

LDEF MATERIALS OVERVIEW

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SUMMARY

The flight and retrieval of the National Aeronautics and Space Administration's Long Duration Exposure Facility (LDEF) provided an opportunity for the study of the low-Earth orbit (LEO) environment and long-duration space environmental effects (SEE) on materials that is unparalleled in the history of the U. S. Space Program. The 5-year, 9-month flight of LDEF greatly enhanced the potential value of all materials on LDEF to the international SEE community, compared to that of the original 1-year flight plan. The remarkable flight attitude stability of LDEF enables specific analyses of individual and combined effects of LEO environmental parameters on identical materials on the same space vehicle. NASA recognized this potential by forming the LDEF Space Environmental Effects on Materials Special Investigation Group (MSIG) to address the greatly expanded materials and LEO space environment analysis opportunities available in the LDEF structure, experiment trays, and corollary measurements so that the combined value of all LDEF materials data to current and future space missions will be addressed and documented.

This presentation provides an overview of the interim LDEF materials findings of the principal investigators and the Materials Special Investigation Group. These revelations are based on observations of LEO environmental effects on materials made in space during LDEF retrieval and during LDEF tray deintegration at the Kennedy Space Center, and on findings of approximately 1.5 years of laboratory analyses of LDEF materials by the LDEF materials scientists. These findings were extensively reviewed and discussed at the MSIG-sponsored LDEF Materials Workshop '91. The results are presented in a format that categorizes the revelations as "clear findings" or "obscure preliminary findings" (and progress toward their resolution), plus resultant needs for new space materials developments and ground simulation testing/analytical modeling, in seven categories: Materials/Environmental Parameters and Data Bases; LDEF Contamination; Thermal Control Coatings and Protective Treatments; Polymers and Films; Polymer-Matrix Composites; Metals, Ceramics, and Optical Materials; and Systems-Related Materials. The utilization of LDEF materials data for future low-Earth orbit missions is also discussed, concentrating on Space Station Freedom.

In general, the LDEF data is remarkably consistent; LDEF will provide a "benchmark" for materials design data bases for satellites in low-Earth orbit. Some materials were identified to be encouragingly resistant to LEO SEE for 5.8-years; other "space qualified" materials displayed significant environmental degradation. General contamination levels on LDEF were low, but molecular contamination was widespread; LDEF offers an unprecedented opportunity to provide a unified perspective of unmanned LEO spacecraft contamination mechanisms. New material development requirements for long-term LEO missions have been identified and current ground simulation testing methods/data for new, durable materials concepts can be validated with LDEF results. LDEF findings are already being integrated into the design of Space Station Freedom.

INTRODUCTION

The National Aeronautics and Space Administration / Strategic Defense Initiative Organization Space Environmental Effects on Materials Workshop, June 1988, identified and prioritized candidate materials spaceflight experiments needed to validate long-term performance of materials on future spacecraft (reference 1). The highest priority identified by all participants of that workshop was virtually unanimous: The return of the NASA Long Duration Exposure Facility (LDEF) safely to earth, followed by a detailed analysis of its materials to compare with data obtained in previous relatively short in-space exposures and to validate, or identify deficiencies in, ground testing and simulation facilities and materials durability analytical models. As the First LDEF Post-Retrieval Symposium proved (ref. 2), the expectations of the NASA/SDIO Workshop were well founded. The initial in-space and experiment deintegration observations of LDEF at the end of its remarkable flight provided to the LDEF investigators an unparalleled opportunity to define space environment parameters and their long-term individual and combined effects on critical properties of materials for spacecraft applications.

The National Aeronautics and Space Administration Long Duration Exposure Facility (ref. 3) was launched into low-Earth orbit (LEO) from the payload bay of the Space Shuttle Orbiter Challenger in April 1984 (figure 1). It was retrieved from orbit by the Columbia in January 1990 (fig. 2). The 57 LDEF experiments (Table 1) covered the fields of materials, coatings, and thermal systems; space science; power and propulsion; and electronics and optics. LDEF was designed to provide a large number of economical opportunities for science and technology experiments that require modest electrical power and data processing while in space and which benefit from post-flight laboratory investigations of the retrieved experiment hardware on Earth. It was also designed to maintain these experiments in a stable orbital attitude to enable determination of directional effects of the space environment parameters. Most of the materials experiments were completely passive; their data must be obtained in post-flight laboratory tests and analyses.

The 5.8-year flight of LDEF greatly enhanced the potential value of most LDEF materials, compared to that of the original 1-year flight plan. NASA recognized this potential by forming the LDEF Space Environmental Effects on Materials Special Investigation Group (MSIG) to address the expanded opportunities available in studies of the LDEF structure and experiment tray material, which were not originally considered to be materials experiments, so that the value of all LDEF materials data to current and future space missions would be assessed and documented. Similar Special Investigation Groups were formed for the disciplines of Systems, Ionizing Radiation, and Meteoroids/Debris.

This paper provides an overview of the interim LDEF materials findings of the Principal Investigators and the Materials Special Investigation Group. These revelations are based on observations of LEO environmental effects on materials made in-space during LDEF retrieval and during LDEF tray deintegration at the Kennedy Space Center, and on findings of approximately 1.5 years of laboratory analyses of LDEF materials by the LDEF materials scientists. These findings were extensively reviewed and discussed at the MSIG-sponsored LDEF Materials Workshop '91 (ref. 4). The results are presented in a format which categorizes the revelations as "clear findings" or "obscure preliminary findings" (and progress toward their resolution) in seven categories: Environmental Parameters and Data Bases; LDEF Contamination; Thermal Control Coatings and Protective Treatments; Polymers and Films; Polymer-Matrix Composites; Metals, Ceramics, and Systems-Related Materials. Resultant needs for new space materials developments and ground simulation testing/analytical modeling are enumerated. The utilization of LDEF materials data for future low-Earth orbit missions is also discussed, concentrating on Space Station Freedom. Some directions for continuing studies of LDEF materials are outlined.

THE LDEF MISSION, SCIENCE TEAM, AND MSIG

LDEF was a free-flying, 12-sided cylindrical structure, approximately 30-feet long and 14-feet in diameter (ref. 3). It had the capability to accommodate 86 experiment trays, most of which were 50-inches long and 34-inches wide. LDEF had no central power or data systems and no capability to transmit data to Earth while in orbit. Thus, experiments which took data during the flight had power systems (batteries) and data recorders on the inside of their trays, designed for 1-year of operation. Despite the obvious constraints of such arrangements and the much longer flight than planned, these data systems worked exceedingly well in almost all cases. The in-flight data recovered from the data tapes was of high quality. The skeletal structure of LDEF weighed approximately 8000 lb; the combined structure and experiment weight launched into orbit was approximately 21,400 lb. The initial orbit was nearly circular, at 257 nautical miles, with a 32° inclination. General information concerning the flight period, experiments, and participants is shown in Table 1 and further detailed in refs. 2 and 3.

The orientation of the spacecraft with respect to the Earth during the mission is shown in figure 3. Values of key parameters of the low-Earth orbit environment which LDEF encountered are listed in Table 2. This orientation was sustained throughout the flight, from release by the Shuttle Challenger Payload Bay Remote Manipulator System to retrieval by the Columbia Remote Manipulator. Precision placement (release) into its orbit, plus a design which included gravity gradient stabilization, careful consideration of mass distribution, and a passive viscous magnetic damper system were the key factors in orientation maintenance. The remarkable flight attitude stability of LDEF (within less than 1° of movement in yaw, pitch, or roll) enables specific analyses of various individual and combined effects of LEO environmental parameters on identical materials and systems on the same space vehicle. NASA recognized this potential by forming four LDEF Special Investigation Groups (SIGs) (Table 1) to address the greatly expanded materials and LEO space environment parameter analysis opportunities available in the LDEF structure, experiment trays, and corollary measurements.

The LDEF Science Team management structure is shown in figure 4. The LDEF Science Office is located in the Materials Division of the NASA Langley Research Center; it is responsible for coordination of all LDEF experiment data, supporting data, and data generated by the SIGs.

The LDEF Environmental Effects on Materials Special Investigation Group (MSIG) was chartered to investigate the effects of the long-term LEO exposure on structure and experiment materials, which were not originally planned to be test specimens, and to integrate the results of these investigations with data generated by the Principal Investigators of the LDEF experiments into the LDEF Materials Data Base. The LDEF Materials Data Analysis Workshop (ref. 6) addressed the plans resulting from that charter. MSIG membership includes approximately 25 technical experts in the fields of atomic oxygen, radiation, contamination and other space environment effects on materials. Researchers with experimental and analytical experience in chemical, mechanical and physical properties of spacecraft materials and data basing are included. Several members provide liaison with the other LDEF Special Investigation Groups. The members represent technical laboratories and organizations throughout the United States, and laboratories in Canada and Europe. A number of MSIG members are also Principal Investigators of LDEF experiments.

Initial considerations of MSIG related to significant issues concerning space environmental effects on materials and the data potentially available from LDEF analyses to address these issues, is outlined in fig. 5. The general plan for MSIG operations is as follows:

- Systematically examine identical materials in multiple locations around LDEF to establish directionality of atomic oxygen erosion, ultraviolet radiation degradation, contamination, etc.
- Analyze selected samples from LDEF "non-materials" experiments and samples contributed from LDEF materials experiments.
- Establish central materials analysis capability:
 - Standardized, non-contaminating procedures for sampling / shipping / archiving
 - Uniform test / analysis procedures and ground simulation tests
 - Basis for assessment of laboratory-to-laboratory variations in materials data
- Focal point for coordination of all LDEF materials analyses:
 - Sponsor LDEF materials workshops / symposia
 - Generate unified LDEF Materials Data Base, including data from principal investigators, supporting data groups, and special investigation groups

The Boeing Defense and Space Group Laboratories in Seattle and Kent, Washington were selected as the MSIG Central Analysis Laboratory by the MSIG, shortly after its formation in 1989.

The LDEF Materials Workshop '91 (ref. 4) was scheduled to elucidate, compare, and assess the results of the initial 1.5 years of observations and laboratory analyses of LDEF materials by the LDEF materials scientists. Figure 6 outlines the Workshop objectives and the materials disciplines addressed. The results in each discipline were extensively discussed and reviewed by technical teams consisting of technologists from the International Space Materials Community, with various degrees of familiarity with LDEF. Their findings are detailed in ref. 4. The next section of this paper (LDEF Materials Findings) includes information generated in recent space environmental effects on materials modeling studies and data-basing activities, information presented to and generated during the workshop, plus information based on previous observations of LEO environmental effects on materials made in-space during LDEF retrieval and during LDEF tray deintegration at the Kennedy Space Center in 1990 (See, for example, ref. 2).

LDEF MATERIALS FINDINGS

In this section, 9 categories of LDEF materials results are presented in a format which classifies them as "clear findings" or "obscure preliminary findings". Many of the clear findings were made during the initial months after LDEF retrieval, as the LDEF trays were de-integrated from the structure for shipment to the laboratories of the principal investigators, but others periodically appear as the PIs and the MSIG investigators report on their continuing studies. Currently, the LDEF investigators are quantifying and modeling the clear findings and defining the phenomena involved in the obscure findings. In a previous, complementary report (ref. 5), this author has summarized these findings with examples of observations from a number of experiments and from the materials on the LDEF structure. In the present report, examples of

specific findings are illustrated with interim results of laboratory material analyses which have been in progress since June of 1990. The status of the resolution of the obscure findings is also addressed. The October 1992 Huntsville Alabama Conference on "LDEF Materials Results for Spacecraft Applications" (ref. 7) was the most recent update on LDEF Materials; ref. 8 is a general exposition of the applicability of LDEF results.

Environments and Data Bases

Table 3 is such a listing for the environments encountered by the materials on LDEF and the considerations for LDEF materials data basing. Most of the clear findings were illustrated and discussed in refs. 2, 4, and 5 and will not be repeated, or only briefly summarized here.

However, new information has emerged in some cases. Perhaps the most significant regards the general classification of the degree of LDEF contamination. LDEF had been regarded by many observers as a "dirty" spacecraft, because of the visible molecular and particulate contaminants on its external surfaces during retrieval and deintegration. That perjorative designation may have been due to the unfamiliarity of these observers with the appearance of other spacecraft after extended exposures in orbit, since very few spacecraft have been returned to earth undamaged. At the October 1992 at Huntsville Conference on "LDEF Materials Results for Spacecraft Applications", two respected authorities in spacecraft contamination expressed an opposing view. Based on their recent findings, Dr. Wayne Stuckey of the Aerospace Corporation and Dr. Alain Paillous of CERT - CNES asserted that LDEF may be one of the cleaner spacecraft flown in recent years. Dr. Stuckey illustrated that comment with fig. 7, which shows the increase in solar absorptance for fused silica mirrors as a function of time in orbit (ref. 9). Fused silica is not degraded by LEO environmental parameters; changes in absorptance are considered to be due to contamination. LDEF mirror absorptance increases were equivalent to those observed on SCATHA, which had stringent cleanliness requirements and has generally been regarded as having very low levels of contamination during its flight.

Since the publication of ref. 5, atomic oxygen fluence calculations have been further refined. Fig 8 shows the revised AO fluences for each LDEF tray on the 12 side rows, the earth-facing end, and the space-facing end. The highest AO fluence was 9.0×10^{21} atoms/cm², on the LDEF leading edge, about 8.1° off row 9 (towards row 10). Experiment trays on the side rows experienced different AO fluences because of the 8° ram vector angle. The Earth and Space end AO fluences were more than one order of magnitude lower than the ram fluence. The lowest AO fluence on LDEF was 2.7×10^3 atoms/cm², between rows 3 and 4. During the LDEF flight, the total fluence for rows 2 through 4 was in the same order of magnitude as the lowest fluence listed in fig. 8. However, during the retrieval mission, after LDEF was safely clamped in the shuttle payload bay, an "anomaly" occurred when LDEF rows 1 through 3 (which faced out of the bay) were inadvertently subjected to atomic oxygen at the retrieval altitude for approximately 15 minutes. That inadvertent exposure raised AO fluence from values on the order of the 10^3 to 10^{17} atoms/cm² for the experiment trays on those rows.

