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SKYLAB D024 THERMAL CONTROL COATINGS AND POLYMERIC FILMS EXPERI--ETC(U)
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SKYLAB DO24 THERMAL CONTROL COATINGS AND POLYMERIC FILMS EXPERIMENT

TECHNICAL REPORT AFML-TR-75-77

Report for the Period January 1968 to October 1974

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This technical report has been reviewed and is approved for publication.

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Preliminary results of an experiment designed to determine the effects of the external Skylab space environment on the performance and properties of a wide variety of selected thermal control coatings and polymeric films are presented. Three duplicate sets of thermal control coatings and polymeric films were exposed to the Skylab space environment for varying periods of time during the mission. The specimens were retrieved by the Astronauts, placed in hermetically sealed return containers during EVA, recovered, and

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FOREWORD

This report was prepared by the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson AF Base, Ohio. This work was initiated under Project 7340, "Nonmetallic and Composite Materials", Task No. 734007, "Coatings for Energy Utilization, Control, and Protective Functions", and was administered under the direction of the Air Force Materials Laboratory with Dr. William L. Lehn (AFML/MBE) Project Engineer.

This summary report covers a portion of the work on the evaluation of the DO24 experiment hardware recovered from Skylab, SL 1/2, SL 1/3 and SL 4 and encompasses a period from January 1968 when the experiment was first being developed to October 1974. It was submitted by the authors in January 1975. Additional summary reports covering other portions of the DO24 experiment hardware are in progress and will appear at a later date.

Many of the materials used in this project were not developed or intended for the conditions to which they were subjected. Any failure or poor performance of a material is, therefore, not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

The authors gratefully acknowledge the assistance of R. Winn, G. Clinehens, R. Vissoc, G. Stevenson, J. Weaver and D. Prince in the sample preparation and evaluation phases of the project.

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SKYLAB DO24 THERMAL CONTROL COATINGS AND POLYMERIC FILMS EXPERIMENT

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-- NOTES --

SKYLAB DO24 THERMAL CONTROL COATINGS AND POLYMERIC FILMS EXPERIMENT

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Abstract

Preliminary results of an experiment designed to determine the effects of the external Skylab space environment on the performance and properties of a wide variety of selected thermal control coatings and polymeric films are presented. Three duplicate sets of thermal control coatings and polymeric films were exposed to the Skylab space environment for varying periods of time during the mission. The specimens were retrieved by the Astronauts, placed in hermetically sealed return containers during EVA, recovered, and returned to the Air Force Materials Laboratory for analysis and evaluation. Post flight analysis of the three sets of recovered thermal control coatings indicated that measured changes in specimen thermooptical properties are due to a combination of excessive contamination and solar degradation of the contaminant layer. The degree of degradation experienced overrides, obscures and compromises the measurement of the degradation of the substrate coatings themselves. Preliminary experimental results on the analysis of the contamination are also presented.

I. Introduction and Background

Thermal control coatings are used on satellites and other spacecraft as the primary means of controlling the temperature of the vehicle and its various systems and components. Polymeric films find many uses in spacecraft as tapes, electrical and thermal insulation, as protective shrouds and covers and as components of multilayer thermal control coatings. The objective of the DO24 Experiment was to evaluate the effects of the near earth vacuum and ultraviolet radiation Skylab space environment on selected thermal control coatings and polymeric films in order to provide correlation and calibration data for laboratory in situ space simulation. The data obtained would add new insight into the mechanisms of degradation and improved damage theories to provide direction for the development of new and improved materials. In previous experiments the degradation of thermooptical properties of thermal control coatings exposed to the space environment have been determined by calculations based upon the changes in temperature of various appropriately instrumented surfaces and subsystems, which are telemetered back to earth. Other surfaces which had been exposed to space and then recovered were exposed either to the spacecraft cabin environment, or the reentry, recovery or ambient earth environment. This experiment was unique in that specimens of materials which had actually been exposed to the space environment would be retrieved and returned to earth in hermetically sealed vacuum return containers. Upon return the sealed containers would be opened in a specially designed vacuum in situ reflectance unit and the thermooptical property degradation of the thermal control specimens determined directly without any exposure to the spacecraft cabin, reentry, recovery or ambient earth atmosphere. It was expected that measurement of subtle aspects of the degradation and recovery of optical properties, i.e. bleaching effects, would be possible.

