SECOND LDEF POST-RETRIEVAL SYMPOSIUM

INTERIM RESULTS OF EXPERIMENT A0034

Roger C. Linton
Rachel R. Kamenetzky
NASA Marshall Space Flight Center
MSFC, AL 35812
Phone: 205/544-2526, Fax: 205/544-0212

INTRODUCTION

Thermal control coatings and contaminant collector mirrors were exposed on the leading and trailing edge modules of LDEF experiment A0034 to provide a basis of comparison for investigating the role of atomic oxygen in the stimulation of volatile outgassing products. The exposure of identical thermal coatings on both the leading and trailing edges of the LDEF and the additional modified exposure of identical coatings under glass windows and metallic covers in each of the flight modules provided multiple combinations of space environmental exposure to the coatings and the contaminant collector mirrors. Investigations have been made to evaluate the effects of the natural space and the induced environments on the thermal coatings and the collector mirrors to differentiate the sources of observed material degradation.

Two identical flight units were fabricated for the LDEF mission, each of which included twenty-five thermal control coatings mounted in isolated compartments, each with an adjacent contaminant collector mirror mounted on the wall. The covers of the flight units included apertures for each compartment, exposing the thermal coatings directly to the space environment. Six of these compartments were sealed with ultraviolet-grade transmitting quartz windows and four other compartments were sealed with aluminum covers. One module of this passive LDEF experiment, occupying one-sixth of a full tray, was mounted in Tray C9 (leading edge), while the other identical module was mounted in Tray C3 (trailing edge).

Each of the flight units of this experiment included multiple specimens of S13G, S13G-LO, Z93, and YB-71 (zinc orthotitanate) thermal control coatings. The leading edge (C9) flight unit contained, additionally, specimens of the polyurethane-based coatings A276 and Z306. Each flight unit also included some compartments with uncoated substrates (aluminum) substituting for a thermal coating as one more level of control for evaluating contamination effects. Each thermal control coating mounted in its individual compartment under an open aperture was directly exposed to the space environment, including atomic oxygen, while the adjacent collector mirrors on the side walls of the compartments were only indirectly exposed to the natural space environment by reflection or scattering from the thermal coatings or aluminum plates at the base of the

compartment.

The apertures proved significant in limiting the cumulative exposure of the specimens to solar ultraviolet radiation during the extended periods of the LDEF mission when the apertures shadowed the underlying coatings from oblique incidence solar radiation. Visible darkening, fluorescence changes, and changes in solar absorptance of sensitive thermal control coatings exposed under quartz windows on the leading edge unit and exposed directly or under quartz windows on the trailing edge unit indicate levels of incident solar radiation substantially less than that observed for similar coatings exposed without limiting apertures on other LDEF experiments. The apertures did not limit the incidence of atomic oxygen on the leading edge coatings, although the re-directed flux of oxygen atoms to the adjacent collector mirrors was dependent on the relative degree of accommodation associated with the various thermal coating materials.

Post-Flight Observations

Post-flight visual observations of the thermal control coatings indicated that only three leading edge specimens were significantly changed in appearance as a result of the exposure. These included one of the S13G coatings exposed under an "open" aperture with anomalous (by contrast with neighboring S13G specimens) reddish hued darkening, a darkened A276 specimen exposed under a quartz window, and the darker, more diffusively reflecting Z306 specimen (compared to the one exposed under a quartz window) exposed through an "open" aperture. Trailing edge exposure produced contrasting darkening of all RTV resin-bonded S13G and S13G-LO specimens; the Z93 and YB-71 specimens from both the leading and trailing edges were only slightly changed in appearance. These visual observations were confirmed by measurements of diffuse spectral reflectance (Varian/Cary 2300) for determination of solar absorptance and measurements of infrared thermal emittance with a Gier-Dunkle DB-100 portable reflectometer. These measurements were summarized and discussed in a previous publication (references 1, 2). It is assumed that the relatively unchanged optical properties of the leading edge S13G and S13G-LO specimens are a result of atomic oxygen bleaching of the damage induced by solar radiation, recognizing the relatively lower levels of solar radiation incident on the coatings in compartments with restricted fields-of-view.

The extent of reaction and induced changes in the exposed coating materials have been investigated with combinations of optical and surface profiling measurements. For each of the coating specimens, the diffuse spectral reflectance, optical scattering (BRDF), and surface morphology profiling (TalySurf) have been used to compare the effects of leading and trailing edge exposure.

For the polyurethane-based Chemglaze Z306 coatings exposed on the leading edge, the results indicate increased coating roughness and, consequently, solar absorptance, as a result of material erosion induced by atomic oxygen. Two specimens of Chemglaze Z306 paint were included in the leading edge module. These included the specimen exposed to atomic oxygen through an open aperture (#01-44) and the other exposed under a sealed quartz window (#01-14). Visual observations of a "blacker", more diffuse appearance for the Z306 coating exposed through

an open aperture are confirmed by the measurements of spectral diffuse reflectance (Figure 1) and the comparative profiles of light scattering provided by the BRDF measurements (Figure 2). The more specular profile, through 70 degrees angle of incidence, of the BRDF associated with the Z306 specimen exposed under a window (#01-14) in Figure 2 is characteristic of freshly prepared and unexposed Chemglaze Z306 and contrasts strikingly with the Lambertian profile of the atomic oxygen-exposed specimen (#01-44). These optical indications of increased surface roughening in the specimen exposed to atomic oxygen have been quantified by stylus profiling with the TalySurf profilometer (Figure 3). The two TalySurf profiles in Figure 3 correspond to 20 mm length traces across the surface of the Z306 specimen exposed through an open aperture ("O") and the windowed specimen ("W"), quantifying the increased roughness of the specimen exposed to atomic oxygen (PRg(rms) = 2.36 (#01-44) compared to PRg(rms) = 1.64 (#01-14).

Preliminary results of BRDF and TalySurf profiling measurements on the zinc oxide (S13G, S13G-LO, Z93) and zinc orthotitanate (YB-71) white thermal control coatings indicate that the changes in surface roughness induced by the space exposure are subtle, if not indistinguishable. The overlapping curves of cosine corrected BRDF dependence, through 70 degrees angle of incidence, for Z93 specimens exposed through open apertures from both the leading (#01-24) and trailing (#02-22) edges (Figure 4) are typical of the measured dependencies for these four types of coatings. Comparing the cosine corrected BRDF dependency of an exposed Z93 coating specimen to that of a laboratory diffuse standard (Figure 5), the results show that the Z93 specimen is more Lambertian than the standard itself. TalySurf profiles of these Z93 specimens indicate, unlike the overlapping BRDF profiles, that there are significant and systematic differences in surface roughness of leading edge Z93 coatings compared to trailing edge coatings of Z93 (Figure 6). These differences, for Z93 specimens of all types of exposure from the leading and trailing edges, are summarized in Figure 7. The bar-chart format differentiating TalySurf Group A scans from Group B scans refers to the pattern of dual scans on each coating specimen, the second scan done in a direction normal to the first scan. Since the leading edge "Control" Z93 trace differed in magnitude as well as the "window" exposure specimen (#01-52) and the "open" exposure specimen (#01-24) from any of the trailing edge traces in magnitude, the systematic differences in traces from the opposing module specimens probably indicate batch processed differences. The pattern of TalySurf traces for another of the zinc oxide pigmented paints (S13G-LO) gives evidence of a similar pattern, though significantly reduced in magnitude of difference (Figure 8). The investigation of induced surface roughness of the flight thermal control coatings is continuing.

Fluorescence Observations

Fluorescent emission from the thermal control coatings was detected during inspection of the flight hardware and specimens with black-light illumination. Closer inspection revealed systematic patterns of stimulated and quenched fluorescence in the coatings as a result of the space exposure. The determining environmental factors are apparently atomic oxygen and solar ultraviolet radiation.

