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SUMMARY

Kapton® polyimide oxidizes at significant rates (4.3×10^{-24} gram/incident oxygen atom) when exposed in low earth orbit to the ram atomic oxygen flux. Ion beam sputter deposited thin films of Al_2O_3 and SiO_2 as well as a codeposited mixture of predominantly SiO_2 with a small amount of polytetrafluoroethylene were evaluated and found to be effective in protecting Kapton® from oxidation in both laboratory plasma ashing tests as well as in space on board Shuttle flight STS-8. A protective film of ≥ 96 percent SiO_2 and ≤ 4 percent polytetrafluoroethylene was found to be very flexible compared to the pure metal-oxide coatings and resulted in mass loss rates that were 0.2 percent of that of the unprotected Kapton®. The optical properties of Kapton® for wavelengths investigated between 0.33 and 2.2 μm were not significantly altered by the presence of the coatings or changed by exposure of the coated Kapton® to the low earth orbital ram environment.

INTRODUCTION

Early Shuttle flights have demonstrated that materials such as polyimide (Kapton®), carbon coatings, and some paints undergo weight loss and changes in optical properties when exposed in low earth orbit.[1] The postulated mechanism for these material changes is oxidation by atomic oxygen atoms which energetically (~5 eV) impact into the exposed spacecraft surfaces because of the spacecrafts orbital ram velocity relative to the geostationary low-earth-orbital environment which is predominantly atomic oxygen at altitudes between 180 km (97 n mi) and 650 km (351 n mi).[2] Materials which form volatile oxides when exposed to ram atomic oxygen typically become mat in appearance due to microscopic surface fibrils or cone like structures which are a result of oxidation by the directed atomic oxygen flux.[3] The observed rates of oxidation of Kapton® and Mylar® are sufficiently high as to cause concern for their survival as solar cell blankets or thermal blankets when used in low earth orbital applications of any significant duration.[4] Thus considerable interest exists in identifying oxidation resistant substitute polymeric materials or protective coatings suitable to prevent oxidation on existing polymers such as Kapton® and Mylar®.

This paper presents an approach which utilizes thin films of predominantly metal oxide coatings as a means of preventing oxidation of polymers. Thus the protection of the polymer surface from oxidation is afforded by nonvolatile metal oxides which are already in their highest oxidation state. Because metal oxides such as SiO_2 and Al_2O_3 are brittle a molecularly mixed film of predominantly metal oxide with a little fluoropolymer was thought to be an attractive approach to gain both oxidation protection from the oxide component and perhaps added flexibility as a result of the polymeric constituent.

APPARATUS AND PROCEDURE

Coating Deposition and Selection

Two types of thin film coatings were investigated for oxidation protection for Kapton® polyimide. These were pure metal oxides and a molecular mixture of metal oxide and fluoropolymer. The thin films were deposited by ion beam sputter deposition after 2 minutes of ion beam sputter cleaning the Kapton® substrates as shown in figure 1. An 8 cm diameter ion source was used to produce a 1000 eV, 65 mA argon ion beam for sputter cleaning and deposition.[5] A ion beam current density of up to ~2.8 mA/cm^2 resulted in the vicinity of the sputter target and Kapton® substrates which were located approximately 20 cm downstream of the ion source. The ion source was operated with a hot wire neutralizer in a vacuum facility 4.5 m long by 1.5 m in diameter which maintained pressures of 3×10^{-5} torr during ion source operation. Smooth fused silica slides were also mounted with the Kapton® substrates to allow documentation of film thickness. Deposited film thickneses were measured by means of a surface profiling instrument (Alpha-Step Profiler®, Tencor Instruments) by tracing the surface with a stylus passing from a virgin portion of the fused silica surface (which was protected by means of a polyimide tape) to the deposited surface. Sputter targets were 15.24 cm diameter disks of SiO_2 or Al_2O_3 for deposition of single constituent metal oxide films, and SiO_2 with polytetrafluoroethylene (Teflon®) bars or tubes ranging from 19.1 to 0.44 mm wide stretched across the diameter of the SiO_2 target for the codeposited films.

Because solar array and thermal blankets of Kapton® may require such oxidation protective coatings, the flexibility of the coated blanket is a pertinent consideration. The deposited thin film coatings on 0.127 mm Kapton® were subjected to compressive and tensile stresses by wrapping the coated Kapton® (with the coated surface concave then convex) around various size mandrels ranging in radii from 10.16 to 0.008 cm. The coated surfaces were then microscopically examined for crazing and/or spalling.

