. However a very visible thick brown contaminant layer built up at numerous locations corresponding to the nut plate holes. The source of contaminants was thought to be volatiles from silicones and urethane paint within the LDEF. The films at experiment tray corner openings were 22-24 microns thick, spalling and deposited in a layered manner (at least 34 distinct layers) with the thickness of each layer decreasing from the bottom (first layer) to the outer layers [Blak 92, Crut 91]. The composition of the film based on Electron Spectroscopy for Chemical Analysis (ESCA) indicated a relative atomic composition of 72-74% carbon, 15-23% oxygen, 2-5% silicon and 3-8% other elements [Blak 92]. The above results indicate that the volatile flux probably varied with the LDEF temperature as it orbited the Earth until very little volatile material remained. The high carbon content also suggests that, in the early days of the mission, the oxidation occurred in an environment in which the flux of atomic oxygen was insufficient to fully oxidize the hydrocarbon or the silicone. This is in sharp contrast to the much thinner and less dark silica contaminant observed on the external ram surface of the LDEF which was probably due to the low return flux of volatiles back scattering from the LEO atmosphere. Thus it appears that the lower rate of arrival of silicones and hydrocarbons on the external surface of the LDEF, with the same atomic oxygen flux, produced a much thinner, more fully oxidized and more transparent contaminant layer than interior to the LDEF.

Solar cells from the retrieved Mir photovoltaic array were found to have non-uniform silica contaminant films on their front and back surfaces. The contaminant was sufficiently thick and rough that it produced a diffusely reflecting surface where it was thickest. Fig. 4 is a photograph of the back surface of a retrieved Mir solar cell that is an Optical Solar Reflector (OSR). The front and back surfaces of the solar cells received a silicone contaminant flux from silicones used in the laminate construction of the cover glass, fiberglass fabric, solar cell, another fiberglass fabric layer, and an optical solar reflector. This laminate construction contained a significant amount of silicone that appeared to evolve very slowly at suture penetrations around the perimeter of each cell at the sites where the cells were sewn to a structural mesh backing.

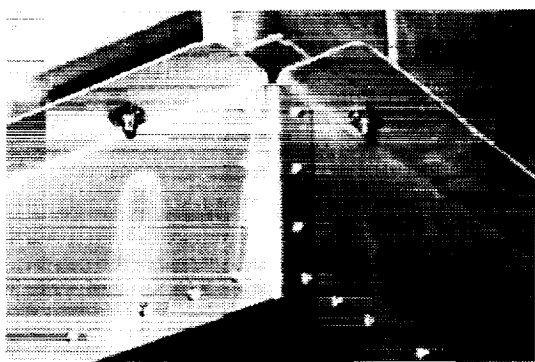


Fig. 3 - LDEF SiO_x- based contaminant streaks.

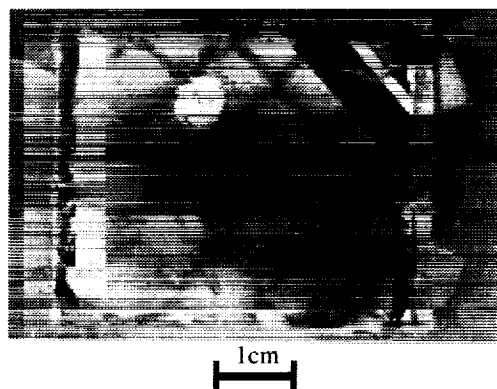


Fig. 4 - SiO_x-based contamination on Mir OSR.

As can be seen from Fig. 4, the SiO_x contaminant is highly visible in contrast to the area that was cleaned by tape peeling (where the contaminant readily separated from the surface of the OSR). The contaminant was found to be of varying thickness across the back of the solar cell because the

sources of the silicone deposition occurred at discrete locations around the perimeter of the cell. Microscopic debris on the back surface of the solar cell produced shadows of the depositing contaminant, indicating that a major transport mechanism occurred through line of sight vapor phase transport. An image of the support mesh that was sutured around each solar cell perimeter can also be seen. The contaminant was found to be thinner in these regions where the mesh prevented atomic oxygen from converting the silicone to SiO_x thus allowing some amount of desorption of the depositing silicone prior to its conversion to SiO_x . At a representative location on this particular solar cell, the contaminant was found to be 1.24 microns thick in the areas which were not shielded from atomic oxygen by the mesh and 1.06 microns where the mesh obstructed arriving atomic oxygen from converting the silicone to SiO_x [Bank 99]. Measurements of the contaminant thickness which occurred similarly on the front surface of a typical solar cell were found to be 2.0-4.6 microns thick and found to be comprised mostly of oxidized silicone by energy dispersive spectroscopy.

