

N 9 2 - 2 3 2 8 9

MOLECULAR FILMS ASSOCIATED WITH LDEF*

E. R. Crutcher and K. J. Warner
Boeing Defense and Space Group
Seattle, WA 98124-2499
Phone: 206/773-7002, Fax: 206/773-1473

SUMMARY

The molecular films deposited on the surface of LDEF originated from the paints and RTV silicone materials intentionally used on the satellite and not from residual contaminants. The high silicone content of most of the films and the uniformity of the films indicates an homogenization process in the molecular deposition and suggests a chemically most favored composition for the final film. The deposition on interior surfaces and vents indicated multiple bounce trajectories or repeated deposition-reemission cycles. Exterior surface deposits indicated a significant return flux. Ultraviolet light exposure was required to fix the deposited film as is indicated by the distribution of the films on interior surfaces and the thickness of films at the vent locations. Thermal conditions at the time of exposure to ultraviolet light seems to be an important factor in the thickness of the deposit. Sunrise facing (ram direction) surfaces always had the thicker film. These were the coldest surfaces at the time of their exposure to ultraviolet light. The films have a layered structure suggesting cyclic deposition. As many as 34 distinct layers have been seen in the films. The cyclic nature of the deposition and the chemical uniformity of the film one layer to the next suggest an early deposition of the films though there is evidence for the deposition of molecular films throughout the nearly six year exposure of the satellite. A final 'spray' of an organic material associated with water soluble salts occurred very late in the mission. This may have been the result of one of the shuttle dump activities.

INTRODUCTION

This paper provides a spectrographic and photographic summary of the molecular films created in orbit along with the spectra of suspected source materials. Over four hundred infrared spectra have been collected from different areas of LDEF and compared to specific source materials. Twenty spectra are presented here. The molecular films on LDEF resisted solvents very well. Alcohol wipes of the films and even those using more aggressive solvents generally failed to remove the film for analysis. All of the data presented here is the result of direct analysis of the deposit in place on the LDEF substrate material or was mechanically removed by scraping the surface. Extraction performed under the microscope using a variety of solvents confirmed the film's resistance to solvent collection.

The distribution of the film is shown in this paper as it appeared after recovery and evidence is presented for a greater distribution of the brown film earlier in the orbital exposure of LDEF. Evidence is also provided suggesting the contribution of different source materials to the total deposit. The instruments used and associated analytical procedures have been presented previously (Ref. 1).

*Work done under NAS 1-18224, Task 12

COMPOSITION OF LDEF MOLECULAR FILMS

The discoloration of the LDEF surface was one of the earliest observations made. The discoloration was expected but the extent of the coverage was a bit surprising. Some of the films were so thick that they were peeling from surfaces as large flakes. In other areas the films were very thin but as a result of their dark color were still quite evident. Typical brown film spectra is shown in Figures 1 and 2. These are spectra from the earth end and space end of LDEF respectively. Both are from openings in the satellite surface that vent the interior of the satellite and from sides of the vent that faced in the ram direction, the direction of travel. The principle absorption bands are essentially the same. The broad band between 3200 and 3600 wave numbers corresponds to O-H and N-H groups. Nitrogen containing groups in the film have been confirmed by micro-chemical tests and by electron beam elemental analysis. Most of the peak is due to the presence of the O-H group. Some of the O-H present may be the effect of hydration following recovery. The C-H stretch at about 2960 is evident in both spectra as is a distinct carbonyl at 1710 and 1630. The region below this is a bit more complex due to the similarity of the absorption region of urethanes from the paints used (Figures 3 and 4), those of the silicones used on LDEF (Figure 5), and the organo-phosphates used in materials on some trays (Figure 6). For the space end film about 45% of the weight of the film was recovered after ashing as a transparent, colorless, film of silicon dioxide. This would correspond to a weight percent of 21% silicon in the film tested.

Tray C-12 was a special case. When LDEF was first rotated in SAEF-2 a liquid began running from this tray. The spectrum of the liquid (Figure 7) essentially matched that of the triocyl phosphate used as a fire retardant material in the plastic insulation around the fiber optic bundles on that tray (Figure 6). The brown film around tray C-12 contained very little silicones as is indicated by the absence of the peak near 800 wave numbers in this spectrum (Figure 8).

