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FURTHER INVESTIGATIONS OF EXPERIMENT A0034

ATOMIC OXYGEN STIMULATED OUTGASSING

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ABSTRACT

Thermal control coatings within the recessed compartments of LDEF Experiment A0034 experienced the maximum leading edge fluence of atomic oxygen with considerably less solar UV radiation exposure than top-surface mounted materials of other LDEF experiments on either the leading or the trailing edge. This combination of exposure within A0034 resulted in generally lower levels of darkening attributable to solar UV radiation than for similar materials on other LDEF experiments exposed to greater cumulative solar UV radiation levels. Changes in solar absorptance and infrared thermal emittance of the exposed coatings are thus unique to this exposure. Analytical results for other applications have been found for environmentally induced changes in fluorescence, surface morphology, light scattering, and the effects of coating outgassing products on adjacent mirrors and windows of the A0034 experiment. Some atmospheric bleaching of the thermal control coatings, in addition to that presumably experienced during re-entry and recovery operations, has been found since initial post-flight observations and measurements.

INTRODUCTION

This passive LDEF experiment, occupying one-sixth of Tray C9 on the leading edge and Tray C3 on the trailing edge, consisted of an aluminum framework housing 25 individual compartments sandwiched between a base plate and a top cover providing apertures for each individual compartment (Fig. 1). Most, but not all, of the 25 compartments in each flight unit contained a thermal control coating, sized larger in diameter than the opposing top cover aperture. Each compartment also contained a mirror mounted on an adjoining side wall intended to collect outgassed molecular species or particulates from the underlying coating. These mirrors were facing transverse to RAM-impinging AO on the leading edge and shielded from all but the most oblique incidence angles to solar radiation by the aperture covers. At least one compartment in each flight unit was left empty, except for the contaminant collector mirror, as a means of assessing contamination attributable to external sources. Each of the four corner compartments in each flight unit was sealed with aluminum covers to assess, as a control,

the outgassing of coatings stimulated by thermal vacuum exposure in the absence of UV radiation and atomic oxygen. Another level of experimental control was provided by sealing six other compartments in each flight unit with UV-grade quartz windows. The basic experimental control was provided by duplicating the leading edge flight unit on the trailing edge to assess outgassing in the absence of atomic oxygen.

The thermal control coatings exposed in this experiment are S13G, S13G/LO, A276, Z306, Z93, and zinc orthotitanate. S13G paint is a potassium silicate-treated zinc oxide in a methyl silicone binder. S13G/LO is a lower outgassing version of S13G. A276 is a glossy white titanium dioxide paint in a polyurethane binder. Z306 is similar to A276, with the addition of carbon for a glossy black color. Z93 paint is zinc oxide pigment in the original PS7 potassium silicate binder. Effects of LEO environmental exposure and subsequent changes in optical properties, including solar absorptance, infrared thermal emittance, and spectrofluorescence, are detailed in previous symposia proceedings (refs. 1-3).

Most of the contaminant collector mirrors in the flight units were quartz substrates coated with an opaque layer of aluminum protected by silicon monoxide. Four other mirrors in each flight unit consisted of thin film reflector coatings: silver, osmium, gold, and magnesium fluoride overcoated aluminum. These four mirrors in each flight unit were all mounted in compartments with open apertures. The silver and osmium mirrors were flown to provide a passive indicator of scattered atomic oxygen impingement in the compartments, while the gold and MgF_2/Al mirrors were intended to provide a means of assessing the role of mirror material in the degree of optical effects of contamination.

ENVIRONMENTAL EXPOSURE

During the 5.8 year flight, the A0034 trays were exposed to the LEO environment of atomic oxygen, ultraviolet radiation, particulate radiation, thermal cycling, hard vacuum, and micrometeoroid/space debris impacts. Atomic oxygen exposure is estimated to have been 8.99×10^{21} atoms/cm^2 and 1.32×10^{17} atoms/cm^2 (ref. 4) for leading and trailing edge trays, respectively. UV radiation exposure was limited, as discussed previously, by the tray cover apertures to approximately 2000 equivalent sun hours. Particulate radiation exposure was approximately 3.0×10^5 rads. Both trays experienced over 33,000 thermal cycles during the mission and a vacuum estimated between 10^{-6} and 10^{-7} torr. Damage by micrometeoroids or space debris consisted primarily of impact craters in the aluminum tray covers.