Changes in fluorescence as a result of the space exposure were strongly material dependent. The three species of white thermal control coatings formulated with zinc oxide as the pigment

(S13G, S13G-LO, and Z93) all exhibit an intrinsic yellow coloration under black-light illumination which was quenched or suppressed as a result of space exposure on both the leading and trailing edges of the LDEF. In contrast, specimens of the polyurethane-based paints A276 and Z306 provided evidence of both stimulated and quenched fluorescence behavior as a result of the space exposure. The YB-71 (zinc orthotitanate) coatings were not obviously affected under black-light illumination as a result of the space exposure.

These changes in fluorescence as a result of the space exposure were found to be influenced by the type and degree of exposure. Comparison of fluorescent coloration for specimens from the leading and trailing edges and for specimens exposed "open", under windows, or "closed" provides insight into the mechanisms of interaction and the relationships to degree of exposure. These observations show that the quenching of fluorescence in the zinc oxide pigmented coatings, as detected by changes in the yellow coloration under black-light illumination, is found in specimens from both the leading and trailing edges and, to a significantly lesser degree, from specimens exposed under quartz windows. The stimulated orange fluorescence in the A276 specimen exposed under a quartz window has apparently been extinguished in the specimens exposed under an open aperture. A small peripheral area of the A276 specimen exposed under an open aperture exhibits the stimulated orange glow observed in the specimen exposed under a quartz window; this peripheral area corresponds to that portion of the A276 specimen shielded from atomic oxygen on the leading edge by the aperture and the documented 8 degree offset in RAM angle of attack for atomic oxygen.

The general observations of black-light illuminated fluorescence and the changes induced by the LDEF exposure were previously discussed (reference 1). The results are being quantified by measurement with an SLM Model SPF-500C spectrofluorometer. These types of measurements, for the flight S13G coatings, are summarized in Figures 9 and 10 for the comparison of effects for leading and trailing edge exposure on coatings exposed under open, windowed, and closed apertures. The quenching (suppressing) of the observed yellow fluorescence is apparently duplicated in the other more narrow wavelength bands, particularly for the strong ultraviolet band centered at 360 nanometers. Solar ultraviolet radiation transmitted through the quartz windows induced the same pattern of quenching as exposure through open apertures, though diminished in effect in relation to the spectral transmittance of the (contaminated) windows. The role of solar uv radiation in quenching zinc oxide pigmented coating fluorescence is clear. Subsequent laboratory testing, however, has shown that the role of atomic oxygen in producing the same effect is, for some materials, similar in nature and degree of effect. Measurements of the fluorescent emission from a conductive white paint (NS43C) exposed to thermal energy atomic oxygen at MSFC and a beam of 5 eV neutral atomic oxygen at the Princeton Plasma Physics Laboratory (PPPL) indicate similar patterns of quenching (Figure 11). The principal difference in the fluorescence quenching of this coating (similar in composition to Z93) and that of the flight S13G coatings is the more pronounced quenching of the ultraviolet band. Similar testing with the polyurethane based coatings has shown that the threshold level of uv radiation required to stimulate fluorescence in these coatings is very low (< 100 ESH), that the visible (black-light illuminated) coloration is strongly dependent on duration of exposure, and that the coloration fades rapidly (but does not disappear) following air exposure. These investigations are continuing with the objective of determining the mechanisms of interaction.

The original experimental approach to determining the role of atomic oxygen in the stimulation of volatile outgassing products anticipated differences in the optical degradation of contaminant collector mirrors adjacent to thermal control coatings exposed on the leading edge compared to mirrors adjacent to identical coatings exposed on the trailing edge. Comparative measurements of spectral reflectance of these mirrors indicated that the larger changes in optical properties were associated with mirrors adjacent to thermal coatings on the leading edge exposed under open apertures to atomic oxygen (reference 1). These increased levels of optical degradation are one indication of increased (stimulated) outgassing induced by atomic oxygen exposure of associated coatings exposed under open apertures. However, an alternative source of mirror degradation is interaction with the natural space environment.

Most of the collector mirrors were silicon monoxide overcoated aluminum thin films on quartz substrates. Each module also included, in selected compartments, thin film mirrors of silver and osmium as indicators of atomic oxygen exposure and thin film mirrors of gold and magnesium fluoride overcoated aluminum as indicators of the effects of alternative materials for contaminant "sticking" probability. Post-flight inspection of these substitute collector mirrors indicated that a measurable and relatively significant flux of re-directed atomic oxygen was incident on the mirrors of the leading edge module and, to a lesser extent, the trailing edge module as well (Figure 12). This was inferred from the total oxidation and virtually complete removal of the leading edge silver and osmium films and the partial oxidation of the counterpart silver and osmium mirrors on the trailing edge (reference 1). A perceptible difference in the visible appearance of the gold mirrors from the leading and trailing edge modules was also noted. An estimated fluence of atomic oxygen to the collector mirrors (10^{20} max) was inferred from the reactivities of silver and osmium and the observed film thickness losses (ibid).

Atomic oxygen exposure of the collector mirrors could be expected to have two effects. Contaminants deposited on the mirrors as a result of underlying thermal control coating outgassing would be subject to chemical conversion and potential re-volatilization and removal. The silicon monoxide overcoating itself would be subject to oxidation and subsequent conversion of optical properties. Although few of the collector mirrors from either flight module were conclusively visibly contaminated, the changes in optical properties of several mirrors were substantial. It has been previously stated that the more substantial changes in mirror optical properties were associated with mirrors adjacent to thermal coatings exposed directly to atomic oxygen through open apertures. Indications that these effects are attributable to atomic oxygen interactions with the collector mirrors have been found with additional analysis of the mirrors using ESCA, ellipsometry, and TalySurf profiling techniques.

Mirror coating thickness measurements using a Gaertner Model L119 ellipsometer indicate a systematic change in thickness (or optical properties) for the silicon monoxide overcoated aluminum collector mirrors located adjacent to thermal control coatings exposed through open apertures on the leading edge (Figure 13). The ellipsometer measurements shown in Figure 13 are based on a thin film configuration assuming only light (632.8 nm.) interaction with an opaque aluminum substrate and a film of silicon monoxide. Attempts to include an assumed top layer of

contamination were unsuccessful in producing systematic results. The collector mirrors with the most substantial indicated thickness change were located adjacent to source coatings of widely different outgassing potential: Z93, A276, Z306, a blank aluminum substrate plate, and one of the "open" S13G coating samples.

Attempts to determine the chemical composition of contaminant films on the collector mirrors by Fourier Transform Infrared Reflectance (FTIR) analyses were unsuccessful. The quantity (thickness) of contamination was apparently less than the sensitivity of the technique. Some compositional information was obtained through the use of Electron Spectroscopy for Chemical Analysis (ESCA) on selected collector mirrors. Results obtained to date are summarized in Figure 14 for carbon, silicon, and oxygen atomic concentration compartment on the leading edge. These results indicate the presence of silicon dioxide at the surface for nearly all of the mirrors. The degree (depth) of conversion of silicon monoxide to silicon dioxide has not been determined. These ESCA results also indicate that the lowest carbon concentrations are associated with the collector mirrors found, by ellipsometry, to have the more substantial indicated thickness change, namely the ones exposed to Z93, A276, Z306, and the blank aluminum coating substrate through "open" apertures on the leading edge. If the atomic concentration of carbon on the surface of the collector mirrors is assumed to be one indicator of contamination, then the ESCA results indicate the possibility of atomic oxygen "cleaning" of some of the mirrors exposed to contamination in compartments with "open" apertures on the leading edge. These ESCA results also provide evidence that the collector mirrors that were found to have the greater change in spectral reflectance were also found to be relatively free of contamination (as indicated by carbon concentration). It is possible, then, that the changes in optical properties of these mirrors were induced by accelerated oxidation during the leading edge exposure.