Tray H-06, being on the space end, had a complex exposure with the trailing side of the tray being exposed to atomic oxygen (AO) and the leading side of the tray being shielded. The fluence of AO has not been estimated for the microenvironments of tray H-06 but in the AO exposed area the patches of brown film persisted (Photograph 1). The film was analyzed in three layers. The top layer spectra is shown in Figure 9 and is dominated by the silica absorption band at 1060. The broad band around 3200 to 3600 wave numbers is probably due to moisture absorbed since recovery. Some carbonyl is also present. Beneath that layer the silicone pattern becomes more evident, the carbonyl peaks become more defined and larger and the O-H/N-H band becomes more pronounced, again probably due to hydration (Figure 10). The C-H absorption peak is absent or so small that it is lost in the broad water absorption band. Still lower the silicones disappear and the characteristic white urethane paint pattern is seen (Figure 11). Figure 12 shows the spectra of brown film in tray H-06 facing the trailing direction. The brown film here appears to be a UV exposed modification of the A276 white paint with very little deposited silicones, based on the intensity of the peak at 800 wave numbers. The strong absorption around 700 and below is due to the pigment of the paint. A more typical brown film pattern was collected from the head of bolt A on clamp 12 of tray H-06 (Figure 13). Photograph 2 illustrates the deposition of the brown film in the opposite corner of tray H-06 and shows the small circular deposits associated with each wire tie wrap. Figure 14 shows the infrared spectrum of these deposits. They had essentially no silicones and were dominated by the C-H absorption band. Photograph 3 shows the appearance of this area of tray H-06 under visible light illumination and ultraviolet light illumination. Ultraviolet light illumination was found to often make visible patterns not visible with normal illumination. Ultraviolet light was never used until all initial spectra had been collected to minimize induced changes in the films.

The thickest brown films always formed on vents from the interior on the side facing into the ram direction. Figure 15 is an example from tray F-06. Notice that this spectrum is very similar to that in Figures 1 and 2. A yellow deposit on the front of tray E-02, clamp 6 had a pattern that was quite different than the typical brown film (Figure 16). No precursor of this deposit has been found at this time.

The backs of the tray clamps and shims were examined to evaluate the types of molecular film contaminants that were launched with LDEF. The material on the back surface of tray E-06, clamp 1 had a large silicone component (Figure 17). Closer to the edge of the clamp the hydrocarbon component increased (Figure 18) until at the edge of the clamp the pattern had become very similar to the typical brown film pattern (Figure 19).

Another interesting spectrum was shown by brown spots found on a number of surfaces (Figure 20). These brown spots were often associated with a variety of particulate matter, paint spheres, wear metals, fibers, and other debris (Photograph 5) and a significant concentration of sodium chloride, potassium chloride, and other water soluble salts. These materials were also found on leading edge trays indicating they were not present during the nearly six years LDEF was in orbit. These may be the residue of waste dumps made after the retrieval of LDEF by the shuttle.

Photograph 6 shows a handprint in the bottom of tray F-06. The handprint is lighter than the surrounding area indicating the print acted as an ultraviolet light filter or as a sacrificial surface layer reducing the effect on the paint vehicle underneath or it represented an area of positive pressure preventing the deposition of brown molecular film. Fingerprints in other areas were seen to become dark brown or black but this was always on metal surfaces rather than paint. Similar "lightening" effects were seen on other trays such as the pre-flight scuff patterns seen in the brown deposits in Photographs 1 and 2.

The brown film was deposited in layers. As many as 34 distinct layers have been counted in a single deposited film. Photograph 7 shows such a piece of film from a corner vent of tray C-12. These layers suggest a cyclic deposition. The most obvious cyclic event is an orbit but this would indicate that these solvent insoluble, polymerized films form and become stable with one orbit. Many other cycles exist of much longer duration but it is difficult to conceive of a slow steady release rate maintaining the same proportion of functional groups from multiple sources that would persist over years in orbit to deposit these layered films. These films do not change significantly from layer to layer which would also suggest an early release and deposition. There is some evidence on the canister trays that suggest later deposition of materials. This evidence is still being evaluated.

On the leading edge trays there was often little evidence of deposition by discoloration. Elemental analysis of the surface in many areas did indicate silicate films, presumably the remnant of the hydrocarbon/silicone film after reacting with atomic oxygen. Figure 21 is the infrared spectrum of one of these films on clamp 4 of tray F-09. Figure 22 shows the elemental mapping of this "shadow" seen next to bolt A of clamp 4 on tray F-09. The aluminum map shows the bare aluminum exposed under the washer and the aluminum in the anodized surface of the clamp. The oxygen map illustrates the distribution of oxides. In the area of the weaker aluminum signal the silicon map illustrates a concentration of silicon. This is a silicon dioxide film over the anodized aluminum. Photograph 8 shows the LDEF structure with the trays removed and a slight discoloration in the exposed area of the structure associated with the presence of the silica film compared to the areas covered by the tray edges and tray clamps. This is in contrast to the obvious dark film seen on the trailing structure clearly delineating the position of the tray edges and clamps (Photograph 9).

DISTRIBUTION OF THE MOLECULAR FILMS

The distribution of molecular films on LDEF was one of the most obvious features of its orbital exposure. All exterior trailing surfaces and surfaces shielded from atomic oxygen on LDEF exhibited a brown discoloration. Those surfaces that faced into the atomic oxygen were bleached white or were mottled in shades of pastel green and red as a result of thin film interference effects on the surface of aluminum panels. The whites of the painted surfaces were not bright but tended toward the gray as a result of the formation of color centers in the rutile pigment that absorbed the visible wavelengths of light. When LDEF was finally back at Kennedy the distribution of the color effects could be studied in more and

closer detail. The gray of the white paint pigment disappeared quickly back on earth but the brown discoloration and the discoloration caused by thin film effects persisted. In areas associated with the venting of the interior of the satellite thick brown films had developed, some of which were a few hundred micrometers thick and were peeling from the surface on which they had been deposited. When the inside of LDEF was opened for viewing by the removal of experiment trays molecular films deposition patterns were seen on interior surfaces. Circular patterns, sharp silhouettes of interior structures, and broad linear areas of discoloration were evident.