ESCA ANALYSIS

ESCA analysis was performed on a number of the collector mirrors adjacent to thermal control coatings. Figure 2 demonstrates the difference in atomic concentrations of silicon, oxygen, and carbon for mirrors exposed to S13G paint under various exposure conditions. Depth profiling analyses have indicated that the original coating of silicon

monoxide has been oxidized for both flight exposed and control samples. Mirrors exposed to S13G outgassing on the leading edge have the least carbon on the surface as a result of reflected atomic oxygen from the underlying paint. The most striking observation is the level of carbon found on the trailing edge windowed sample. A similar (48% atomic concentration) level of carbon has been found for mirrors exposed to other paints on the trailing edge without a covering window sealing the compartments. This is presumed to be the result of outgassing.

Figure 3 compares collector mirrors adjacent to two of the thermal control coatings, S13G and zinc orthotitanate, to a collector mirror in an empty open compartment on the leading edge. Pre-flight, it was presumed that the atomic oxygen-stimulated outgassing from the S13G sample would result in high atomic concentration levels of carbon and oxygen as compared to the zinc orthotitanate and certainly higher than carbon and oxygen levels found in a compartment without an adjacent thermal control coating. Post-flight observations indicated that any contaminant deposition was likely etched off the collector mirrors by atomic oxygen, as the ESCA analysis revealed little evidence for contamination and lacked a trend in compositional analysis. The ESCA survey indicates that the small levels of carbon on the mirrors from leading edge open compartments are likely adventitious.

These results may be compared to previously reported ESCA data for Experiment A0034 (ref. 3). These mirrors and the compartment window covers are being re-investigated to include sputter etch depth profiling. The photoelectron binding energies and surface chemistries of all of the mirrors are being compiled for analysis and will be reported in a future paper.

LABORATORY INVESTIGATIONS

Small areas of these contaminated windows, foil wrapped to outline the desired exposure area, were exposed to thermal energy atomic oxygen in the laboratory to investigate atomic oxygen "cleaning" susceptibility. The relatively thick layers of photolyzed contaminant on windows from compartments with Chemglaze A276 or Z306 polyurethane based paints were readily removed by only minutes of exposure to an atomic oxygen flux of approximately 2×10^{16} atoms/cm^2/second . In contrast, the silicone-based contaminant films on windows exposed to outgassing from the S13G and S13G-LO RTV-based coatings were not "cleaned", even after hours of exposure, changing only in appearance by silicate formation at the surface and hardening. No visible effect was observed for exposure to this laboratory-generated atomic oxygen of the contaminant films on windows exposed to Z93 coatings.

Visible changes in appearance of most of the exposed thermal control coatings have been minimal since the time of initial post-flight characterization. Repeat measurements of diffuse reflectance indicate some bleaching, particularly for the solar UV-darkened A276 coating sample flown under a UV-grade quartz window, and for the Z306 coating samples exposed either under a window or open to leading edge environment. These results are averaged for all of the A0034 coatings in Table 1.

Some atmospheric bleaching of UV-darkened thermal control coatings exposed in vacuum has long been noted, particularly for the zinc-oxide pigmented paints (ref. 5), and the acceleration of this bleaching by subsequent near-ultraviolet irradiation has also been noted (ref. 6). Laboratory demonstrations have been performed to investigate this phenomenon for LDEF coatings darkened by flight exposure on A0034. Solar absorptance of a sample of S13G, flown in an open compartment on the trailing edge, increased from 0.18 to 0.26 during the 5.8 year exposure. Bleaching of quadrants of this sample were induced by laboratory exposure to UV radiation in air then in vacuum. The source of illumination was a commercial long wave (365 nm) Blak-Ray B100-A lamp. Alternate portions of the coating were shielded by tightly wrapped aluminum foil (fig. 4) during black light illumination. Bleaching in air was slightly more effective at lowering the solar absorptance ($\alpha = 0.236$) than bleaching in vacuum ($\alpha = 0.244$). The small difference between the air and vacuum bleaching indicates that the effect is not dominated by air/ozone interaction with the coating. The area with combined bleaching in air and vacuum had a solar absorptance measurement of 0.223.

