Results of Apparent Atomic Oxygen Reactions with Spacecraft Materials During Shuttle Flight STS-41G

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An experimental package (ACOMEX) flown on Shuttle mission STS-41G was designed to investigate the effect of atomic oxygen in Shuttle (low Earth) orbit on polymeric-based spacecraft materials. The experiment included specimens of advanced composite materials, i.e., carbon-epoxy and Kevlar®-epoxy both with and without protective coatings, in addition to a number of thermal protective paints and films. These materials specimens were attached directly to the lower arm boom of the Shuttle Remote Manipulator System (SRMS) and positioned normal to, and in the direction of, flight for a total of approximately 38 h of equivalent normal exposure at 225 km altitude. In addition, a carbon-coated atomic oxygen fluence monitor together with a photographic record obtained by the Canadian payload specialist onboard provided detailed information on the environment experienced by the exposed specimens. The present paper describes the effect of atomic oxygen interaction experienced by the exposed specimens. Mass loss measurements together with high-resolution Scanning Electron Microscope photomicrographs are presented to quantify the effect and identify the resultant surface morphology. Post-flight analysis indicated the specimens experienced the effect of a very aggressive environment which resulted in significant changes to exposed surfaces.

Introduction

EXPERIENCE on Shuttle flights has shown that atmospheric interactions with spacecraft in low Earth orbit (LEO) can have significant effects on the performance of materials, particularly those of a polymeric base, after only short exposure. Polymeric materials are important elements of spacecraft design with applications for structural members in the form of advanced composite materials or thermal protection in the form of films and coatings. Future spacecraft will continue to use polymeric materials in thermal coatings or as advanced composite material structural members in order to achieve the size, stiffness, and pointing requirements of large third-generation spacecraft.

Unfortunately, there is the potential for every satellite, whether in LEO or higher, to be affected by the low Earth orbit environment. The use of the Shuttle to launch satellites (which is benefited by a check-out of the satellite before deployment and boost) and the realization of satellite repair increases the possible exposure. Even a short time spent in LEO as a result of launch scenarios using the Shuttle, or expendable launch vehicles that employ a parking orbit prior to boost, may have serious effects on exposed materials. Such a concern exists for the Galileo spacecraft being developed by the Jet Propulsion Laboratory. Galileo is an interplanetary spacecraft that will orbit Jupiter. The current deployment altitude and parking orbit is 196 km at 30 deg inclination. Erosion of materials could affect the spacecraft in three ways. The primary concern would be the loss of surface conductivity. This would violate the equipotential spacecraft requirement and create a potential electrostatic discharge situation. Second, if the outer layer of the thermal blanket material (a black polyester coating deposited over Kapton®) is removed down to the substrate, the Kapton could prove to be a glint source to the sensitive science instruments. Finally, there is concern that the material that is eroded away could become another source of contamination. The advent of the space station will provide another situation of concern.

The Earth's upper atmosphere is not a simple function of altitude, but varies in composition, density, and temperature with (among other things) solar activity, latitude, local time and season. Fig. 1 represents the average composition.[1] At altitudes between 200 and 700 km, the predominant species is atomic oxygen and, at altitudes above this, it remains a significant constituent. The atomic oxygen density in LEO is not particularly high even at Shuttle altitudes; the 10^9 atoms/cm^3 corresponds to the density of residual gas in a vacuum of 10^{-7} Torr. However, due to the high orbital velocity (approximately 8 km/s at Shuttle altitude), the flux is indeed high, being of the order of 10^{15} atoms/cm^2 – s. In addition, this high orbital velocity corresponds to collisions with highly energetic (5 eV) oxygen atoms. The result has been observed to be surface erosion and mass loss for exposed materials.[2]

If atomic oxygen incompatibility is discovered to be extensive and difficult to remedy for Galileo, the option exists to raise the Shuttle orbit altitude at which Galileo is deployed. The Galileo design fluence [2.2×10^{20} atoms/cm^2 (7 orbits), to 6.9×10^{20} atoms/cm^2 (22 orbit contingency)] allows for Shuttle orbits as low as 196 km. Raising the altitude by 40 km will reduce the total fluence to the spacecraft by one-half. A marginal design may become acceptable in this manner but, of course, there are mission impacts with this approach that affect the mission trajectory and flight time. Another option to reduce extensive atmosphere interactions with the Galileo materials is to overcoat the existing materials with a protective layer or include an additive in the bulk coating that would reduce the effective erosion or both. The platform and fluence to understand the effectiveness of this option was provided by STS-41G.