Another indication of oxidation of the silicon monoxide collector mirrors was obtained using a TalySurf stylus profiling analyzer. These profiles of surface morphology were obtained by scanning with the stylus from the exposed center area of the mirrors to the unexposed outer rim where the mirrors were protected from exposure. The results of TalySurf scanning on a collector mirror exposed to a blank aluminum coating substrate in an "open" compartment on the leading edge are provided in Figure 15. This TalySurf profile of collector mirror CM 01-45 indicates a decrease in thickness of the silicon monoxide of approximately 200 Angstroms in the exposed center area compared to the protected outer rim. Since the oxidation of silicon monoxide would be expected to lead to silicon dioxide (increasing "x" in SiOx), and silicon dioxide is more dense, the compaction of SiO converted to SiO2 would be expected to lead to such a thickness decrease.

Interim Conclusions

Preliminary analysis of optical degradation for the contaminant collector mirrors of this experiment indicated a systematic pattern of change. Mirrors that were located adjacent to thermal control coatings exposed to atomic oxygen under open apertures on the leading edge were systematically more severely degraded at ultraviolet wavelengths than the other mirrors. This evidence of stimulated outgassing has been shown to be tenuous as a result of evidence of atomic oxygen effects as another possible source of change in mirror optical properties. More direct

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means of quantifying collector mirror oxidation as a result of natural environmental exposure, including ESCA/Auger depth profiling, are being investigated.

Thermal control coating stability to the space environment has been clearly differentiated by material and exposure in the compilation of coating optical properties. Despite obvious erosion in the Z306 black absorber coating exposed to atomic oxygen on the leading edge, the changes in solar absorptance and emittance are relatively small, indicating, as expected, a small improvement in light absorbing properties. The A276 white coating exposed to atomic oxygen was relatively unchanged in diffuse reflectance despite complete erosion by atomic oxygen of the polyurethane binder. Severe degradation of the A276 coating exposed under a severely contaminated window confirms the relatively minimal level of solar uv radiation required for darkening of this coating.

For the zinc oxide pigmented and zinc orthotitanate coatings, only the S13G and S13G-LO specimens exposed on the trailing edge were found to be visibly darkened (with one exception). BRDF measurements indicate that the intrinsic diffuseness of these coatings is not significantly affected by the exposure. Surface morphology profiling (TalySurf) of these coatings indicated differences in surface roughness that are presently not subject to systematic relation to exposure and, as indicated for Z93 coatings, may be more indicative of batch processing variations. The fluorescence observations and measurements clearly reveal interaction with the space environment for all of the exposed coatings. These investigations of the effects of exposure on the flight coatings, mirrors, and windows are continuing in conjunction with associated laboratory simulated exposure testing of similar materials.

Acknowledgement

References

1. Linton, R.C., Kamenetzky, R.R., Reynolds, J.M., and Burris, C.L., "LDEF Experiment A0034: Atomic Oxygen Stimulated Outgassing", NASA Conference Publication 3134, Part 2, June, 1991.

2. Linton, R.C., "Effects of Space Exposure on Thermal Control Coatings", AIAA 92-0795, Reno, Nevada, January 6-9, 1992.

Spectral Diffuse Reflectance of Z306

LDEF A0034
Z306
W Window Aperture
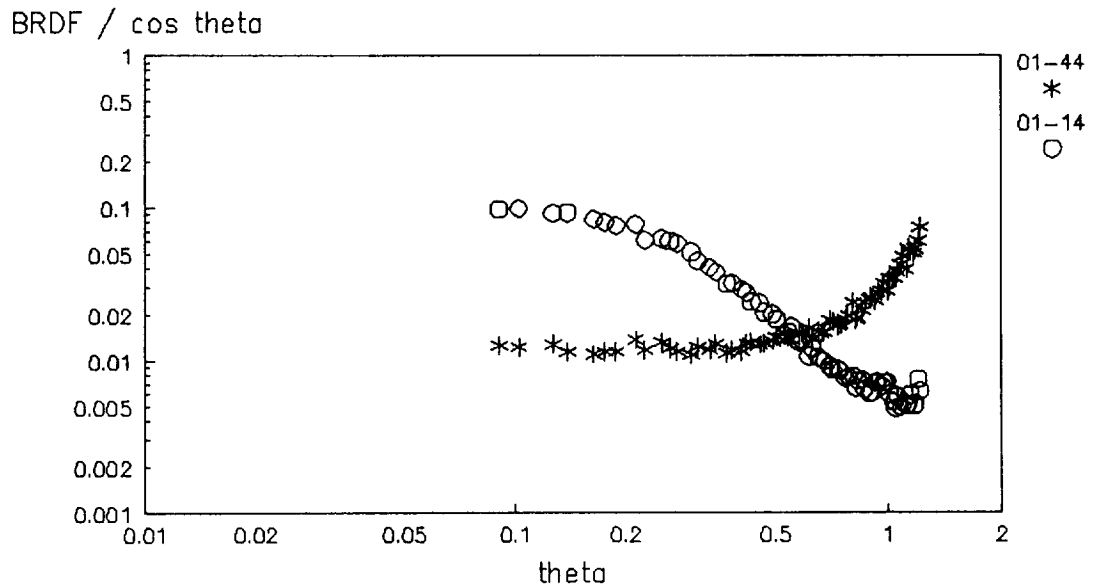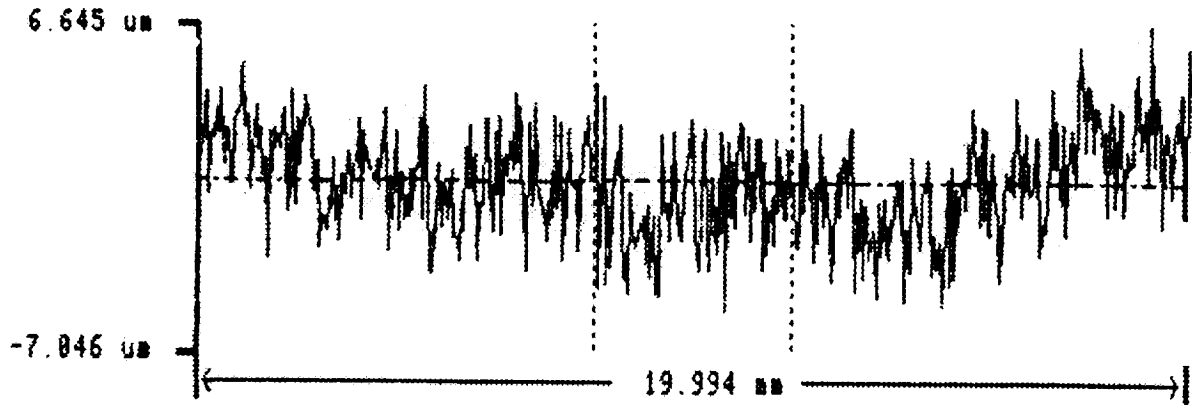O Open Aperture
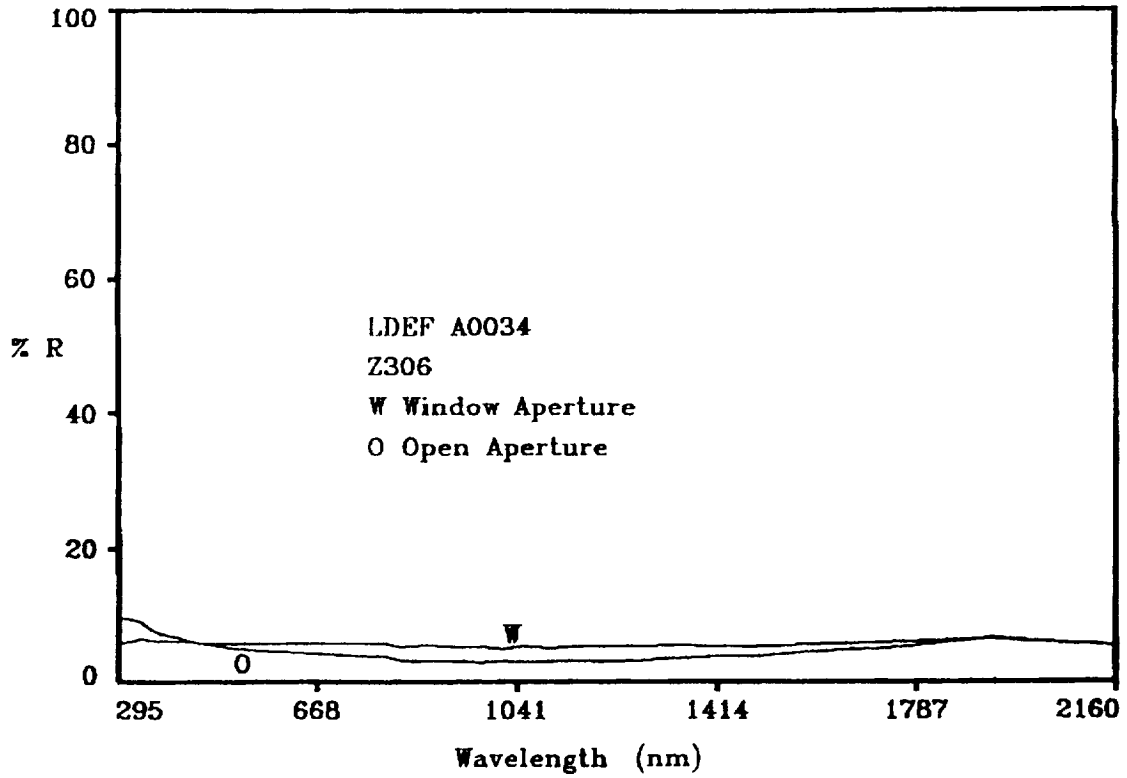
FIGURE 1

