

FLUORESCENCE MEASUREMENTS OF THE THERMAL CONTROL
EXPERIMENTS COATINGS ON LDEF S0069 AND A0114

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SUMMARY

Fluorescence measurements have been made on the thermal control coatings from the LDEF S0069, Thermal Control Surfaces Experiment (TCSE); and the A0114, Interaction of Atomic Oxygen with Material Surfaces in Low Earth Orbit. Fluorescence was observed in two types of thermal control coatings and is attributed to pigments or binders. In addition, fluorescence measurement on the silver Teflon* from the front cover of TCSE led to confirmation of damage (cracking) to the metal layers during application.

INTRODUCTION

When the TCSE experiment was inspected upon its return to the laboratory, one technique employed was the use of an ultraviolet source ("black light") to look for fluorescing contaminants such as cloth fibers and oils or greases. It was obvious, when compared with similar unexposed materials and with sample controls, that changes had occurred in the visible fluorescent brightness of the thermal control samples and of the TCSE experiment hardware itself (Figure 1). The fluorescence was so striking in some cases, such as the black urethane based coating Z302, that it was decided to try to obtain quantitative measurements of the changes. The goals were to try to characterize the various types of coatings in terms of their fluorescent properties and to possibly learn if the observed changes could further elucidate effects of exposure to the space environment.

Measurement Equipment and Set-ups

Absolute fluorescence measurements were made using the following experiment set up and calibration procedure.

*Teflon is a trademark of Dupont

A Beckman DK-2 Spectrophotometer using its 1P28 photo multiplier tube mounted in the spectroradiometric position was used to detect any fluorescent behavior from the samples. Fluorescence was induced by irradiating the sample, mounted at 45° to the optical beam, in line with the sample entrance port of the spectrophotometer (Figure 2). For these measurements, a one kw mercury-xenon lamp with a Schoeffel monochromator was used. It was found that use of the strong peak of 280 nm was convenient. Overall, the illuminating band was from 265 to 290 nm with the monochromator slits set at 1.5 mm. Measurements of output with this set up using a molelectron radiometer indicated an irradiance level of 0.5 m²/cm² at the sample (equivalent to about 1 sun in this band). To provide a calibration of the DK-2 spectrophotometer, a one kw quartz-halogen tungsten Standard of Total and Spectral Irradiance (Model 200H) supplied by Optronics Laboratories (traceable to NIST), was used in place of the Hg-Xe source (Figure 3). A 99% diffuse reflectance standard (from Labsphere, Inc. SRS-99-010-6561A) was placed at the sample location. Since this non-fluorescing standard provided essentially Lambertian reflectance of a known irradiance level, a calibration of the DK-2 as a system was made over its sensitive wavelengths (~300-650 nm). For ZnO pigmented coatings, it was also determined that the fluorescent energy is proportional to irradiance, over a factor of 5.5; and that there was no detectable change in fluorescent wavelength peaks for irradiance bands of 265 to 290 nm, 295 to 320 nm, and 310 to 340 nm. Other coatings were not tested in this manner, but probably would behave similarly.

Fluorescence Measurements

Two types of thermal control coating samples were found to exhibit rather strong fluorescence. These were: 1) coatings that used urethane as a binder and, 2) coatings that used ZnO as a pigment. In addition, there were variations of the above coatings with a thin overcoat of silicone to test the feasibility of an additional protective layer against the deleterious effects of atomic oxygen (AO) bombardment at orbital velocities. Controls for the TCSE experiment were maintained in covered containers in a limited-access steel cabinet.

Other TCSE thermal control coatings samples that were measured and found not to have significant fluorescence were Z306 (a urethane based black paint), YB71 (silicate), and D111 (silicate). A white Tedlar* flight sample did not fluoresce, while a laboratory specimen exhibited very weak fluorescence peaks at about 420 to 440 nm. Also measured, were silver Teflon samples cut from the front cover of TCSE. Similar materials that were unexposed to the space environment were used for comparison.

Figures 4 and 5 allow comparison of the flight and control fluorescent spectra of Z302 and A276 urethane based coatings. The similarity in the control spectra from 400-575 nm is likely attributable to the fluorescence characteristics of the polyurethane binder. However, the spectra for the flight exposed sample of Z302 is somewhat unique in that the magnitude and band width of the fluorescence is less than most of the other polyurethane samples. This may be due to the erosion of the sample by AO and/or as a natural frequency shift of the material caused by exposure to the LEO environment. Fluorescence data is not available for Z302, exposed in the RAM direction for 5.8 years, since it was completely eroded.

The similarities shown in the spectra of Z302 and A276 with a OI650 silicone overcoat are even more striking (Figures 6 and 7). These figures tend to illustrate that the polyurethane samples, both Z302 and A276, overcoated with OI650 and then exposed to the flight environment fluoresce very similar to one another. In addition, the similarities between the overcoated and neat A276 polyurethane coatings fluorescence spectra are shown in Figures 5 and 7. The OI650 overcoated control samples have enhanced ultraviolet fluorescence attributable to the overcoat itself. This effect is not present in the flight exposed samples and, in fact, there is no fluorescence evidence that the overcoat is still present. The similarity in exposed A276 (neat and overcoated) spectra may be due to extensive crosslinking of the silane polymer on the surface. The crosslinking of the polymer modified the electronic and molecular structure and may have more effectively bonded the available electrons. The result is the electrons could no longer be excited to a

*Tedlar is a trademark of Dupont

higher, unstable energy level when exposed to UV irradiation and therefore the overcoat no longer fluoresced, but the fluorescence of the A276 was transmitted through the overcoat. Further evidence that crosslinking of the silane overcoat is a likely explanation for this phenomenon is that visual inspection of the surface of the overcoated samples shows significant cracking. This can be the result of the hardening and embrittlement of the polymer from increasing crosslinking based on optical properties measurements¹. The overcoat has served its purpose to protect the Z302 from eroding.

The ZnO pigmented Z93 and S13GLO coatings show remarkably similar fluorescence spectra for the control samples as well as those that were protected by an aluminum cover during flight (Figures 8-13). The spectra from the exposed samples generally appear similar, with unexplained weaker fluorescence on the TCSE P7, 5.8 years exposure S13GLO sample (figure 9) and on AO114 Wake mounted S13GLO sample (Figure 13). Especially, the Wake mounted sample shows a weak fluorescence and the absence of the 380 nm peak.

From Figure 8, Z93 spectra for 1.6 and 5.8 years exposure are shown, providing evidence that the change occurring is not linear with time and that the 380 and 520 nm fluorescence change rates may be different.

The slight fluorescent glow noticed on the TCSE front cover was measured and is shown in Figure 14. Measurements on non-flight Teflon failed to produce any detectable fluorescence. However, measurements of the 3M 966 high temperature acrylic adhesive used to apply the silver Teflon produced fluorescence that, like the silicone overcoat, extended into the ultraviolet (Figure 15). Upon exposure to strong ultraviolet for various periods of time, the spectra shifted toward the visible region during the first short exposure and did not continue to shift significantly, but fluorescence intensity continued to grow in this band.