The one common thread in all of these deposits was the exposure to ultraviolet light. The exterior surface was bathed in ultraviolet light every orbit. The interior was a region of sharp shadows and rastering beams cut short by the geometry of LDEF's structure. Two conditions for the creation of these durable brown films were the presence of a condensed material suitable for polymerization and ultraviolet light to polymerize the film.

The ram direction always exhibited the thickest films. There are two attributes characteristic of the ram direction. The first is that the ram direction always received ultraviolet light exposure before any adjacent surface that faced in the trailing direction. The earth end ram surfaces were exposed as the satellite came from the shadow of the earth. The second attribute is that the surfaces facing the ram direction always received more exposure to the effects of atomic oxygen than the surfaces facing the trailing direction. The temperature of the satellite is at its lowest when it leaves the shadow of the earth. The cool surfaces are relatively good collectors (high sticking coefficient) for condensible molecular materials. As a result the ram facing surfaces are still cool when they are first exposed to the ultraviolet light from the sun. As the ultraviolet light polymerizes the exposed film the sun's light warms the satellite and the condensed molecular materials not polymerized become more mobile. By the time the trailing surfaces receive ultraviolet light they have warmed considerably and lost much of the condensed film.

The source materials for this film were everywhere on the interior and vented outward through every available vent as can be seen by the wide distribution of the films. The urethane paint was literally on every interior surface and the silicone materials were widely distributed about the interior on experiment A0178 (see Ref. 2, figure 2). Vent paths from the interior were often tortuous due to the depth of some of the trays and the dimensions of the longeron and brace I-beams. Most exiting molecules encountered a number of surfaces before exiting the satellite and being available for redeposition as part of the return flux. The heaviest return flux should have been on the surfaces facing the ram direction (Ref. 3). That may have been but the ram directed surfaces have been scoured of thin hydrocarbon films by the atomic oxygen exposure. Silica films would be expected to be present if a film had first been deposited and then burned away but the presence of silica is not as uniform in distribution as the brown film seen deposited on the trailing edge surfaces (compare Figure 22 and Photograph 9). The tray surfaces facing in the trailing direction and exposed to return flux only have films of less than 100 nanometers in thickness. These films also exhibit a directionality that may be related to the nearest corner vent of the tray. This directional dependency is independent of the ram direction and may help explain the distribution of silica films found on the ram facing trays. In Figure 22 the silica is on the side of the bolt toward the space end cover panel. The space end cover panel directed venting materials toward this clamp (tray F-09, clamp 4) and its bolts. The heaviest deposits of silica extend from the edge of the washer toward the edge of the clamp toward the space end panel. In the areas of the clamp where there was no bolt the silica concentration is on the order of the background for the aluminum clamp. The presence of the bolt enhanced the concentration of the film between the source and the bolt. These examples indicate that much of the return flux was not redirected by 180 degrees but rather by less than 90 degrees as a result of configurational geometries that tended to direct escaping molecules at relatively low angles over the surface of the satellite.

CONCLUSION

1. The films consisted primarily of modified outgassing products of the RTV silicone materials used and the urethane paints.
2. Fixation of the deposit was dependent on ultraviolet exposure and possibly a low level of atomic oxygen exposure.
3. The films were deposited cyclically with up to 34 layers being counted in a single fragment of film.
4. Local sources of outgassing material contributed to local films.
5. On the leading rows the films were converted to silicon dioxide type films or were removed by the attack of atomic oxygen on carbon based substrates.
6. Organic materials were deposited on LDEF after retrieval that had a high hydrocarbon content and were associated with potassium and sodium chlorides.

REFERENCES

1. Preliminary Report on LDEF Contaminants, 1991 NASA Publication.
2. Crutcher, E. R., L. S. Nishimura, K. J. Warner, and W. W. Wascher: Silver/Teflon Blanket: LDEF Tray C-08. First LDEF Post-Retrieval Symposium, NASA CP-3134, 1992.
3. Rantanen, R. O. and T. D. Gordon: Contaminant Buildup on Ram Facing Spacecraft Surfaces. OPTICAL SYSTEMS CONTAMINATION: EFFECTS, MEASUREMENT, CONTROL, SPIE Vol. 777, 1987.