It has become clear that geometric details of the exposed surfaces in conjunction with their flight attitude are keys to understanding some of the space environmental effects that occurred differently on different parts of experiment trays. Such effects as atomic oxygen atoms which do not "stick" to a surface but deflect onto another surface and react with it, and partial shadowing of atomic oxygen and solar ultraviolet radiation on exposed surfaces will affect fluences of these environmental factors. MSIG is developing analysis schemes to account for these "microenvironments". The methodology is outlined in refs. 10 and 11; initial results were

presented in those references; further results were presented by Dr. Roger Bourassa at the October 1992 at Huntsville Conference. The objective and general scope of the microenvironments modeling task for atomic oxygen is shown in fig. 9. The outline of the AO exposure models is given in fig. 10 and Fig. 11 shows the orientation of surfaces on LDEF that were studied. The following discussion (and figures 12 and 13) focus on case number 2, tray B7 FEP Teflon thermal blanket edge shown in fig. 11. Predicted FEP surface recession from the model is seen in the plot of silvered Teflon blanket thickness as a function of the distance from the blanket edge, fig. 12. Fig. 13 shows a cross-section sketch of the geometry involved and the comparison of the predicted Teflon blanket thickness changes due to AO erosion with those experimentally measured on two specimens. The microenvironments model shows very good correlation with the experimental data and holds promise as a very useful tool for quantitative predictions of environmental effects on spacecraft surfaces in LEO.

As indicated in the "LDEF Mission, Science Team, And MSIG" section of this paper, development of LDEF materials data bases is an important MSIG responsibility. The LDEF Materials Workshop '91 participants clearly indicated their expectations of two kinds of materials data bases: one for the spacecraft design community and another for the space environmental effects on materials research community (ref. 4). Potential users of these data bases have requested early release of the interim data. In order to satisfy these needs, MSIG is concentrating on two electronic data basing activities. Early data releases are being accomplished by means of the "mini-databases" described in ref. 12. Fig. 14 indicates the mini-data bases which are currently available through Dr. Gary Pippin of Boeing Defense and Space Group, P. O. Box 3999, M. S. 82-32, Seattle WA 98124. The second MSIG electronic data basing activity is underway at the NASA Marshall Spaceflight Center as the LDEF Materials Database on MAPTIS - the NASA Materials and Processes Technical Information System, as described in ref. 13. Quoting from that reference, this database is intended to encompass the "wide variety and vast quantities of materials data being generated by the MSIG members and other LDEF investigators". A preliminary version of the LDEF Materials Data Base Menu is shown in fig. 15. Completion of this database will not be accomplished for several years, but a preliminary version was released to the LDEF community in June of 1992. Continuous updating is in progress. A third LDEF materials data base has been developed for the comprehensive materials and system components on experiment M0003, located on four LDEF trays. This data base, The M0003 Deintegration Observation Record Database, is described in ref. 14, which also contains information for obtaining a copy.

In the lower part of Table 3, the obscure preliminary findings in this category are noted. Some of these findings have been resolved or at least qualitatively explained, while others remain enigmatic. Work in progress should resolve some of the remaining unexplained findings.

LDEF Contamination

Contamination control was not a priority for the LDEF mission. Preflight cleaning procedures were those utilized for any shuttle payload to maintain the cleanliness of the payload bay. As described in the previous section, observers not familiar with contamination levels on other LEO spacecraft initially believed that LDEF had high contamination levels, a belief that was recently disproved. LDEF was actually a "relatively clean" satellite in LEO, compared to other LEO spacecraft (fig. 7).

As low as contamination levels on LDEF were, the contamination was both widely dispersed for some contaminants and quite localized in others, which sometimes exhibited heavy concentrations. Detailed study of residual contaminants is straightforward via visual and spectroscopic surface examination of experiment samples, trays, and structural elements in LDEF archival storage. LDEF provides a unique opportunity to provide a unified perspective of unmanned spacecraft contamination mechanisms in low-Earth orbit. LDEF was the ultimate

witness plate for the shuttle orbiter payload bay. It was a molecular film deposition experiment. LDEF provided data for many potential studies of orbital effects on surface contaminants, both molecular and particulate. LDEF research provides data for validation of current and future contamination monitoring systems for spacecraft. However, current funding limitations severely limit the future progress of LDEF contamination research.

Table 4 is a listing of the clear findings, the obscure preliminary findings and their resolutions, new materials development requirements, and ground simulation testing requirements based on 1.5-years of LDEF contamination studies. Most of the clear findings were illustrated and discussed in ref. 5. The following will concentrate on developing an interim perspective based on these studies.

Although all materials used on the spacecraft structure and experiments were nominally "space qualified", LDEF carried a significant amount of both particulate and molecular contaminants when it was placed in orbit. Fig. 16 is a general overview of the contamination history of LDEF. Figs. 17 through 21 summarize information from a number of sources, including refs. 2 and 4 and 15 through 27. These figures were prepared by E. R. Crutcher and H. G. Pippin for the October 1992 Huntsville Conference (ref. 7). Fig. 17 defines the three categories of LDEF contamination exposures: Pre Flight, On-Orbit, and Post Flight. Fig. 18 categorizes the contamination sources into three classes: those which produce carbon based contamination films, those which produce silicon or silica based films, and those which produce particulate contamination. The widespread "nicotine stain" molecular contamination formation and degradation processes observed on many LDEF surfaces are summarized in fig. 19. On-orbit effects on the LDEF contamination are described in fig. 20. Fig. 21 summarizes these interim LDEF contamination findings.

In the center of Table 4 are listed the initial LDEF contamination findings that were not explained during the initial observations of the retrieved LDEF in 1990. As indicated in the figures and references discussed in the preceding paragraph, the sources of silicon-containing films and the mechanisms of film deposition have been identified and defined in many cases. They can be complex. The contribution of products of atomic oxygen degradation of LDEF materials to the contamination and the quantitative effects of LDEF contamination on analyses for other space environmental effects has not yet been significantly addressed in published LDEF research.

At the bottom of Table 4 are comments on new materials development requirements to avoid, in future spacecraft, the most significant contamination sources found on or in proximity to LDEF. Foremost among these include the development of non-contaminating alternates to the silicones used in spacecraft for adhesives, coatings, and flexible films. Non-contaminating lubricants and polymers are also important spacecraft materials development needs. Ground simulation testing requirements which have resulted from the initial LDEF contamination studies include the re-evaluation of current outgassing criteria and testing methods for selection and screening of materials for long-term (>10-year) missions in LEO.

Thermal Control Coatings and Protective Treatments

Table 5 outlines the interim findings of the LDEF materials studies on thermal control coatings and protective treatments. Most of the clear findings were illustrated and discussed in ref. 5, based on information presented in refs. 2 and 4 and 28 through 41. Additional studies, presented in refs. 42 through 46, have not significantly changed the "clear findings" listed in Table 5, but have quantified some of the effects, correlated LDEF data with ground tests and analyses, and put individual experiment findings into context with each other. An example of such a study is shown in figs. 22 and 23, from ref. 45. Fig. 22 shows a laser profilometer scan along the surface of a polyurethane-based thermal control coating, A276, on LDEF tray D9, where unprotected areas

were exposed to the highest atomic oxygen fluences. Such areas eroded to a depth of approximately 10 μ m (0.4 mils). Fig 23 shows that the solar absorptance of such LDEF leading edge specimens was unaffected, because the surface of the polyurethane binder of the A276 which was being degraded (darkened) by ultraviolet radiation was being eroded away. Fig. 23 also shows the correlation of solar absorptance with solar UV fluence for LDEF trailing edge exposures (low AO fluence) for specimens from various LDEF experiments and MSIG evaluations. The degradation in solar absorptance due to UV darkening of polyurethane is consistent. Also shown in fig. 23 is a ground test correlation line, based on an assumed equivalency of LEO solar fluence with ground test exposures using 40 keV electrons and protons and a scaling factor. This correlation is one of a number of possible ways to utilize combinations of LDEF and ground test data.

These additional studies have also concentrated on analysis of the LDEF data to define trends in coating thermal control properties which will enable prediction of stability of coatings and protective treatments for LEO exposures longer than the LDEF coatings received (such as for those to be used on Space Station Freedom). Fig. 24, from ref. 46, shows a regression analysis using a power law to predict absorptance changes in Z93 white thermal control coatings for 30-year exposures in LEO. This coating promises excellent thermal control property stability, based on the LDEF data.

The obscure findings in Table 5 include a fluorescence shift in surfaces of several LDEF coating specimens. Whereas the unexposed coatings fluoresced in the ultraviolet portion of the spectrum when subjected to UV radiation, the exposed coatings fluoresced in the visible portion of the spectrum (refs. 30 and 42). This phenomenon has been noted previously (see, for instance, ref. 41). The details of the surface chemistry changes for the LDEF specimens have not yet been defined, but studies such as those reported in ref. 42 are making good progress.

Two important coatings, S-13GLO (ref. 33) and black chromium (ref. 45) showed variabilities in their thermal control properties which have not yet been explained; studies continue. The microenvironment analysis methodology, discussed earlier in this paper, may provide avenues to the resolution of such enigmas. The synergistic roles of UV, electron and proton radiation in the atomic oxygen erosion of certain polymeric materials such as FEP Teflon have not yet been quantitatively defined.

New materials development requirements in thermal control coatings and protective treatments for long-term LEO missions are listed in Table 5. Included are thin, transparent silicate overcoats resistant to crazing and alternate sources of pure silicates for coating binders. New processes for application of adhesive-backed Ag/FEP to substrate panels are being developed which show promise of avoiding microcracking. The final item in the new materials category regards the need for a flexible white thermal control coating with demonstrated long-term LEO durability. The PCBT coating developed by the MAP Company in France has shown promise in a 9-month exposure (in a FRECOPA canister) during the LDEF missions and in another short LEO flight (ref. 34). Self explanatory ground simulation testing requirements in the coatings category are also listed in Table 5.

Polymers and Films

Table 6 outlines the interim findings of the LDEF materials studies on polymers and polymer films. Most of the clear findings were illustrated and discussed in ref. 5, based on information presented in refs. 2 and 4 and 47 through 58. Additional studies, presented in refs. 59 through 64, have not significantly changed the "clear findings" listed in table 6, but have modeled some of the effects and explained previous inconsistencies. An example of such a modeling study

is reported in ref. 61, a study of polymer "undercutting" at defects in a protective coating. The atomic oxygen erosion yield at such sites is approximately twice that of an uncoated polymer surface, because of multiple impacts of AO atoms in the undercut cavity. The Monte Carlo model assumptions and parameters were adjusted to reasonably correlate with LDEF results. However, it is interesting to note that assumptions in the model, which accurately predicted ground laboratory "asher" facility simulation test results, did not accurately predict LDEF results.

Detailed chemistry studies of the FEP surfaces of LDEF silvered Teflon blankets (ref. 64) show that atomic oxygen dominated the environmental interactions on LDEF leading edge surfaces, leaving virgin FEP on the surfaces. Beginning at row 6, the interactions transitioned to solar UV dominated interactions on LDEF trailing edge surfaces.

Ref. 59 provides an excellent explanation of a phenomenon which was previously considered to be an inconsistency in LDEF results: Molecular-level effects present in polymer specimens exposed for 10 months in canisters (which were closed during the flight) were no longer present after 5.8 years of exposure. The relative flux ratios of solar UV to atomic oxygen were quite different early in the LDEF mission than they were at the end of the mission. AO erosion at the 10-month point did not "scrub away" the surface material which was affected by UV. Near the conclusion of the mission, AO flux was so high that all UV-affected material was eroded away.

The obscure preliminary findings for polymers and polymer films (Table 6) include higher erosion for some polymeric materials on LDEF than predicted on the basis of previous short-term flight exposure data, the sources of thermal effects, and the degree of confounding of polymer surface analyses due to the molecular contamination. The high erosion rates of some polymers appear to be an example of AO/UV synergism wherein a threshold of UV exposure is reached, after an extended time in orbit, which affects the polymer surface and makes it more susceptible to reactions with atomic oxygen (ref. 5). After that time, the erosion is accelerated, as postulated in ref. 50.

The localized thermal effects noted in some LDEF external regions during the initial inspections of the retrieved spacecraft in 1990 have not yet been fully explained; the microenvironment analysis methodology, discussed earlier in this paper, will probably explain many of these effects. The effects of molecular film contamination on LDEF polymers has not yet been defined in many cases and contributes to the difficulty of analyzing for the effects of the LEO environment on a non-contaminated surface.

Near the bottom of Table 6 is a list of new polymeric material development requirements for durability in long term LEO environments and ground simulation testing requirements based on LDEF polymers and polymer film analyses thus far. No current polymeric material appears to be completely resistant to atomic oxygen and/or UV attack. If such polymers can be developed, they must have the additional attribute of non-contamination of other materials on a spacecraft due to outgassing, reaction products from AO or other LEO environmental parameter interactions, etc. Some suggested avenues for polymer synthesis are noted in the Polymers and Films section of the Panel Discussion Summary in ref. 4. Ground simulation testing requirements, listed at the bottom of Table 6, were also extensively discussed at the workshop. These discussions are also summarized in ref. 4.

Polymer-Matrix Composites

Table 7 outlines the interim findings of the LDEF materials studies on polymer-matrix composites. Most of the clear findings were illustrated and discussed in ref. 5, based on information presented in refs. 2 and 4 and 65 through 71. Additional studies, presented in refs. 72 through 78, have not significantly changed the "clear findings" listed in Table 7, but have quantified and modeled some of the effects and explained previous inconsistencies.

Atomic oxygen impinging on a bare Gr/Ep composite on the leading edge of LDEF eroded 0.0034-inch (on average) of material from the specimen surface, ref. 73. Figures 25 and 26, from ref. 74, indicate the quality of the data. The AO reactivity calculated from these erosion measurements was calculated to be $0.99 \times 10^{-24} \text{cm}^3/\text{atom}$, which correlates with other LDEF data (e.g. refs. 67 and 78) and data from other space experiments (e.g. ref. 79). Correlations such as those made for specimens of polymers, polymer-matrix composites, paints, and metals in ref. 78, and other correlations on areas of LDEF which had widely varying AO fluences, give high credibility to LDEF data and indicate that contamination is not confounding analyses of AO interactions with composites.

Outgassing of LDEF composite specimens, which had been previously shown to be the key factor in dimensional stability of graphite/epoxy composites in space (ref. 67), was modeled; these modeling studies are reported in ref. 77. The model assumptions followed the data trends well, but diffusion constants measured on earth do not result in an accurate prediction of flight data outgassing; further studies are required.