Discussion and Summary

It is clear that the fluorescence of the urethane based paints is produced by the urethane binder itself and not the various pigments. Hill² has correlated laser-induced fluorescence (LIF) with tensile strength of several polyurethane based materials. He also found LIF changes in LDEF Tray Clamps samples of A276 and Z306 supplied to him by Boeing³. It is not apparent if the specific LIF changes detected in the thermal control coatings are the same as polyurethane/tensile strength LIF changes. Hill attributes the latter to "complex molecular and intermolecular relationships (such as cross-linking, scission, oxidation) that are altered during degradation."² Silicone overcoated urethane paints, although severely cracked and sometimes peeling seem to provide protection from atomic oxygen erosion. From the measurements, not only does the initial enhanced ultraviolet fluorescence disappear after space exposure, but the resulting spectra closely matches that of the urethane paints without the silicone. If polyurethanes are to continue to be used in the space environment, it is necessary to better understand the degradation mechanisms involved. Fluorescence may prove to be a useful tool in this understanding as well as in the valuation of the condition of polyurethane based materials.

The coatings containing ZnO (S13G/LO and Z93) exhibited fluorescent spectra apparently dominated by ZnO. Nicoll⁴ showed that the ultraviolet (~380 nm) band wavelength peak shifts with wavelength toward the visible at about 0.12 nm/°C (Figure 16). This shift seems to correlate with the fundamental absorption edge shift. There is no shift in the visible band, but its intensity decreases with temperature. Kroeger⁵ attributes this visible fluorescence (~520 nm) in ZnO to the presence of oxygen vacancies, that is, a non-stoichiometric zinc rich condition. It is tempting to attribute the reduction seen in this band for the LDEF S13G/LO and Z93 to the reaction of ZnO with atomic oxygen. Streed⁶ shows, in ground chamber tests, that fluorescence reduction in this band may be caused by ultraviolet and/or proton irradiation. Perhaps, in space, the reaction is indeed proceeding toward a stoichiometric mixture aided by the presence of zinc and oxygen in the lattice reacting as a result of exposure to the various high-energy environments.

Fluorescence of silver Teflon (TCSE front cover) is attributed to the microcracking that occurred during installation. The matching spectra of ultraviolet irradiated adhesive used to apply the silver Teflon leaves little doubt of the source of the flight material fluorescence and also is an example of fluorescence as an additional analytical tool available to materials researchers and technologists.

REFERENCES

1. Wilkes, D.R., et. al., Thermal Control Surfaces on the MSFC & LDEF Experiments, LDEF Materials Workshop, Hampton, VA, November, 1991.
2. Hill, R.H. Jr., Feuer, H.O. Jr., Laser-Induced Fluorescence Inspection of Polyurethane, Proceedings of the 17th Symposium on Nondestructive Evaluation, April 17-20, 1989, San Antonio, TX.
3. Hill, R.H. Jr., Laser-Induced Fluorescence of Space-Exposed Polyurethane, Southwest Research Institute Report 15-9682, April 6, 1992.
4. Nicoll, F.H., Temperature Dependence of Emission Bands of ZnO Phosphors, Journal of the Optical Society of America, Vol. 39, 1948.
5. Kroeger, Vink, et. al., The Origin of Fluorescence in Self-Activated ZnS, CdS, and ZnO, Journal of Chemical Physics, Vol. 22, No. 2, p. 250, 1954.
6. Streed, E.R., Experimental Study of the Combined Space Environment Effects on ZnO/Potassium Silicate, Thermophysics of Spacecraft and Planetary Bodies, ed. by G. Heller, 1967.

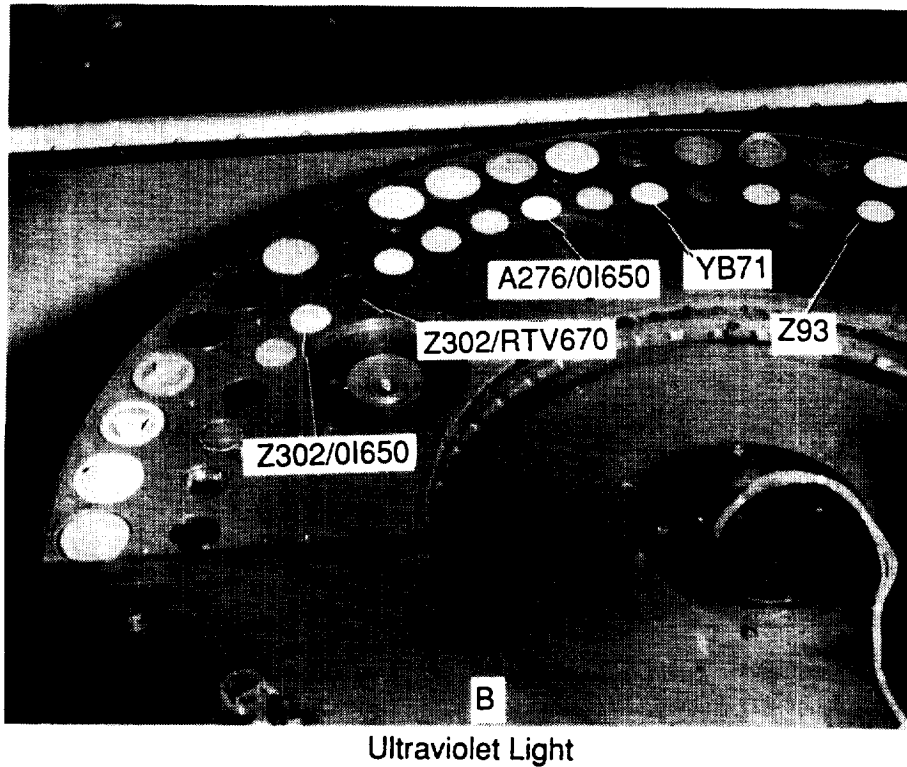
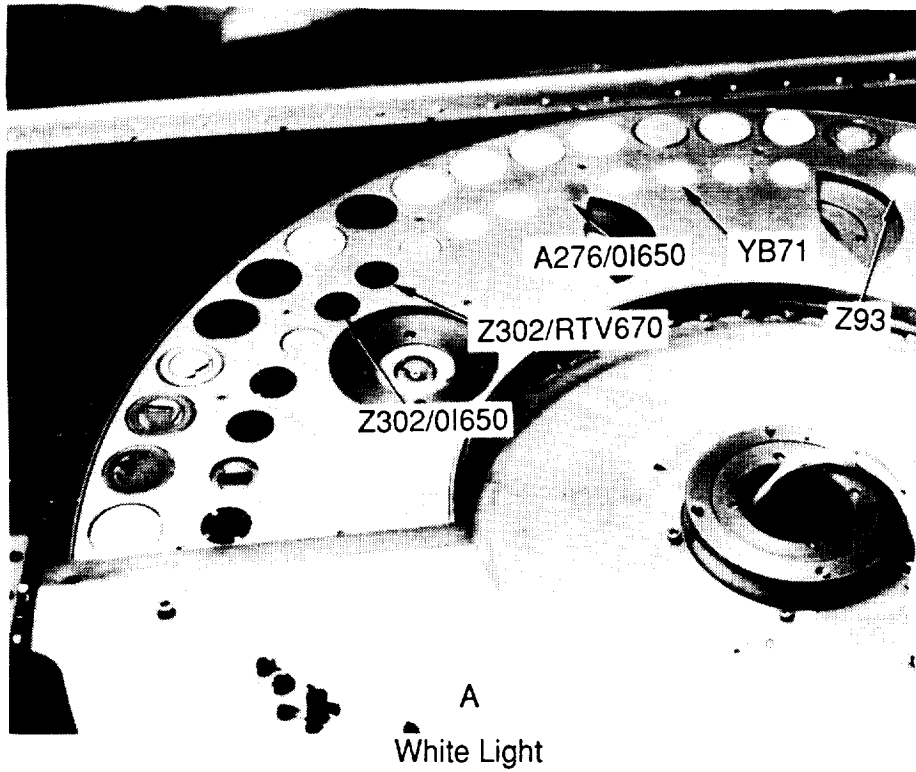