The oxidation protection capability of various thickness and composition coatings were evaluated with an RF plasma asher (SPI Plasma Prep II®) to produce atomic oxygen bombardment of samples. Both coated and uncoated Kapton® samples were subjected to low pressure RF air discharge for approxi- mately 15 hours during which typically 18 percent of the unprotected Kapton's® 0.127 mm total thickness would be removed by oxidation. Samples were protected by glass slides such that only one surface (the coated surface for the protected samples) was exposed to the RF plasma. Samples were evaluated to compare weight loss after allowing sufficient time for reabsorption of moisture.

Thin film coating composition and thickness selected for space flight testing were based on the results of the flexibility tests and plasma asher tests.

Space Experiment

Circular 2.54 cm diameter 0.127 mm thick unprotected and three thin film protected Kapton® samples were mounted in aluminum trays which allowed space exposure of a 2.06 cm diameter central portion of each sample. The unprotected sample of Kapton® was a control for the coated samples as well as others not described in this paper and had an aluminum film deposited on its unexposed surface. The control sample aluminum film as well as the protective coatings were all deposited on the smoothest side of the Kapton® substrates. The samples as mounted in their flight tray are shown figure 2. This tray was located within the shuttle bay of STS-8 as shown in figure 3. This allowed normally incident ram atomic oxygen flux to impinge upon the samples.

Samples were docummented by optical microscopic photography, scanning electron microscopy (Amray® 1400), energy dispersive spectroscopy (Kevex® EDS system), mass change, optical reflectance, absorptance and transmittance (by means of a Gier-Dunckle® integrating sphere in conjunction with a tungsten strip lamp and monochrometer) to allow an evaluation of the characteristics and effectiveness of the thin film protective coatings.

RESULTS AND DISCUSSION

Coating Selection for Space Flight Test

Thin film coatings selected for space flight testing were 700Å of Al_2O_3, 650Å of SiO_2, and 650Å of $\geq$96 percent SiO_2 with $\leq$4 percent (by volume) polytetrafluoroethylene (PTFE). The codeposition target for the $\geq$96 percent SiO_2 $\leq$4 percent PTFE film utilized a 0.44 mm PTFE tube stretched across the SiO_2 target as the source of the $\leq$4 percent PTFE in the codeposited film. Film thickneses evaluated ranged from 400Å to 1000Å. The minimum radius of curvature that each selected coating could survive on 0.127 mm thick Kapton® without crazing or spalling was found to be 6.35 mm for 700Å of Al_2O_3, 3.18 mm for 650Å of SiO_2, and near zero for 650Å of $\geq$96 percent SiO_2 $\leq$4 percent PTFE. The codeposited film showed no evidence of failure even with a 180° fold back of the Kapton® on itself. Codeposited films with a significant fractional fluoropolymer content such as 65 percent SiO_2 35 percent PTFE were found to be ineffective in protecting the Kapton in the plasma ashing tests.

Space Flight Test Results

The samples were exposed to the ram atomic oxygen environment of 222 km (120 n mi) during Shuttle Flight 8 in three separate exposure periods on September 3, 4, and 5, 1983 for a total of 41.17 hours. This was accomplished by orbiting the earth with the shuttle bay doors open to allow the sample trays to ram with normal incidence into the environmental atmosphere.

The unprotected Kapton® sample developed a mat surface (or increase in diffuse reflectance) as a result of the space exposure whereas no significant change beyond the experimental measurement error was found to occur in the Al_2O_3, SiO_2, or $\geq$96 percent SiO_2, $\leq$4 percent PTFE samples. Figure 4 an 5 compare the changes in optical properties of unprotected and $\geq$96 percent SiO_2, $\leq$4 percent PTFE protected Kapton®. The transmittance is not shown in figure 4 because its value is zero for the wavelength region shown due to the aluminum coating on the unexposed surface. The optical properties of reflectance, absorptance, and transmittance for Al_2O_3 and SiO_2 are not presented in this paper because they were indistinguishable from each other and the $\geq$96 percent SiO_2 $\leq$4 percent PTFE sample. From Figs. 4 and 5 one can conclude that the thin film coatings of Al_2O_3, SiO_2, and ≥ 96 percent SiO_2 ≤ 4 percent PTFE do not significantly (over the wavelength region of 0.33 - 2.2 μm) alter the optical properties of uncoated Kapton® and upon exposure to the low earth orbital environment also did not change as does the unprotected Kapton®.

Table I compares the mass losses of the protected and unprotected Kapton® samples that resulted from the exposure to the low earth orbital environment.