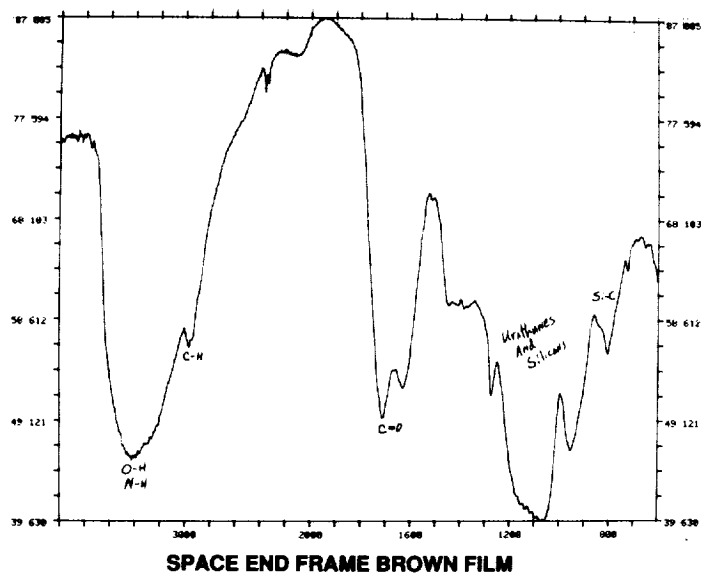


Figure 1: Brown film from longeron exposure at tray G-12 facing ram direction.

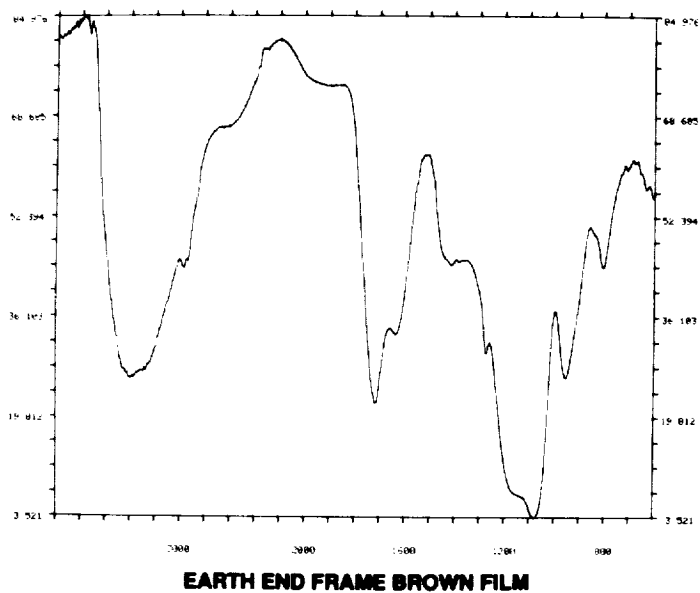


Figure 2: Brown film from longeron 13, space end, exposure facing ram direction.

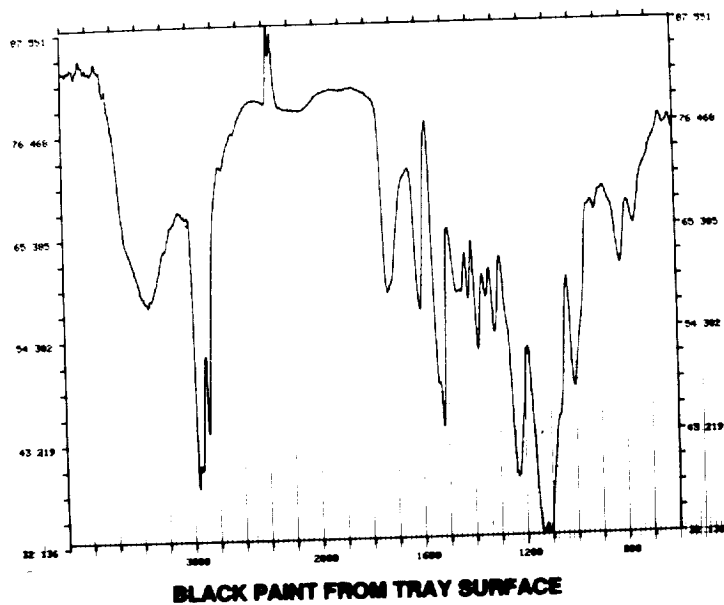


Figure 3: Black paint from back surface of tray F-06.

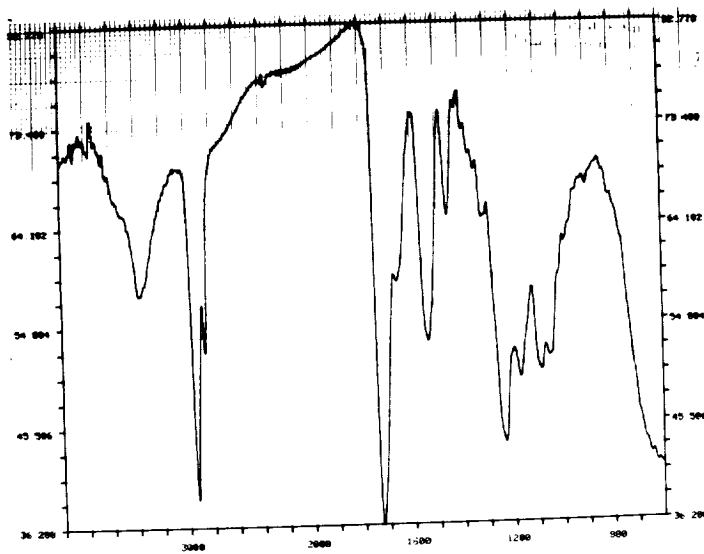


Figure 4: White paint from beneath bolt, interior of tray H-06.