Figure 1. Fluorescence of Thermal Control Coatings Comparison of Samples Under White and Ultraviolet Light.

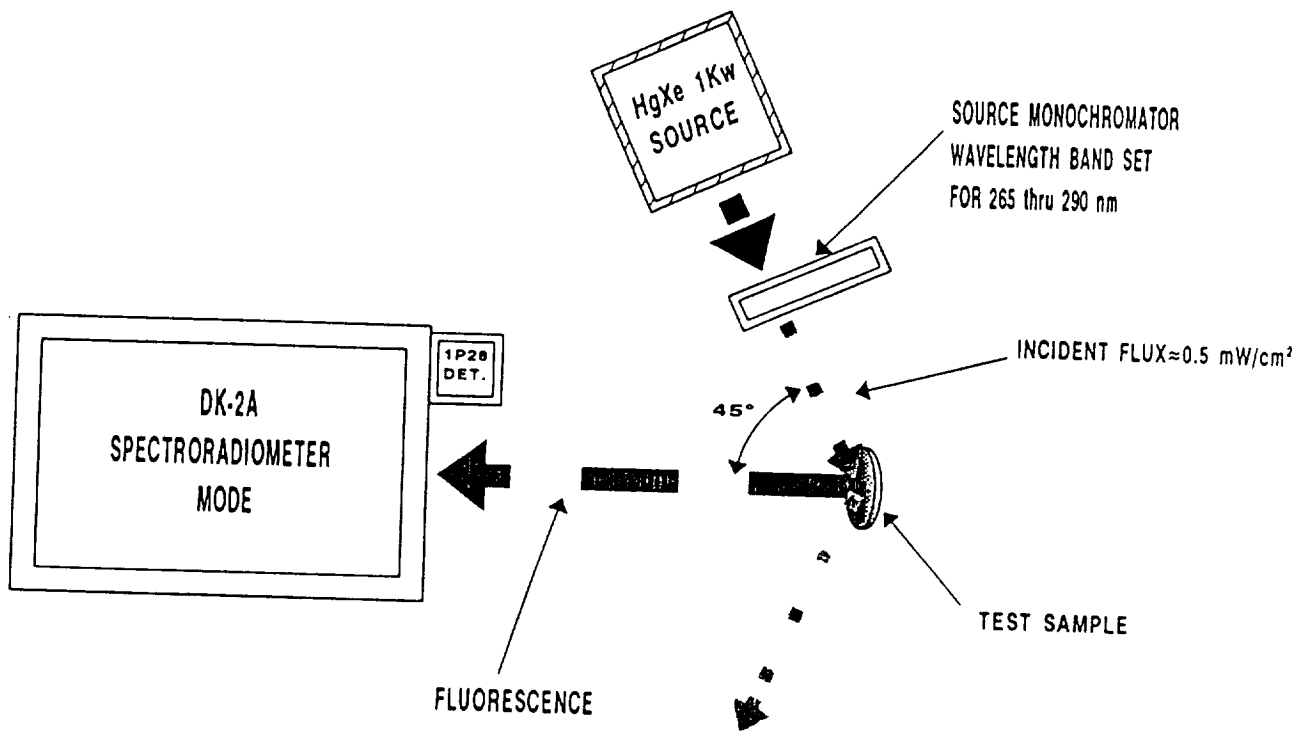


Figure 2. Schematic of Fluorescence Measurement.