The unprotected Kapton® was found to lose an equivalent thickness of 2.6×10^{-4} mm/hr (1×10^{-5} in./hr) while being exposed to the ram atomic oxygen flux. This rate was found to be consistant with several other investigators also onboard STS-8. The rate of mass loss of the Al_2O_3 coated sample would indicate that six times the mass of the protective coating was removed. However energy dispersive spectroscopy substantiated the presence of the coating. Even though the mass loss of the Al_2O_3 protected Kapton® was only 11 percent of that of the unprotected, there is a significant probability that a missing Kapton shard (lost during sample mounting or removal) contributed to this mass loss. Thus the Al_2O_3 coatings actual performance is probably more similar to the SiO_2 coating which lost only 0.1 percent of the mass of unprotected Kapton®. One can also see that the more flexible ≥ 96 percent SiO_2 ≤ 4 percent PTFE coating was also very effective in protection of the polyimide with only 0.2 percent of the unprotected loss rate. Energy dispersive X-ray spectrometry (EDS) also confirmed the presence of both the SiO_2 and ≥ 96 percent SiO_2 ≤ 4 percent PTFE coatings. Scanning electron microscopy also gave strong support that the atomic oxygen which significantly textured the unprotected Kapton® did not alter any of the three coated Kapton® surfaces. Figure 5 compares scanning electron microscope photographs of the unprotected and ≥ 96 percent SiO_2 ≤ 4 percent PTFE protected Kapton® samples before and after space flight exposure. As can be seen significant surface texturing of the unprotected Kapton® occurs. The textured surface obviously is the predominant cause of the mat appearance of the post flight unprotected Kapton®. All of the three protective coatings yielded the same results upon scanning electron microscope inspection. That is, the thin film coatings showed now significant alteration in surface morphology upon deposition on the Kapton® or change as a result of exposure in low earth orbit.

CONCLUSIONS

Ion beam sputter deposited thin film of 700Å of Al_2O_3, 650Å of SiO_2, and ≥ 96 percent SiO_2 ≤ 4 percent PTFE were found to be effective in preventing oxidation of Kapton® exposed to ram atomic oxygen in low earth orbit. The codeposited film of ≥ 96 percent SiO_2 ≤ 4 percent PTFE was found to be more flexible than the either of the pure metal-oxide films. Kapton® coated with the codeposited film and exposed for 41.17 hr to the orbital ram environment at 222 km (120 n mi) resulted in mass loss rates of 0.2 percent of that of the unprotected Kapton®. The optical properties of reflectance, absorptance, and transmittance over the wavelengths of 0.33 to 2.2 μm were not significantly altered by the presence of the films, and furthermore, did not change upon exposure of the thin-film-coated Kapton® to the low earth orbital ram environment.

ACKNOWLEDGMENTS

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TABLE I. - MASS LOSS OF PROTECTED AND UNPROTECTED KAPTON® SAMPLES TO LOW EARTH ORBITAL ENVIRONMENT

Protective coating on Kapton®	Thickness of protective coating, Å	Mass loss, μg	Mass loss per incident oxygen atom*, g/atom
None (Unprotected)	0	5020 ± 9.9	4.3×10^{-24}
Al_2O_3	700	567 ± 5.2	4.8×10^{-25}
SiO_2	650	5.9 ± 5.2	5.0×10^{-27}
$\geq 96\%$ SiO_2 $\leq 4\%$ PTFE	650	10.3 ± 5.2	8.8×10^{-27}

*Based on an estimated atomic oxygen fluence of 3.5×10^{20} atoms/cm^2

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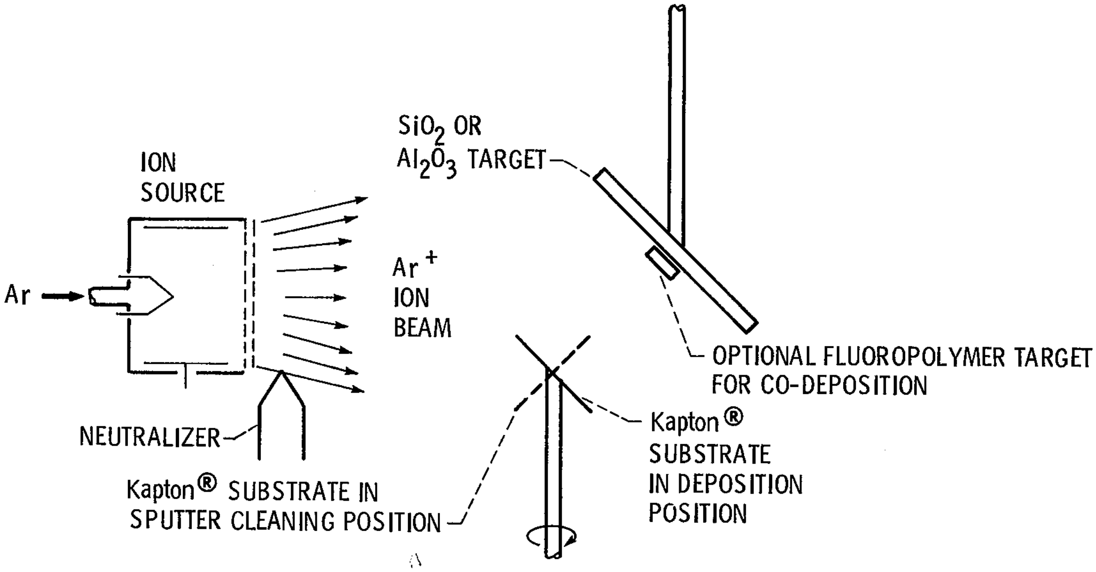