With such thick contaminant layers on the surface of the solar cells, one would also expect some reduction in the transmitted solar light radiation with a reduction in photovoltaic array output power. However, calibration of the solar cell, before and after removal of the contaminant (by polishing with a CeO paste), indicated that the silica contamination only caused a reduction in efficiency from 10.51% to 10.4%. Thus it appears that a low flux of silicone volatiles was able to be near fully oxidized to form a very transparent silica contaminant layer on the sun facing surface of the Mir solar cells. The back surface of the Mir array had a polymer mesh that was covered with an organic adhesive (BF_4) which may have been a source of hydrocarbon contaminant that caused darkening of the SiO_x deposit. However, the contaminant also had a negligible carbon content, as measured by energy dispersive spectroscopy, on the AK-573 white paint coatings for the solar array ridged handrails. This paint experienced an increase in solar absorptance from an initial range of 0.243-0.261 to between 0.537-0.555 after retrieval [de Gr 99]. Similarly, the OSR indicated a solar absorptance of 0.163 with contaminant removed and 0.213 with the contaminant on the OSR. Thus, in an atomic oxygen environment, the presence of hydrocarbon volatiles along with the silicone volatiles, may increase the absorptance (and reduce transmittance) of the resulting SiO_x contaminant film without necessarily adding much carbon to the deposit.

3.2-Ground Silicone Contamination Experiments

Tests in both the plasma asher and the atomic oxygen beam systems were typically conducted over approximately one week continuous duration for each set of samples. Contamination experiments in the RF plasma asher with only the RTV-560 silicone contaminant sources produced SiO_x deposits which had negligible loss in transmittance. Experiments in the RF plasma asher when both the RTV-560 silicone and Tygon[®] hydrocarbon contaminant sources were present produced deposits which had measurable losses in transmittance. As can be seen in Table I, the silicone-to-Tygon[®] mass ratio of ~3.3 produced the thinnest deposit that in fact had the highest absorption coefficient.

Table I – RF Plasma Asher Contamination Tests

<u>Contaminant (mass, shape)</u>	<u>Atomic Oxygen Effective Fluence, atoms/cm²</u>	<u>Transmittance</u>		<u>Contaminant Thickness, Angstroms</u>
		<u>Initial</u>	<u>Final</u>	
RTV-560 (10 g, solid) + Tygon® ¹ (3 g, solid)	6.1 x 10 ²¹	0.926	0.84	~14,000
RTV-560 (40 g, chopped) + Tygon® (12 g, chopped)	6.2 x 10 ²¹	0.926	0.89	~2,000
RTV-560 (21.5 g, chopped) + Tygon® (24.5 g, chopped)	6.0 x 10 ²¹	0.926	0.85	~12,200

Note ¹: This sample of RTV-560 had been exposed in vacuum for 236 hours including a 100°C vacuum bake for 162 hours.

Contamination experiments performed in the thermal energy directed-beam atomic oxygen facility also resulted in absorbing contaminant films only when Tygon® hydrocarbon contaminants were allowed to simultaneously arrive with silicone contaminants from RTV-560 silicone. As can be seen in see Table II, increasing the hydrocarbon portion of the contaminant flux by heating the Tygon® tubing to 49°C rather than 24°C produces causes a thinner, yet less transmitting contaminant film. As in the case of the asher environment the silicone-to-Tygon® mass ratio of ~3.3 produced the thinnest deposit which also resulted in the highest absorption coefficient, α .

3.3-Modeling of Transmittance Consequences of Silicone Contamination

Assuming that the arrival flux, f_s , of silicone volatiles (with or without hydrocarbon contaminants) arriving at an optical surface is proportional to the amount of volatile material remaining, then the flux would be expected to decrease with time in an exponential manner.

$$f_s = k_1 \exp(-k_2 t) \quad 3.3.1$$

where k_1 and k_2 are constants and t is time. This would be characteristic of a finite source of silicone contaminants on a spacecraft which gradually depletes its volatiles with time. If one assumes the reaction rate of atomic oxygen with silicone contaminants is dependent upon surface area concentration as opposed to a volume concentration, as in wet chemistry, then the thickness, x , of the contaminant film can be modeled. Using this surface reaction model, the rate, dx/dt , of oxidized contaminant build up on a fused silica window is proportional to the product of the fractional coverage, C_s , of the window surface with momentarily adsorbed silicone molecules and the fractional coverage, C_o , of the same surface with adsorbed oxygen atoms.

Table II – Directed Atomic Oxygen Beam Contamination Tests

Contaminant (mass, temp., shape)	Atomic Oxygen Effective Fluence, atoms/cm ²	Transmittance		Contaminant Thickness ¹ , Angstroms
		Initial	Final	
RTV-560 (10 g, 49°C, solid) + Tygon [®] (3 g, 24°C, solid)	1.69 x 10 ²¹	0.926	0.922	4,197
RTV-560 (10 g, 49°C, solid) + Tygon [®] (3 g, 49°C, solid)	1.99 x 10 ²¹	0.926	0.859	1,897
RTV-560 (21.7 g, 49°C, chopped) + Tygon [®] (9 g, 49°C, chopped)	1.65 x 10 ²¹	0.926	0.809	12,130
RTV-560 (12.6 g, 49°C, chopped) + Tygon [®] (8.5 g, 49°C, chopped)	0.44 x 10 ²¹	0.926	0.863	6,000

Note ¹ : Measured near the outside edge of the deposit. Deposits in the center of the sample were 3 - 4 times greater than near the edge.