An excellent study of microcracking in LDEF graphite/epoxy composites was reported in ref. 74. A T300/934 panel was divided into areas, one of which was bare and others which had black and white coatings. The thermal histories of these areas are shown in fig. 27; the dashed curve shows that the subsurface thermal cycling temperature range was much smaller than those of the panel areas. Microcrack densities are shown in fig. 28. White coatings, which significantly reduced the thermal cycling temperature range, thus prevented significant microcracking. The bare and black coated portions of the panel had significant microcracks in the 3 outer plies on both outer (exposed to LEO environment) and inner surfaces. AO exposure eroded microcracked areas, even under coatings. Other LDEF experimenters reported composite microcracking (e.g. ref. 75) or showed data indicating that it may have been present (e.g. ref. 76).

The effects of meteoroid and debris impacts on composites were reported in refs. 73 and 74. Many impacts were studied, with the general conclusion that composite material structural integrity was not affected by any LDEF impact. Ref. 73 reported that quartz/phenolic composites exhibited less degradation due to impact and subsequent AO erosion than do Gr/Ep composites. The latter, "...because of their melt/vapor features and fiber weave can serve as an efficient absorber of impacting particle residue..." (ref. 73), compared to impacts on metals, which vaporize the particles, or on fiberglass composites, where fiber fragmentation confounds the studies. This leads to an interesting conjecture that further cross-section studies of LDEF graphite fiber reinforced polymer matrix composites could provide elemental space particles to elucidate the chemical compositions of objects both within and outside the solar system.

The obscure preliminary findings for polymer-matrix composites (Table 7) include effects of contamination on AO erosion rates, explanations for detailed differences in eroded surfaces, and mechanical property degradation differences. The effects of contamination on degradation mechanisms for certain materials and in confounding the analyses of the degradation mechanisms was discussed previously in this report. Although the qualitative understanding is slowly

appearing, quantitative information and modeling have not progressed. This is a fruitful area for further LDEF studies.

Recent studies of surprising differences in AO erosion morphologies and "ash" residues in graphite fiber reinforced composite surfaces were reported in refs. 59 and 74. "Stripes" on the composite surfaces were first illustrated (but the phenomenon was not defined) in ref. 64. Figure 29 (from ref. 74) shows that these stripes or bands are areas of differing surface heights while the schematic in fig. 30 shows that the widths of the bands definitely correspond to graphite fiber tow widths. Detailed chemical analyses reveal sodium and sulfur differences in the different bands, indicating that chemical differences in the fiber/matrix interface (and, thus, possibly, in the matrix and/or fiber tow sizing) provide the explanation for these stripes. Recent studies of the "ash" residue on AO-eroded composites are reported in refs. 59, 73, and 74. The definitive chemical analysis, reported in ref. 59, identifies the ash to be the remnant of sulfates from the DDS curing agents used in epoxy- and polysulfone-matrix composites. Differences in the appearance and quantity of the ash are related to the concentration of the DDS in the specific regions of the AO-eroded LDEF composites being studied.

The obscure preliminary finding of a lack of mechanical property degradation in uncoated LDEF composites, excepting on the leading edge specimens is probably a result of the considerably lower AO fluences on all LDEF surfaces, compared to the leading edge fluence. AO erosion on non-leading edge specimens probably affected the outer polymer layer, but did not reach into the first ply of the composite and did not disbond that ply from the matrix. Given this scenario, mechanical properties would not be affected.

Near the bottom of Table 7 are new materials development requirements for polymer-matrix composites resulting from the LDEF materials studies reported to date. The excellent protection afforded to small polymer specimens by very thin inorganic coatings (see, for example, ref. 5) requires scale-up and verification in tests of full-size parts. Flexible coatings for specialized uses such as springs which must operate in the LEO environment should be developed and verified. Given such development, there is good reason to believe that surface-protected polymer-matrix composites will perform well in structural applications for extended missions in LEO.

Ground simulation testing requirements (bottom of Table 7) for polymer-matrix composites are similar to those noted for other materials categories, including increases in size of specimen areas subjected to atomic oxygen exposures, simultaneous simulation of space environment parameters for synergistic effects, and analytical modeling of such effects. The size limitations for specimens in current facilities may be inadequate for the parts mentioned in the previous paragraph.

Metals, Ceramics, and Optical Materials

Table 8 outlines the interim findings of the LDEF materials studies on metals, ceramics, and optical materials. Most of the clear findings were illustrated and discussed in ref. 5, based on information presented in refs. 2 and 4 and 80 through 94. Additional studies, presented in refs. 62 and 96 through 99, have not significantly changed the "clear findings" listed in Table 8, but have made good contributions in quantification and modeling of some of the effects. Additional studies of LDEF clamps (refs. 96 and 97) continue to document the inherent stability of chromic acid anodized aluminum alloy in the LEO environment, noted in ref. 5. Although the effect is small, it appeared that solar UV incident flux contributed more to a slight (<1%) decrease in emittance than did atomic oxygen (ref. 96). Ref. 97 documented the stable surface chemistry of the clamps and the change in molecular contamination chemistry from organo-silicon (silicone) to inorganic silicon (silicate), due to AO interactions with the contamination film.

Details of the interactions of copper with atomic oxygen were reported in ref. 98. On a thin film sample, 55 nm of Cu was converted stoichiometrically to Cu_2O . The outer surface of that oxide on a solid copper specimen appears to have been hydrated to $\text{Cu}(\text{OH})_2$ after the samples were returned and stored on earth. Copper grounding straps from LDEF indicated the same phenomenon. This is another indication of post-exposure effects in earth storage, which was previously noted for polymeric materials in refs. 53 and 56. The thermal control properties (absorptance and emittance) of LDEF copper grounding straps were reported in ref. 64. For LDEF leading edge exposures, large increases in absorptance correlate with atomic oxygen fluence (fig. 31). On the LDEF trailing edge, where AO fluences were low, absorptance increases were still noted and correlated with solar exposure during the early part of the LDEF LEO exposure (fig. 32). The trailing edge copper specimen increases were of lower magnitude than those in the leading edge specimens. Emittance values were not significantly affected by these environmental parameters.

A detailed study of graphite fiber reinforced metal-matrix composites, Gr/Al and Gr/Mg, flown on LDEF is reported in ref. 99. As noted previously (ref. 5) for oxidation behavior, Gr/Al was shown in ref. 99 to be more stable in thermal expansion behavior than Gr/Mg. Gr/Al showed linear, near zero hysteresis, thermal expansion behavior which stabilized with prolonged thermal cycling. Even after extensive thermal cycling, Gr/Mg showed non-linear expansion with hysteresis. Thermal bending of Gr/Mg samples was noted, due to low thermal conductivity (as compared to that of Gr/Al, where no bending was noted).

The only obscure preliminary findings for metals, ceramics, and optical materials (Table 8) related to the sources of molecular contamination. As noted previously herein, those sources have been identified to be organics and silicones, both internal and external to LDEF.

Near the bottom of Table 8 are new materials development requirements for metals, ceramics, and optical materials resulting from the LDEF materials studies reported to date. Clear, craze-resistant coatings and flexible coatings, which are stable in LEO and do not contaminate other surfaces, are of prime interest. Ground simulation testing requirements (bottom of Table 8) for metals, ceramics, and optical materials are similar to those noted previously for other materials categories.

Systems-Related Materials

This materials category covers lubricants, adhesives, seals, mechanical fasteners, solar cells, and batteries. The studies on materials aspects of systems on LDEF were conducted jointly by the LDEF Systems and LDEF Materials Special Investigation Groups; a detailed exposition of findings is presented in ref. 100. In general, LDEF systems functioned well; the system materials met their requirements.

Table 9 outlines the interim findings of studies on LDEF systems-related materials. Most of the clear findings were briefly discussed in ref. 5, based on information presented in refs. 2 and 4 and 100 through 106. A recent summary paper, ref. 107, is an excellent compilation of comments on the systems materials performance. Figs. 33 and 34 are examples of data from that reference. Fig. 33 lists the findings on lubricants flown on LDEF. The overall conclusions on lubricants are that they should be protected or shielded from direct contact with the LEO environment and that fasteners must be carefully lubricated to prevent galling during installation, if post-flight disassembly is required. Aside from galling problems which complicated fastener removal during experiment tray disassembly, fastening systems on LDEF performed satisfactorily (ref. 104). No "cold welding" was observed on LDEF systems.

Seals on LDEF (ref. 107) were predominantly in the form of O-rings, with a few cases of sheet rubber seals. The seal materials included butyl, ethylene propylene, ethylene propylene diene monomer, acrylonitrile butadiene, silicone, and Viton. All rubber seals were protected from the LEO environment and all performed well, excepting for an ethylene propylene O-ring on a LiCF battery. That O-ring failed due to a "compression set" from contact with the dimethyl sulfite electrolyte, a failure not attributed to the space exposure.

Fig. 34, from ref. 107, lists findings on LDEF epoxy adhesives. Where no information is listed for an adhesive in the comments column of fig. 34, evaluations were not performed due to a lack of resources. Most LDEF adhesives performed satisfactorily. A failure of a strain gage adhesive is noted in ref. 107. Some acrylic and RTV adhesives (ref. 108) degraded in one experiment, but silicone adhesives performed well in another (ref. 101).

Solar cells on LDEF (ref. 105), showed major performance degradation resulting only from meteoroid and debris impacts. Minor degradation was caused by contamination, UV effects on cover glass adhesives, and atomic oxygen/UV effects on antireflection coatings.

The first of the obscure preliminary findings for LDEF systems-related materials (Table 9) regards "dynamic" effects; the microenvironment analysis methodology, discussed earlier in this paper, will probably explain many of these effects. The degradation in solar cell output, was found to be a result of contamination, UV, and AO effects, as described earlier in this section.

Near the bottom of Table 9 are new materials development requirements for systems-related materials resulting from the LDEF materials studies reported to date. Non-contaminating, low outgassing lubricants and seals, which are stable when directly exposed to the LEO environment, are of prime interest. Ground simulation testing requirements (bottom of Table 9) for systems-related materials are similar to those noted previously for other materials categories.

LDEF MATERIALS CONTRIBUTIONS TO SPACE TECHNOLOGY

The promise that LDEF offered (ref. 1) for providing unparalleled data on long-term space environmental effects on materials in low-Earth orbit is being fulfilled. Ref. 5 places the LDEF materials data in context with that from previous LEO environmental effects on materials studies conducted in flight tests and ground simulation tests. The needs of Space Station Freedom designers and the applicability of the LDEF data to those needs were addressed. Ref. 5 also indicated some of the early LDEF materials findings that are already being utilized for SSF. The third of the LDEF materials forums, the October 1992 conference at Huntsville, Alabama on "LDEF Materials Results for Spacecraft Applications" was planned to provide a review and critical assessment of the relevance, significance, and impact on spacecraft design practice of the interim results of LDEF materials research. The proceedings of that conference will undoubtedly be an important addition to the libraries of spacecraft designers and materials analysts.

Ref. 5 also reviewed the general directions for continuing LDEF materials studies under MSIG. The focus of these studies gradually is changing from preliminary observations and physical analyses of LDEF materials specimens to phenomenological understanding, documentation, archiving, and data basing. LDEF specimens and hardware will be archived and will be available to researchers worldwide, into the foreseeable future, through the LDEF Science Office and NASA.

CONCLUSIONS

This paper, as a supplement to ref. 5, has presented a broad overview of interim findings of observations and analyses from ongoing studies of materials from the National Aeronautics and Space Administration Long Duration Exposure Facility, and concentrates on explaining those initial findings which were obscure in the preliminary evaluations. These interim findings on LDEF materials are summarized in Table 10. The column at the upper left lists materials which demonstrated high resistance to degradation for the entire 5.8-year flight. The column at the upper right lists materials which may be perfectly adequate for flights up to several years in LEO but which, if unprotected, will exhibit various degrees of degradation during flights as long or longer than the LDEF mission (5.8 years). As a result of these findings, new materials development requirements and general ground simulation testing requirements have been identified, as listed in the lower parts of Table 10.

In general, LDEF met or surpassed all of its goals regarding the generation of long-term low-Earth orbit space environmental effects on spacecraft materials. The ongoing studies outlined herein indicate LDEF to be the definitive source of long-term exposure verification of low-Earth orbit effects on materials. The quantitative data / micro-environment / mechanistic understanding being developed will strongly contribute to future spacecraft design and new materials development guidelines. LDEF furnishes an unprecedented opportunity to provide a unified perspective of unmanned low-Earth orbit spacecraft contamination mechanisms and interactions. The LDEF materials data bases under development should become the basis of a new family of design guidelines for space environmental effects on materials.

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TABLE 1

LONG DURATION EXPOSURE FACILITY

LAUNCH:

- April, 1984
(into 255 nautical mile orbit)

RETRIEVAL:

- January, 1990
(from 178 nautical mile orbit)

EXPERIMENTS:

- 57 Technology, Science, and Applications Experiments
- Potential for >25000 test specimens from experiment trays and structure

PARTICIPANTS:

- >200 Principal Investigators from 9 Countries
 - 33 Industry
 - 7 NASA Centers
 - 21 University
 - 4 DoD Laboratories
- 4 Special Investigation Groups, >75 Participants
 - Materials
 - Meteoroid and Debris
 - Systems
 - Ionizing Radiation

TABLE 2

LDEF EXPOSURE CONDITIONS

HIGH VACUUM:

- 10^{-6} to 10^{-7} torr

UV RADIATION:

- 100 - 400 nm; 4,500 to 15,500 equivalent sun hours

ELECTRON AND PROTON RADIATION:

- $\sim 2.5 \times 10^5$ Rads surface fluence

ATOMIC OXYGEN:

- $\sim 10^3$ to 9×10^{21} atoms/cm² (wake- to ram-facing)

METEOROID AND DEBRIS IMPACTS:

- >36000 particles from ~ 0.1 mm to ~ 2 mm
- High fluence on ram-facing surfaces

COSMIC RADIATION:

- ~ 6 Rads
- ~ 20 tracks Thorium and Uranium

THERMAL CYCLING:

- $\sim 34,000$ cycles
- [$\pm 20^\circ\text{F}$] to [$\sim -30^\circ\text{F}$ to $\sim +190^\circ\text{F}$]

TABLE 3

ENVIRONMENTAL PARAMETERS AND DATA BASES

Clear Findings

- All polymers on LDEF were attacked by atomic oxygen (AO).
- Metals and oxides protect against AO.
- Although widespread contamination occurred, continuing studies indicate LDEF to have low levels of general contamination, compared to other spacecraft.
- LDEF mission environments were defined:
 - Atomic oxygen
 - Total solar exposures
 - Contamination history
- "Microenvironment" analysis methodology is in development for detailed understanding of space environmental effects.
- AO fluence models must be revised to account for thermal velocity distribution.
- Impacts occur in temporal bursts.
- Data bases are required for both design and research technical communities.