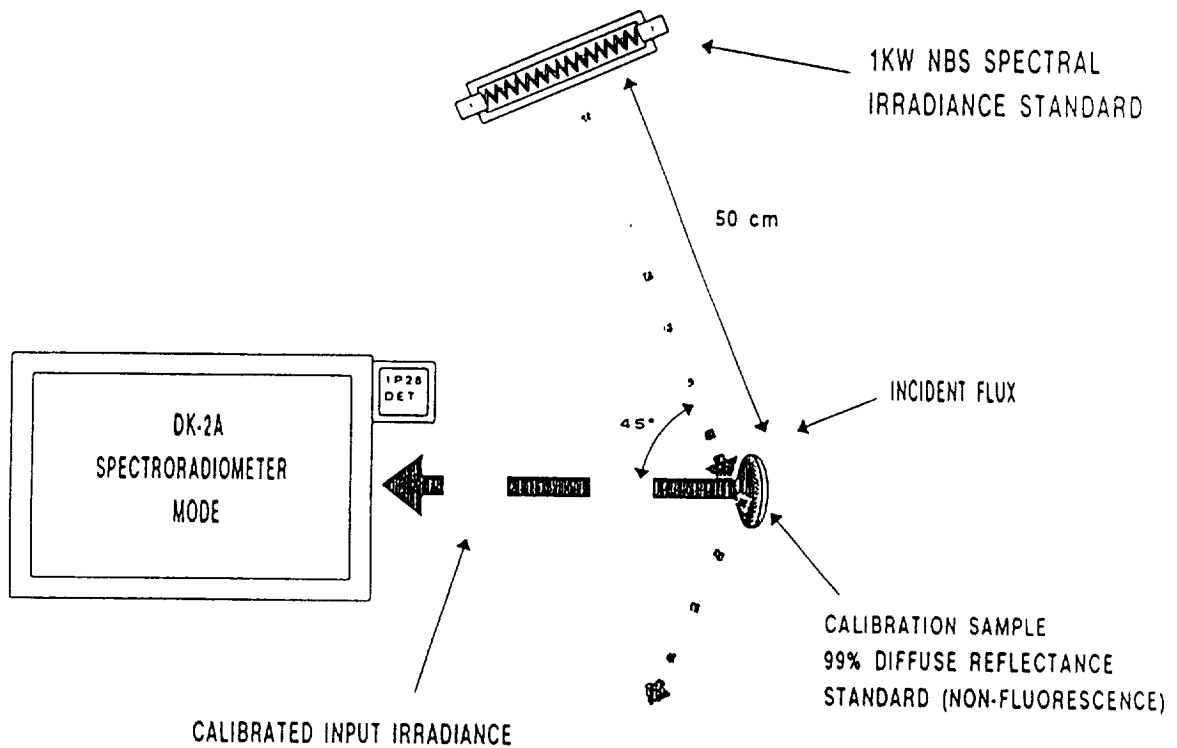
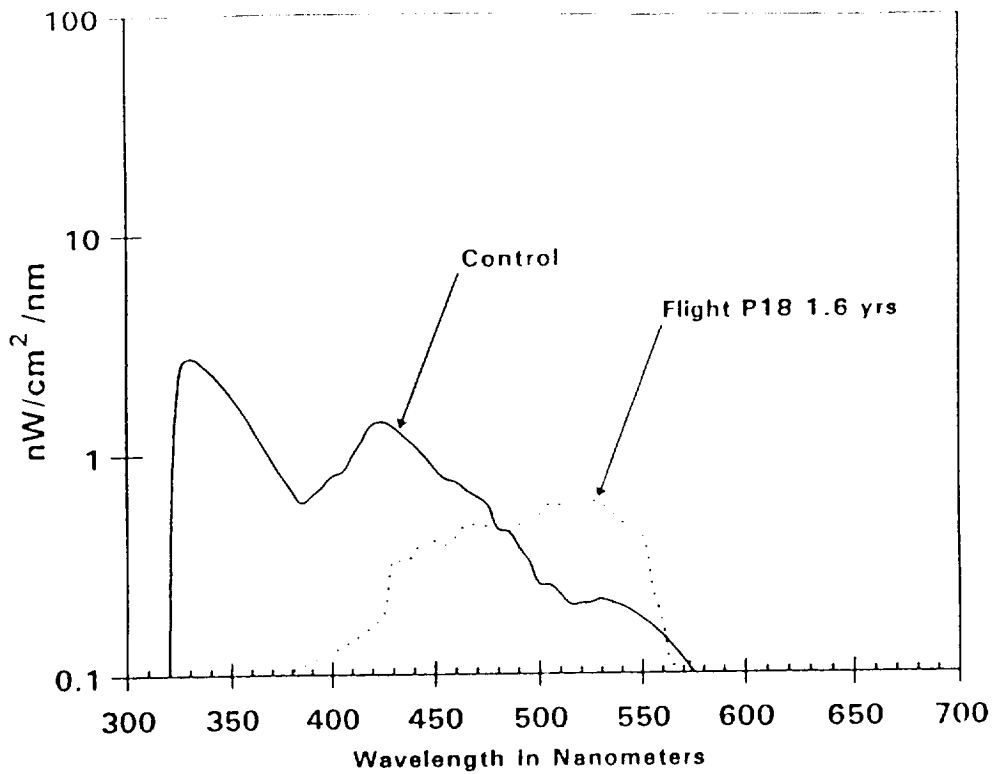
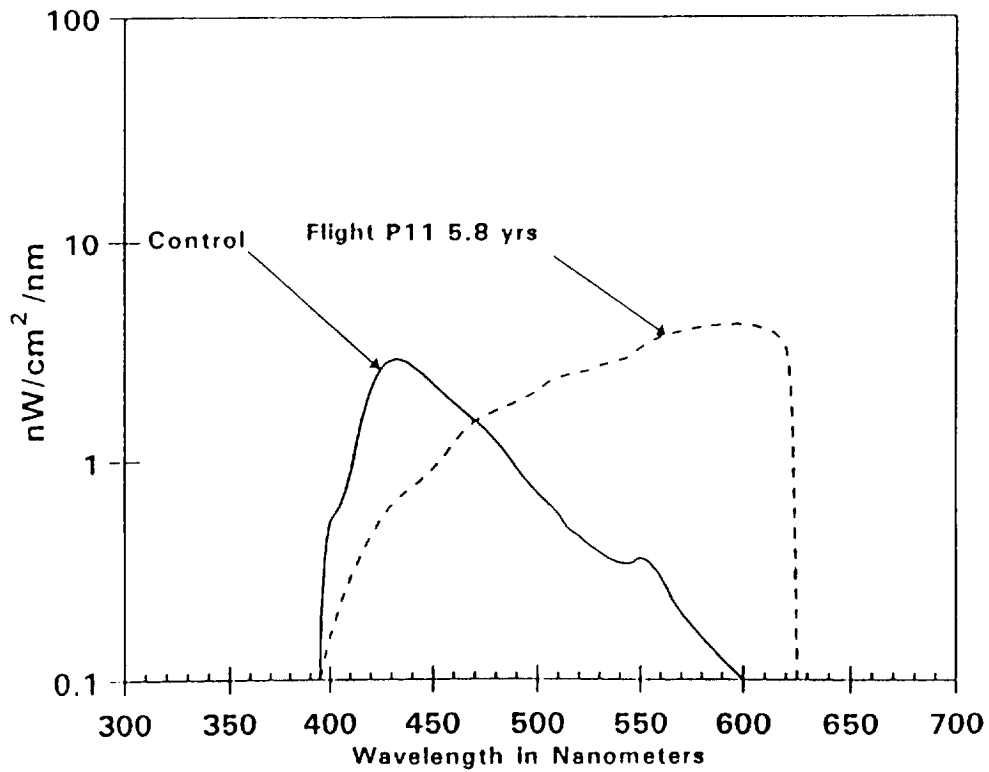


Figure 3. Schematic of Calibration Setup for Fluorescence Measurements.



**Figure 4. Fluorescence Spectra of Z302.
Thermal Control Surfaces Experiment S0069**



**Figure 5. Fluorescence Spectra of A276.
Thermal Control Surfaces Experiment S0069**

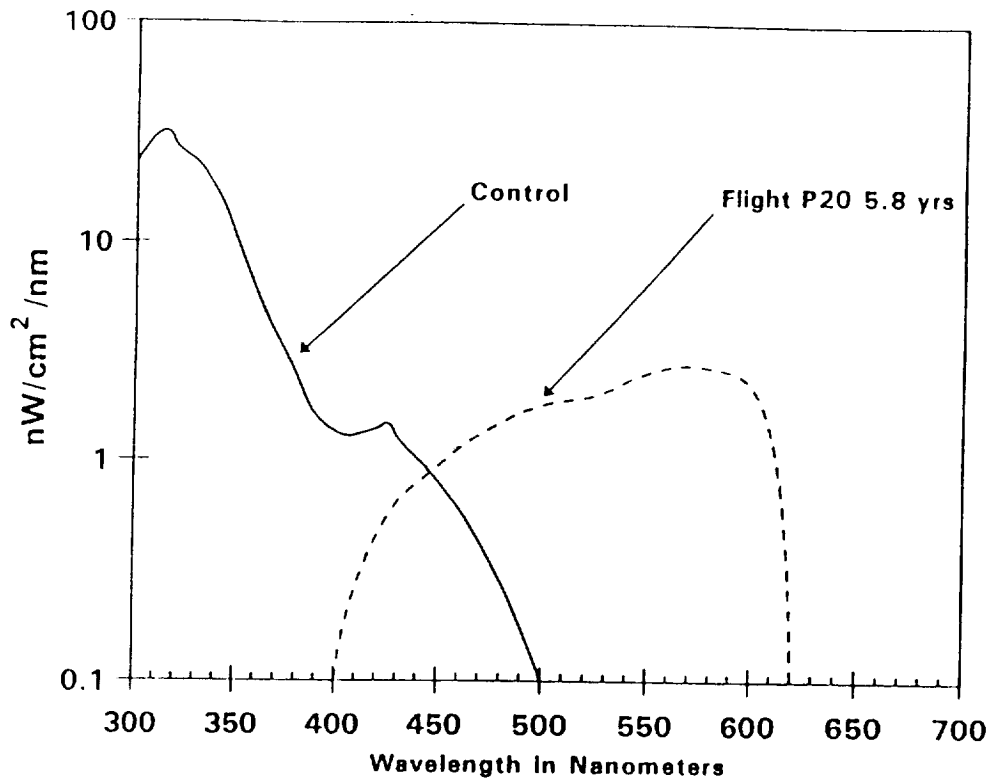


Figure 6. Fluorescence Spectra of Z302 with OI650 Overcoat. Thermal Control Surfaces Experiment S0069