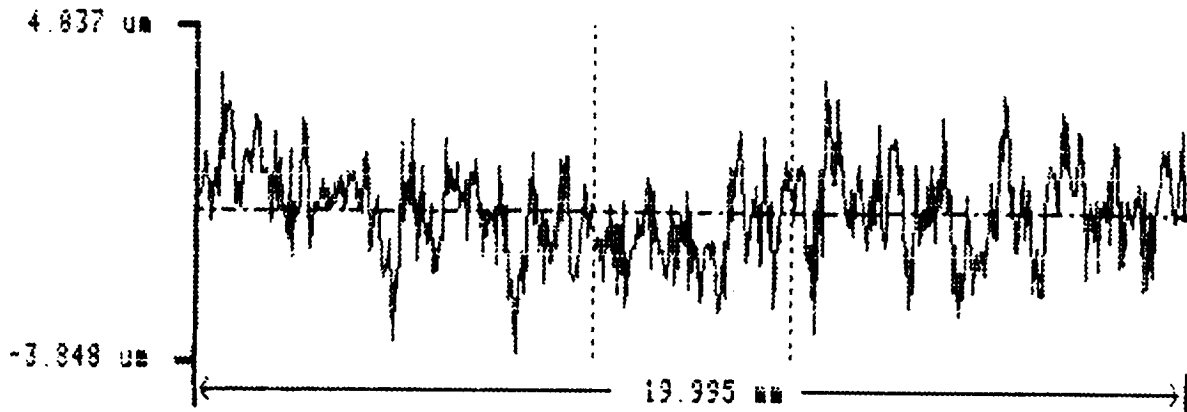## 01-44: Z306
01-14: Z306

FIGURE 2   BRDF OF Z306 COATINGS

6.645 um

-7.046 um

19.994 mm

Peak To Valley =   13.691 um

Z-306 (O) Leading Edge

4.837 um

-3.848 um

19.995 mm

Peak To Valley =   8.685 um

Z-306 (W) Leading Edge

Talysurf Profiles of Z-306 - Experiment A0034
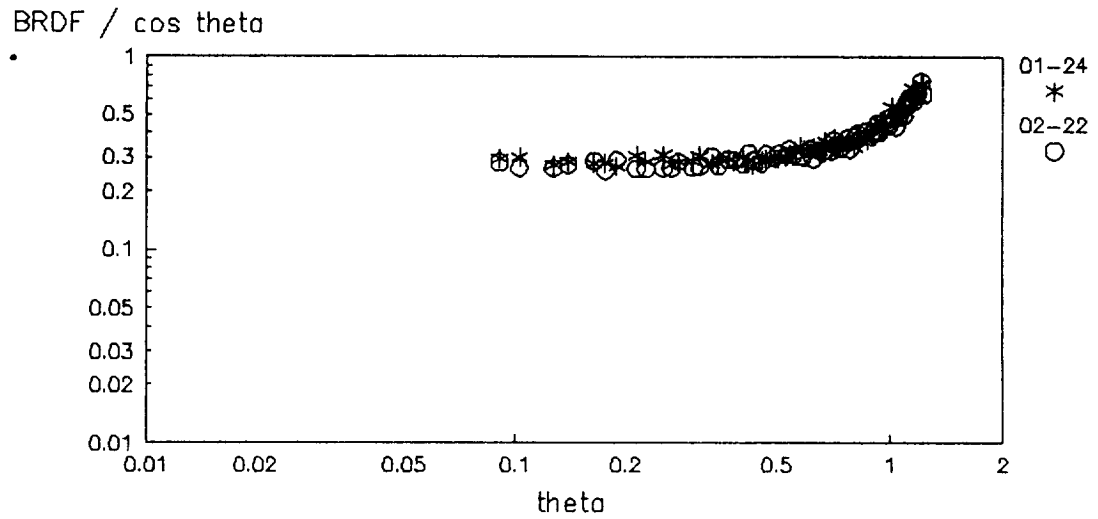
FIGURE 3