The DO24 flight hardware shown in Figure 1 consisted of four sample panels, two duplicate sample trays each containing 36 individual sample buttons coated with some 27 different selected thermal control coating materials and two duplicate sample trays each holding 8 different polymeric film specimens. Pertinent properties of all specimens were individually measured prior to flight. The four specimen trays along with two hermetically sealable return containers were mounted on the exterior of the Airlock Module (AM) near the Extravehicular Activity (EVA) hatch prior to launch as shown in Figures 2 and 3. The thermal control trays were mounted oriented perpendicular to the sun vector for maximum direct solar radiation exposure while the polymeric films were located some 39° off axis as

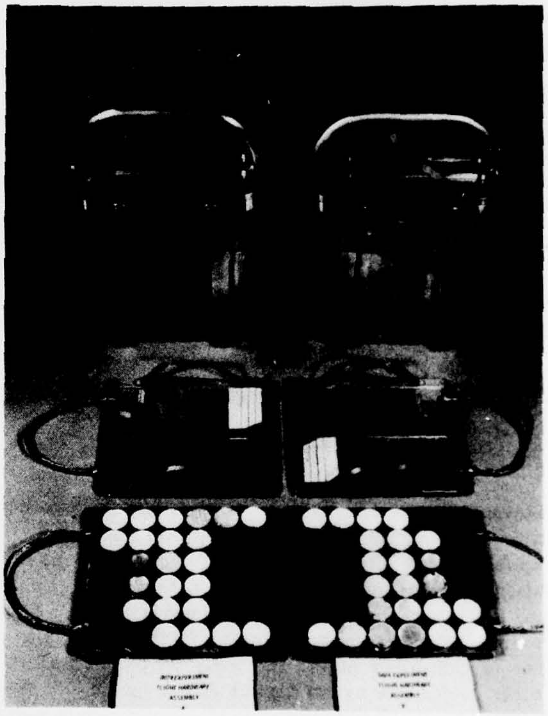

Figure 1. DO24 Flight Hardware

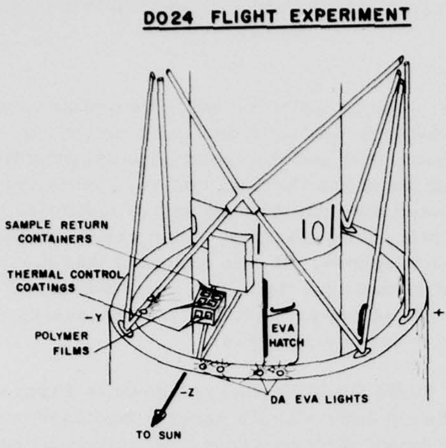

Figure 2. DO24 Flight Experiment

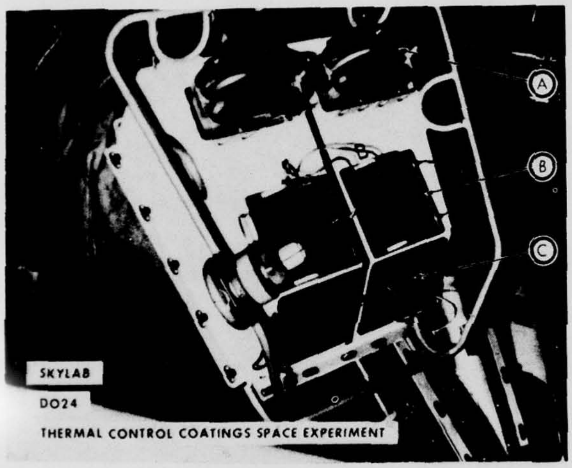

Figure 3. DO24 Flight Hardware Installation

shown in Figure 4. The specimens were protected during launch by the payload shroud and were exposed after shroud ejection. Due to the passive nature and location of the experiment the mechanical and electrical problems experienced by Skylab during the initial phases of the flight due to the loss of the solar panel and workshop thermal shield had little or no direct effect on DO24. However, a more far reaching and subtle effect was the increased contaminant concentration added to the Skylab external environment as a result of the overheating of the workshop external surfaces and interior. This requires the venting of that internal atmosphere prior to Astronaut occupancy plus the additional contamination resulting from the deployment of the sun shade and solar sail. The specimen trays after exposure were removed and sealed in the return containers by the Astronauts during EVA, retrieved and returned to earth for measurements and evaluation.

Figure 4. DO24 Experiment and Supporting Structure

The first set of specimens, SL 1/2, were retrieved by the first crew of Skylab astronauts after 35 days (approximately 550 hours of solar exposure) and returned to earth for analysis. The second set of specimens, SL 1/3, were retrieved after 131 days (approximately 2040 hours of solar exposure) and returned to earth for analysis. Post flight examination of the exterior of the return containers as shown in Figure 5 and of the recovered materials specimens indicated that the materials had been exposed to a high level of contamination which had severely degraded in the solar space environment. The contamination tended to override, obscure and compromise the measurements of the subtle bleaching as well as gross thermooptical property degradation and obviated the in situ vacuum handling. The contamination was originally ascribed to Service Module Reaction Control System (SMRCS) propellant by-products as a result of the fly by and docking maneuvers. An additional back-up set of specimen trays was approved for launch, deployment, exposure and retrieval on Skylab 4 (SL-4) in an effort to preclude contamination effects. The specimens were deployed and recovered by the third crew of astronauts after 74 days (approximately 1150 hours of solar exposure). The third set of specimens, SL-4, experienced no SMRCS exposure, being deployed after docking and recovered before undocking, but still exhibited the effects of contamination. The three sets of returned thermal control coatings along with a set of preflight specimens are shown in Figure 6. A set of preflight and recovered SL 1/3 Polymeric Films Strips are shown in Figure 7. Note the shading or shadowing effect of the retainer spring on the observed coloration (contamination).