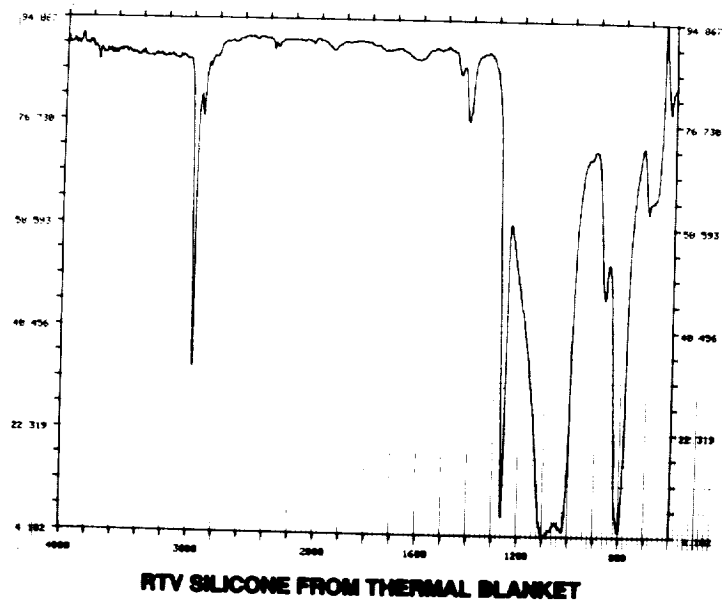


Figure 5: Silicone adhesive used to attach velcro tape to back of Silver/Teflon Blankets, tray F-02.

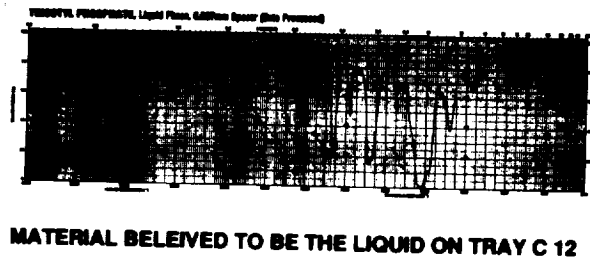


Figure 6: Trioctyl phosphate standard spectrum.

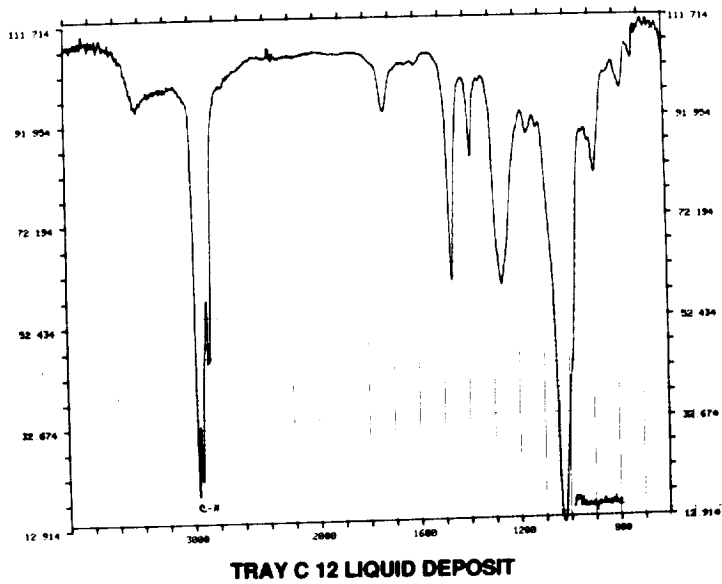


Figure 7: Tray C-12, liquid collected on glass fiber paper during deintegration.

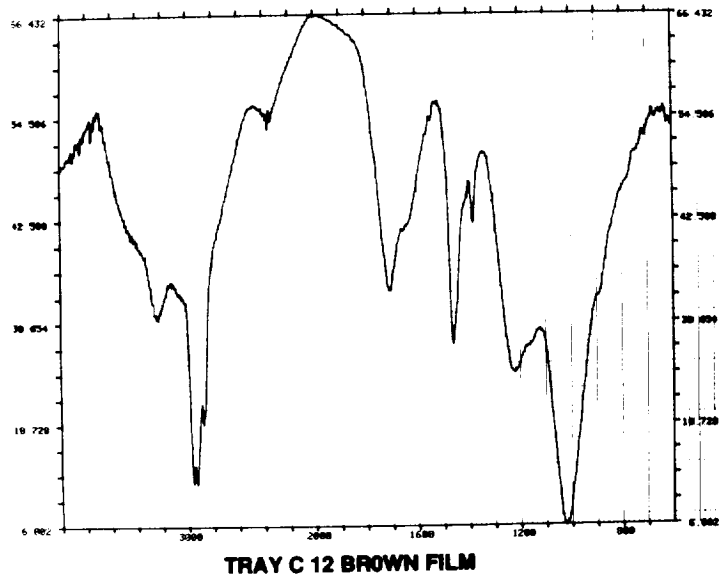


Figure 8: Tray C-12, brown film from corner vent.