0 1-24: Z93

02-22: Z93

BRDF / cos theta

FIGURE 4   BRDF OF Z93 COATINGS FROM LEADING AND TRAILING EDGES

LDEF Sample 02-31: Z93
Lambertian Calibration

BRDF/cos theta
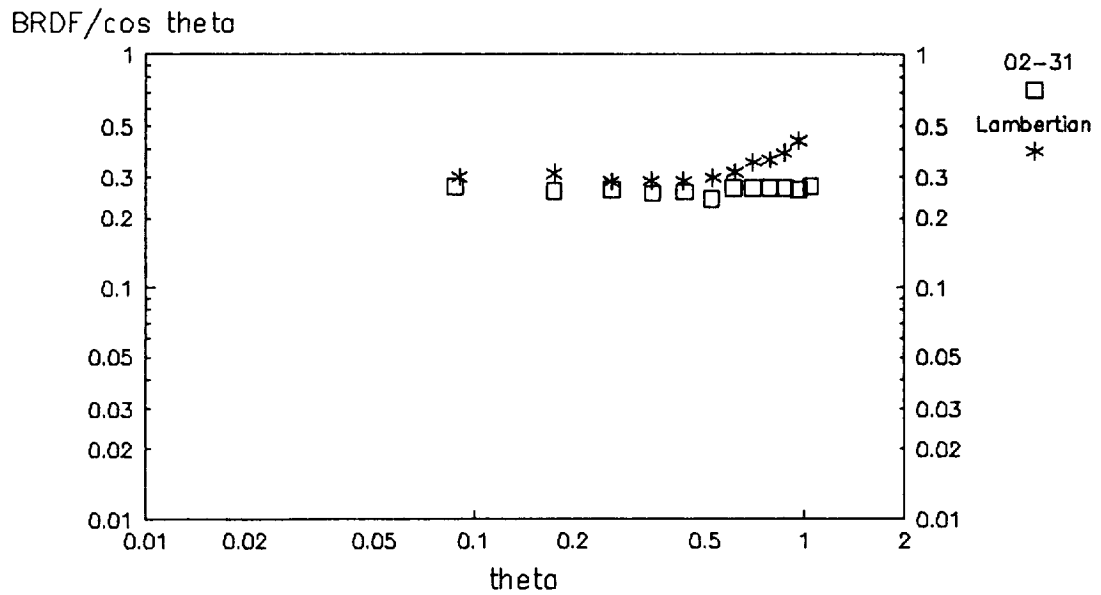
FIGURE 5   BRDF OF Z93 COATINGS AND LAMBERTIAN STANDARD

1160

40.538 um

-29.296 um

|←————————————— 19.987 mm —————————————→|
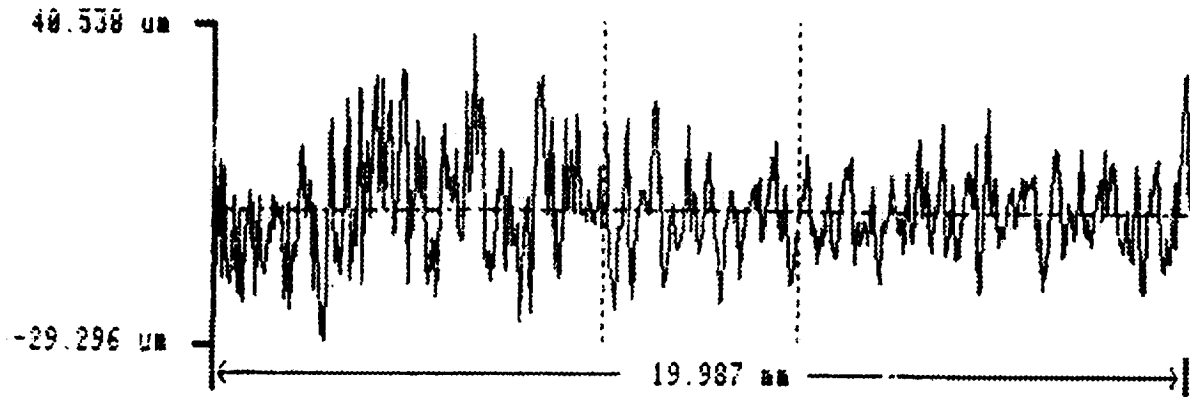
Peak To Valley = 69.834 um

Z-93 - Leading Edge

29.810 um

-13.276 um

|←————————————— 19.985 mm —————————————→|
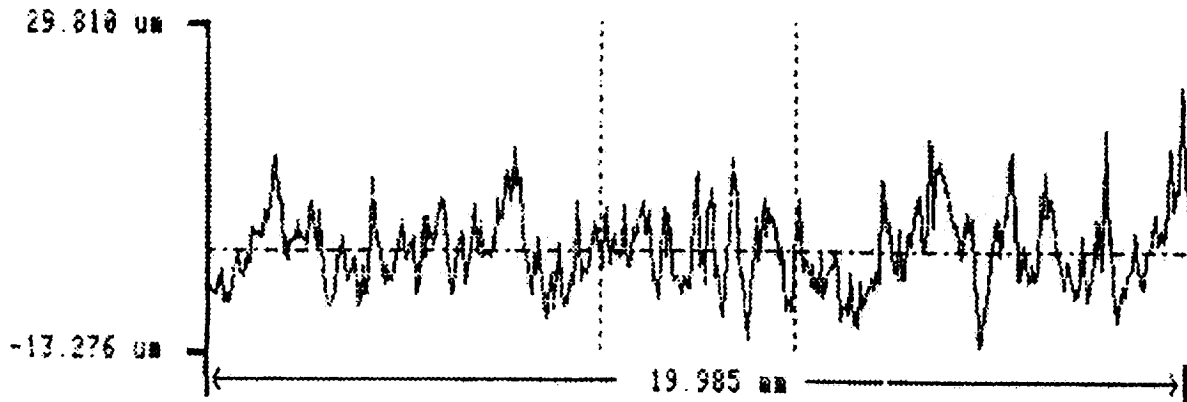
Peak To Valley = 43.085 um