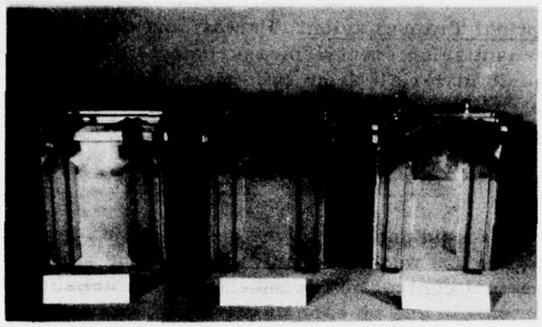

Figure 5. DO24 Return Containers

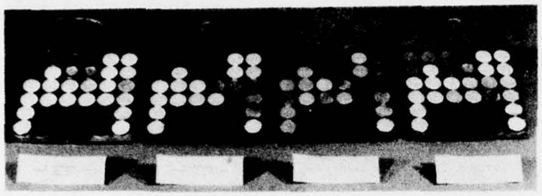

Figure 6. DO24 Thermal Control Specimens and Trays

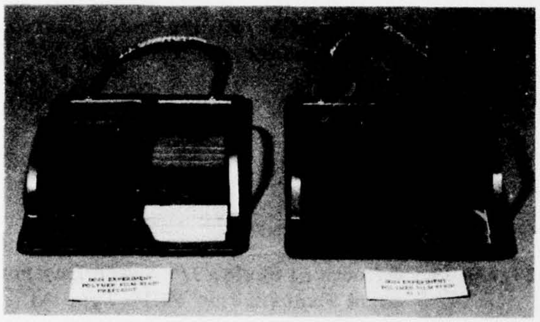

Figure 7. DO24 Polymeric Film Strip Trays

II. Optical Measurements

Reflectance/Absorptance. The thermophysical properties of each of the individual thermal control coating specimens were measured pre and post test using a Beckman DK-2A spectroreflectometer equipped with a Gier-Dunkle integrating sphere (Model SP220). A magnesium oxide coating on the integrating sphere wall was used as the standard. Solar absorptance (α_s) values were obtained from the reflectance curves from 0.2 to 2.5μm. Solar absorptance data from ten selected representative materials of the twenty seven actually flown are given in Table 1. In general, all of the SL 1/2, SL 1/3 and SL-4 thermal control materials exhibited gross changes in solar absorptance which can be accounted for only on the basis of a combination of contamination plus solar degradation. The relatively large changes in solar absorptance measured versus changes measured in laboratory in situ exposures are given in Table 2. Representative reflectance curves are shown in Figures 8, 9, 10 and 11. Predicted solar absorptance changes indicated in Table 2 were based upon in house in situ exposure measurements or values published in the literature (1), (2), (3), (4), (5), (6), (7).

Emittance. A Gier-Dunkle Model DB-100 Portable Infrared Reflectometer was used to measure the total normal reflectance of all of the DO24 thermal control materials both pre- and post flight. The theory employed and the equipment description has been described in detail by Nelson, et al(8). The data obtained from this instrument can be converted to total normal emittance by subtracting the measured reflectance from unity. Differences be-