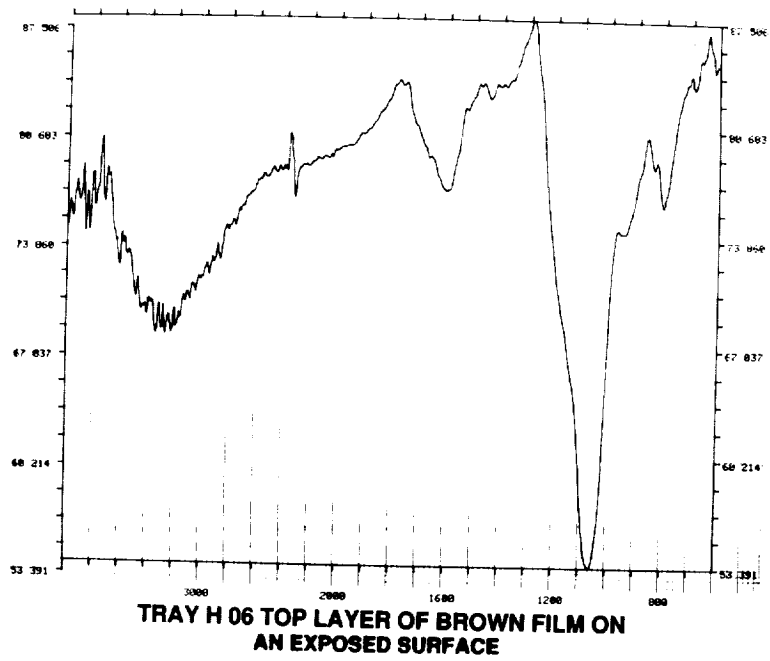


Figure 9: Tray H-06, top layer of AO exposed brown film.

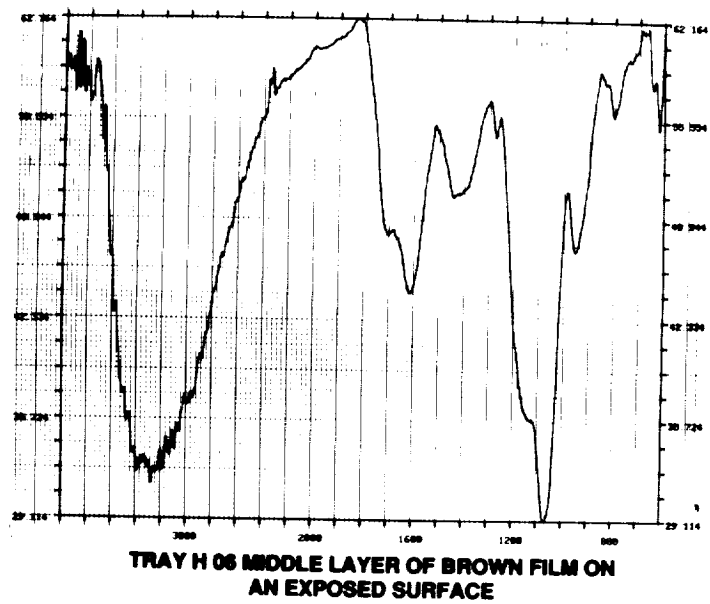


Figure 10: Tray H-06, middle layer of AO exposed brown film.

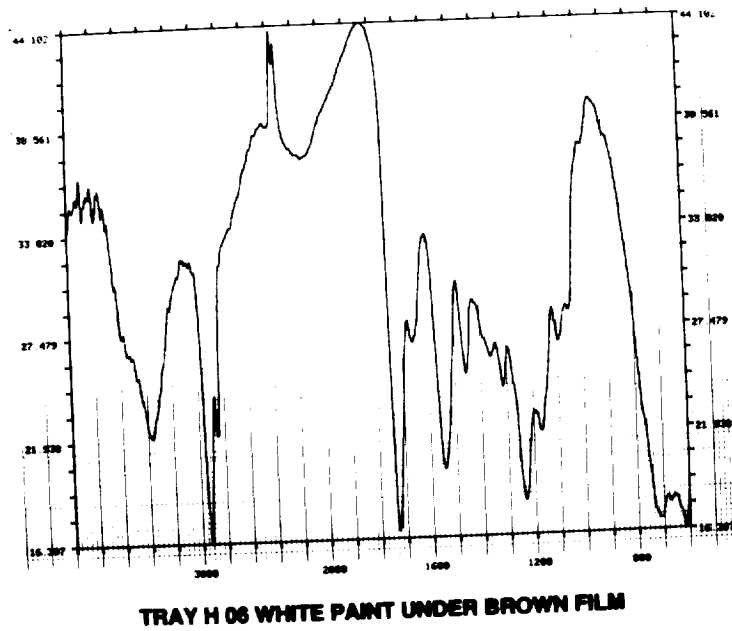


Figure 11: Tray H-06, bottom deposit (paint surface) of AO exposed brown film.