Z-93 -Trailing Edge

Talysurf profiles of Z93 - Experiment A0034

FIGURE 6

Z-93 TALYSURF SUMMARY

PRg VALUES (microns)
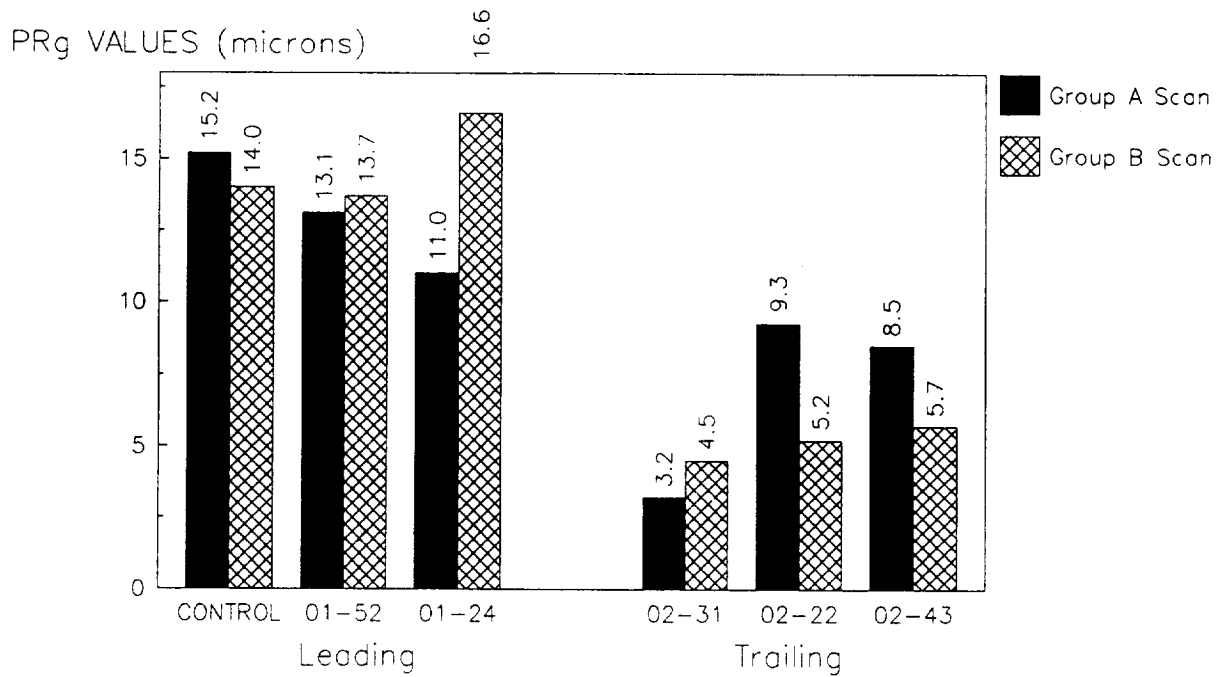
FIGURE 7

S-13G-LO TALYSURF SUMMARY

P.Rg VALUES (microns)
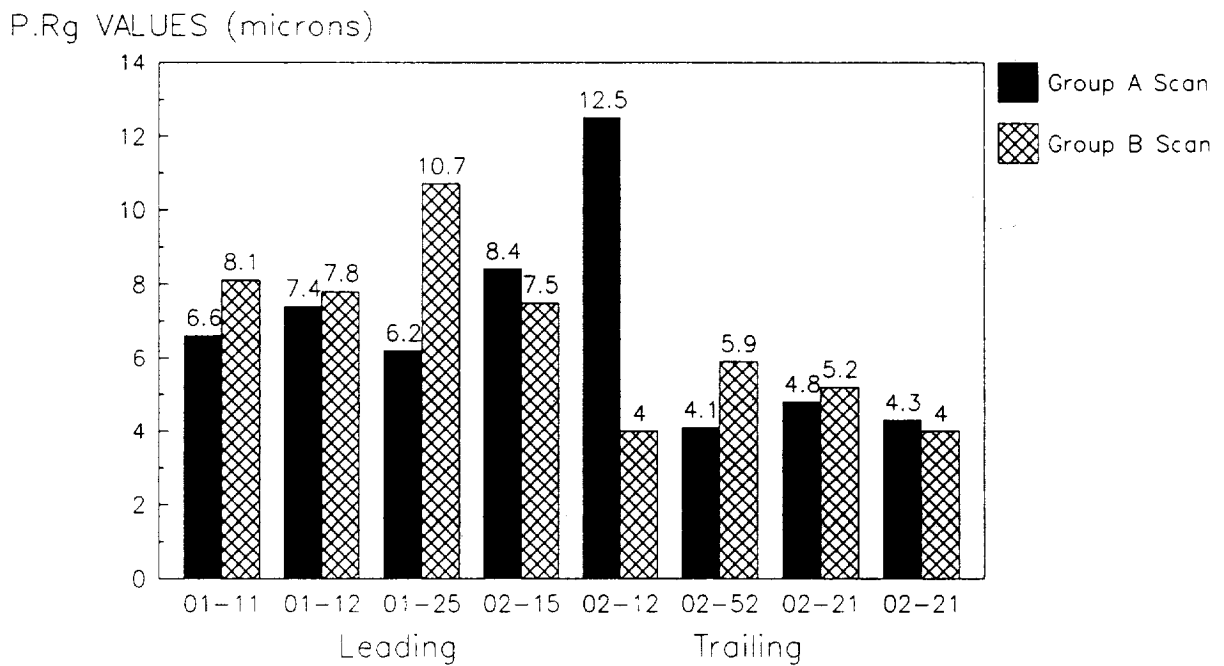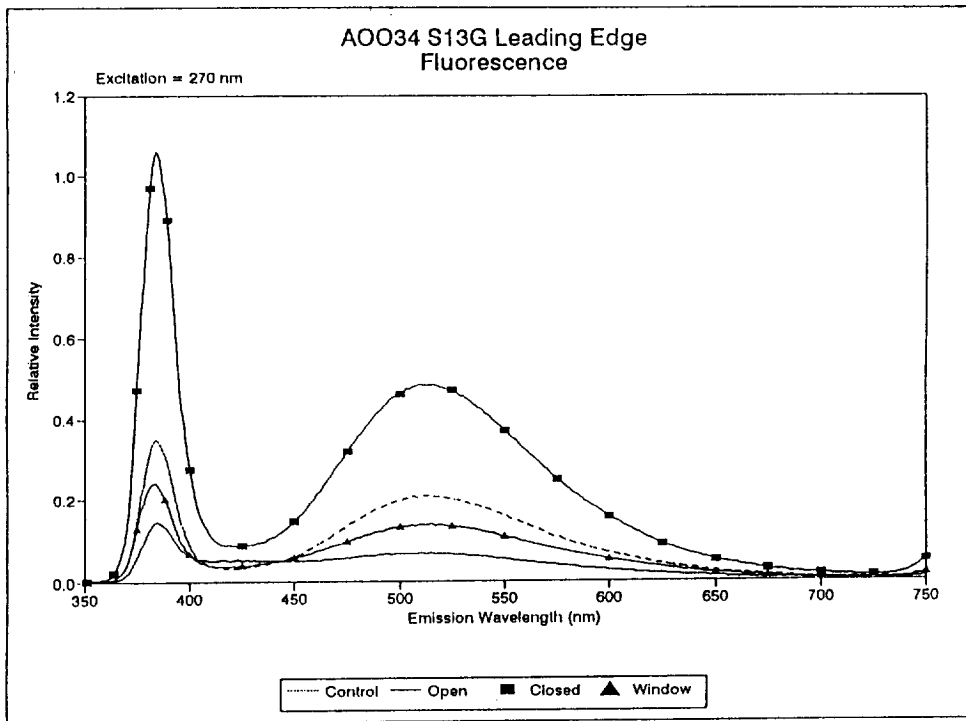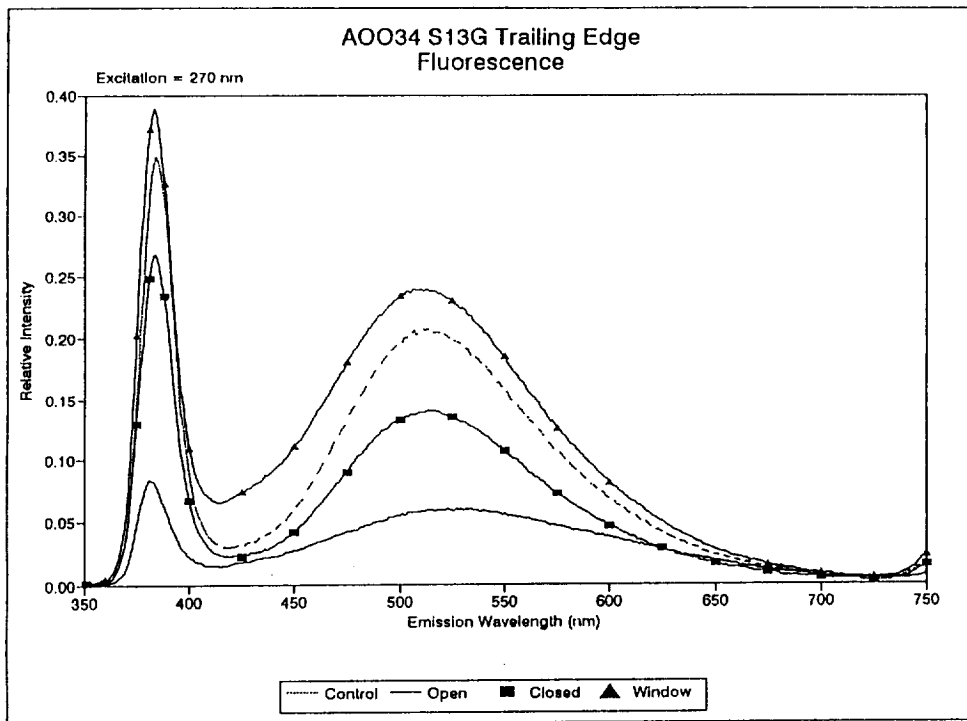
FIGURE 8