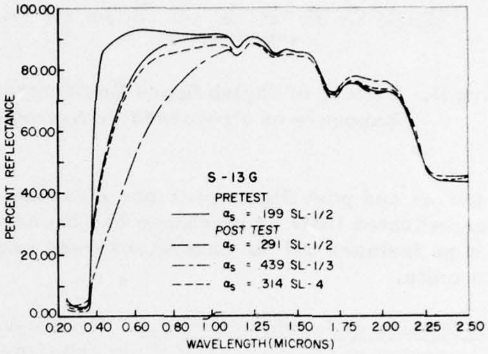

Figure 8. Effects of Skylab Space Environment Exposure on S-13G

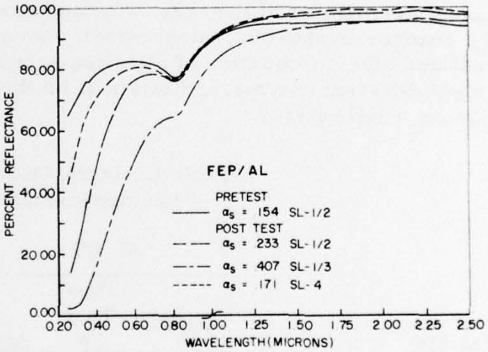

Figure 9. Effects of Skylab Space Environment Exposure on FEP/Al

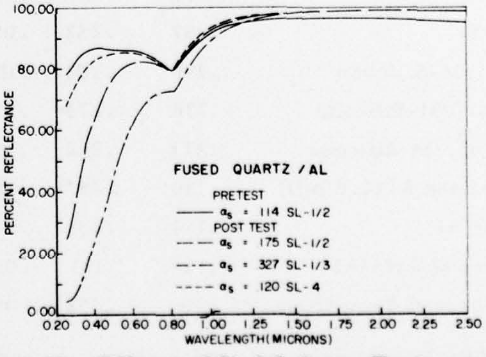

Figure 10. Effects of Skylab Space Environment Exposure on Fused Quartz/Al

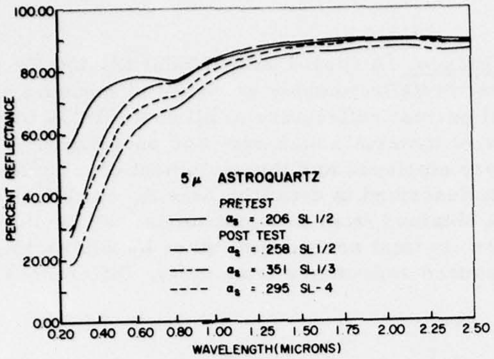

Figure 11. Effects of Skylab Space Environment Exposure on Processed 5μ Astroquartz

tween pre- and post flight emittance measurements indicated little or no change had occurred and in no instance did the change observed exceed 0.015 units.

FMIR Spectra of Polymeric Films. Post test FMIR spectra of the recovered flight experiment polymeric film specimens were obtained using a Perkin Elmer 621 infrared spectrophotometer with a 45° KRS-5 FMIR prism (Figures 12 and 13). A complete description of the evaluation and analysis of the changes in physical, mechanical, electrical, optical and other properties of all three sets of the eight different polymeric films will be the subject of a later paper.

Optical Transmission. Pretest and post test transmission spectra measurements of the polymeric materials from 0.25μm to 2.5μm were determined using a Beckman ratio recording spectrophotometer (Figure 14).

III. Auger and SIMS Analysis

One gold and one silver coated quartz oscillator crystal were mechanically mounted on a thermal control button substrate and included in the specimens on each of the thermal control coating trays to serve as a possible contamination monitor during the exposure of the various specimen trays. The metallized surface of the specimen, except where it was covered by a narrow metal retaining ring was exposed. The recover-

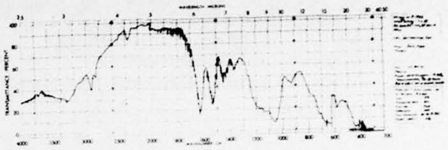

Figure 12. Effects of Skylab 1/3 Space Environment Exposure on Nylon 6/6

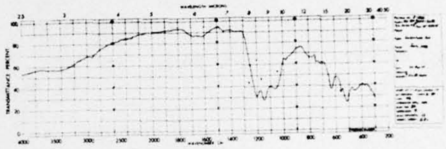

Figure 13, Effects of Skylab 1/3 Space Environment Exposure on FEP (Type A)

Table 1. DO24 Thermal Control Coatings Experiment Thermophysical Properties - Solar Absorptance

	SL 1/2			SL 1/3			SL-4		
Materials	Pretest α	Post Test α	Δα	Pretest α	Post Test α	Δα	Pretest α	Post Test α	Δα
S-13	.239	.330	.091	.214	.498	.284	.218	.335	.117
S-13G	.199	.291	.092	.202	.439	.237	.223	.314	.091
Z-93	.157	.252	.095	.155	.334	.179	.154	.160	.006
SiO_2/M-Silicone	.190	.302	.112	.203	.405	.202	.209	.357	.148
Eu_2O_3/M-Silicone	.170	.275	.105	.164	.417	.253	.164	.287	.123
$^{\alpha}Al_2O_3$/M-Silicone	.111	.262	.151	.114	.395	.281	.153	.326	.173
Anodized Al (0.5 mil)	.150	.281	.131	.153	.426	.273	.156	.360	.204
FEP/Al	.154	.233	.079	.161	.407	.246	.158	.171	.013
Fused Quartz/Al	.118	.175	.057	.119	.327	.208	.114	.120	.006
Processed 5μ Astroquartz	.206	.258	.052	.231	.351	.120	.260	.242	.018

NOTE: Reporting data to three places is used to denote trends in the data, not accuracy of measurement techniques.

ed silver coated quartz crystal oscillators were greatly discolored and had undergone extensive chemical degradation. The silver coating on the SL-4 recovered crystal was, in fact, no longer conductive and appeared almost translucent when viewed from the backside. Attempts to determine the contaminant layer thickness by the change in pre and post frequency shifts gave questionable results. The silver layer under the metal retaining ring was still visible when viewed from front or back. On SL 1/2 and SL 1/3 the silver layer in the exposed portion of the sample was still visible when viewed from the back. One observer noted that this difference may reflect a change in the chemical nature of the contaminant species present between SL 1/2 and SL 1/3 and SL-4.