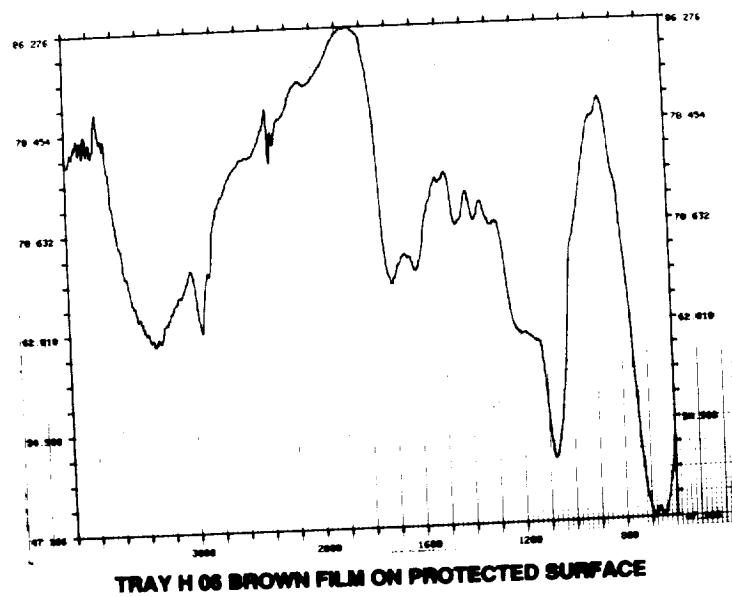


Figure 12: Tray H-06, brown deposit on trailing exposure.

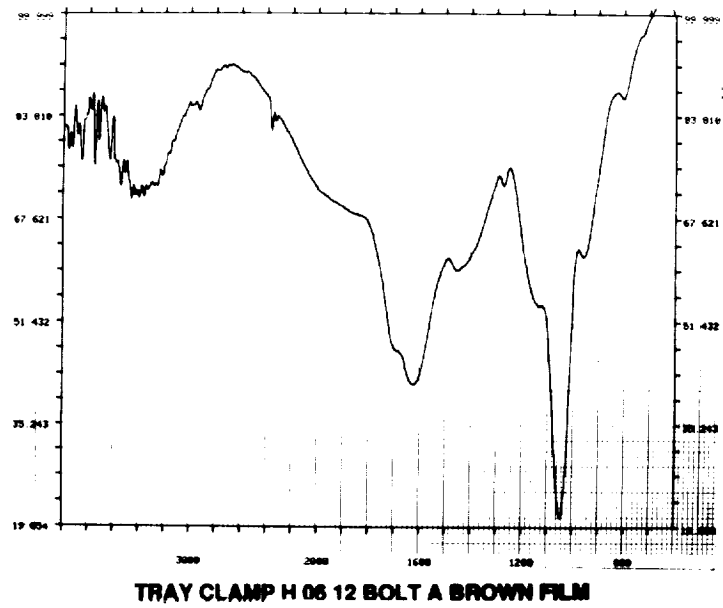


Figure 13: Tray H-06, clamp12, bolt A.

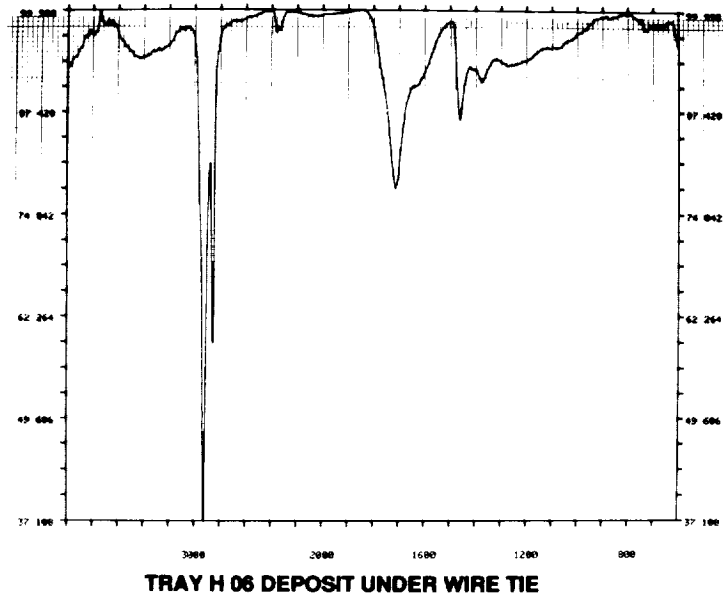
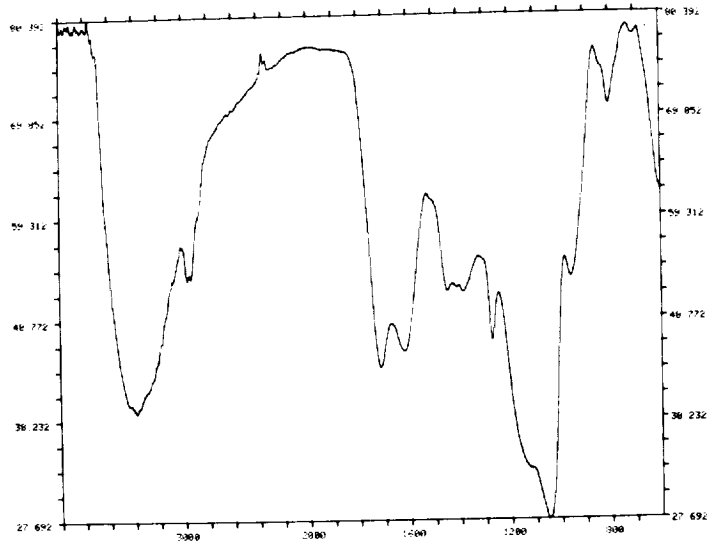
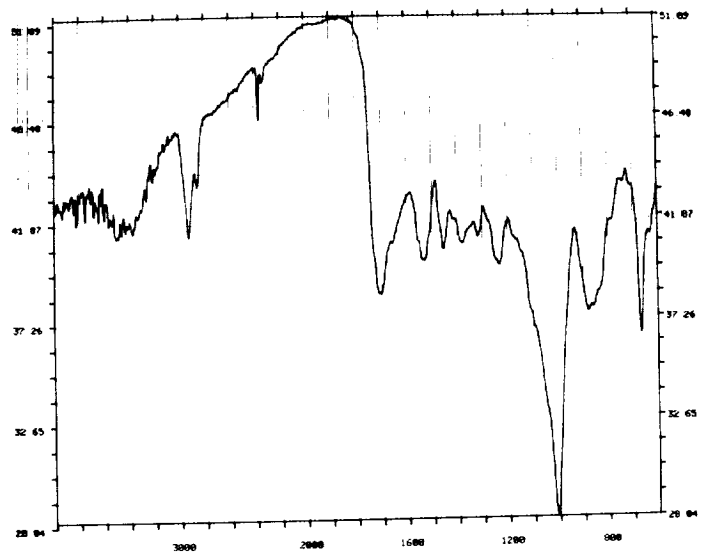