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
• Sources of general "nicotine stain" contamination	• Silicones and organic materials, both internal and external to LDEF
• Contamination mechanisms	• Not yet defined in many cases
• AO degradation mechanisms	• Defined in most cases
• AO/UV synergism	• Work in progress for a number of cases

TABLE 4
LDEF CONTAMINATION

Clear Findings

- LDEF was not a "dirty spacecraft"
- Molecular contamination was widespread:
 - Multiple sources, external and internal
 - Surface temperature dependent
 - Cross-contamination from Shuttle sources
 - Environmental interactions with AO & UV
 - Leading edge deposits more transparent
- Particulate contamination was deposited pre-flight, in-flight, post-flight; can be differentiated
- LDEF provides an opportunity for a unified perspective of unmanned LEO spacecraft contamination mechanisms

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
• Sources of silicones/silicates	• Silicones internal and external to LDEF
• Deposition mechanisms	• Defined in many cases
• Contribution of AO degradation products	• Undefined in most cases
• Effects on analyses for other space environmental effects	• Undefined in most cases

New Materials Development Requirements:

- Alternate, non-silicone materials
- Non-contaminating lubricants, polymers

Ground Simulation Testing Requirements:

- Re-evaluation of current outgassing criteria/tests for long-term missions
- Combined exposure testing and analytical modeling
- System level testing and analytical modeling

TABLE 5

THERMAL CONTROL COATINGS AND PROTECTIVE TREATMENTS

Clear Findings

- Chromic Acid Anodized Aluminum is stable for long LEO exposures.
- Z-93, YB-71, PCB-Z white TC paints and D-111 black TC paint are stable.
- A276 is affected by AO and UV.
- Potassium silicate binders are stable; organic binders are not stable.
- UV accelerates AO erosion of Teflon; FEP erodes more rapidly than predicted.
- Microcracking was found in adhesively bonded Ag/FEP.
- Surface crazing was found in clear silicone coatings.
- Atomic-oxygen undercutting of polymer substrates under protective coatings was evident.

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
• Fluorescence shift from UV to VIS	• General phenomena explained; LDEF chemistry details undefined
• Variable results for black chromium	• "Microenvironment" effect ?
• Variable results for S-13GLO	• VUV plus "Microenvironment" ?
• Roles of UV, e ⁻ , p ⁺ in AO erosion of FEP	• Not defined in most cases

New Materials Development Requirements:

- Thin silicate overcoats for AO protection
- New silicate source for Z-93
- Application process for Ag/FEP
- Durable flexible coating to replace S-13GLO

Ground Simulation Testing Requirements:

- Temperature effects on AO, UV degradation
- Single/combined effects data for analytical modeling
- In-situ measurement capabilities for AO and UV testing
- Addition of e⁻ and p⁺ to simulation facilities
- Verified accelerated testing and analytical modeling

TABLE 6
POLYMERS AND FILMS

Clear Findings

- Ag/FEP blankets remained functional, but were eroded by atomic oxygen (AO).
- No significant changes were found in α/ϵ of Ag/FEP; diffuse reflectance was increased.
- Sizable delaminations of Ag from FEP were found at meteoroid/debris impacts; thermal "lag" resulted from these delaminations.
- Mechanical properties of polymers such as FEP and polyethylene were affected by UV.
- Siloxane-modified materials resist AO.
- Non-silicone polymers are attacked by AO.
- Contamination is an important effect.
- AO erosion of Kapton is linearly predictable; Kapton will be a good "witness" specimen.
- Greater erosion was found than that predicted for FEP, polystyrene, and PMMA.
- Minimal chemical change detected in bulk polymers from AO exposures.
- Extensive heating was apparent for some films on LDEF.
- Atomic oxygen attack on carbon films was observed.

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
<ul style="list-style-type: none"> • More erosion was found on some materials than predicted. • Localized thermal effects were evident. • Effects of contamination 	<ul style="list-style-type: none"> • UV/AO synergism effects are most likely responsible. • "Microenvironment" effect ? • Not yet defined in many cases

New Materials Development Requirements:

- Non-contaminating materials resistant to AO attack
- Non-contaminating materials resistant to UV degradation

Ground Simulation Testing Requirements:

- High fluence AO testing (directed beam)
- High fluence UV/VUV testing
- Simultaneous AO/UV exposure testing and analytical modeling
- Verified accelerated testing and analytical modeling
- Large area exposures for mechanical testing
- Thermal cycling
- Temperature effects
- Quantitative definition of thermal "lag" at delaminations in silvered Teflon second-surface-mirror thermal blankets

TABLE 7
POLYMER-MATRIX COMPOSITES

Clear Findings

- AO causes surface degradation of uncoated composites, but no bulk polymer property changes.
- Thin inorganic coatings prevent AO erosion
- Outgassing dictates dimensional stability of Gr/Ep; other CTE changes minor
- Optical properties: No change for Gr PMC except on LDEF LE; fiberglass darkened
- Sequential effects of impact/AO erosion
- Thermal cycling causes microcracking
- No catastrophic failure from impacts

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
• Effects of contamination on AO erosion rates.	• Not yet defined in most cases.
• Differences in AO erosion morphologies; stripes on T300/934 with 5-mil tape.	• Low material variability, particularly sodium and sulfur concentrations.
• Differences in appearance and quantity of "ash" on AO-eroded specimens.	• Sulfates from DDS curing agent.
• No AO degradation of mechanical properties except on LDEF leading edge.	• AO erosion did not reach deep into outer ply of composite.

New Materials Development Requirements:

- Scale up of coating process to full size parts
- Flexible coatings (for composite springs, etc.)

Ground Simulation Testing Requirements:

- Current capabilities adequate for individual effects
- Capacity and size for AO inadequate
- Synergistic effects (AO, UV, thermal cycling, vacuum, contamination)
- AO simulation on UV degraded LDEF specimens
- Analytical modeling of individual parameter and synergistic effects

TABLE 8

METALS, CERAMICS, AND OPTICAL MATERIALS

Clear Findings

- Structural Al and Ti alloys are unaffected.
- Many surfaces are contaminated.
- 1000Å Al coating on stainless steel is a very stable mirror/reflector.
- Thin anodized coatings on Al show small but measurable α/ϵ increases.
- Heavy oxidation of Ag and Cu.
- All metallic films except Sn and Pt show some oxidation.
- Al-matrix composites are not degraded; Mg-matrix composites oxidize at edges.
- Gr/glass composites are stable.
- Ceramics and glasses are generally stable unless damaged by impacts.
- Optical properties of glasses are affected in UV spectral regions only.
- Black coatings become more absorbing

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
• Sources of contamination	• Multiple sources internal and external to LDEF. Predominantly organics and silicones.

New Materials Development Requirements:

- Non-contaminating, craze-resistant clear coatings
- Non-contaminating flexible coatings

Ground Simulation Testing Requirements:

- Synergistic effects (AO, UV, thermal cycling, vacuum, contamination)
- Analytical modeling of synergistic effects

TABLE 9
SYSTEMS-RELATED MATERIALS

Clear Findings

- Lubricants--OK only when protected
- Fasteners--no cold welding failures were observed; galling was evident
- Seals--no failures (all protected)
- Adhesives--a few indications of failure
- Solar cells--degradation due to impacts
- Batteries--no space-related failures

<u>Obscure Preliminary Findings</u>	<u>Resolution</u>
<ul style="list-style-type: none">• Dynamic effects• Solar cells--minor degradation in output	<ul style="list-style-type: none">• "Microenvironment" effect ?• Possibly due to contamination plus UV and AO

New Materials Development Requirements:

- Non-contaminating dry film lubricants for exposed applications
- Non-contaminating seals for exposed applications

Ground Simulation Testing Requirements:

- Combined thermal vacuum / UV / AO / dynamic testing

TABLE 10

SUMMARY OF LDEF MATERIALS INTERIM FINDINGS

<u>Resistant Materials</u>	<u>Degraded Materials</u>
<ul style="list-style-type: none"> • Chromic acid anodized Al alloys • Many metals and Al-matrix composites • Ceramics, glasses, and Gr/glass composites • YB-71, Z-93, PCB-Z, D-111 paints • Inorganic coatings • Some siloxane-based polymers • Al-coated stainless steel reflectors 	<ul style="list-style-type: none"> • Various thermal control coatings • Silicone conformal coatings • Polymers • Polymeric-matrix composites • Silver & copper • Ag/FEP second surface mirrors • Exposed lubricants

New Materials Development Requirements:

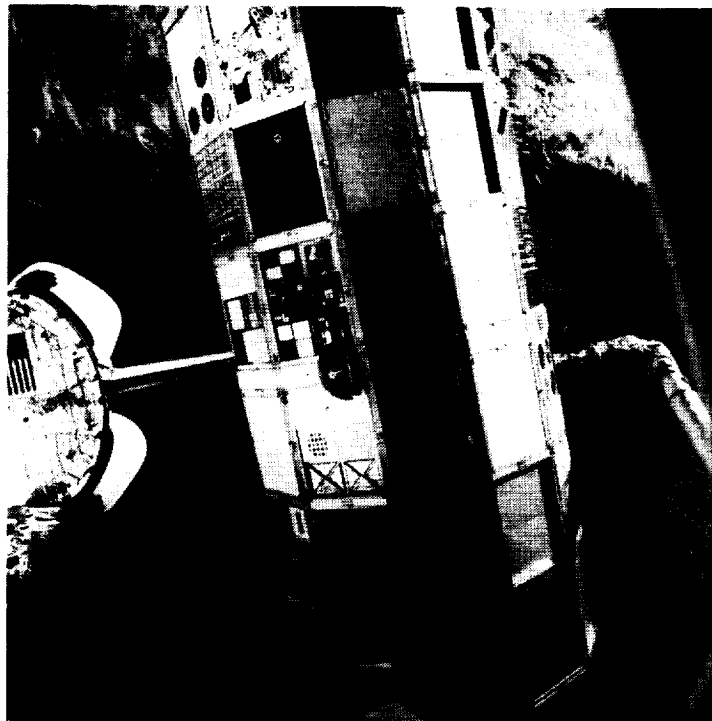
- Non-contaminating, atomic-oxygen-resistant polymers and polymer-matrix composites
- AO-durable flexible polymer for electrical insulation
- Replacement for Ag/FEP with low α_s/ϵ
- Flexible white paint replacement for S-13GLO
- Non-contaminating lubricants and seals for exposed applications
- Durable transparent polymer coatings
- Efficient concepts for hypervelocity impact resistance

Ground Simulation Testing Requirements:

- Synergistic effects testing and analytical modeling
- Validated accelerated tests for combined UV, AO, thermal cycling

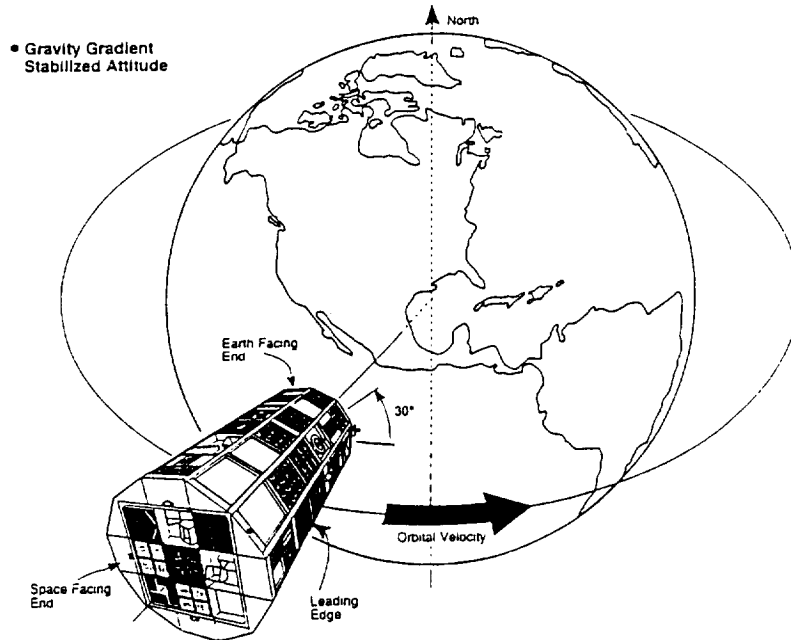


1. LDEF in orbit, April 1984.

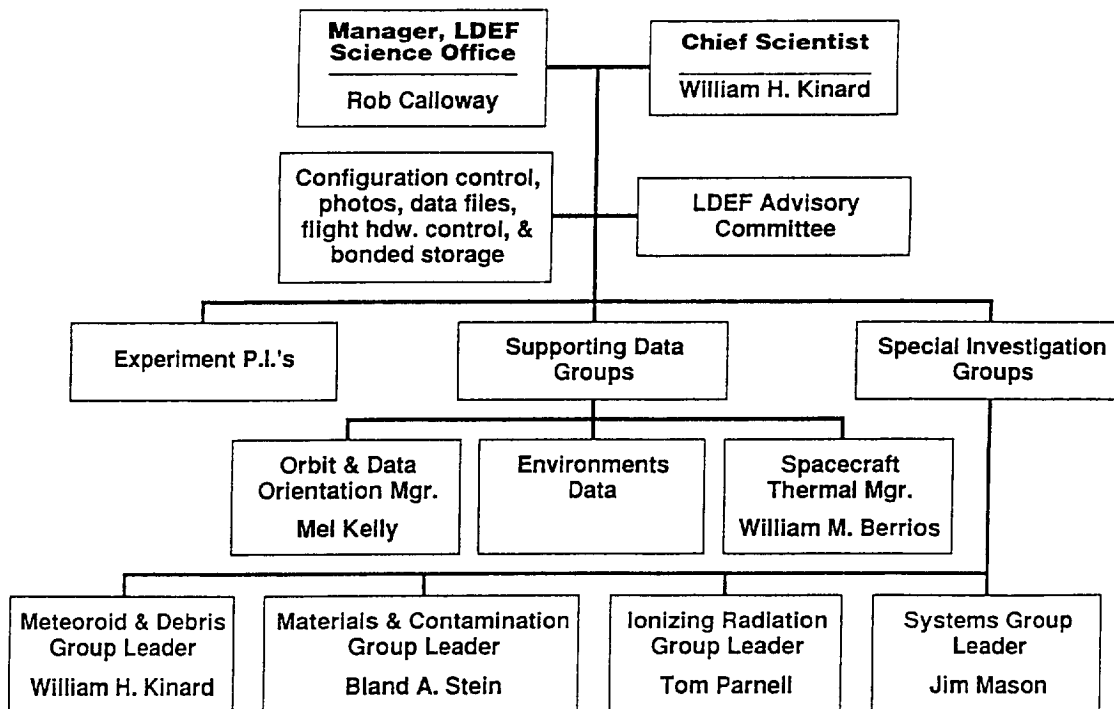


2. LDEF retrieval after 5.8 years in low-Earth orbit, January 1990.

LDEF ORIENTATION



3. LDEF orientation.



4. LDEF Science Team.

Materials Issue	Data Available from LDEF
<ul style="list-style-type: none"> • Stability of Material Properties <ul style="list-style-type: none"> - Optical - Mechanical - Thermal - Physical - Chemical 	<ul style="list-style-type: none"> • Polymers, Metals, Composites, Ceramics, Glasses, Coatings, Films
<ul style="list-style-type: none"> • Combined Space Environment Effects Models 	<ul style="list-style-type: none"> • AO, Electrons, Protons, UV, ΔT, M & D, Vacuum • Control Specimens on LDEF and in Ground Storage
<ul style="list-style-type: none"> • Atomic Oxygen Effects 	<ul style="list-style-type: none"> • Erosion Rates and Mechanisms • Modifications to Fluence Models
<ul style="list-style-type: none"> • Meteoroid/Debris Impact Effects 	<ul style="list-style-type: none"> • Delamination of Blankets, Composites • Crater/Impact Particle Chemistry
<ul style="list-style-type: none"> • Contamination 	<ul style="list-style-type: none"> • Molecular & Particulate Levels/Chemistry