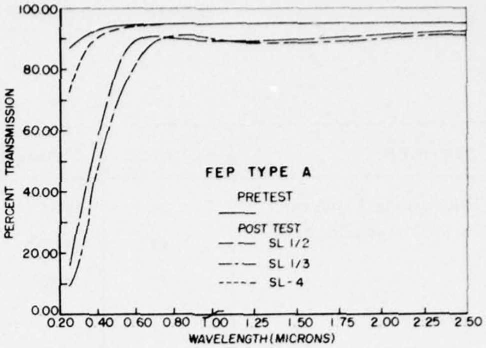

Figure 14. Effects of Skylab Contamination on Transmission of FEP (Type A)

The contaminant layer on the quartz oscillators were analyzed using Auger electron spectroscopy and secondary ion mass spectroscopy techniques. The Auger analysis, as given in Table 3, indicated the presence of a contaminant layer consisting of materials containing principally silicon, oxygen and carbon plus other minor constituents. Contaminant thicknesses were estimated using Auger sputtering techniques. Sputtering rates for the species defined are best estimates due to the possible/probable non homogeneous nature of the materials comprising the contaminant layer. Auger analysis of the area under the retaining ring indicated only traces of material. SIMS analysis verified the presence of Si+, SiO+ and SiOH+ species. There is no evidence for the presence of any other than minor traces of nitrogen containing materials, expected contaminants from the reaction control system, or for the presence of any methylsilicone groups or fragments. Presence of the latter were predicted to be the major contaminants for the DO24 experiment as a result of the outgassing from the S-13G thermal control coating used on the back side of the ATM solar panel. The backside of this panel presents the best line of sight contaminant source for DO24. Efforts to determine the nature of the contamination by mass spectroscopy gave negative results and indicated that the material was essentially non volatile.

TABLE 2

SOLAR ABSORPTANCE CHANGES AS FUNCTION OF ULTRAVIOLET RADIATION

Sample	Material	SL 1/2 $\Delta\alpha$	500 EUVSH $\Delta\alpha$	SL 4 $\Delta\alpha$	1000 EUVSH $\Delta\alpha$	SL 1/3 $\Delta\alpha$
1	S13	0.091	---	0.117	0.08	0.284
2	S13G	0.092	0.02	0.091	0.02	0.237^e
3	Z93	0.095	---	0.006	0.01^b	0.179^f
4	SiO_2/M Silicone	0.112	---	0.148	0.076	0.202
5	Eu_2O_3/M Silicone	0.105	0.04^a	0.123	0.040	0.253
6	αAl_2O_3/M Silicone	0.151	---	0.173	0.090	0.281
7	Anodized Al (0.5 mil)	0.131	0.09^a	0.204	0.18^c	0.273
8	FEP/Al	0.079	0.04^a	0.013		0.246
9	Fused Quartz/Al	0.057	<0.01	0.006	0.006^d	0.208
10	Processed 5μ Astroquartz	0.052	---	-0.018	0.036	0.120

a. 300 EUVSH
b. 800 EUVSH
c. 700 EUVSH
d. 1510 EUVSH
e. $\Delta\alpha$ of 0.10 after 2000 EUVSH
f. $\Delta\alpha$ of 0.03 after 2000 EUVSH

NOTE: Reporting data to three places is used to designate trends in the data, not accuracy of measurement techniques.

Table 3. Auger Analysis of Quartz Crystal Oscillators

Specimen	SL 1/2		SL 1/3		SL-4	
	Element	Deposit (Å)	Element	Deposit (Å)	Element	Deposit (Å)
Gold coated quartz crystal oscillator	Si	1700	Si	250	Si	100
	O	1700	O		O	150
	C	700	C	40	C	
Silver coated quartz crystal oscillator	Si	2450	Si	75	Si	100
	O	2450	O	75	O	100
	C	700	C		C	
			N	Trace		

IV. Coating Materials Selection and Preparation

The rationale for the selection of the thermal control materials for the DO24 experiment consisted of the following: (1) The materials should be of current interest; either being used by the aerospace community or promising materials under research and development. (2) The material should cover the broad spectrum of thermal control materials with emphasis on the solar reflectors or low α_s/E white paint type materials. (3) For purposes of correlation analysis, the selection should include well characterized materials with respect to both ground based simulation testing and other flight tests. (4) The selection should include materials which were expected to be both stable and unstable to the near earth environment. The unstable materials were to have known degradation modes in different regions of the spectrum and effected to varying degrees by atmospheric related optical recovery.