Figure 1. - Ion beam sputter cleaning and deposition configuration.

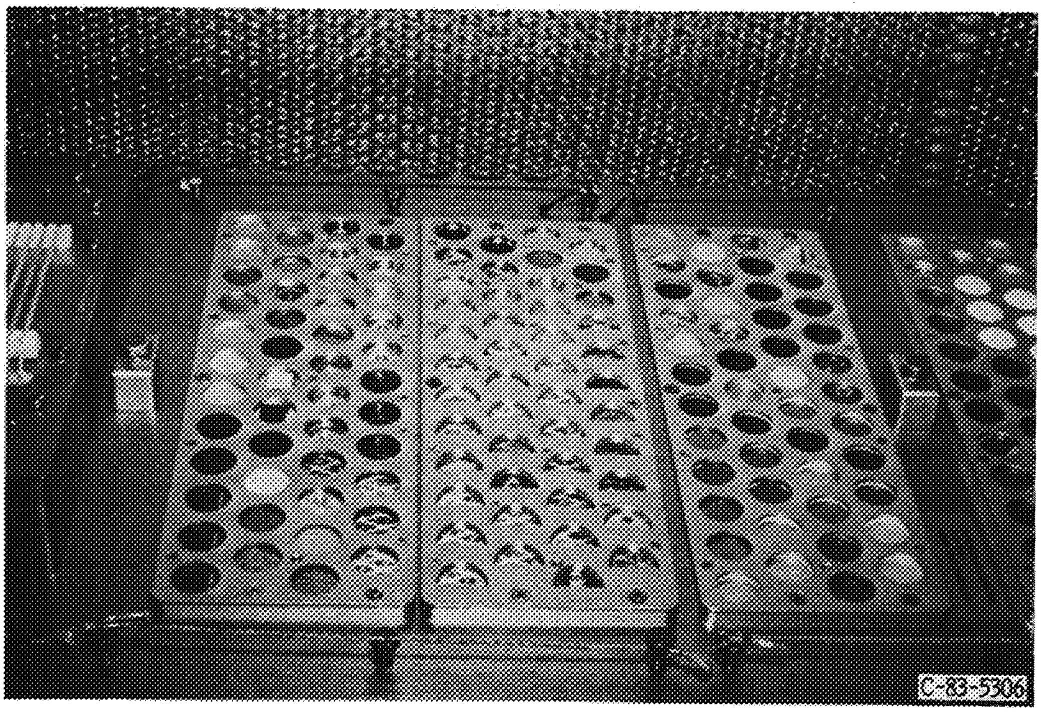


Figure 2. - Shuttle experiment sample tray.