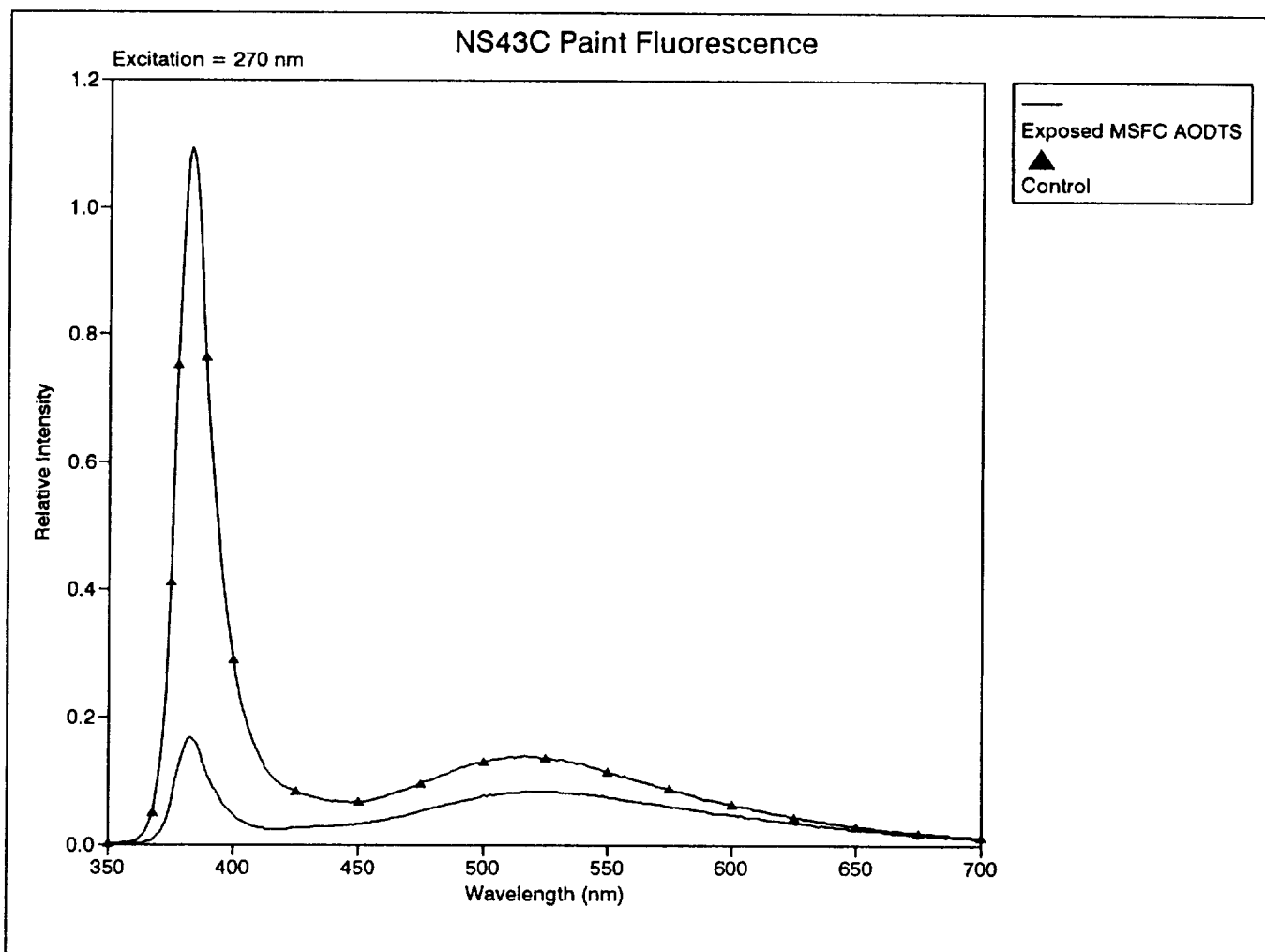**FIGURE 9**

FIGURE 10

FIGURE 11   FLUORESCENCE OF NS43C EXPOSED TO ATOMIC OXYGEN
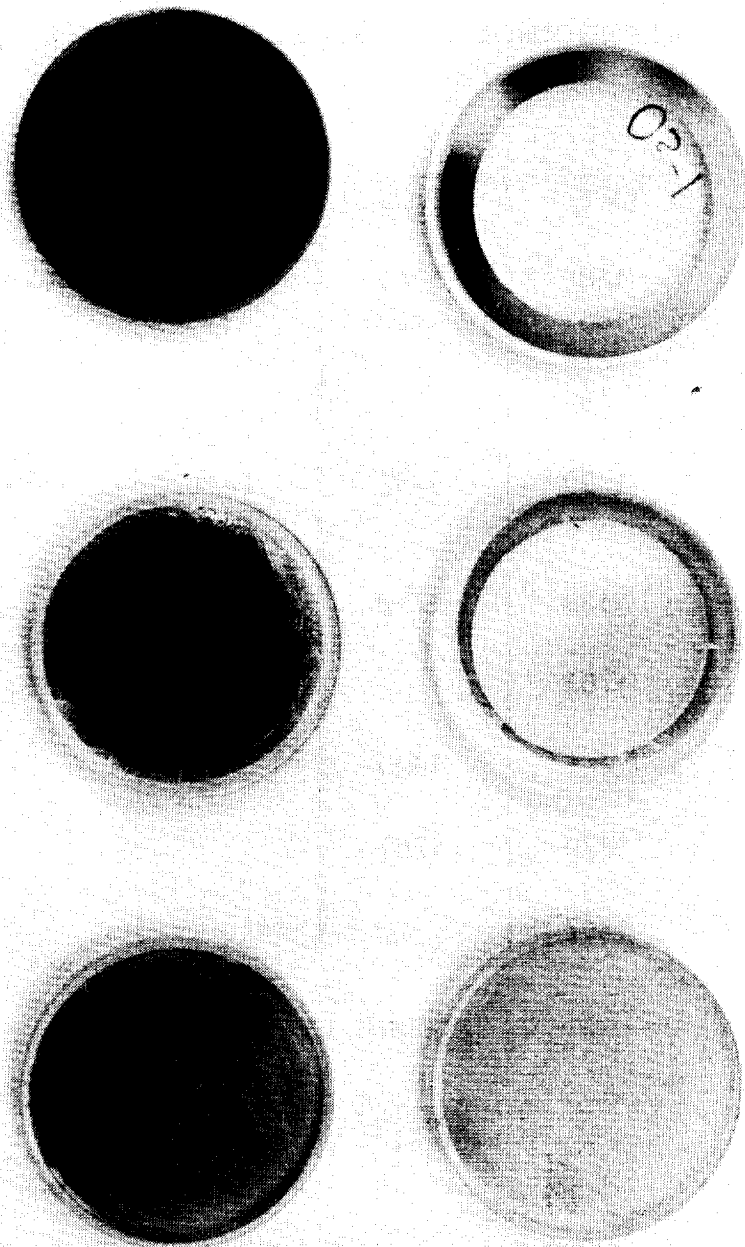
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FIGURE 12   POST-FLIGHT APPEARANCE OF OSMIUM, SILVER, AND GOLD
MIRRORS FROM A0034 LEADING AND TRAILING EDGES