Description of Experiment

The Advanced Composite Materials Exposure to Space Experiment (ACOMEX) on STS-41G[3] in October 1984 was

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designed to investigate the above phenomenon on selected polymeric materials and to assess the effectiveness of a thin fluorocarbon coating to act as a protective barrier to the attack. Of particular interest were high performance advanced composite materials of carbon-epoxy and Kevlar-epoxy, and thermal control coatings. The advanced composite materials were in the form of thin, 4-ply strips (nominally $15\times2.25\times0.05$ cm) and included three aerospace grade materials (two carbon-fiber-based: Fiberite T300/934 and Narmco T300/5208; and one Kevlar fiber-based: 3M SP328) in typical ply orientation configurations. The thermal coatings were selected from possible materials to be used on the Galileo spacecraft. These included carbon-filled polyester (Sheldahl black) coated Kapton films (0.003 cm) with thin overcoats (275 Å) of indium tin oxide (ITO) that were sputtered or vapor deposited; and three thermal coatings: carbon-filled epoxy (BOSTIC 463-14), carbon-filled polyurethane (Chemglaze Z004) [both modified with a siloxane additive (10% by weight)] and a carbon-filled silicone (GE-PD-224). These materials were applied to round disks (2.5 cm diam) and mounted in an aluminum boat together with a carbon-coated atomic oxygen fluence monitor. Finally, two thin films of Kapton $20\times10\times0.0013$ cm, and 2.5 cm diam $\times0.0075$ cm completed the material complement. The material specimens prior to flight are shown in Fig. 2.

The specimens were mounted directly to the thermal blankets of the lower arm boom of the Canadarm as shown in Fig. 3, by means of both transfer adhesive on the back of each and circumferential bands of Kapton tape. During the mission, the Canadarm was positioned over the port wing to expose the specimens normal to the direction of the flight velocity vector in order to achieve the greatest effect. The arm was to remain in this position for up to 30 h to accumulate a total fluence of approximately 2×10^{20} atoms/cm^2. Unfortunately, operational restrictions onboard the Shuttle, due to equipment malfunction of the flash evaporator system, required periodic water dumps from the side water dump nozzle. Because of past problems on STS-41D with ice buildup after this procedure, the Remote Manipulator System (RMS) was repositioned for each water dump (approximately every 12 h) to inspect the side water dump nozzle. Together with other RMS maneuvers, this had the disadvantage of providing off-normal exposure of the specimens but was beneficial in that it allowed the specimens to be closely inspected by the Canadian payload specialist on board. During the mission, the Canadian payload specialist was scheduled to provide a photographic record of the material specimens in order to monitor the rate of change with time and accumulated fluence, as recorded by the carbon-coated fluence monitor and the Kapton film.

The carbon-coated fluence monitor[4] consisted of a ground KG-1 glass plate with three parallel bands of gold of different thicknesses, 2500 Å, 5000 Å, and 7500 Å, deposited on the surface. This was then overcoated with vapor-deposited amorphous carbon to a total thickness of 10,000 Å resulting in carbon bands of thicknesses 2500 Å, 5000 Å, and 7500 Å, plus the base. The carbon was expected to erode because of the attack of the oxygen at a predetermined rate and, accordingly, provide visual indication of the accumulated fluence as each band of gold appeared from beneath the carbon layer. In addition, the erosion rate of Kapton that has been measured on previous flights was designed to provide an end-of-flight fluence measurement and a calibrated sample of the surface morphology after erosion.

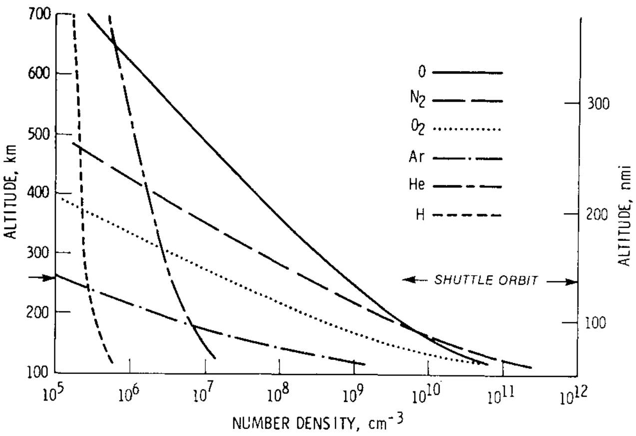

Fig. 1 Atmospheric composition in low Earth orbit.[1]

Observations

Surface Analysis

Visual inspection with only the unaided eye after the flight confirmed material changes that manifested themselves in the form of loss of surface gloss or color changes as compared to laboratory reference samples. In addition, sharp shadow effects on areas unexposed to the flight direction, but exposed to other influences of vacuum, thermal excursions, or solar radiation, supported the belief that the observed change was caused by atomic oxygen impingement.