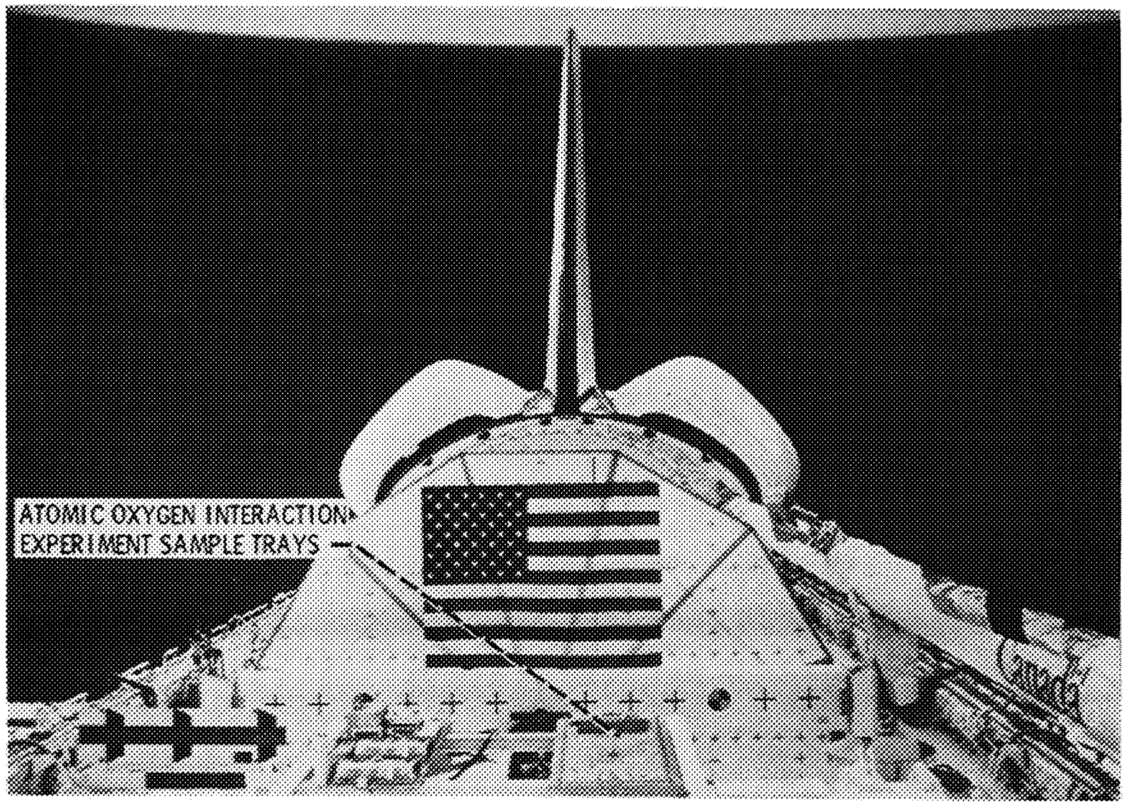
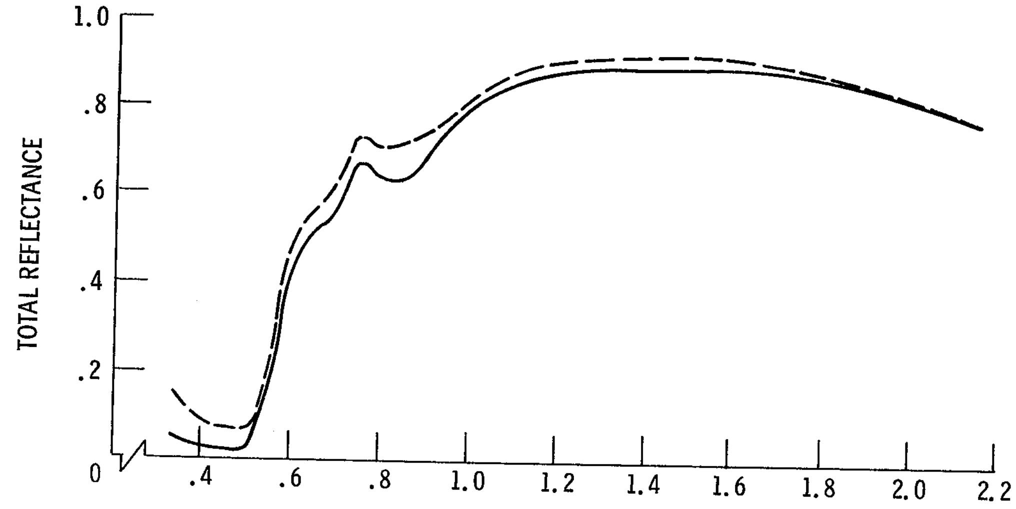
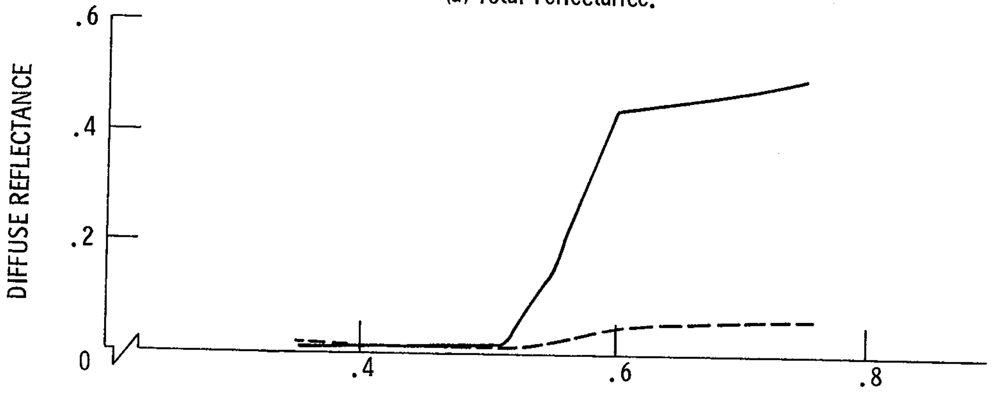