As indicated earlier the results from the analysis and evaluation of only ten of the twenty seven thermal control coating materials and only two of the eight polymeric film materials actually flown are presented here. Data from the other materials have been obtained and the results are consistent with those presented.

S-13 was prepared using ZnO obtained from New Jersey Zinc SP500 and GE RTV 602 as the binder. Five mil coatings were prepared by AFML in accordance with NASA SP-5014.

S-13G was formulated, processed and applied by IITRI in accordance with IITRI Report U-6053-5-7.

SiO_2/M-Silicone was prepared using University of Pennsylvania AF-C-SiO_2-C2 and GE RTV 602 as the binder.

Z-93, A ZnO in Potassium Silicate was formulated, processed and applied by IITRI in accordance with IITRI Report C-62027-16.

Eu_2O_3 /M-Silicone was prepared using AFML silicate coated pigment in GE RTV 602.

αAl_2O_3 /M-Silicone was prepared using Martin Marietta AF-C-Al_2O_3-4052 pigment in GE RTV 602.

Anodized Al (0.5 mil) was prepared using processed 1199 Aluminum and bonded onto a Skylab specimen button with Eccobond Epoxy Type 57C.

FEP/Al composite was supplied by G. T. Schjeldahl Co., type G400900. The composite was bonded to substrates using 3M's No. 465 adhesive transfer tape.

Fused Quartz/Al is an aluminized Corning 7940 quartz prepared by Optical Coating Laboratory, Santa Rosa, California.

Processed 5 μ Astroquartz is a satin weave fabric constructed from 300 2/0 Astroquartz yarn. Fabric was bonded to substrate by means of a 1 mil film of GE's SR 585 silicone adhesive.

V. Results and Discussion

Based upon the visual observation of the returned DO24 specimens as well as the results of the thermooptical property measurements it became obvious that the DO24 experiment had become a prime Skylab environmental contamination experiment rather than a thermal control coatings optical property degradation experiment. From in orbit Skylab exterior photographs it appears that the contamination experienced by DO24 is localized to an area on the EVA side of the MDA extending up to and including the DO24 area and also the under-side of the ATM solar power panel and ATM structure in this immediate area as shown in Figure 15. Considerable effort has been expended in an effort to identify the nature as well as the source of the contaminants.

Based upon the initial visual observations of the returned DO24 SL 1/2 and SL 1/3 return containers it was obvious that the DO24 specimens had become badly contaminated during exposure in space. The clear "shadow" patterns on the return containers and those observed later upon opening the containers on the thermal control coating and polymeric film trays gave a clear indication of the excessive contamination and the degree to which it had been degraded by solar exposure. Sharpness of the patterns is evidence of the excellent degree of solar orientation that was maintained by Skylab during the solar inertial portions of the missions.

Examination of the reflectance spectra of the S-13G, FEP/Al, Fused Quartz/Al and Processed 5 μ Astroquartz clearly indicate that the degradation observed is occurring in the ultraviolet and visible portion of the spectra, 0.2 μm to 0.72 μm, there being little or no evidence of any damage in the 1.0 to 2.5 μm region as shown in Figures 8, 9, 10, and 11. The spectra of the other samples exhibited the same features.

From Table 2 it is apparent that all ten of the thermal control coating materials exhibited a much higher increase in absorptance than would be predicted based upon laboratory in situ simulated solar exposures. S-13G, representative of the current state-of-the-art ultraviolet stable thermal control paints had a solar absorptance some four to ten times higher than that predicted for SL 1/2 and SL-4 and ten times higher than for SL 1/3. The ultraviolet stable Z-93 and Eu_2O_3/M-Silicone exhibited similar behavior. These results are consistent with the presence of an ultraviolet unstable contaminant layer on the surface which degrades to a yellow to golden brown color.

The S-13, SiO_2/M-Silicone, $^{\alpha}Al_2O_3$/M-Silicone and Anodized Al (0.5 mil) coatings are more sensitive to ultraviolet degradation and exhibited correspondingly larger increases in absorptance, the measured degradation being a combination of the contaminant degradation plus substrate coating degradation.