Thus

$$dx/dt = k_R C_S C_O \quad 3.3.2$$

where k_R is a constant relating to the probability of reaction. The fractional coverage with silicone is not simply proportional to the arrival flux, f_S , because the statistics of coverage are similar to that of throwing coins into a box. For a small number of coins (or contaminant molecules) in a big box, coverage is proportional to flux. However, for large fluxes there is a finite probability that the coins (or contaminant molecules) will deposit on top of each other. The situation is also true for atomic oxygen fractional coverage, which is similarly dependent on the atomic oxygen flux, f_O . The resulting combinatorial consequences for the fractional coverage for silicones and atomic oxygen is

$$C_S = (1 - \exp -(k_S f_S)) \quad 3.3.3$$

$$C_O = (1 - \exp -(k_O f_O)) \quad 3.3.4$$

where k_S and k_O are constants. Thus combining equations 3.3.1-3.3.4 yields

$$dx/dt = k_R (1 - \exp -(k_S k_1 \exp -(k_2 t))) (1 - \exp -(k_O f_O)) \quad 3.3.5$$

The resulting contaminant film transmittance, τ , caused by a coating of thickness x , is given by

$$\tau = \exp(-\alpha x) \quad 3.3.6$$

where α is the optical absorption coefficient of the deposited contaminant film. With sufficient data, one might be able to determine the functional dependence of the optical absorption coefficient

on the f_o/f_s ratio and use the information to more accurately predict the contaminant film transmittance degradation with time. Equation 3.3.5 can be computationally integrated and substituted into Equation 3.3.6 to show the resulting gradual loss in transmittance, τ , with time. To predict the dependence of contaminant buildup on variations in atomic oxygen fluence, one can assume an atomic oxygen flux that has periodic spikes (a 25% increase over the nominal flux) in an otherwise constant flux and use computational integration to predict the resulting transmittance degradation with time. Fig. 5-a shows plots of the atomic oxygen flux and contaminant flux that were used with Equations 3.3.5 and 3.3.6 to computationally integrate and predict transmittance, τ . The result, shown in Fig. 5-b, indicates that early in a mission when silicone contaminants are being evolved at a high rate, the contaminant buildup is highly atomic oxygen flux dependent.

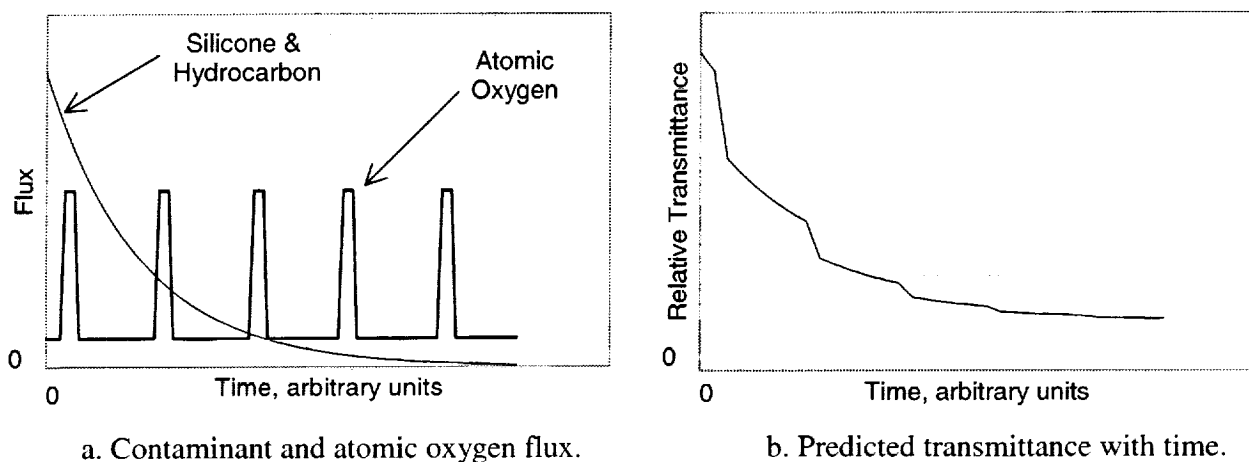


Fig. 5- Modeling of contamination interaction with atomic oxygen in LEO.

After the amount of contaminant volatiles reduces with time, the deposition rate and consequently the transmittance, show very little dependence on atomic oxygen flux. This is somewhat analogous from a reaction changing from fuel rich reaction to oxygen rich with the latter showing little dependence on oxygen because there is already more than is needed.

4 – SUMMARY

Atomic oxygen interactions with silicone volatiles and mixtures of silicone and hydrocarbon volatiles produce glassy SiO_x -based contaminant coatings. The addition of hydrocarbon volatiles in the presence of silicone volatiles appears to cause much more absorbing (and consequently less transmitting) contaminant films than when no hydrocarbon volatiles are present. Based on LDEF and Mir results, conditions of high atomic oxygen flux relative to low contaminant flux appear to cause more transparent contaminant films than do films deposited under conditions of low atomic oxygen flux with high contaminant flux. Modeling predictions indicate that the deposition of contaminant films early in a LEO flight should be much more dependent on atomic oxygen flux than later in a mission.

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