The visual appearance of the coating quadrant exposed to the black light both in air and then vacuum was effectively indistinguishable from the flight control samples of S13G. These patterns of bleaching are most striking for visual observations under black-light illumination, showing the progressive restoration of the original fluorescent yellow emission. Spectrofluorescence measurements concur with the visual observations, as seen in figure 5. The decreased intensity of spectral bands of fluorescent emission in the A0034 zinc-oxide pigmented coatings (ref. 1) has been partially restored by the laboratory bleaching. These curves, for the protected (unexposed) areas of the coating, indicate that thermal heating during black light illumination is only a small factor in the bleaching.

Fluorescence effects of exposure for the A0034 thermal control coatings were investigated by comparative black-light observations and detailed spectral measurements using an SLM Aminco SPF-500C dual-monochromator spectrofluorometer. The effects of exposure to solar UV radiation and atomic oxygen in the LDEF flight thermal vacuum environment are revealed in material dependent patterns of stimulated, quenched, and wavelength shifted fluorescence (ref. 7). All of these effects have been shown, in laboratory testing, as a consequence of exposure to UV radiation of both near and vacuum-ultraviolet wavelengths and also indicated by similar analytical results of coatings exposed on both the leading and the trailing edge of LDEF. However, subsequent testing of similar coatings in the laboratory also indicate that exposure to atomic oxygen, in the absence of UV radiation, can decrease ("quench") the intensity of spectral bands of emission, and that all of the effects of exposure on fluorescence for UV-irradiated coatings can be significantly modified in degree or nature by subsequent or coincident exposure to atomic oxygen. Additionally, comparison to flight exposures of similar materials on Shuttle experiments (refs. 7, 8) indicates that the fluorescence effects found in LDEF-exposed coatings are similar in nature, differing only in degree, for these relatively brief missions. Fluorescence, then, is a highly sensitive indicator, though not necessarily accurate gauge, of material interaction with the space environment.

Chemglaze A276 paint exposed on A0034 is a good example of altered fluorescence dependent on exposure. The control sample of A276 fluoresces bluish-purple. When the

polyurethane binder was eroded by the full, open exposure to LEO atomic oxygen, this fluorescence was totally quenched. When exposed under a quartz window, fluorescence was stimulated to a yellow/orange color (fig. 6). Laboratory exposure of A276 to near-UV stimulates the same fluorescence with as little as 100 equivalent sun hours irradiance.

CONCLUSIONS

In retrospect, several features of the experiment design and approach proved flawed for passive assessment of orbital atomic oxygen stimulated outgassing. The impingement of atomic oxygen on the contaminant collector mirrors on both the leading and trailing edge units is clearly shown by the oxidation and/or erosion of the silver and osmium mirrors and the associated evidence of "cleaning," revealed by ESCA analysis. This AO impingement altered to an unknown degree the basic comparative measure of deposits attributable to outgassing from the adjacent coatings. Outgassed species from the thermal control coatings formed contaminant films on the quartz windows, which were then photopolymerized by solar UV radiation, significantly degrading the transmission of the windows at UV wavelengths (200 to 400 nm). This outgassing, deposition, and solar UV-induced polymerization presumably occurred early in the LDEF mission, as would be expected, since the windowed thermal control coatings were considerably less degraded (darkened) than the companion type coatings exposed to the greater levels of solar UV radiation under open apertures.

This highly visible evidence of contamination on the inside of the optically degraded windows contrasts strikingly with the absence of visible contamination on the collector mirrors in the covered compartments. This indicates UV radiation-enhanced deposition and the intrinsically more severe optical degradation of photolyzed contaminant films. The ranking of leading edge coatings by type for outgassing (ref. 1), as determined from measurements of optical degradation of these windows, was completely reversed from the ranking of similar coatings and exposure on the trailing edge. The only obvious discriminators between contaminated windows over specific coatings on the leading and trailing edges are the greater levels of contamination and visible darkening on leading edge windows. Photomicroscopy and FTIR analysis revealed characteristic contaminant layer morphologies and chemical signatures that are different for each type of coating.