FEP/Al and Fused Quartz/Al are representative of the very ultraviolet stable, series emittance, or second surface mirror type coatings. The Processed 5 μ Astroquartz is representative of materials used for shrouds and micrometeorite shields. These materials would be not expected to exhibit any appreciable degree of degradation due to ultraviolet exposure but all were apparently significantly degraded. Again these results are consistent only with the presence of an ultraviolet unstable surface contaminant. Because of the significantly higher available surface area of the Astroquartz material the contaminant depositing on this material is in effect diluted and the apparent degradation in absorptance is lower than that observed on the minimum surface area, more concentrated contaminant mirror type coatings. The decrease in absorptance noted for the Astroquartz in SL-4, Table 2, is the result of little or no degradation in the thermal control coating measured relative to the reference magnesium oxide sphere coating which was not replaced throughout the pre and post flight measurements and which gradually degraded with the prolonged use. The slightly higher degree of absorptance change for S-13G in SL-4 versus SL 1/2 is considered to be a result of the combined contaminant degradation plus a greater contribution from the degradation of the S-13G due to the longer period of solar exposure. This effect is more apparent in the S-13, SiO_2/M-Silicone and Al_2O_3/M-Silicone specimens. A complete analysis of the SL-4 data separating ultraviolet contamination and substrate coating degradation effects will be reported at a later date.

The lack of any appreciable changes in emittance values in the infrared supports the thesis of a thin, ultraviolet degradable contaminant layer.

Analysis of the FMIR spectra of the 5 mil polymeric film materials showed two noticeable effects. The spectrum of each film was qualitatively similar to the spectrum of stock specimens from the original pretest materials, although the intensity of the absorption bands were decreased for each of the film materials. This is considered indicative of the thin film of contamination deposited on the polymeric films. The other effect was an absorption band appearing in each spectrum at about 1050-1100 cm^{-1} which could be attributed to a siliceous material. Post test FMIR spectra of Nylon 6/6 and FEP Type A are representative of the eight polymeric materials. Nylon 6/6 post test spectra exhibited a new absorption band at 1250 to 1000 cm^{-1} with a maximum at about 1060 cm^{-1} resembling the KBR spectrum of silica gel, SiO_2XH_2O as shown in Figure 11. The spectrum of FEP Type A exhibited bands at 1060 cm^{-1} and 450 cm^{-1} not attributable to the polymeric material but which are also observed in the spectrum of silica gel as shown in Figure 12. Relative intensities of the absorption bands indicates that the recovered SL 1/3 polymeric materials has a significantly higher concentration of a contaminant with this chemical functionality than the SL 1/2 polymeric specimen. The recovered SL-4 polymeric materials appear to have a lower concentration of contamination than the SL 1/3 polymeric materials. This is consistent with the duration of flight exposure and the possible reduction in concentration of residual contamination during the final mission period.

Significant changes in the ultraviolet transmission of the polymeric films was observed. The FEP Type A is representative of the polymeric

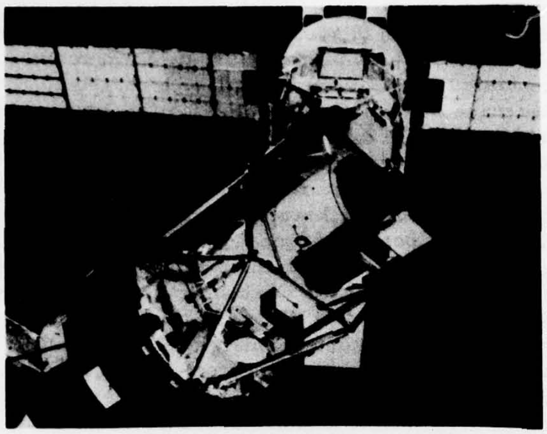

Figure 15. Contamination of EVA, MDA and DO24 Areas

materials and because of its original high transmission in the ultraviolet the presence of a suspected contaminant surface layer with an absorption edge at 0.6 microns not present in the original material is clearly shown in Figure 13. Degradation of such a contaminant layer by ultraviolet is consistent with the changes in reflectance/absorptance observed for the thermal control coating materials shown in Figures 7, 8, 9, and 10. Other experiments aboard Skylab have also reported (9) a lack of data in the ultraviolet, below 111A, which could be accounted for by the presence of an ultraviolet absorbing contaminant layer.

Visual observations of the flight hardware and measured changes in reflectance and transmission spectra indicate the presence of a layer of essentially uniform contaminant over all exposed surfaces of the experiment. The shadow patterns indicate that the contaminant was degraded and essentially fixed by the solar radiation. Absence of any noticeable amount of contaminant under the hold down ring of the metallized oscillator crystal indicates that the contaminant may have been mobile, able to deposit and reevaporate or migrate along the surface unless irradiated and fixed by solar radiation. The measured decrease in contaminant thickness found between SL 1/2 and SL 1/3 is in accord with a volatile contaminant which can reevaporate after initial deposition unless it is fixed by solar radiation. The increase in observed optical degradation is the result of further degradation and color formation in the nonvolatile fixed contaminant.

The Auger and SIMS analysis in combination with other results and observations also point toward a volatile silicon and oxygen containing contaminant. Absence of any carbon to silicon fragments in the SIMS analysis, the lack of any C-methyl in the mass spectroscopy analysis and the evidence for the presence of SiO bands in the FMIR similar to those found in silica gel also point to volatile SiO containing contaminants which can undergo volatilization and condensation and in the presence of solar radiation to give a nonvolatile, ultraviolet unstable siliceous material.