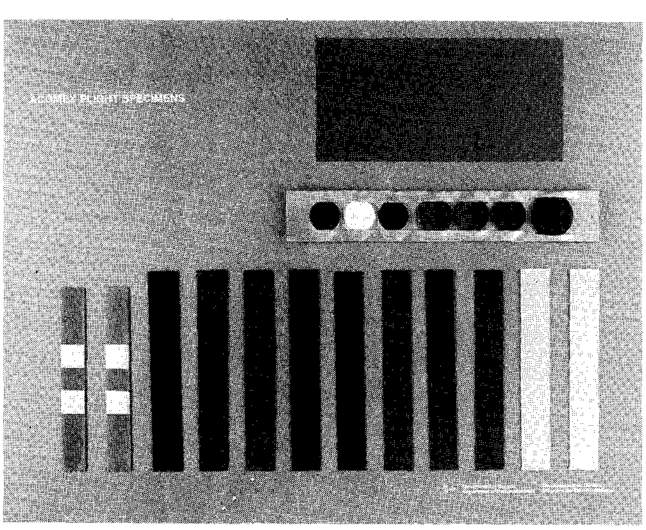

Fig. 2 ACOMEX flight specimens.

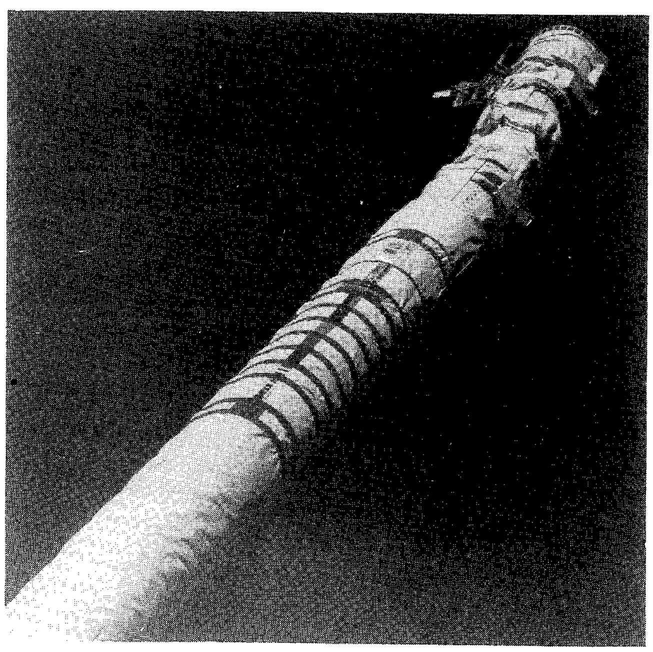

Fig. 3 ACOMEX specimens mounted on Canadarm.

As noted earlier, the specimens experienced exposure in both the designed manner as well as in a somewhat uncontrolled and undefined fashion during mission events such as water dump inspection, ERBS deployment, and others. Consequently, the exposure time and orientation can only be estimated from records taken by the Canadian payload specialist on board, and ground-based observation of telemetered ephemeris data taken during the mission. Fortunately, most of the exposure time was logged with the specimens in the desired normal position, which reduced the error in calculating fluence. Based on an exposure estimated to be equivalent to 38 h of normal exposure, at an altitude of 225 km, the total fluence of atomic oxygen on the specimens was approximately 3×10^{20} atoms/cm^2.

Detailed analysis of the material specimens confirmed the magnitude of the changes observed visually. The surface of carbon-epoxy specimens before exposure was smooth and glossy with only superficial scratches as shown in the Scanning Electron Microscope (SEM) photomicrograph of Fig. 4. Although it is possible to identify the fiber direction of the upper layer in this figure, the fiber features, covered by a layer of epoxy matrix, are not distinct. After exposure in space, the surface resembled a "corduroy" pattern as shown in the SEM photomicrograph in Fig. 5. The depth of this erosion is approximately 5 μm, which corresponds to a reactivity of 2×10^{-24} cm^3/atom for the epoxy matrix.

Of particular interest, as shown in Fig. 5, the fibers themselves have been attacked and appear only as porous ridges with little residual strength or stiffness. This porous nature is in direct contrast to nonexposed fibers from the control specimens of the same material lot as shown in Fig. 6. Similar fiber erosion was observed for Kevlar specimens. The initially smooth specimen surfaces were eroded to expose a similar "corduroy" surface, which exhibited a comparable reaction rate for the epoxy matrix.

Kapton specimens exposed on ACOMEX were originally included in order to provide a standard of comparison to other flight data in this field. However, the two specimens chosen represented material of differing manufacturing times (circa 1984 and circa 1969, from a previous space program) that exhibited very different resistance to the environment. The more recently manufactured specimen reacted as expected, experiencing visibly apparent changes, whereas changes were much more subtle for the other as will be noted.

Initially, the "new" Kapton (circa 1984) surface was typically smooth with small pits suspected to be caused by processing as shown in the SEM photomicrograph of Fig. 7. After exposure, the surface was uniformly irregular with a "rug-like" surface as shown in Fig. 8. Mass loss measurements indicate a reduction of 60% due to the erosion effect. For the 12.7 μm thick Kapton film, this corresponds to a reactivity of approximately 2.5×10^{-24} cm^3/atom, which agrees very favorably with results from other experiments on STS-8.[2]

Although the "old" Kapton (circa 1969) exhibited a similar preflight appearance to "new" Kapton as shown in Fig. 9, after flight the specimen showed a marked decrease in surface roughness compared to "new" Kapton as shown in Fig. 10. In addition, draw lines from the manufacturing process are still