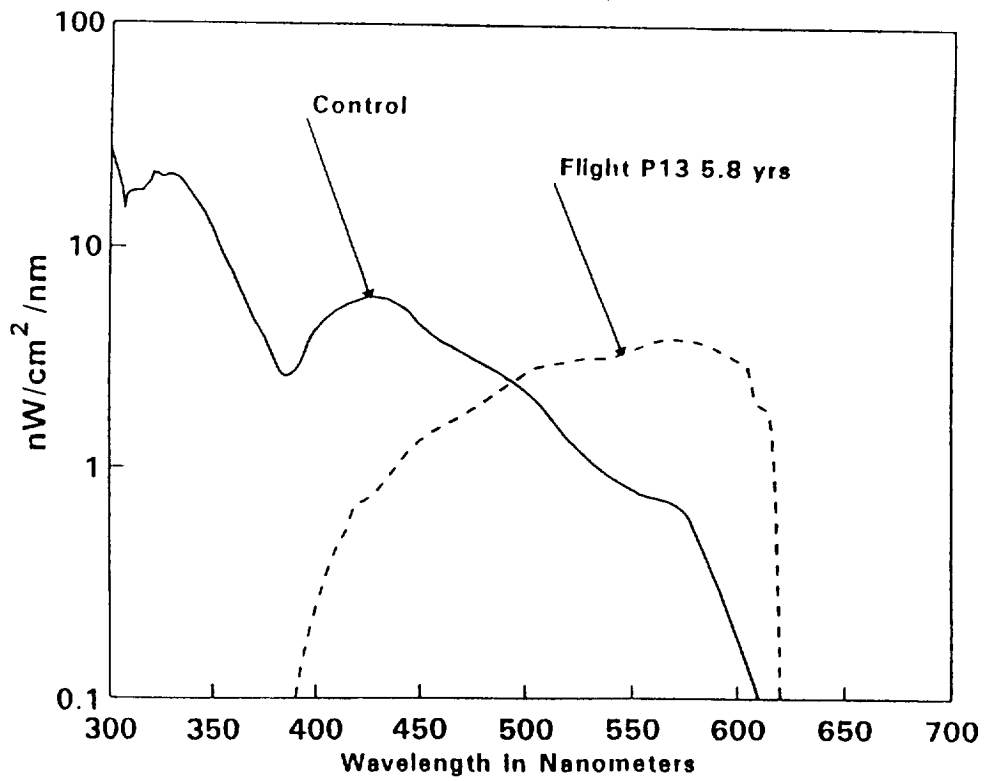
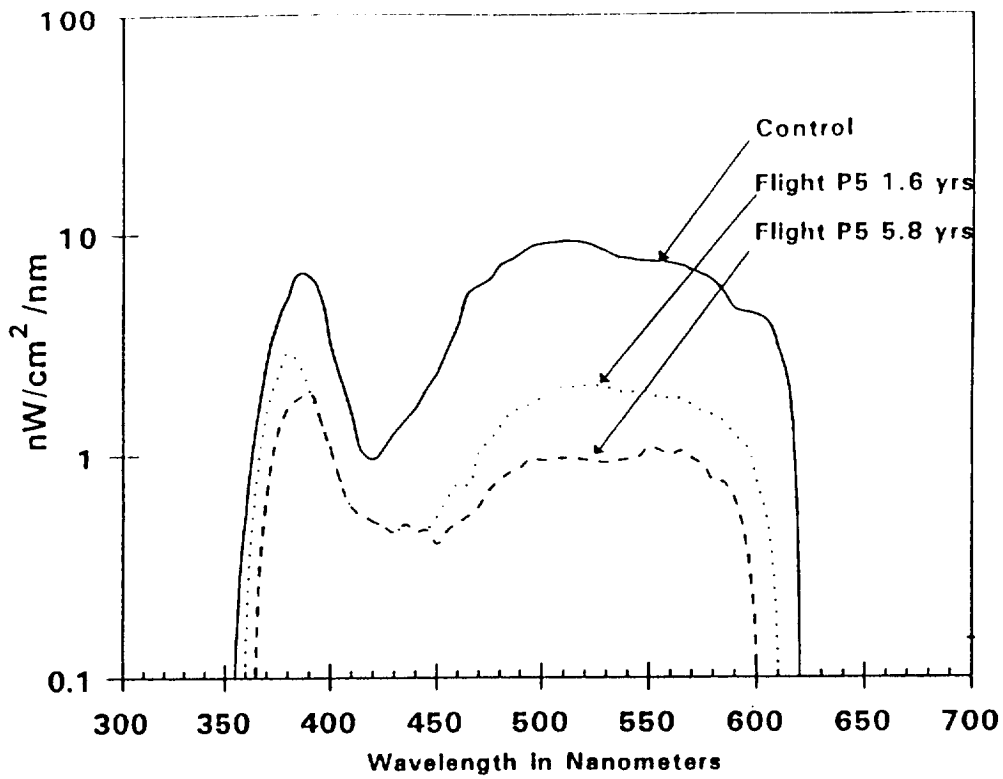
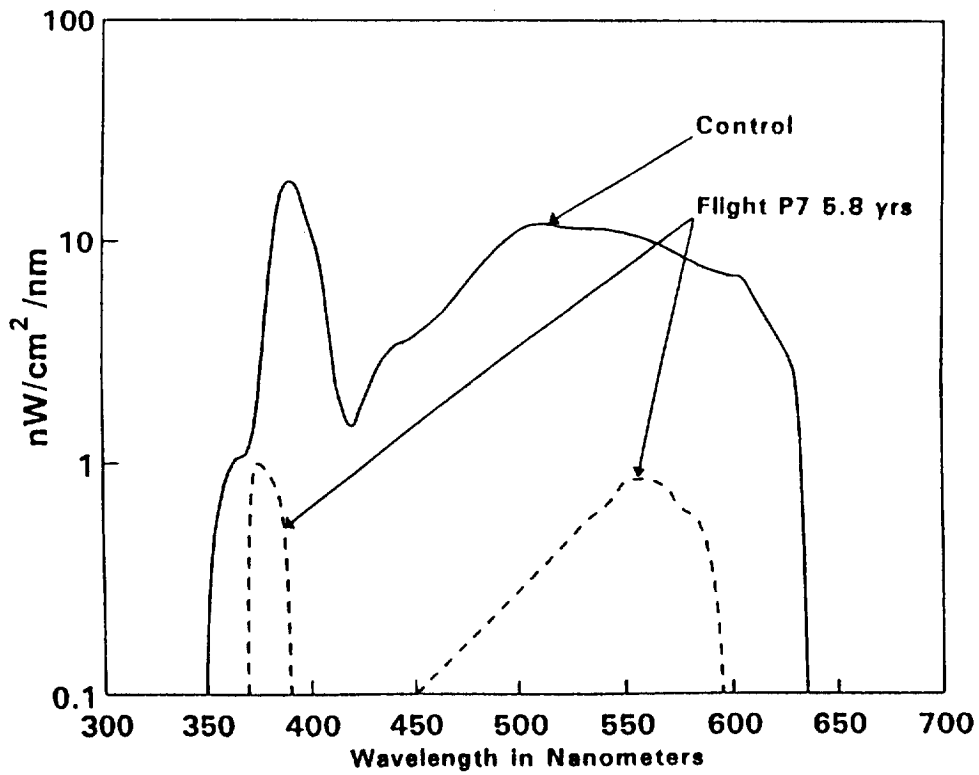