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Table 1.
Solar Absorptance Measurements of A0034 Thermal Control Coatings

Material	Flight Condition	α_s		
		Pre-Flight	Initial Post-Flight	Present Condition
S13G	Leading Open	0.17	0.17 - 0.18	0.22
	Leading Window	0.17	0.17 - 0.18	0.18
	Leading Covered	0.17	0.17	0.17
	Trailing Open	0.18	0.25 - 0.26	0.25
	Trailing Window	0.18	0.20	0.19
	Trailing Covered	0.18	0.18	0.18
S13G/LO	Leading Open	0.18	0.19	0.19
	Leading Window	0.18	0.19	0.19
	Leading Covered	0.18	0.18	0.18
	Trailing Open	0.17	0.27 - 0.28	0.26
	Trailing Window	0.17	0.21	0.20
	Trailing Covered	0.17	0.17	0.17
A276	Leading Open	0.23	0.20	0.22
	Leading Window	0.23	0.35	0.31
Z306	Leading Open	0.96	0.96	0.93
	Leading Window	0.96	0.95	0.93
Z93	Leading Open	0.16	0.17	0.17
	Leading Window	0.16	0.17	0.17
	Trailing Open	0.16	0.17	0.17
	Trailing Window	0.16	0.16	0.16
	Trailing Covered	0.16	0.16	0.16
Zinc Orthotitanate	Leading Open	0.16	0.16 - 0.17	0.17
	Trailing Open	0.16	0.18 - 0.19	0.18
	Trailing Window	0.16	0.19	0.18
	Trailing Covered	0.16	0.16	0.16