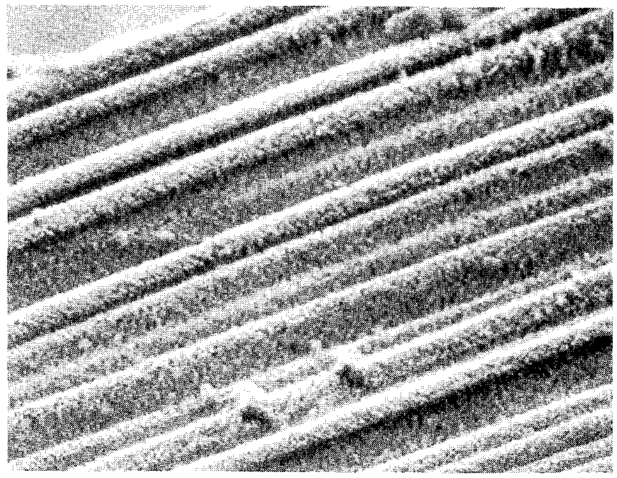

Fig. 5 Exposed carbon-epoxy specimen (1000X).

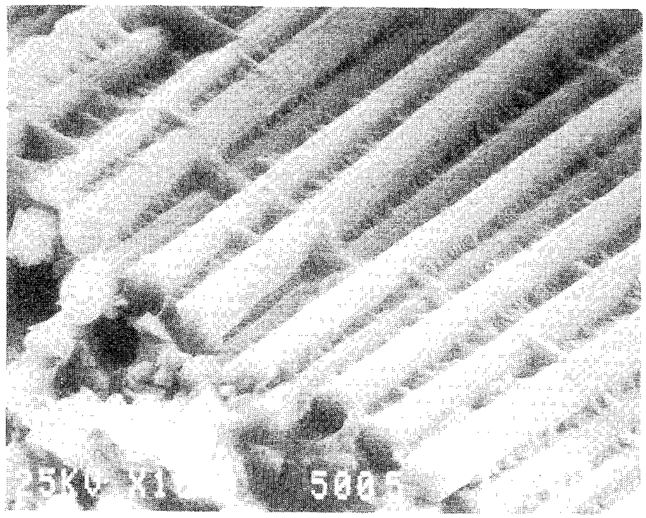

Fig. 6 Control carbon-epoxy specimen internal surface (1000X).

Fig. 4 Control carbon-epoxy specimen (500X).

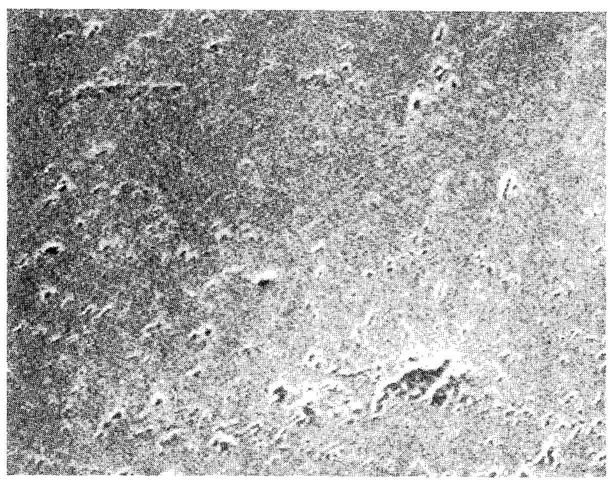

Fig. 7 Control Kapton (circa 1984) specimen (5000X).

visible indicating that the depth of erosion was small. Subsequent investigation[5] with the manufacturer suggested that a manufacturing process change incorporated in the late 1960's may be the cause of the different resistance. The previous manufacturing process included a heat treatment to passivate the surfaces and to alter surface tension properties. This treatment was subsequently eliminated because the primary use had changed from electronics to aerospace applications. This possibility warrants further investigation as a possible approach to increasing the erosion resistance of this important thermal control material for spacecraft.

Protective Coatings for Composite Materials

Duplicate specimens of carbon-epoxy were overcoated with a thin (1000 Å) coating of plasma-sprayed fluorinated ethylene propylene copolymer to act as a protective barrier to the erosion.[6] Although the results of this coating were not uniformly successful, some of the specimens exhibited little if any change after flight while others exhibited increased resistance over sections of the area where the coating remained intact. Successful application of the protective coating is exhibited in the photomicrograph of Fig. 11 taken after flight, which shows little change from the control specimen in Fig. 12. However, the specimen of Fig. 13 shows areas of protected material interspersed with eroded areas similar to those seen for the unexposed specimens. It is thought that the variation in protection is a result of the application procedure that allowed the coating to be removed exposing the surface. Investigation of the source of this problem is necessary to confirm the effectiveness of this technique. The location of the problem, whether it be at the substrate interface or outer surface, could have an important effect on the practicality of the concept. However, the results observed showed promise that the use of a thin overcoat, which would not measurably alter the base properties of the material, could provide an effective barrier to the environment.