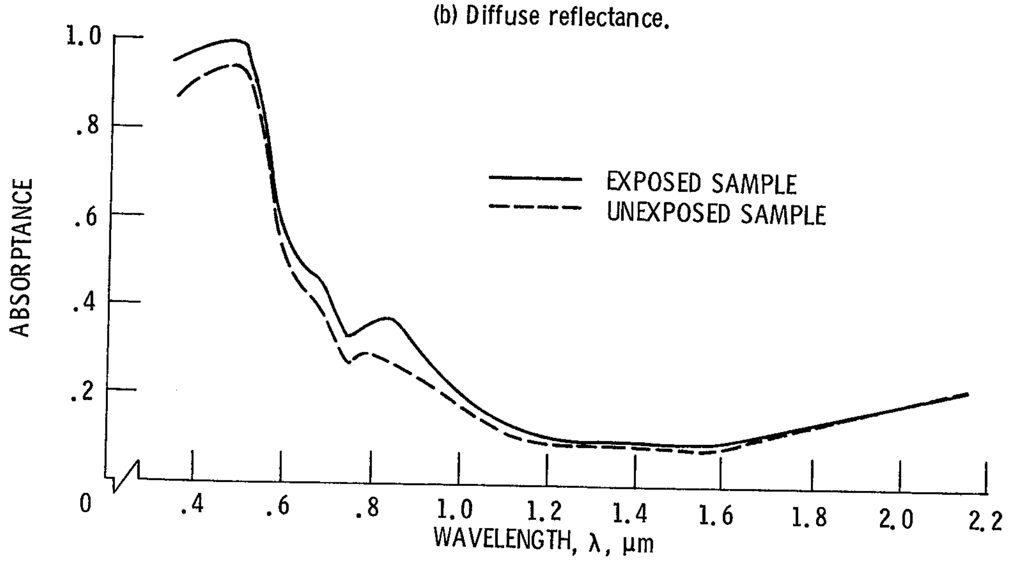
Figure 3. - Shuttle experiment in the bay of STS-8.



(a) Total reflectance.

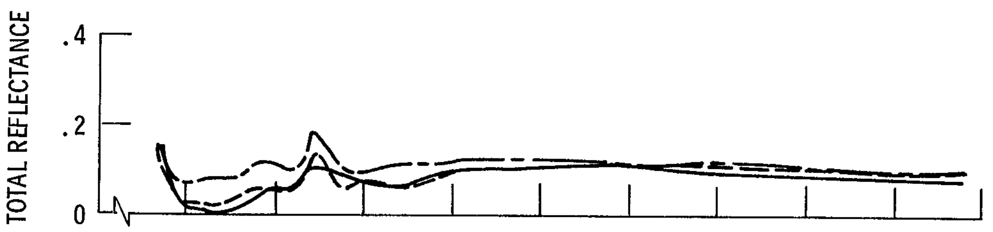


(b) Diffuse reflectance.



(c) Absorptance.

Figure 4. - Optical properties of unprotected Kapton® (0.127 mm thick with an aluminum film on the exposed surface) for samples unexposed and exposed to low earth orbital environment.