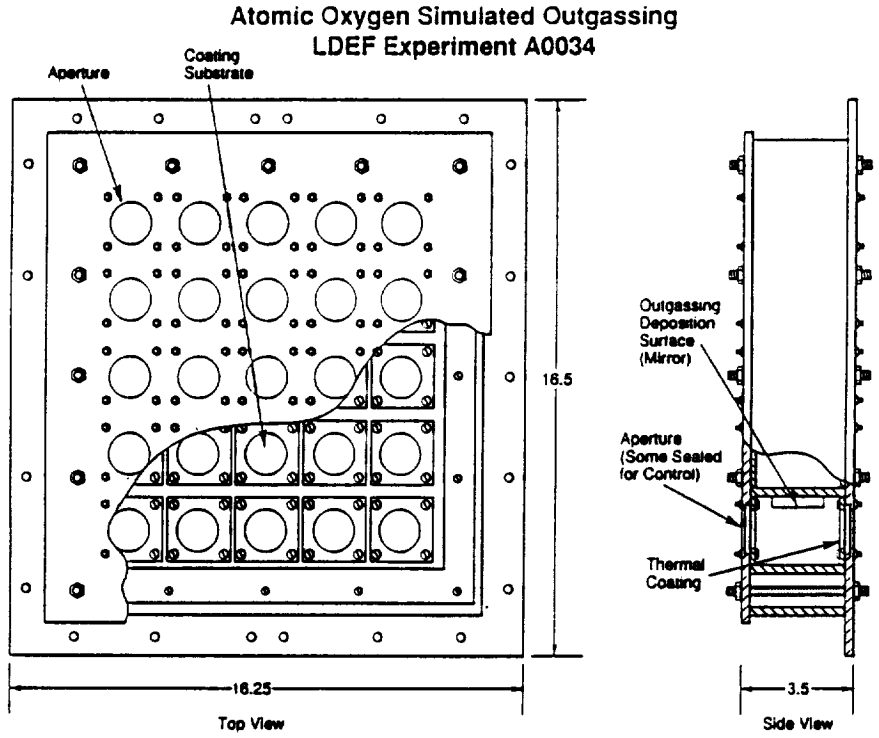

FIGURE 1. SCHEMATIC OF LDEF EXPERIMENT A0034

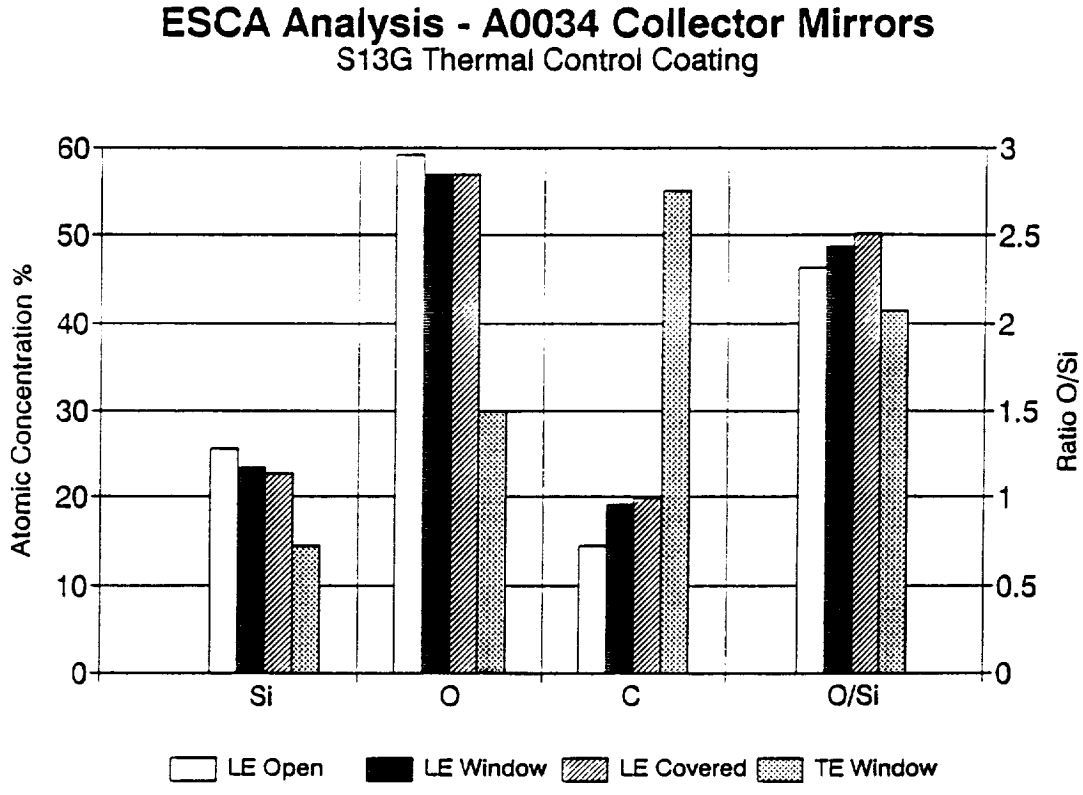

FIGURE 2. ESCA RESULTS OF COLLECTOR MIRRORS ADJACENT TO S13G UNDER VARIOUS FLIGHT EXPOSURE CONDITIONS