Thermal Properties Analysis

Thermal radiative properties of solar absorptance and emittance were measured for carbon-epoxy specimens before and

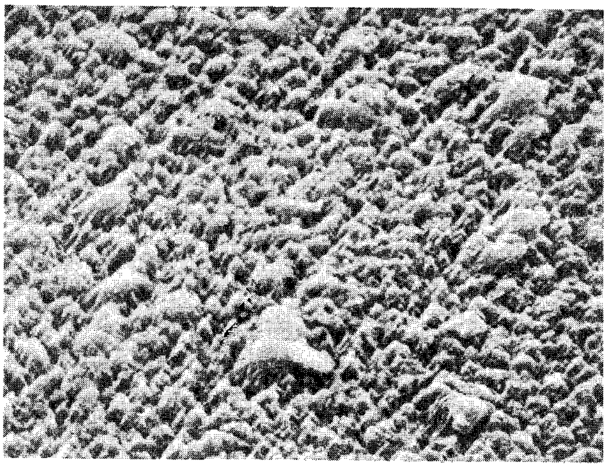

Fig. 8 Exposed Kapton (circa 1984) specimen (5000X).

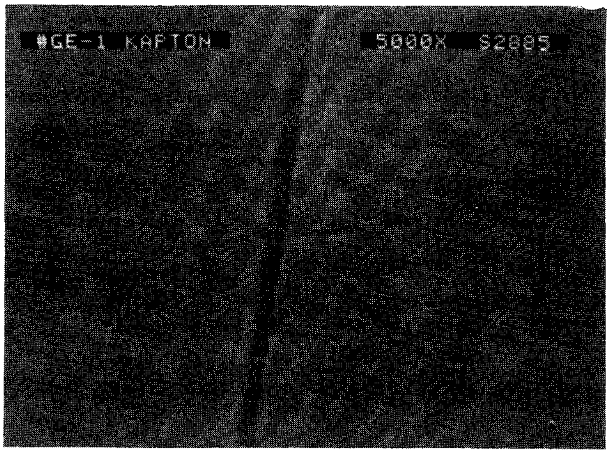

Fig. 9 Control Kapton (circa 1969) specimen (5000X).

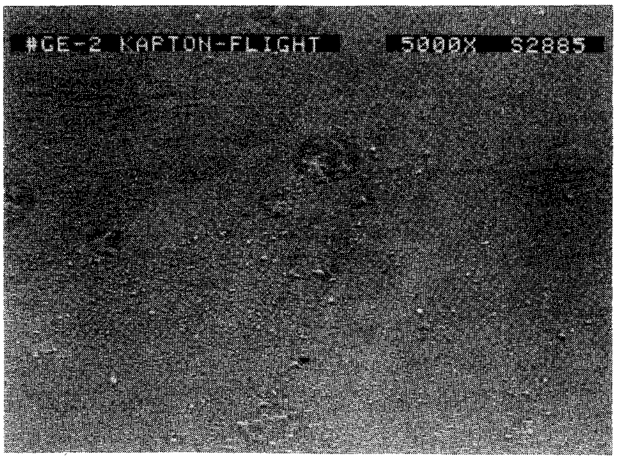

Fig. 10 Exposed Kapton (circa 1969) specimen (5000X).

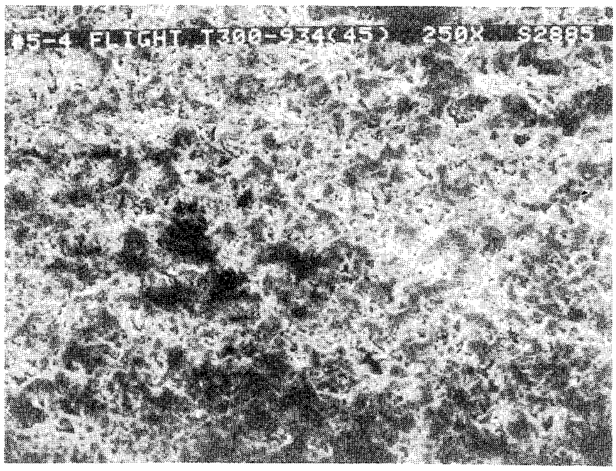

Fig. 11 Exposed fluorocarbon-protected carbon-epoxy specimen (250X).