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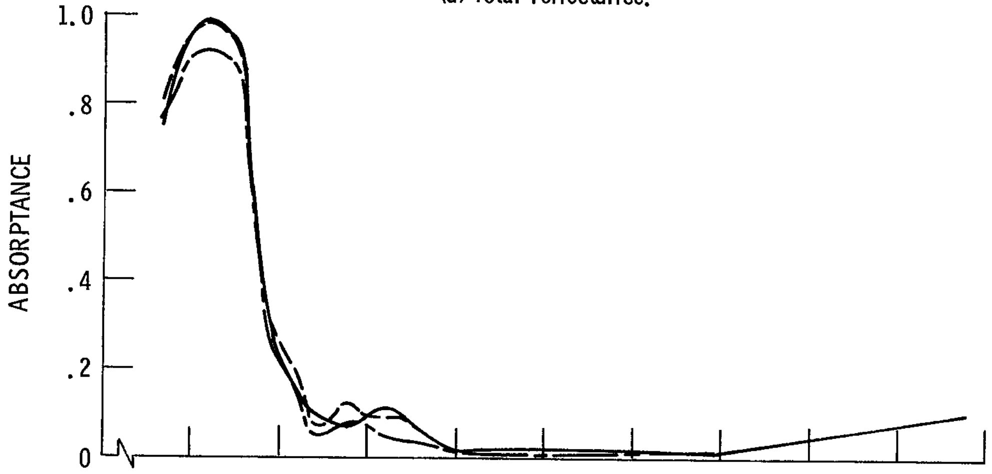
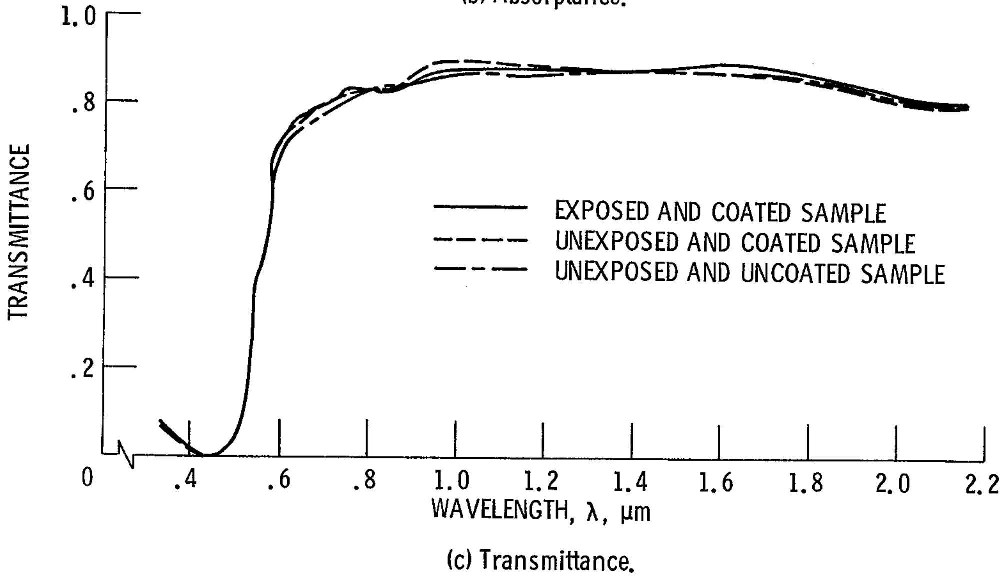
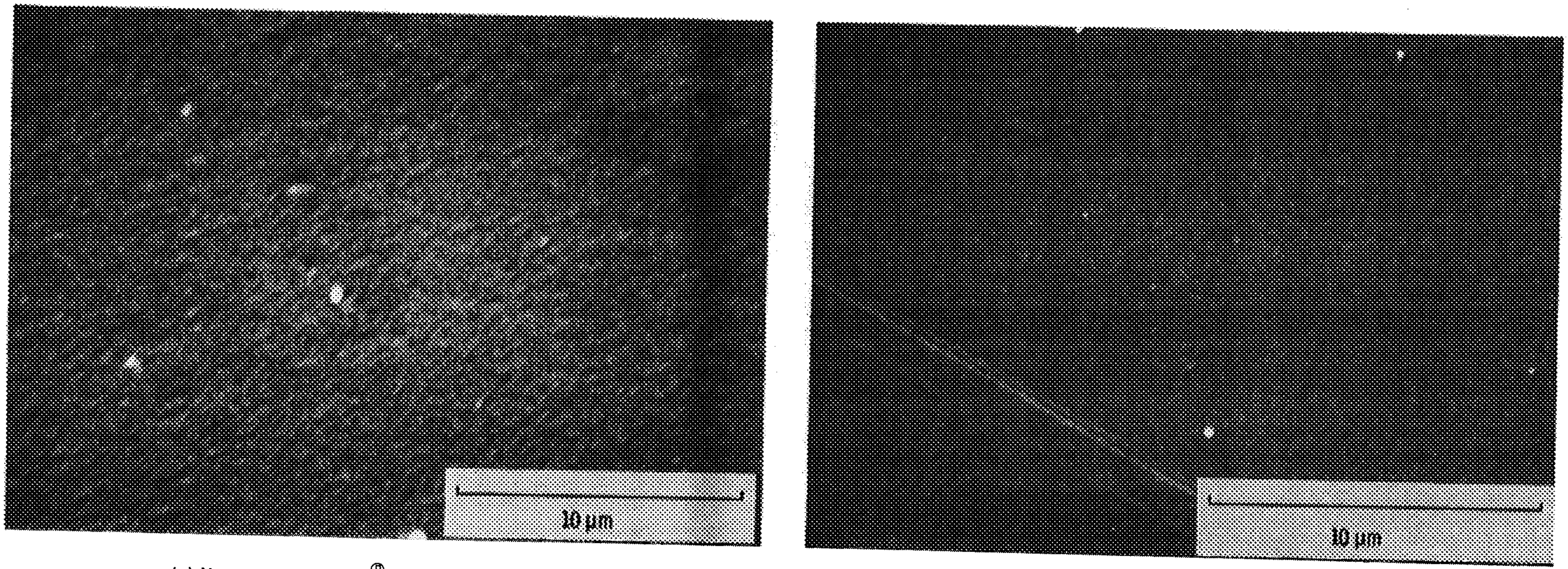