ELLIPSOMETER SUMMARY - LDEF EXPERIMENT A0034

THICKNESS IN ANGSTROMS OF SiOx ON COLLECTOR MIRRORS

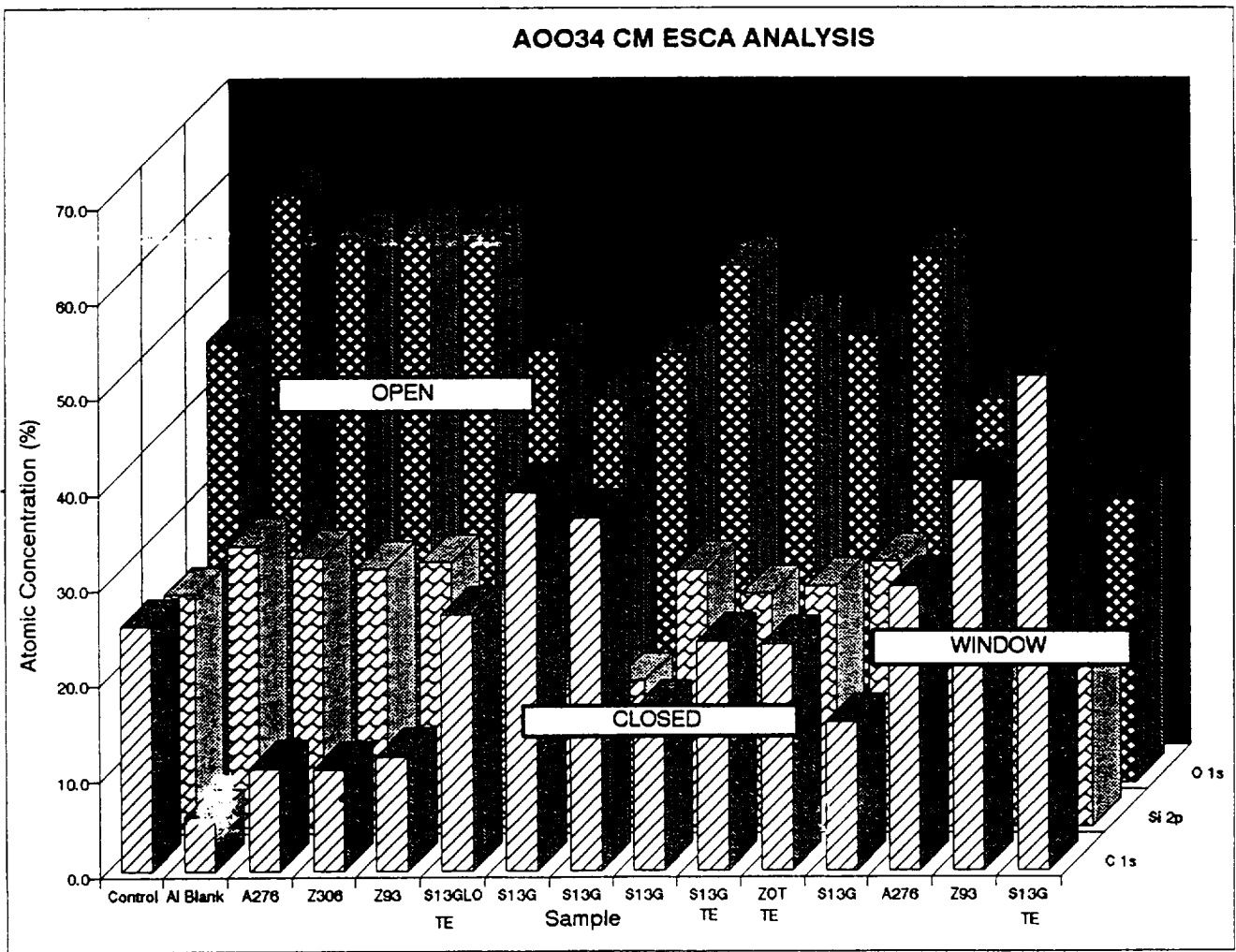| SOURCE TCC	LEADING EDGE			TRAILING EDGE		
	CLOSED	OPEN	WINDOW	CLOSED	OPEN	WINDOW
S13G	1897 1780 1733	1685 1661 1674 1482	1702 1708	1663	1670	1730 1764
S13G-LO	1777	1790	1782	1771	1694	1739 1764
Z93		1438	1712	1758		
YB-71		1703		1762	1691	1678
Z306		1428	1820			
A276		1379	1764			
Al PLATE		1447				

FIGURE 13

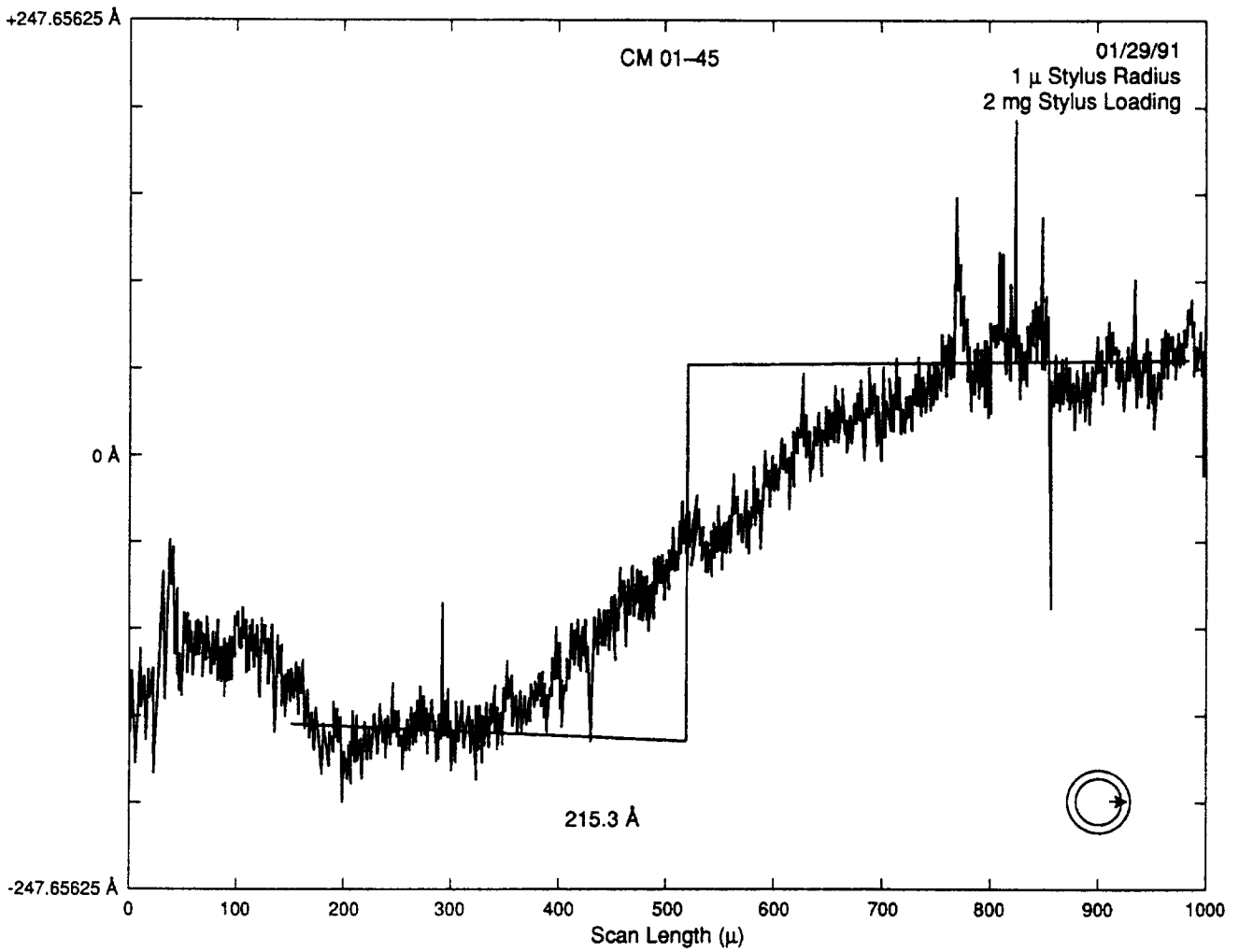FIGURE 14   ESCA RESULTS FOR EXPERIMENT A0034 COLLECTOR MIRRORS

FIGURE 15   TALYSURF PROFILE FOR A0034 COLLECTOR MIRROR EXPOSED TO
ATOMIC OXYGEN ON THE LEADING EDGE