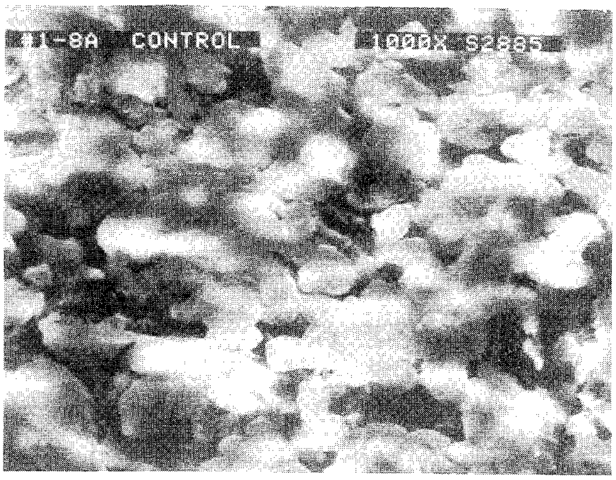

Fig. 12 Control fluorocarbon-protected carbon-epoxy specimen (1000X).

after exposure to the environment. The solar absorptance was measured with a Gier Dunkle Solar Reflectometer Model MS-251 and thermal emittance measured with a Gier Dunkle Infrared Reflectometer Model DB100. Unprotected specimens exhibited an increase in absorptance (α_S) of 7% and a decrease in emittance (ϵ_T) of 11% for a combined α/ϵ ratio change of approximately 20%.

For the thin Kapton film (circa 1984), absorbtance over the near-ultraviolet to infrared wavelengths was compared to a laboratory control specimen by measuring transmission of a collimated beam through the material. The change in absorbtance is shown in Fig. 14, which clearly verifies the increased opacity of the exposed film after exposure to the environment. Although the change is more pronounced on a percentage basis in the far-infrared region, the change over the visible and near-infrared is approximately 30 to 40%, increasing to 60% at longer wavelengths. The measured change in transmission through the specimen is attributed to reflection at the internal and external front surface due to surface roughening rather than changes in bulk material properties.

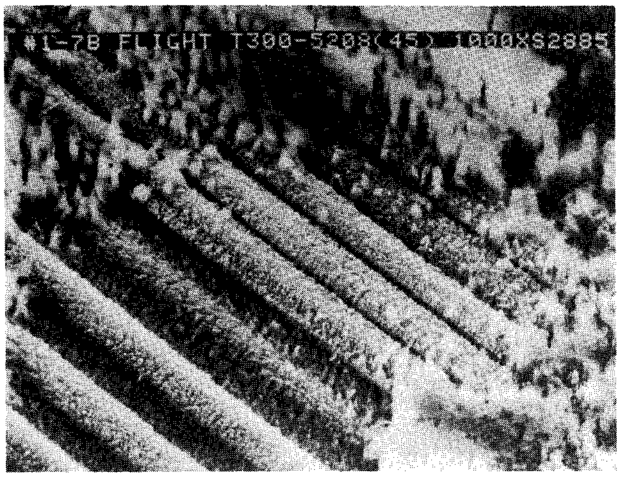

Fig. 13 Exposed incompletely protected carbon-epoxy specimen (1000X).

Similar measurements on Kapton circa 1969 were not possible due to the method of mounting the specimen during the flight test.

The Galileo thermal control coating specimens that were exposed on ACOMEX represented the few remaining Galileo materials that needed to be "qualified" for atomic oxygen exposure particular to that mission. Fig. 15 shows the SEM appearance of the pre-exposed sample of sputtered ITO/Sheldahl black polyester/Kapton. Fig. 16 shows the effects of flight exposure. Although microcracking had apparently been induced by the exposure to the ambient environment, post-flight testing indicated that the material had remained intact, i.e., did not create particulates from sloughing and had retained its surface conductivity. It is interesting to note that the vacuum-deposited ITO-coated specimens reacted in the exact same manner as the specimen with the spluttered coating even though the stoichiometry was different. Figs. 17–22 show the before and after condition of the remaining Galileo materials exposed in ACOMEX. Of particular interest was the complete lack of attack on the GE-PD-224 coating.

This was of great importance because this GE-PD-224 coating is the primary thermal control coating used on the Radio-

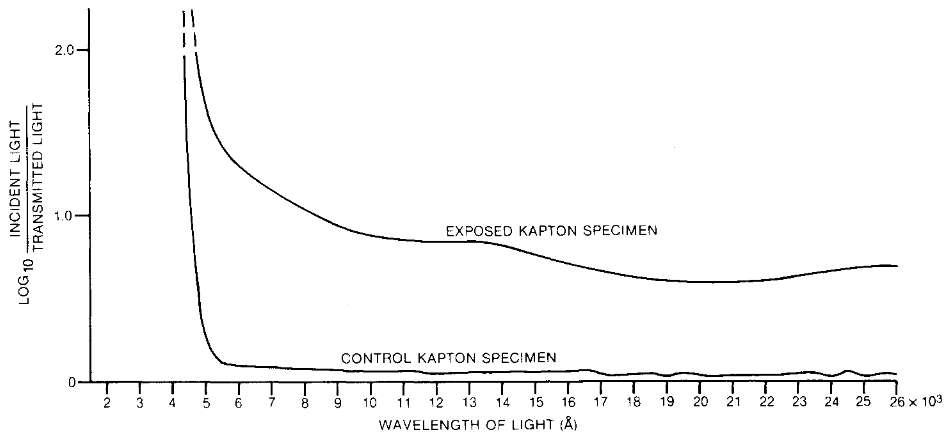

Fig. 14 Transmission of Kapton (circa 1984).