5. LDEF data available to address current issues in space environmental effects on materials.

SPONSOR: Long Duration Exposure Facility - Materials Special Investigation Group

OBJECTIVES:

- In-depth exposition of LDEF Materials Findings from Principal Investigators and MSIG
- Workshop discussions and theme reports on LDEF materials disciplines, data-basing requirements, ground simulation testing and analytical modeling needs, and future flight experiments

TUTORIAL AND WORKSHOP DISCUSSION DISCIPLINES:

- | | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> • LDEF Materials, Environmental Parameters, and Data Bases • LDEF Contamination • Metals, Ceramics, and Optical Materials • Lubricants, Fasteners, Adhesives, Seals, Solar Cells, and Batteries | <ul style="list-style-type: none"> • Thermal Control Coatings, Protective Coatings, and Surface Treatments • Polymers and Films • Polymer-Matrix Composites |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

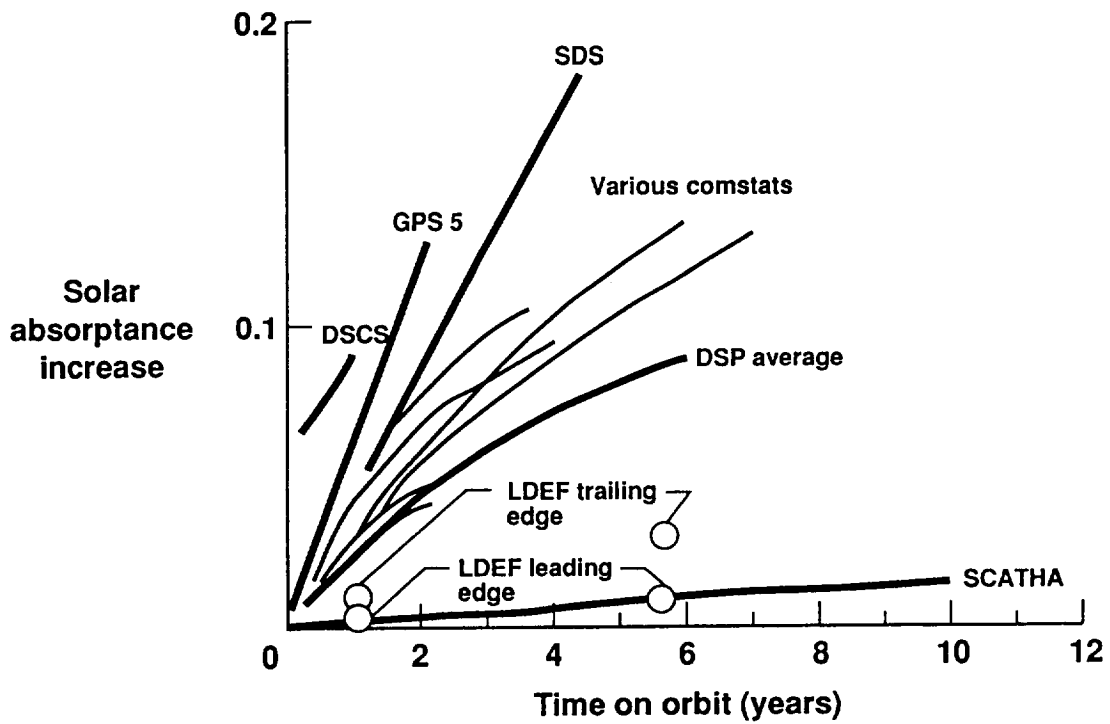
ATTENDANCE:

- ~200 technologists from the International Space Materials Community

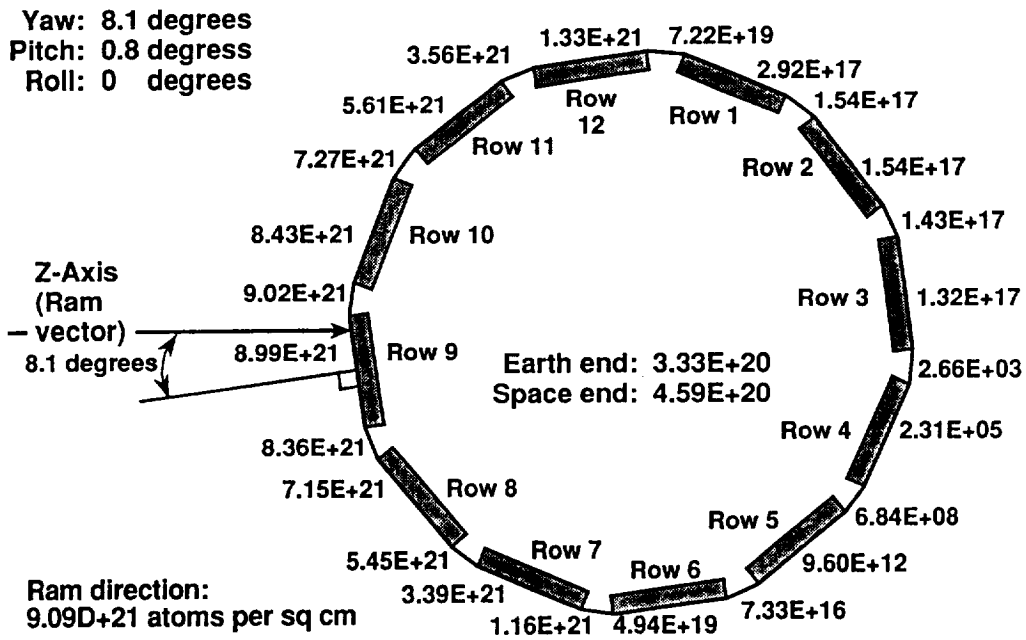
REPORT:

- NASA Conference Publication 3162 (1992)

6. LDEF Materials Workshop '91.



7. Fused silica mirror radiator degradation. (From ref. 9.)

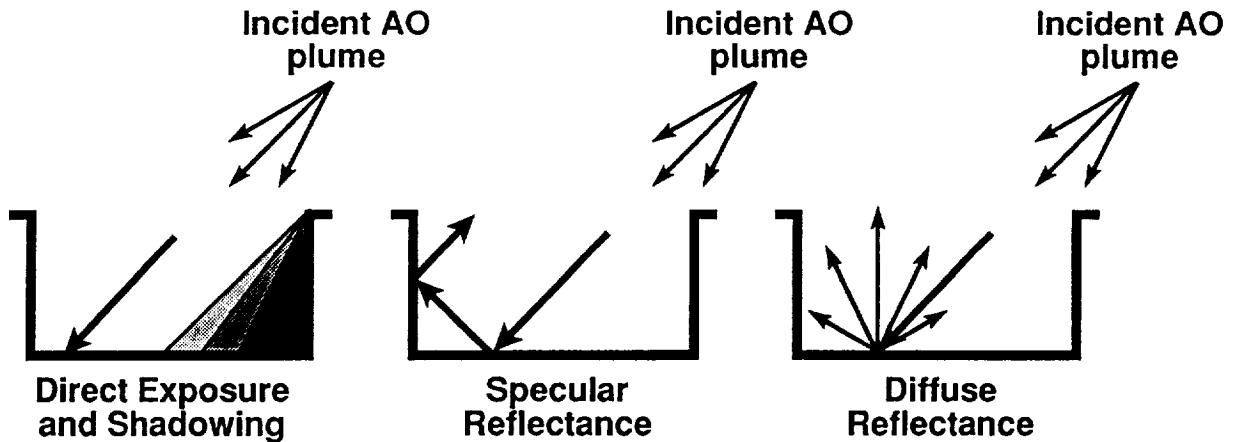


Atomic oxygen fluences at end of mission for all row, longeron, and end bay locations including the fluence received during the retrieval attitude excursion.

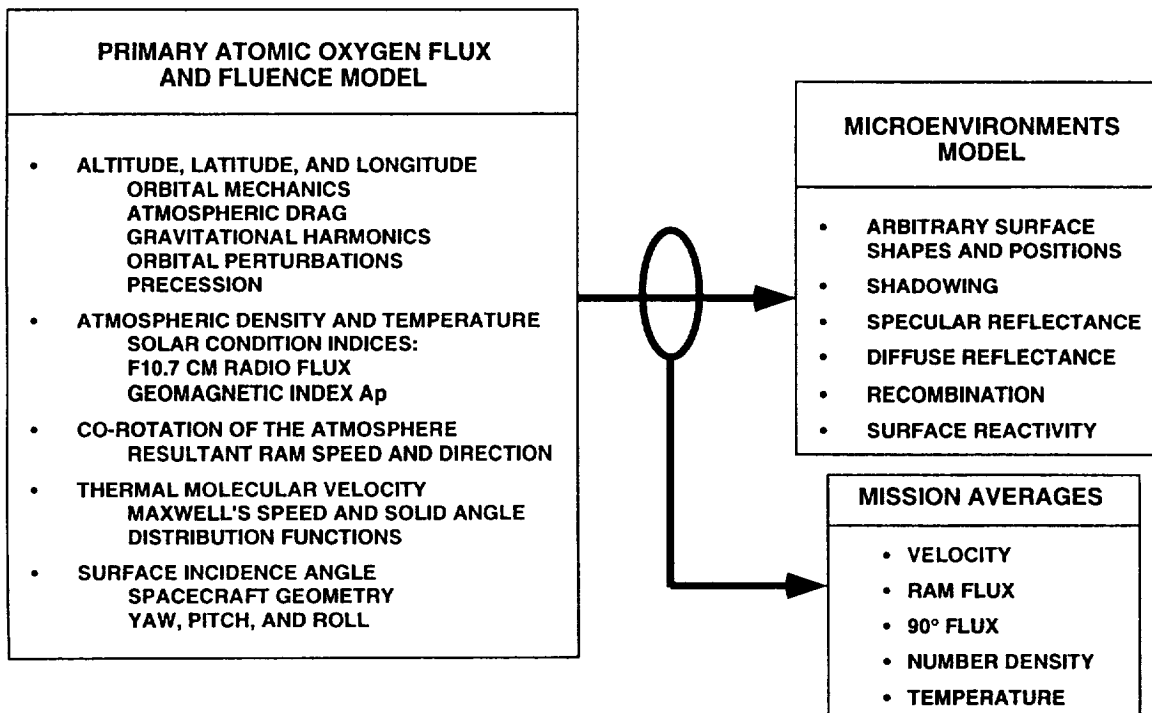
8. Atomic oxygen fluence for each LDEF tray location.

Objective

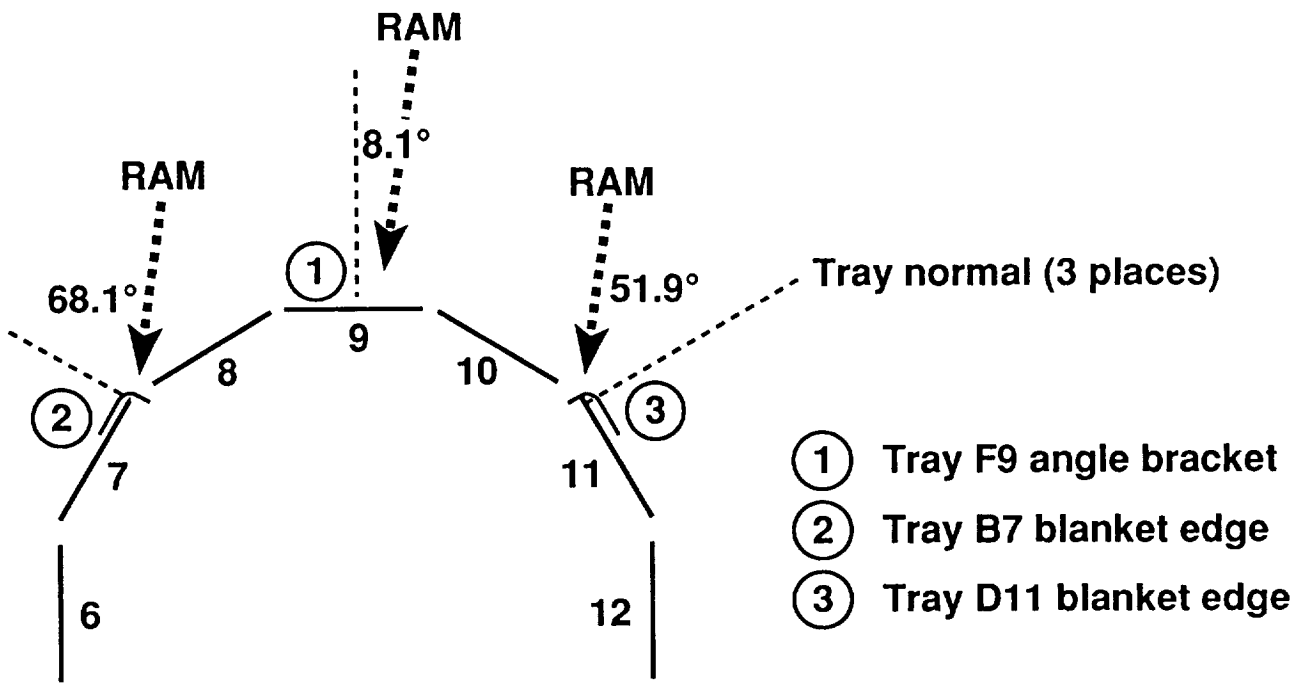
Over the surface of an object of arbitrary shape and placement on a spacecraft, determine atomic oxygen flux while accounting for direct exposure, shadowing, specular reflectance, and diffuse reflectance of oxygen atoms.