Figure 7. Fluorescence Spectra of A276 with OI650 Overcoat. Thermal Control Surfaces Experiment S0069



**Figure 8. Fluorescence Spectra of Z93.
Thermal Control Surfaces Experiment S0069**



**Figure 9. Fluorescence Spectra of S13G/LO.
Thermal Control Surfaces Experiment S0069**

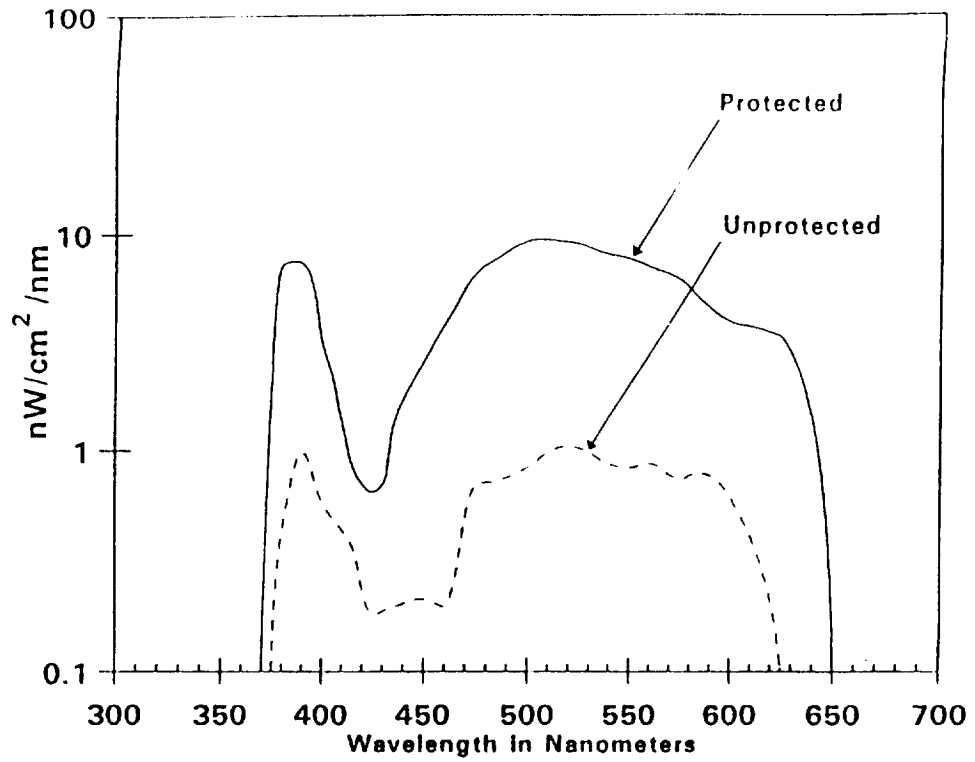


Figure 10. Fluorescence Spectra of Z93 (RAM).
Interaction of AO with Material Surfaces in LEO AO114