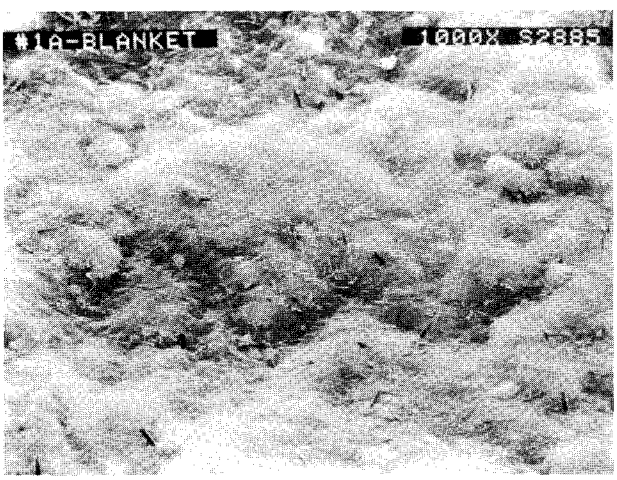

Fig. 15 Control sputtered ITO/polyester/Kapton.

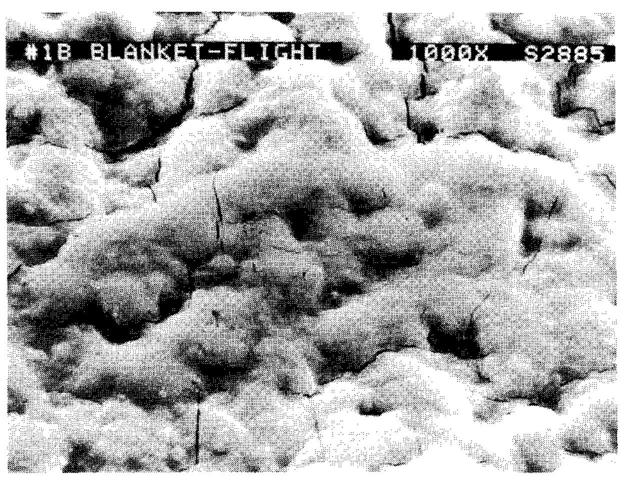

Fig. 16 Exposed sputtered ITO/polyester/Kapton.

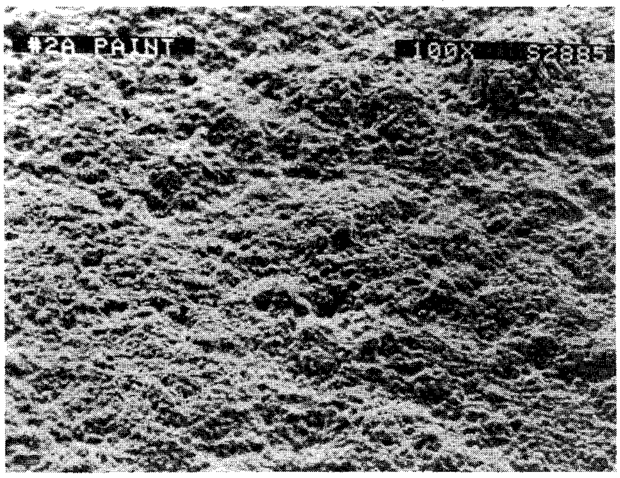

Fig. 17 Control Chemglaze Z004/9832 paint.

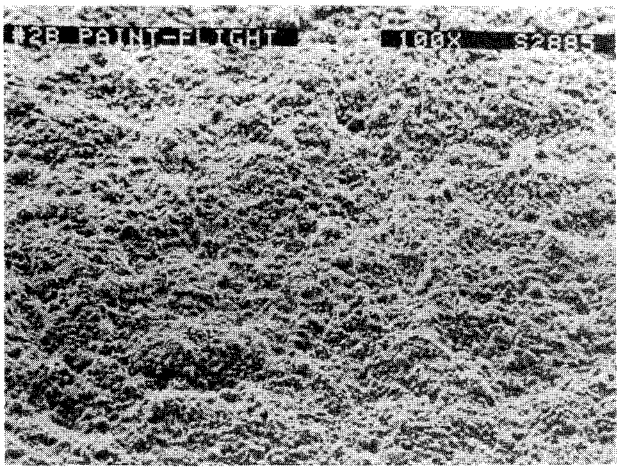

Fig. 18 Exposed Chemglaze Z004/9832 paint.