(b) Absorptance.



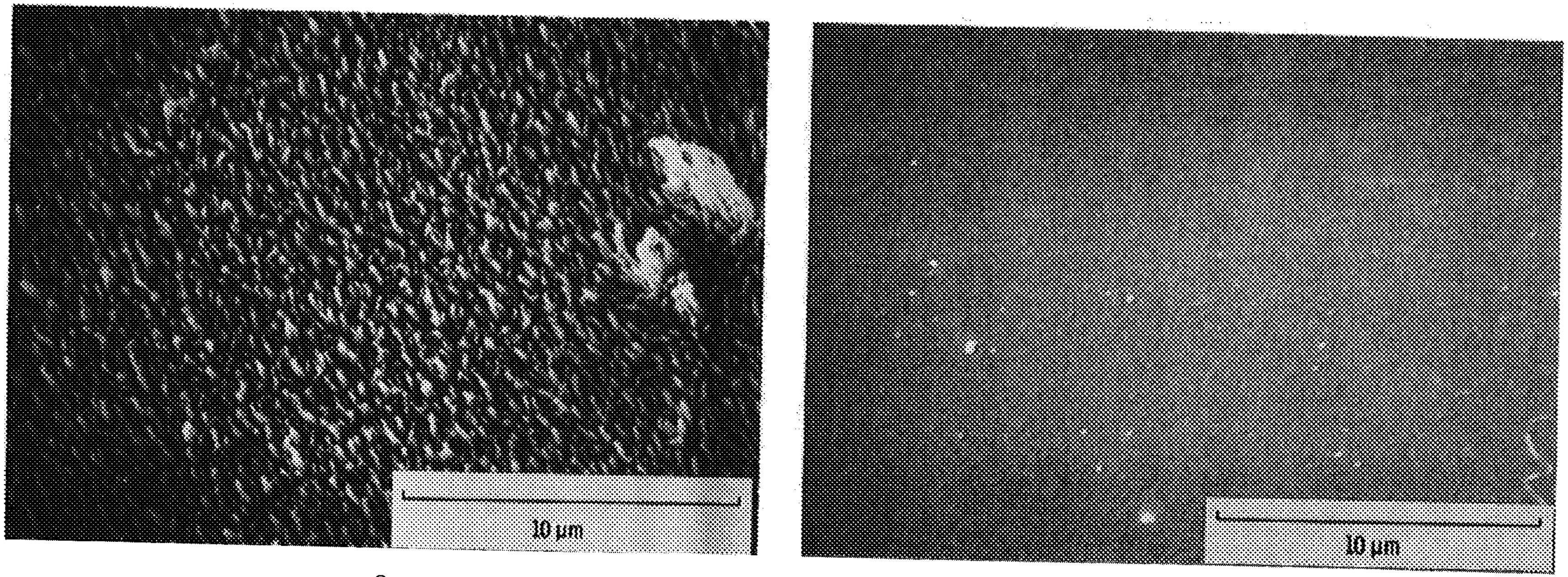
(c) Transmittance.

Figure 5. - Optical properties of ≥96% SiO_2 ≤4% PTFE coated Kapton® samples unexposed and exposed to low earth orbital environment compared with uncoated and unexposed Kapton®.



(a) Unprotected Kapton® before space exposure.

(c) $\geq 96\%$ $SiO_2 \leq 4\%$ PTFE coated Kapton® before space exposure.



(b) Unprotected Kapton® after space exposure.

(d) $\geq 96\%$ $SiO_2 \leq 4\%$ PTFE coated Kapton® after space exposure.

Figure 6. - Scanning electron microscope photographs of unprotected and $\geq 96\%$ $SiO_2 \leq 4\%$ PTFE coated Kapton® before and after space flight exposure.

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