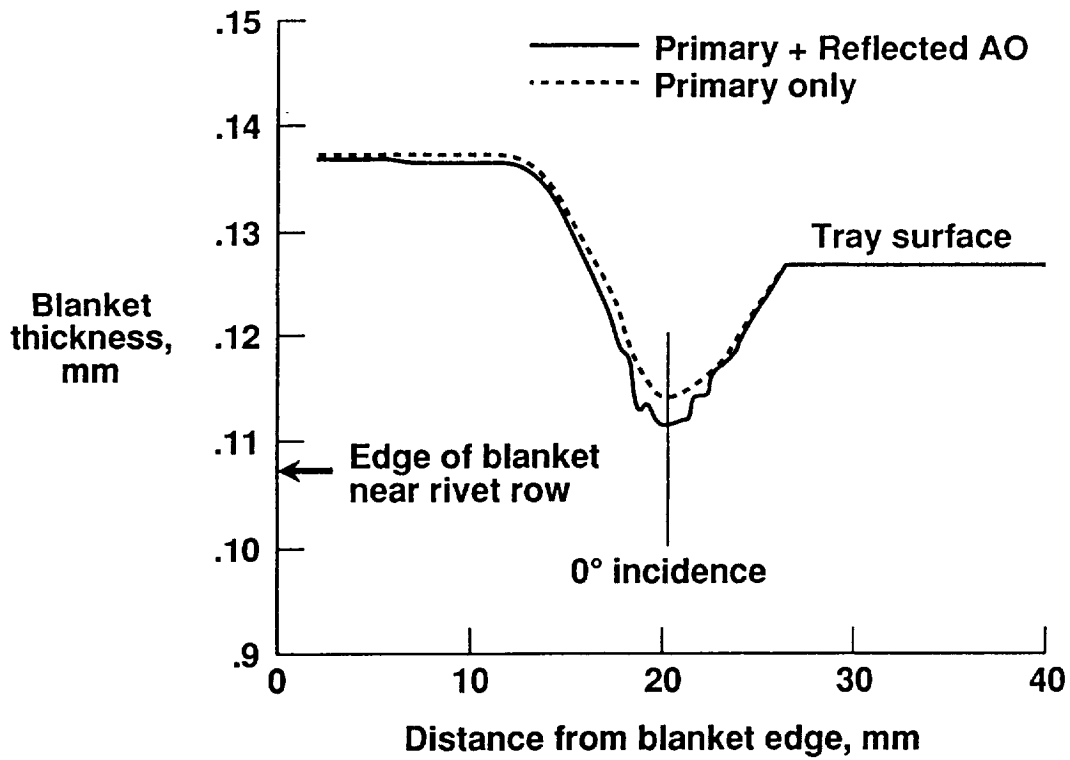
9. Atomic oxygen microenvironments model (from ref. 11).



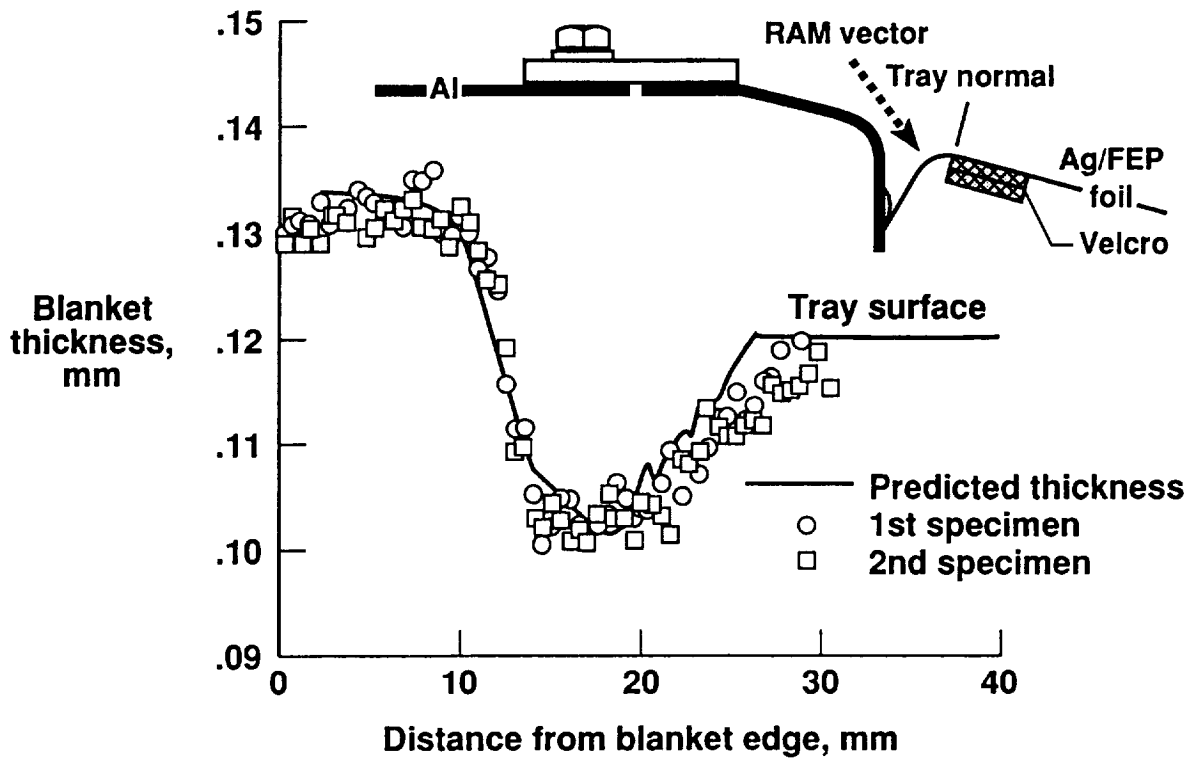
10. Atomic oxygen exposure models (from ref. 11).



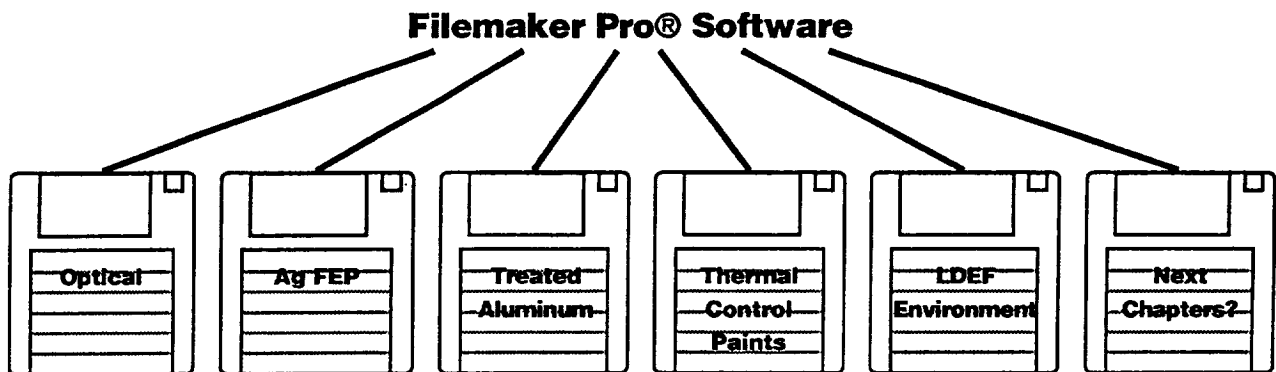
11. Orientation of specimens (from ref. 11).



12. FEP blanket, B7 tray, 68.1° between tray normal and ram vector (from ref. 11).



13. LDEF silvered Teflon blanket AO erosion predicted by new atomic oxygen model (from ref. 11).

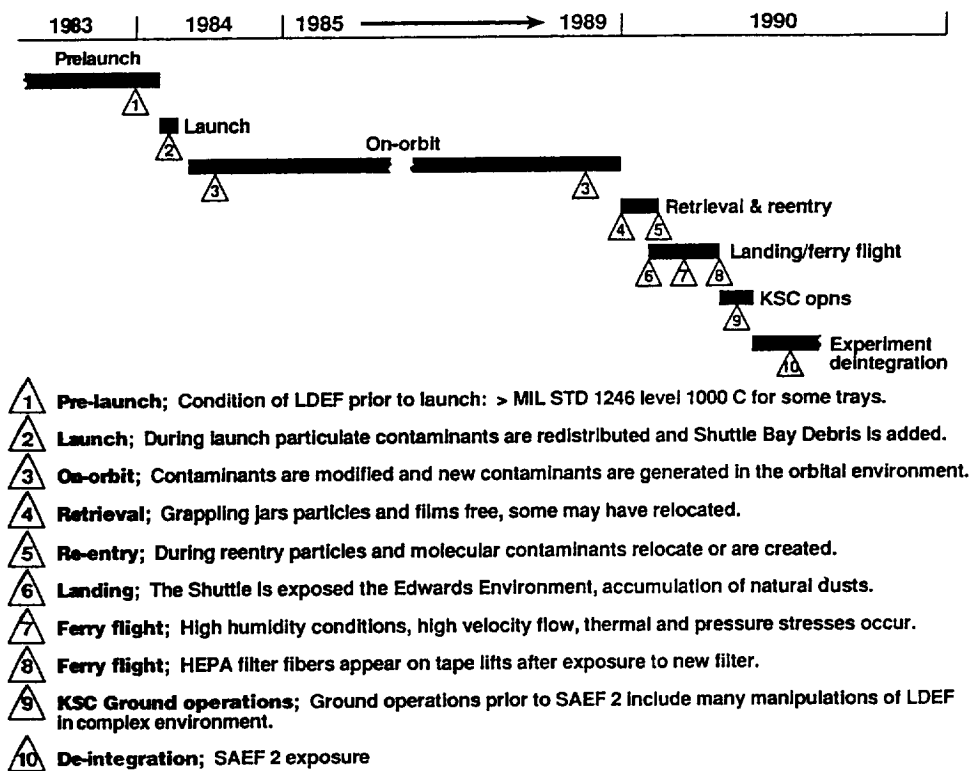


- Independent self-contained units of information
- Application specific
- Optical experiments database supported by the Systems SIG (1991); all other databases supported by the Materials SIG (1992)
- Next chapters? Composites, metals, contamination

14. Status of LDEF "Mini-data bases" (from ref. 12).

1. Basic Data
2. All Data
3. General Properties
 - A. All General Properties
 - B. Change in Mass
 - C. Change in Thickness
 - D. Optical Density
 - E. Surface Roughness
4. Mechanical Properties
 - A. All Mechanical Properties
 - B. Elastic Properties
 - C. Tensile Strength
 - D. Hardness
 - E. Maximum Load
5. Electrical Properties
 - A. Surface Resistance
6. Optical/Thermal Properties
 - A. All Optical/Thermal Properties
 - B. Absorptivity
 - C. Emissivity
 - D. Absorptivity/Emissivity
 - E. Reflectance
 - F. Transmittance
7. Data Sources
 - A. Primary Facility
 - B. Author or Secondary Facility
 - C. Document Title

15. MAPTIS - LDEF materials database (from ref. 13).



16. Contamination exposure history of LDEF.

- **Pre Flight:** Ground based processing created particles and contamination films which were carried into orbit
- **On-Orbit:** Exposures and subsequent degradation. Venting and outgassing produced new particles and molecular contamination films

These events must be evaluated as to how they influence spacecraft performance

- **Post Flight:** Particulate deposition, moisture absorption

These processes must be viewed as artifacts to be factored out of materials performance analyses

17. LDEF contamination exposure categories.

Carbon based film contamination

- Paint solvents
- Polymeric thin films
- Composite materials

Silicon/silica based film contamination

- Adhesives
- Coatings on specimens
- Coatings on support hardware
- Solar cells
- Paints

Particulate contamination

- Fibers, pollen, dust
- Degraded materials

18. LDEF contamination sources.

- **Complex process - Several contributing factors. Outgassed hydrocarbons and silicones deposit on surface**
- **Degraded by solar UV; polymerized crosslinked, fixed to surface**
- **Co-deposited silicones are oxidized to silica/silicates and trap hydrocarbons, which are then darkened by UV exposure**
- **Heat from thermal cycling may accelerate degradation for part of each orbit**

19. Brown ("nicotine stain") contamination observed on external aluminum surface of LDEF.

Creation of contaminants

- **Particulate contamination created as materials deteriorated or failed on leading edges**
- **Thin films created on many surfaces as materials out gassed**

Removal of contaminants

- **Thermal cycling**
- **Oxidation**

Fix contaminants in place and change their identity

- **Breaks bonds, crosslinks polymers**
- **Oxidizes**
 - **Volatile products**
 - **Cross-linked structure**