VI. Contamination Hypothesis

Based upon the results and data gathered to date the following contamination hypothesis is offered to explain the observed results and to account for the localized contamination noted in the DO24, MDA and ATM area.

During the manned phases of each of the Skylab missions leakage of the primary cooling loop working fluid, Coolanol-15, a volatile silicate ester was noted. The location of the leak has not been determined, but appears to have occurred in the EVA quadrant area. In fact, loss of material was such that resupply and recharging of the coolant loop was necessary and was accomplished by the SL-4 astronauts. A leak in the secondary loop has also been reported. Contact of the silicate ester coming from a leak in the primary coolant loop with the external surfaces of the DO24 experiment area is postulated. In the presence of the solar energy and specifically in the presence of water vapor, contained in the external Skylab environment, this material would undergo vapor or surface phase hydrolysis to give an essentially non volatile hydrolysis product. The volatile alcohol by-product would be lost by vaporization. This initial hydrolysis product would through further stepwise hydrolysis, condensation, and loss of alkoxy groups, eventually be transformed into a non volatile impure silica gel like material. Impure, nonstoichiometric silicon-oxygen materials of this nature are known to undergo ultraviolet degradation and color formation from a clear, golden yellow to a deep brown.(10) These materials similarly display an ultraviolet absorption edge near 0.6 microns. In the course of the combined hydrolysis/radiation damage process the contaminant might be expected to pass through an intermediate phase wherein the material might be free to migrate about the surface. However, under the influence of the solar radiation the exposed material would undergo more rapid reaction with the result that contaminant build up would occur in these areas exposed to the solar energy as material migrated from shadowed into exposed areas and give a fixed colored contaminant pattern. Unexposed areas would, therefore, have a much thinner layer of contamination and in the absence of radiation would not be discolored. The observed Auger analysis, visual observations, and analytical results are in accord with this proposed contamination scheme. The lesser degree of contamination/optical property degradation observed on the SL-4 thermal control coatings is in accord with the lower rate of coolant fluid leak observed during that portion of the Skylab mission. Due to a finite vapor pressure, reevaporation, and the degrading effects of solar radiation one would not expect to find Coolanol-15 per se on any of the exposed surfaces of DO24.

Preliminary experiments to investigate and possibly substantiate this hypothesis have been initiated in the laboratory.

It is felt that the results observed are not consistent with a contamination scheme in which the primary contaminant is volatile methylsilicone outgassing products from S-13G paint on the backside of the ATM solar array. Such a scheme would only be consistent if a radiation induced demethylation of the methylsilicone could be shown to occur.

VII. Conclusions

Contamination control on future manned space flights must receive special attention in order to prevent loss of valuable data.

Localized contamination effects from multiple and varied sources may be present in large space systems which do not integrate directly into an overall contamination model and must be considered individually.

A localized Coolanol contamination hypothesis has been proposed to explain the results observed on the Skylab DO24 Experiment.

Continued analysis and evaluation of the recovered DO24 Experiment samples will provide further significant information relative to the nature and effects of contamination on this as well as other Skylab experiments.

The separation of contamination from solar radiation optical degradation effects on the various thermal control coatings flown on SL-4 are anticipated.

Solar radiation exposure degradation data from the first two sets of thermal control coating samples flown and recovered on the Skylab DO24 experiment were largely compromised by excessive contamination but have provided significant information relative to the overall Skylab contamination analysis.

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References

1. L. B. Fogdall and S.S. Cannaday, AFML-TR-70-156, Jul 1970.

2. G. A. Zerlaut and F. O. Rogers, Proceedings of the Joint Air Force NASA Thermal Control Working Group, 16-17 Aug 1967, AFML-TR-68-198, Aug 1968, p. 529.

3. G. A. Zerlaut, et al, NASA Contract NAS8-5379, Report IITRI-U6002-97, Oct 1971.

4. N. J. Douglas, et al, ASTM, IES, AIAA Space Simulation Conference, Sep 1967, p. 110.

5. NASA-CR-1786, Radiation Effects Design Handbook, Section II, Thermal Control Coatings.

6. B. Linder, Proceedings of the Joint Air Force-NASA Thermal Control Working Group, 16-17 Aug 1967, AFML-TR-68-198, Aug 1968, p. 624.

7. G. R. Cunnington, J. R. Grammer and F. J. Smith, NASA CR-1420, Final Report, NASA Contract NAS-3-7630, Sep 1969, p. 86.

8. K. E. Nelson, E. E. Luedke and J. T. Bevans, Journal of Spacecraft and Rockets, Vol. 3, No. 5, 1966, p. 758.

9. Private Communication.

10. N. J. Broadway, Radiation Effects Handbook, Section 2, NASA-CR-1786, June 1971.