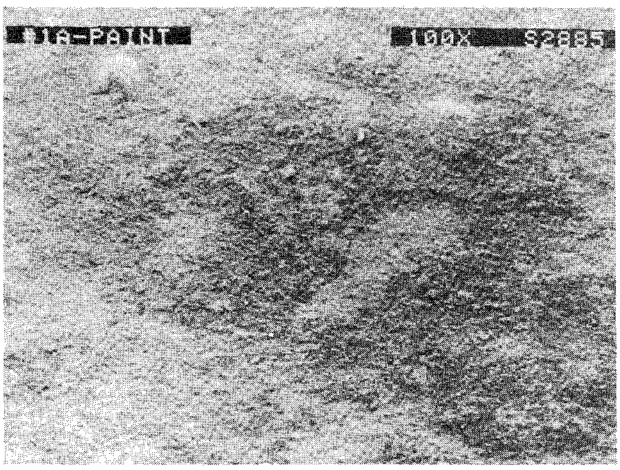

Fig. 19 Control Bostic 463-14 paint.

isotope Thermoelectric Generators. If these surfaces become more diffuse with time, the result would increase the operating temperature of these critical power sources where a margin of 10°C[7] had been established for the operating temperatures. Both the modified Bostic and Chemglaze coatings reacted as expected and pose no threat to the Galileo mission. Results of thermal properties analysis for the Galileo thermal control coatings before and after exposure are shown in Table 1.

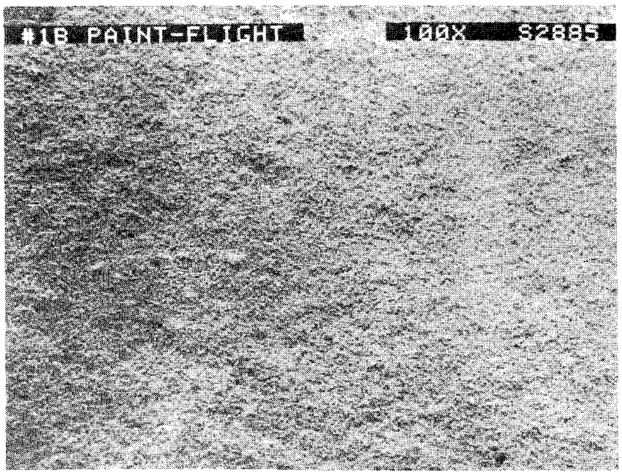

Fig. 20 Exposed Bostic 463-14 paint.

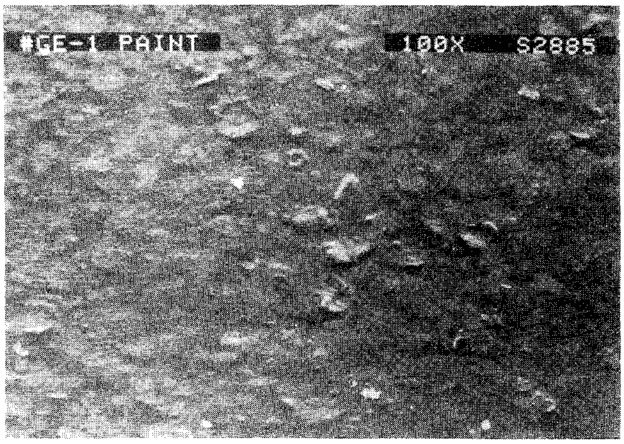

Fig. 21 Control GE-PD-224 paint.

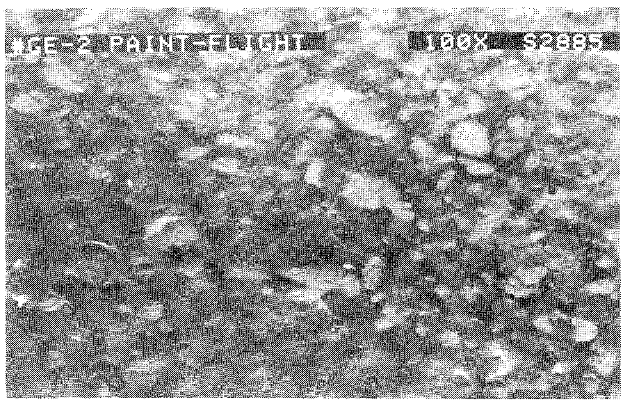

Fig. 22 Exposed GE-PD-224 paint.

Table 1 Galileo thermal control coating properties

	Solar absorptance, α_S		Thermal emittance, ϵ_T	
Material	Before	After	Before	After
ITO (S)[a]/Sheldahl black/Kapton	0.88	0.89	0.83	0.83
ITO (VD[b]) + Sheldahl black/Kapton	0.90	0.90	0.86	0.86
Bostic 463-14	0.93	0.94	0.86	0.86
Chemglaze Z004	0.94	0.95	0.87	0.87
GE-PD-224	0.94	0.94	0.88	0.88

[a]Sputtered. [b]Vacuum deposited.

Conclusions

The Advanced Composite Materials Exposure to Space Experiment (ACOMEX) flown on Shuttle mission STS-41G has provided a valuable data set of selected spacecraft polymeric material specimens. Unprotected exposed surfaces exhibit severe erosion and mass loss with the possibility of seriously degrading structural and thermal performance. However, the use of a thin fluorocarbon overcoat (although not conclusive) showed promise of providing a protective barrier to the attack without altering the base properties of the material. This and other possible protective measures already described deserve additional evaluation to confirm their performance.

Acknowledgment

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