End products indentified after flight

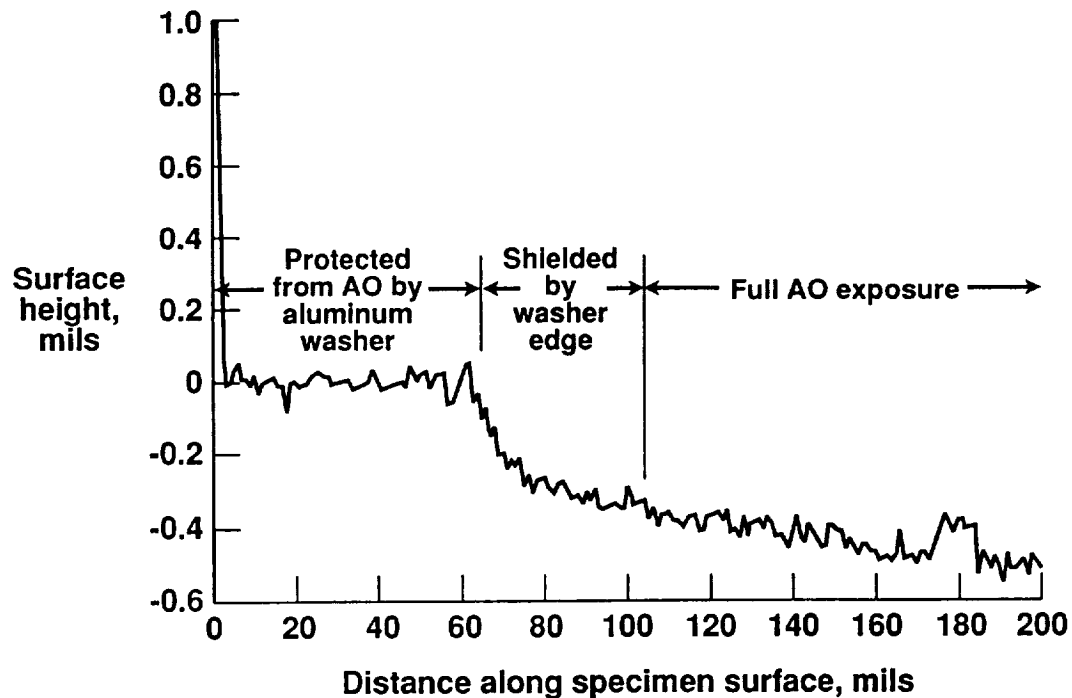
- **Relatively few species - thermodynamically stable**
 - **Non volatile**
 - **Physically trapped**

20. On-orbit effects on LDEF contamination.

- **Minimal influence on thermal status of satellite**
- **Films interfered with LDEF surface analysis and recession rate determination**
- **On-orbit generation of particles may be an issue for sensitive optics**
- **Oxygen atoms will clean some surfaces**
- **Contamination extensive, but site specific**
 - **Heavy molecular contamination deposition is line-of-sight**
- **Uncertainties for outgassing of materials**
 - **Is rate linear or does it decay with time**
 - **Total amount of material outgassed**
 - **Details of interaction of outgassed material with environment**

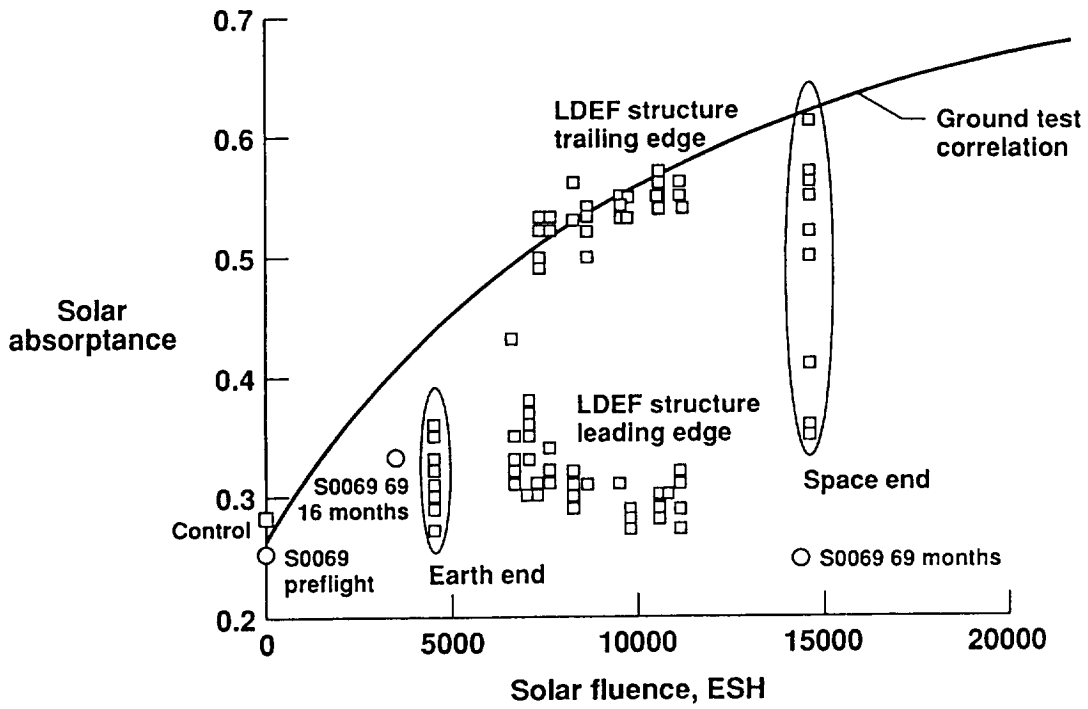
21. Interim LDEF contamination summary.

A276 White Thermal Control Coating, LDEF Tray D9



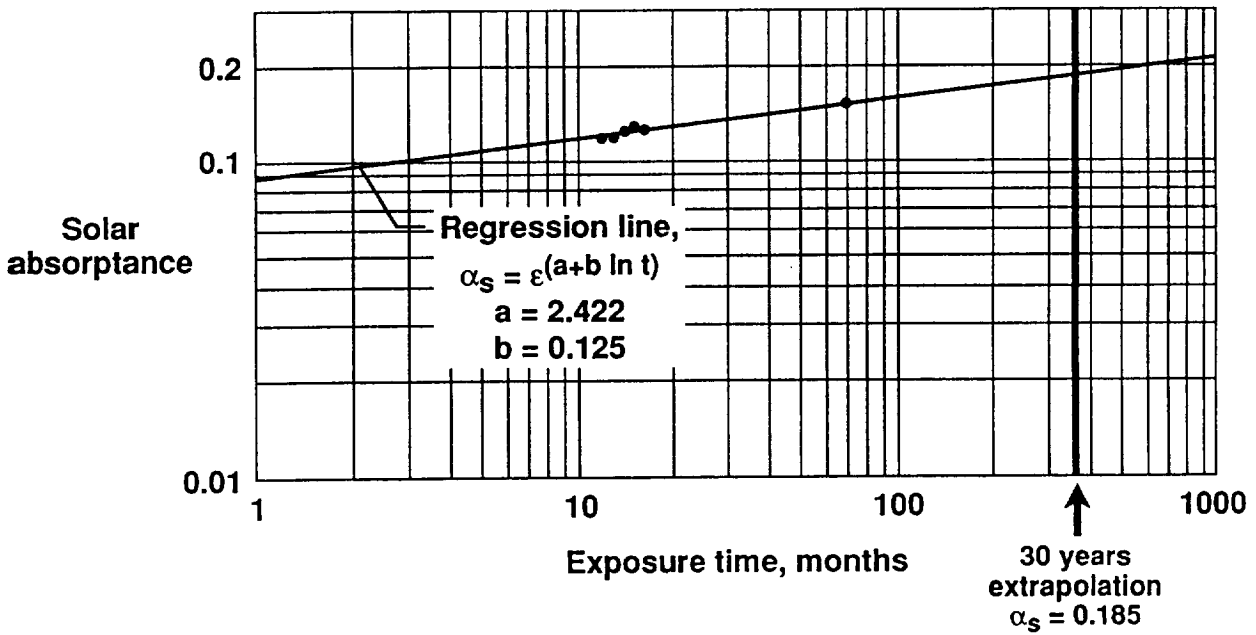
22. Laser profilometry scan for atomic oxygen erosion (from ref. 45).

A276 White Polyurethane-Base Thermal Control Coating Disks



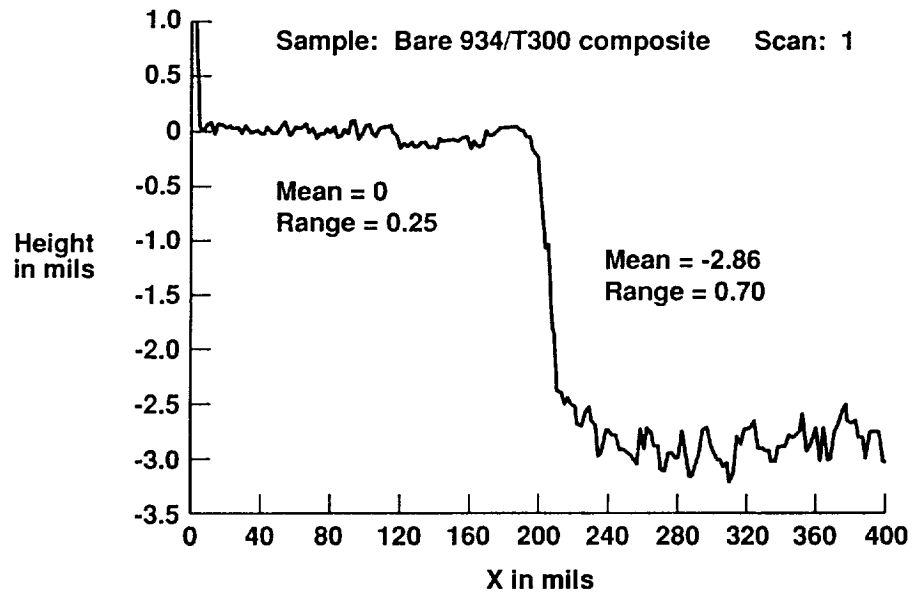
23. Solar fluence effects on solar absorptance (from ref. 45).

Z93 White Thermal Control Coating



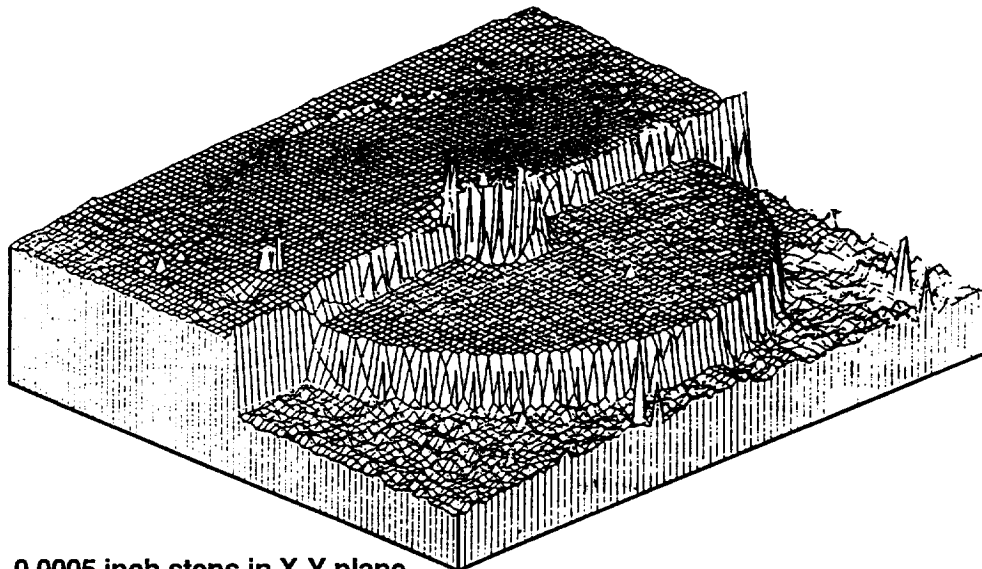
24. Solar absorptance degradation analysis (from ref. 46).

LDEF M0003-8 COATED COMPOSITE PANEL



25. Laser profilometry scan of LDEF atomic oxygen erosion (from ref. 74).

LDEF M0003-8 COATED COMPOSITE PANEL

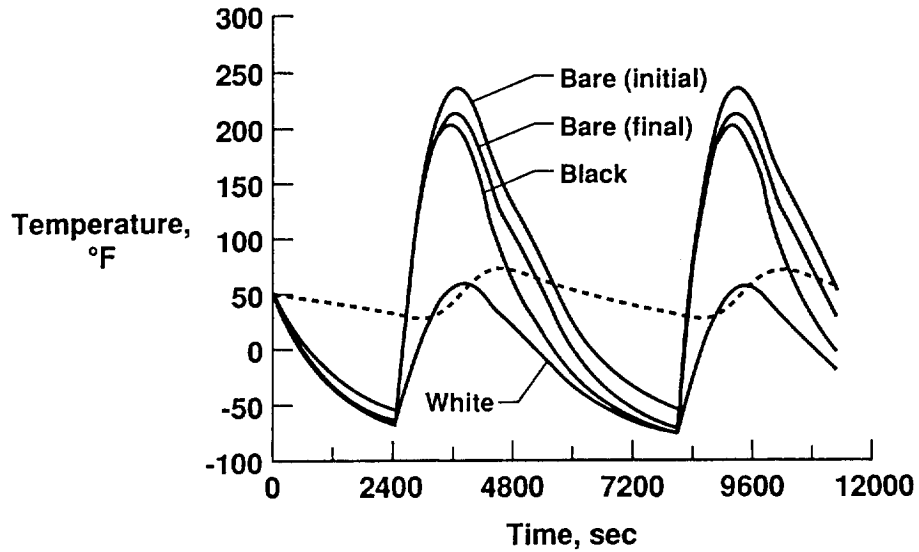


0.0005 inch steps in X-Y plane
0.001 inch per color in Z direction

26. Laser profilometry raster scan of washer region (from ref. 74).

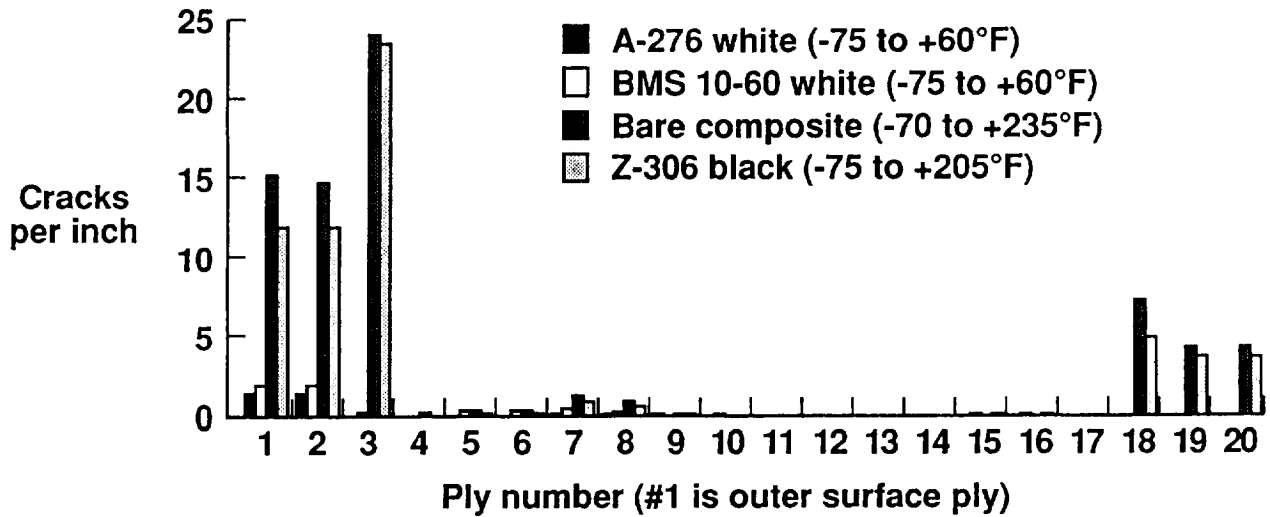
LDEF M0003-8 COATED COMPOSITE PANEL

White, black, bare (initial), and bare (final) panels
(subsurface temperatures from adjusted time scale)