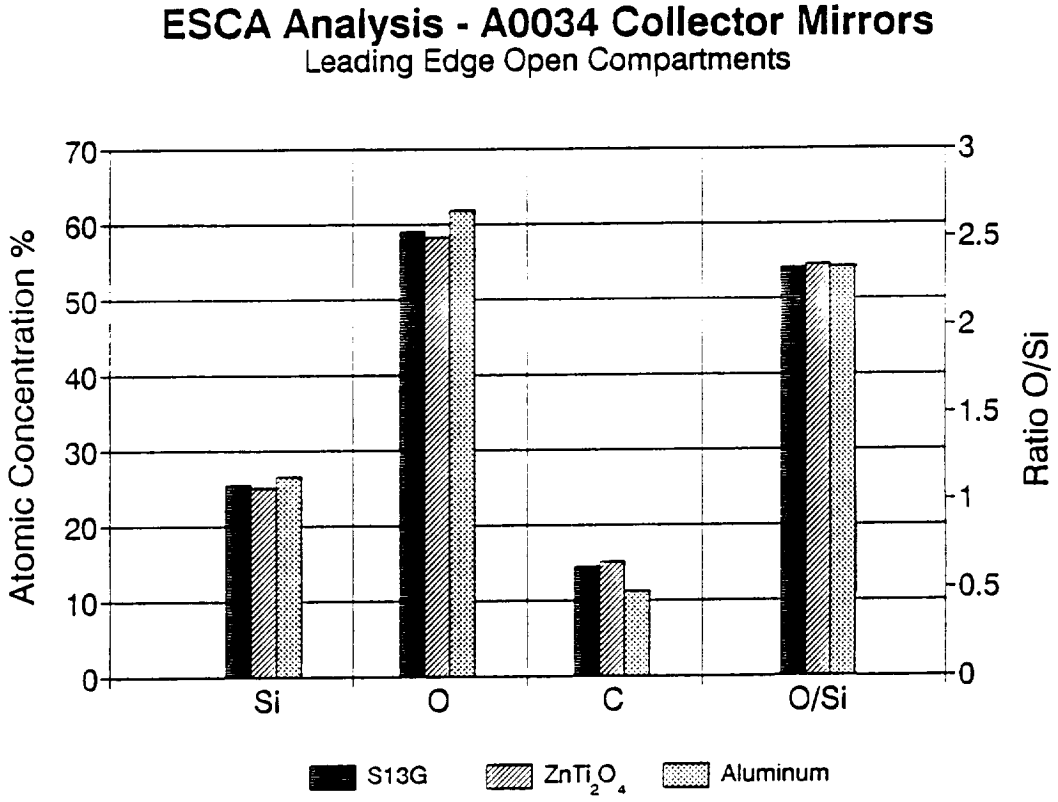

FIGURE 3. ESCA RESULTS OF COLLECTOR MIRRORS ADJACENT TO THERMAL CONTROL COATINGS IN OPEN COMPARTMENTS

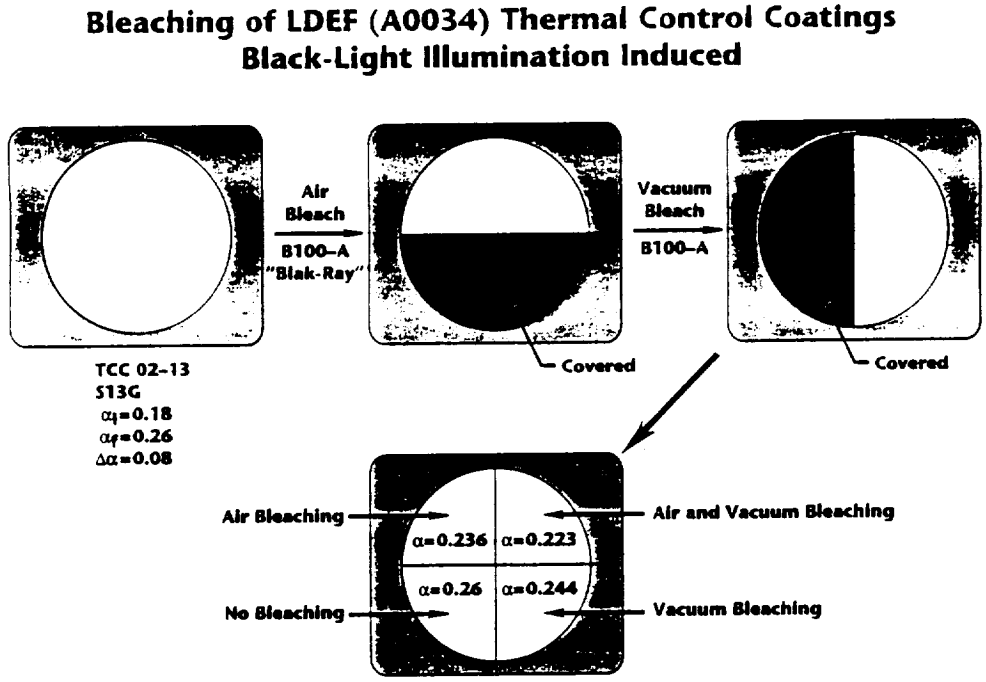

FIGURE 4. LABORATORY BLEACHING EXPOSURE