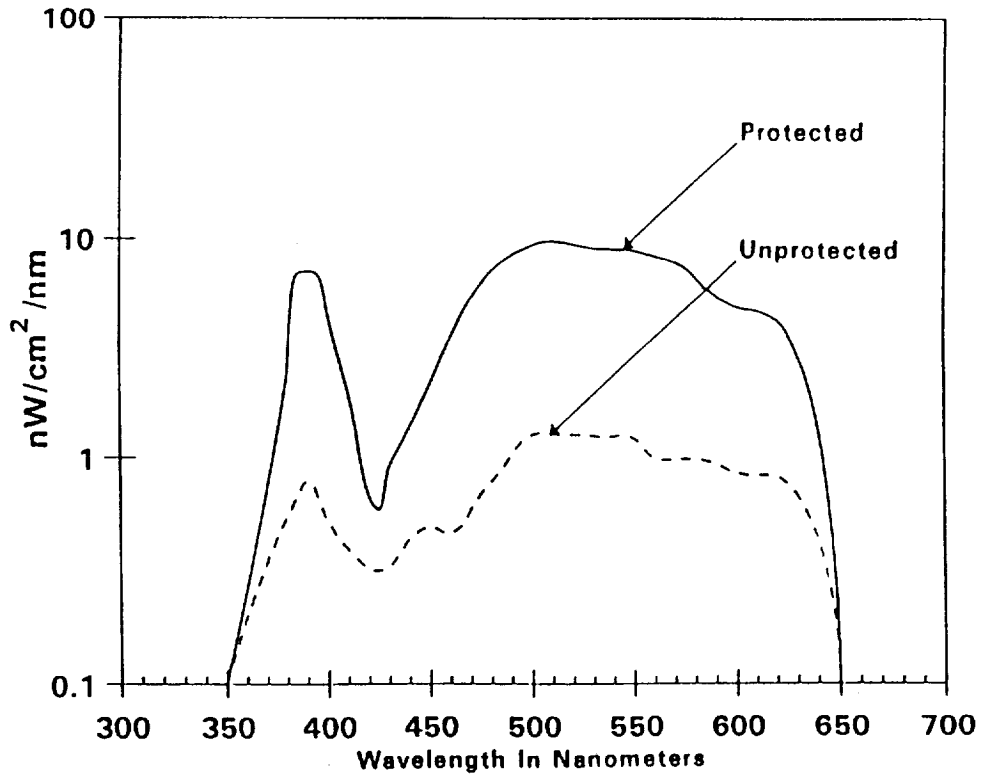
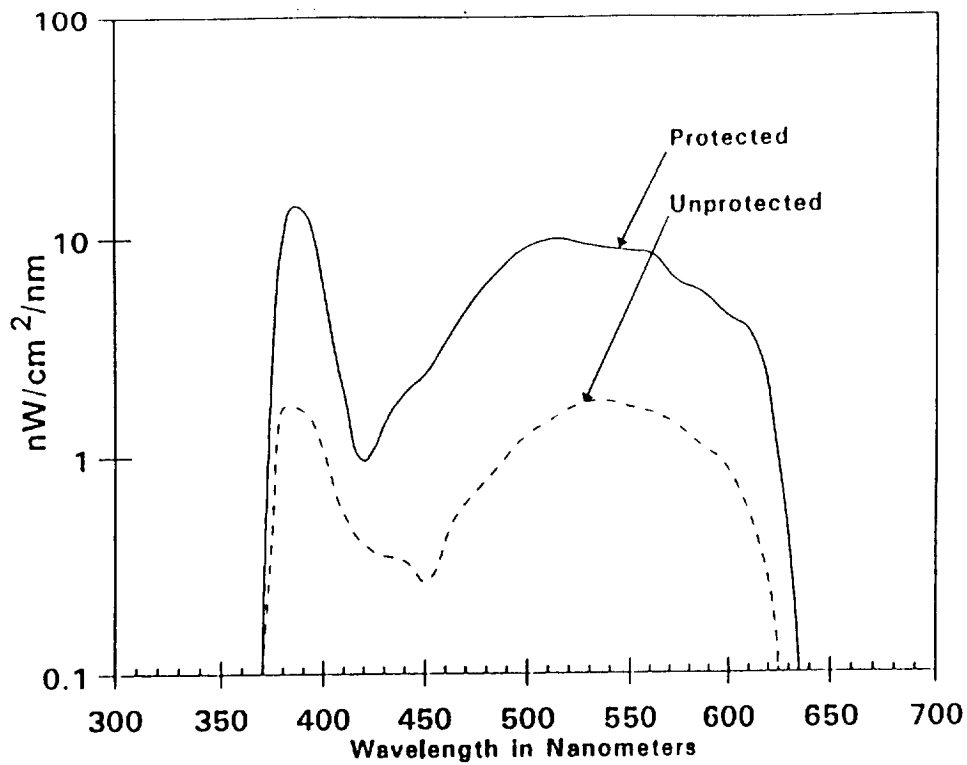
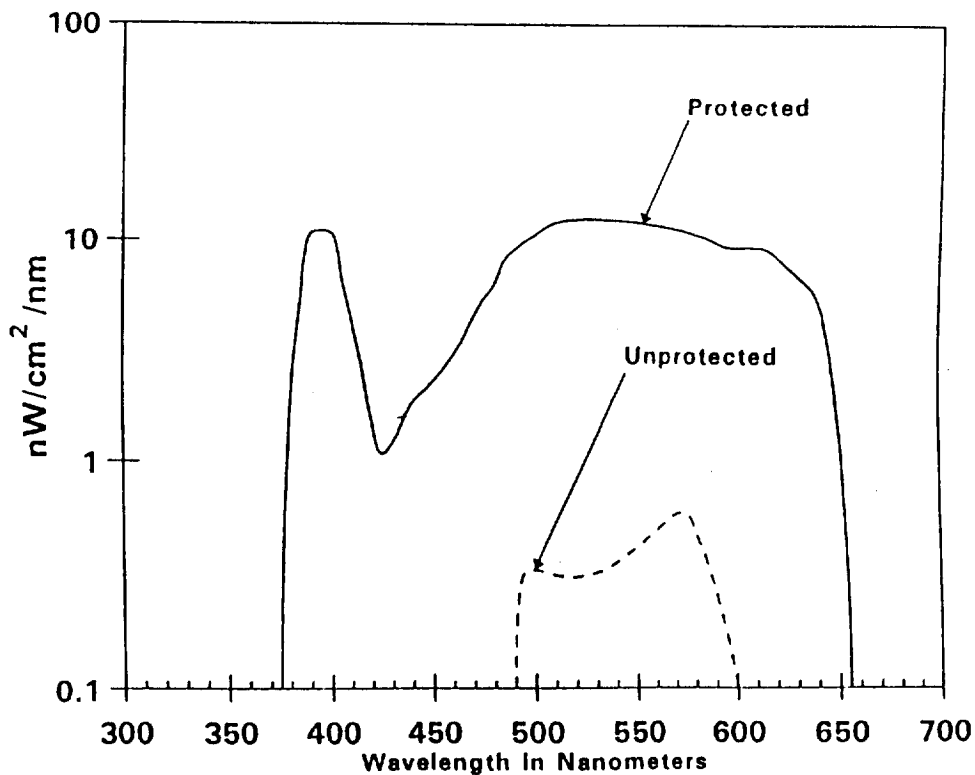


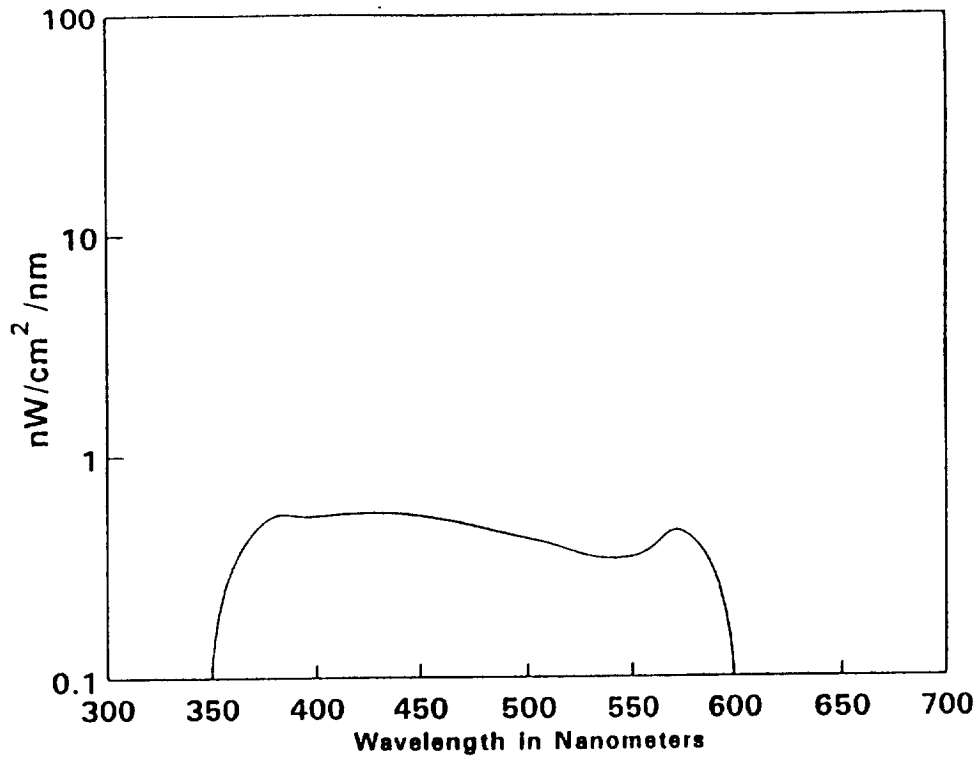
Figure 11. Fluorescence Spectra of Z93 (WAKE)
Interaction of AO with Material Surfaces in LEO AO114