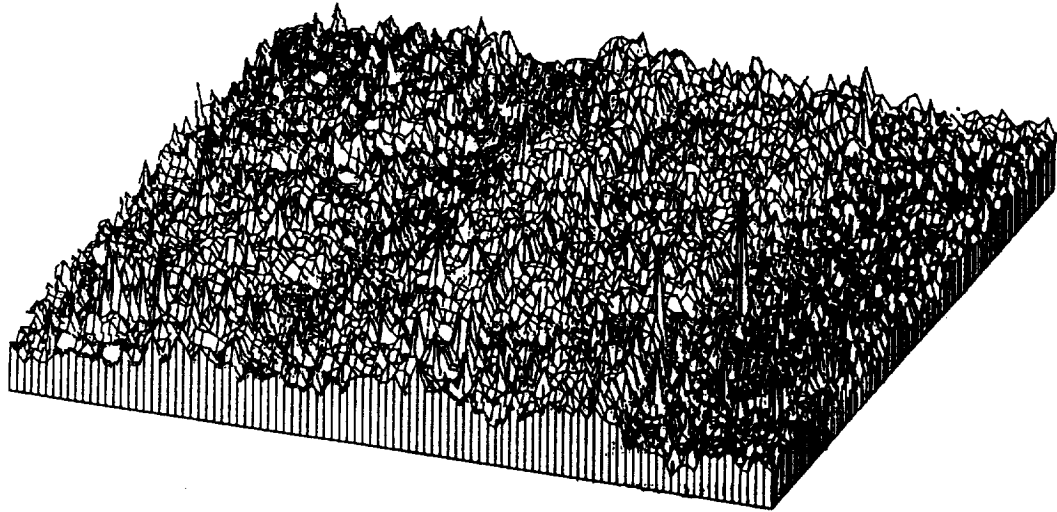
27. LDEF panel and subsurface temperatures (from ref. 74).

LDEF M0003-8 COATED COMPOSITE PANEL



28. Microcrack density vs. location for coated and uncoated composite (from ref. 74).

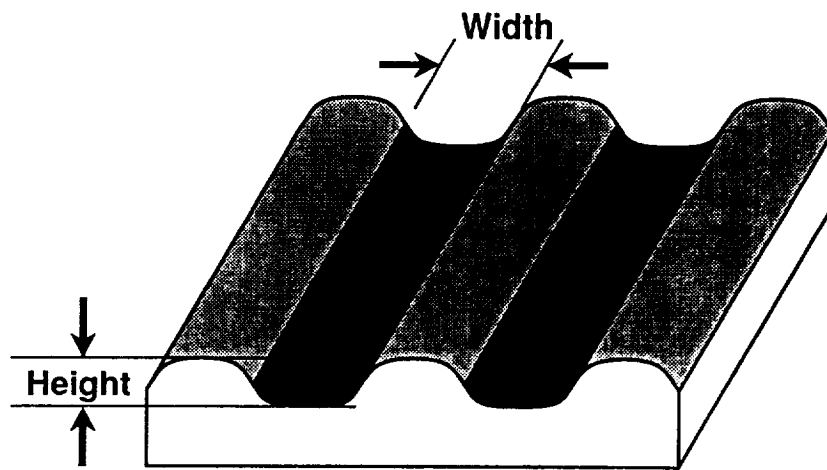
LDEF M0003-8 COATED COMPOSITE PANEL



0.0005 inch steps in X-Y plane
0.00025 inch per color in Z direction

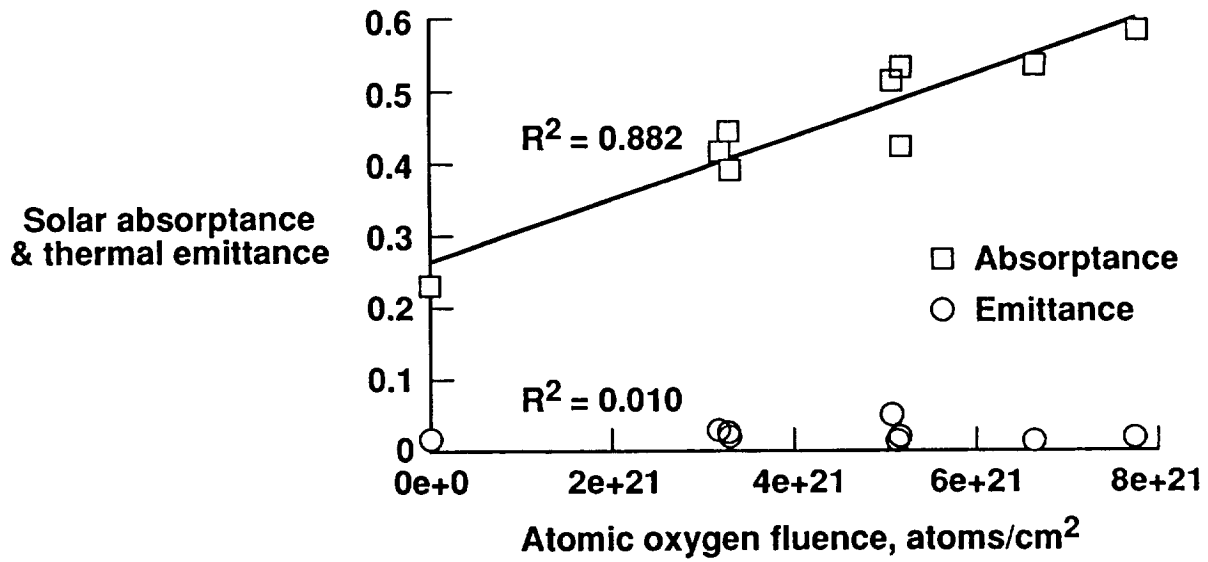
29. Laser profilometry raster scan of band pattern (from ref. 74).

LDEF M0003-8 COATED COMPOSITE PANEL

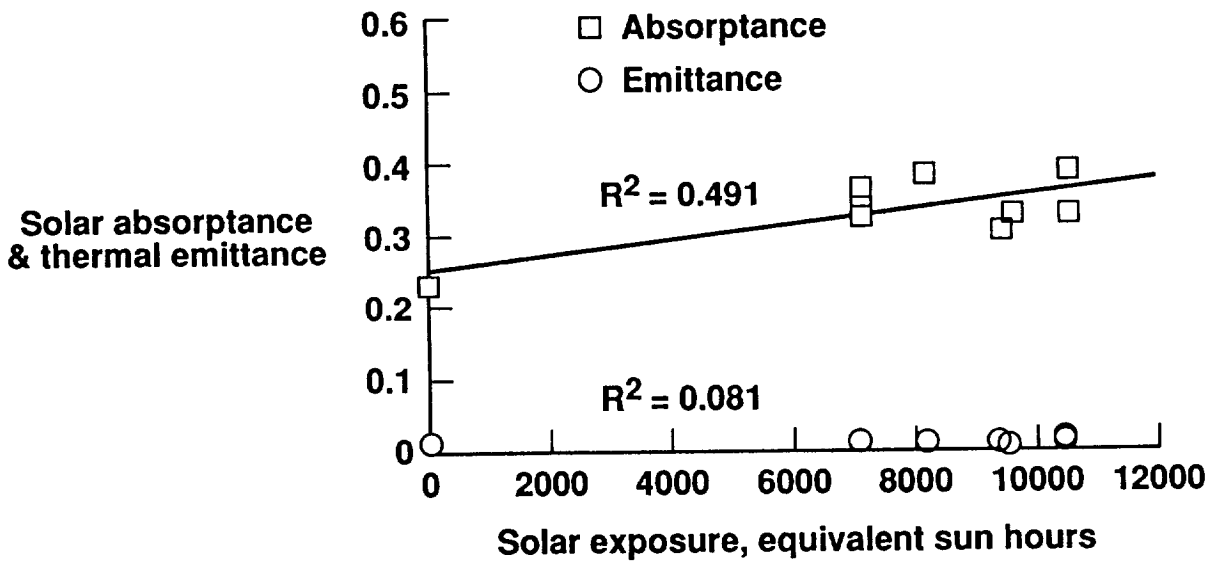


Width (10 measurements): **0.059" ± 0.003"**
Compare to **0.056"** tow width as prepregged
Height (from raster scan): **approx. 0.0005" or 15% of erosion depth**

30. Band pattern dimensions (from ref. 74).



31. Thermal control properties of LDEF copper grounding straps on leading edge surfaces (from ref. 64).



32. Thermal control properties of LDEF copper grounding straps on trailing edge surfaces (from ref. 64).

Material - Description	Location	Findings (5/92)
Cetyl alcohol	A1 & A7	Failed
MoS ₂	A1 & A7	Used on nut plates, appears to be nominal
MoS ₂ - air cured dry film lubricant (MIL-L-23398)	EECCs (shielded & exposed)	Nominal, further testing required
MoS ₂ - chemically deposited	B3	Degraded
Molykote Z - MoS ₂	B3 (shielded)	Not tested
WS ₂ (tungsten disulfide)	Grapples	Bulk properties nominal, no difference between leading and trailing edge
Apiezon H - petroleum based thermal grease	F9 (shielded)	Outgassing tests nominal
Apiezon L - petroleum based lubricant	D12	Not tested
Apiezon T - petroleum based lubricant	H3 & H12 (space end)	Slight separation of oil from filler, some migration
Ball Aerospace VacKote 18.07 - MoS ₂ with polyimide binder	A9 (shielded)	Not tested
Ball Brothers 44177 - hydrocarbon oil with lead naphthanate and clay thickener	EECCs (shielded)	Not tested, extensive offgassing

33a. Lubricants on LDEF (from ref. 107).

Material - Description	Location	Findings (5/92)
Castrol Braycote 601 - PTFE filled perfluorinated polyether lubricant	A3	Extensive testing, to date results show no change
Dow Corning 340 - Silicone heat sink compound	Shielded	IR spectra unchanged
Dow Corning 1102 - Mineral oil based heat sink compound	Shielded	Visual examination nominal
Dow Corning Molykote Z - MoS ₂	Shielded	Not tested
DuPont Vespel 21 - Graphite filled polyimide	D3	Optical, EDX, and friction tests nominal
DuPont Vespel bushings - polyimide	Various	Nominal
E/M Lubricants Everlube 620C - MoS ₂ with modified phenolic binder	D3	Complete binder failure
Exxon Andok C - petroleum grease	Shielded	System test results nominal, lubricant not evaluated
Mobil Grease 28 - Silicone grease	MTMs (shielded)	System test results nominal, lubricant not evaluated
Rod end bearings with PTFE coated Nomex liner	D3	Extensive test results nominal

33b. Lubricants on LDEF (concluded) (from ref. 107).

Vendor	Product	Experiment	Comments
Ciba-Geigy	Araldite AV 100/HV 100	A0056 A0139	
	Araldite AV 138/HV 998	A0023 A0056 A0138-1 S1002	
	Araldite AV 138/HW 2951	A0138-1	
	Araldite AW 136/HY 994	M0002	
	Araldite AW 2101/HW 2951	A0138-1	
	Araldite MY 750/HY 956	A0056	
Crest	3135/7111	A0180	1, 2, 3

Key to comments

- 1: Performed as expected
- 2: Discolored where exposed to U.V.
- 3: Further testing is planned./Results to be published later

34a. Epoxy adhesives on LDEF (from ref. 107).

Vendor	Product	Experiment	Comments
Emerson & Cuming	Eccobond 55	A0056 A0139 A0147 S0014	1 1, 2
		S1002	
	Eccobond 55 + 10% Ecosil	S1002	
	Eccobond 56C	A0076 A0171 S0069	1 1, 3 1
		S1002	
Epoxy Technology	Epo-Tec 301	A0147 S0014	1 1
	Epo-Tec 331	M0004	1
Furane	Epl-Bond 104	S0014	1
Hysol	EA 934	A0180 M0024 S1001	1, 2, 3 1 1
		A0054	1
		M0004	1
	EA 956	M0003	1, 3
	EA 9210/109519	M0003	1, 3

Key to comments

- 1: Performed as expected
- 2: Discolored where exposed to U.V.
- 3: Further testing is planned./Results to be published later

34b. Epoxy adhesives on LDEF (continued) (from ref. 107).

Vendor	Product	Experiment	Comments
Rome & Haas	K-14	A0171	1, 3
	N-580	A0171	1, 3
Shell	Epon 828	A0056 A0180 P0003 S1001	1, 2, 3 1 1
3M	AF-143	M0003	1
	EC 2216	A0076 A0138-1 A0178 M0003 S1005 Viscous damper	1 1 1 1
Varian	Torrseal	M0006	

Key to comments

- 1: Performed as expected
- 2: Discolored where exposed to U.V.
- 3: Further testing is planned./Results to be published later

34c. Epoxy adhesives on LDEF (concluded) (from ref. 107).