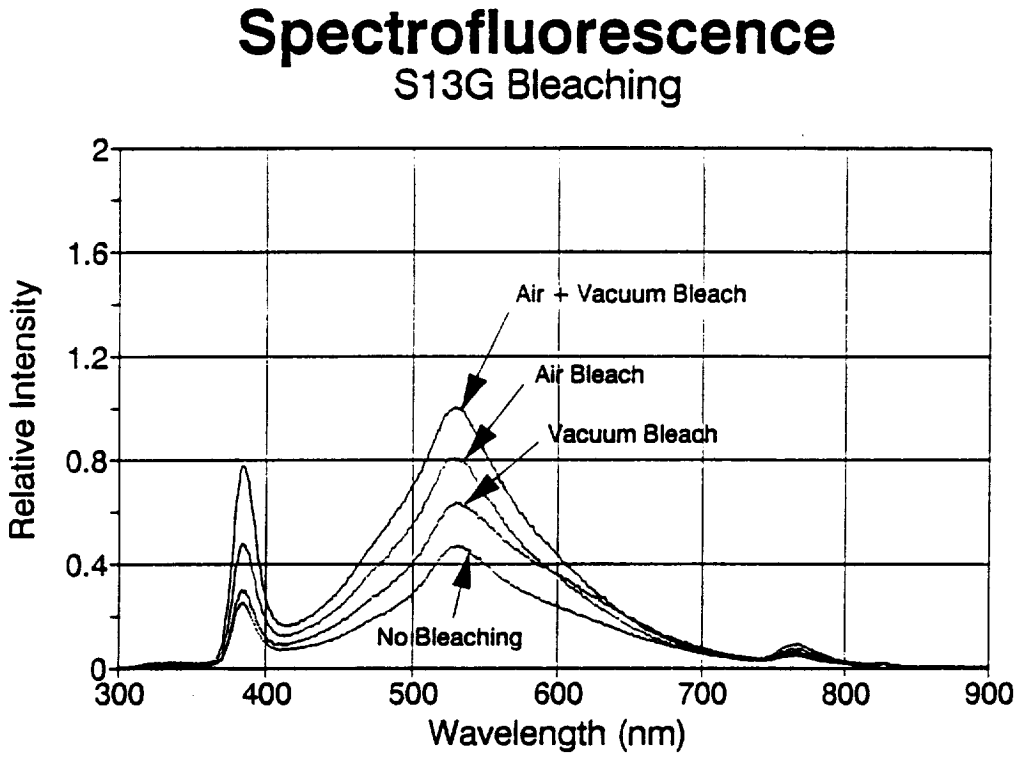

FIGURE 5. SPECTROFLUORESCENCE OF S13G FOLLOWING BLEACHING

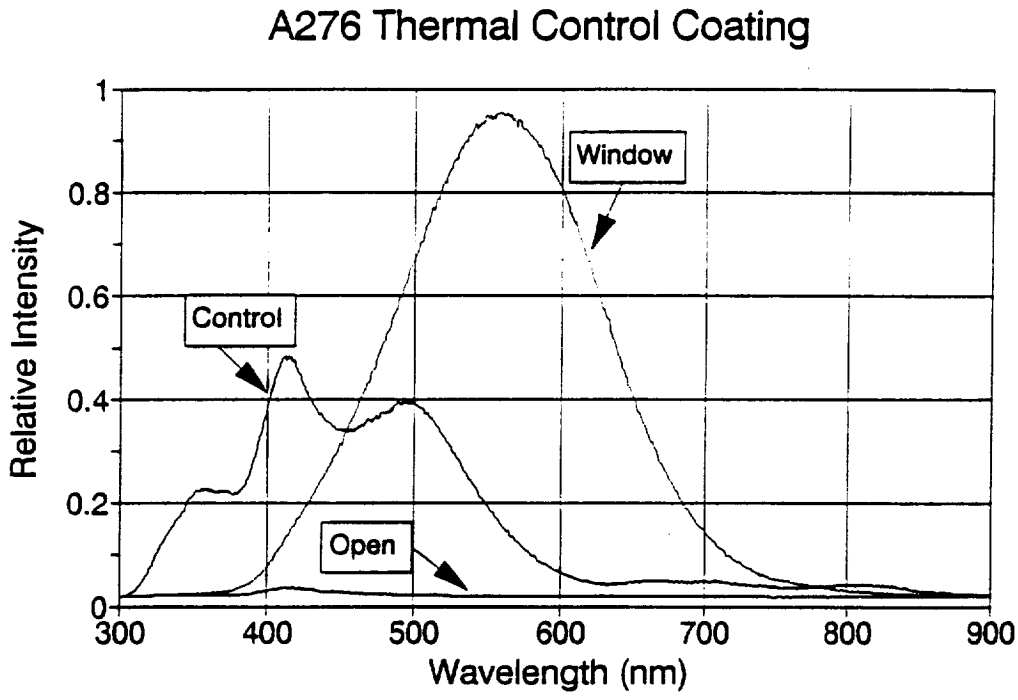

FIGURE 6. SPECTROFLUORESCENCE OF A0034 A276 THERMAL CONTROL COATINGS