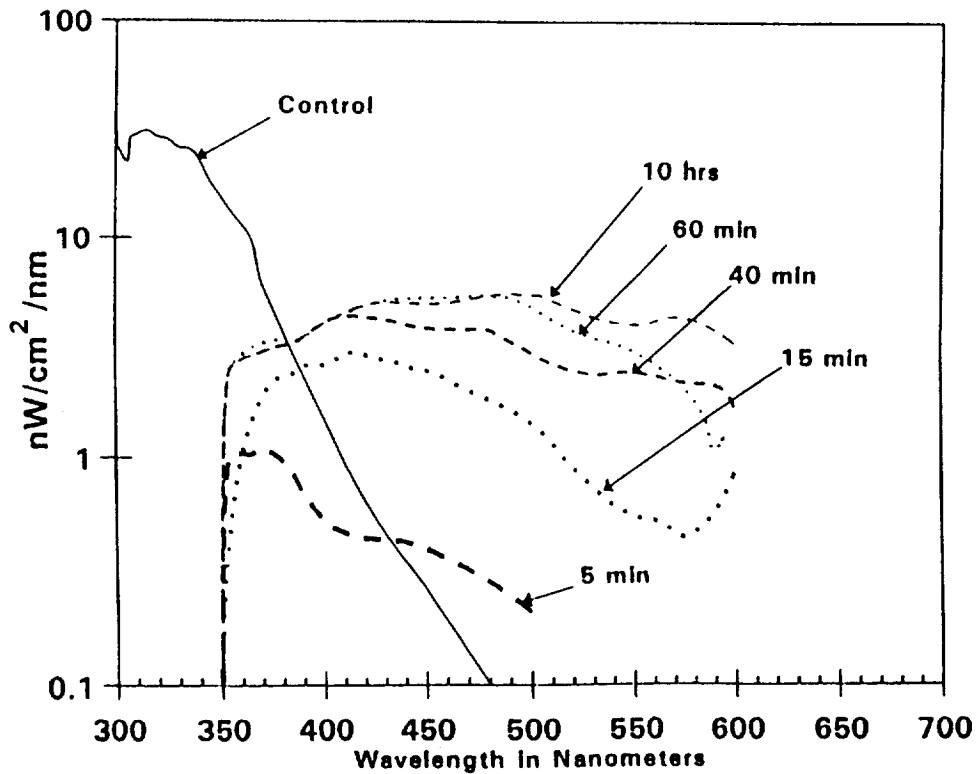
**Figure 12. Fluorescence Spectra of S13G/LO (RAM).
Interaction of AO with Material Surfaces in LEO AO114**



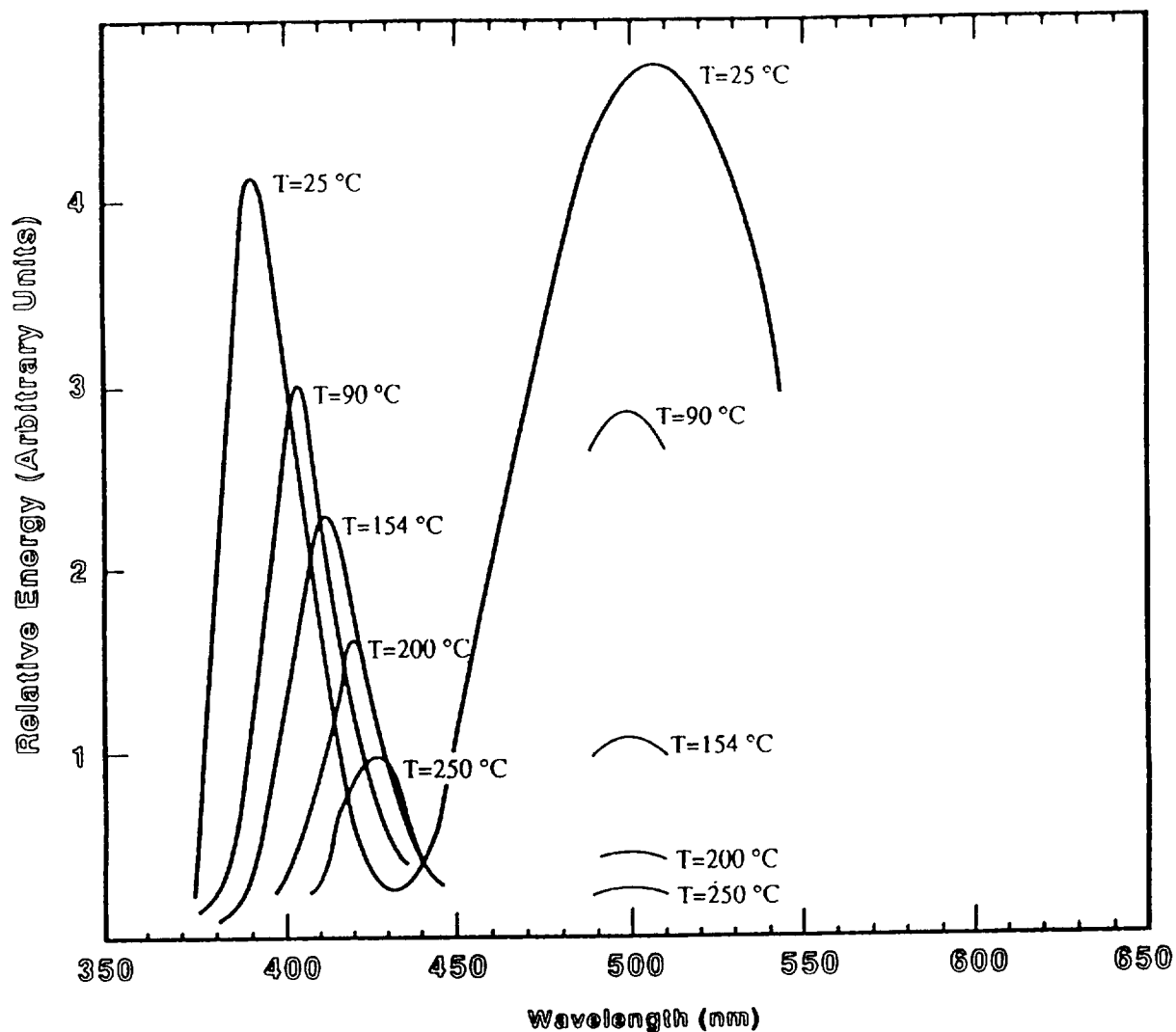
**Figure 13. Fluorescence Spectra of S13G/LO (WAKE)
Interaction of AO with Material Surfaces in LEO AO114**



**Figure 14. Fluorescence Spectra of Front Cover Silver Teflon.
Thermal Control Surfaces Experiment S0069**



**Figure 15. Fluorescence Spectra of Adhesive 966 After UV Exposure.
Thermal Control Surfaces Experiment S0069**



Relative energy emitted by hex, ZnO: [Zn] phosphor as a function of wavelength for different temperatures. Emission produced by a high current density electron beam, 100 MA focused and scanning a 3-in. \times 4-in. television pattern at 20 kV.

Refer: Nicoll, F.H.; J. Opt. Soc. Amer. 38, 817 (1948).

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Figure 16. Fluorescence ZnO.