Figure 14: Tray H-06, deposit beneath wire tie wrap.



TRAY E 06 CORNER VENT FACING RAM DIRECTION

Figure 15: Tray F-06, corner vent deposit facing ram exposure.



TRAY CLAMP E 02 6 YELLOW DEPOSIT ON FRONT SURFACE

Figure 16: Tray E-02, clamp 3, yellow deposit.

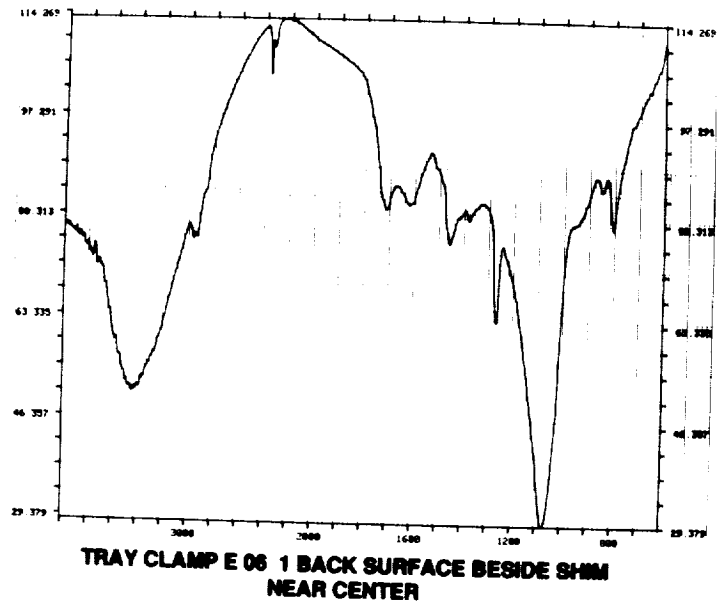


Figure 17: Tray E-06, clamp 1, deposit between clamp and shim at center.

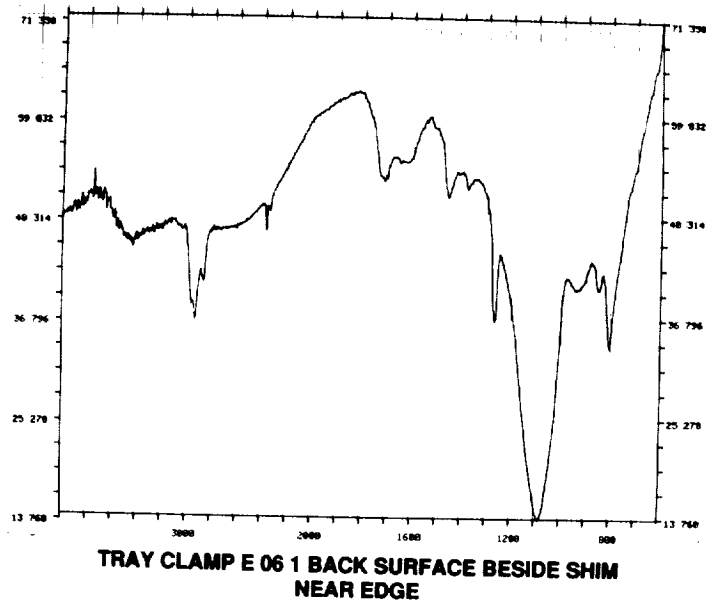


Figure 18: Tray E-06, clamp 1, deposit between clamp and shim near edge of clamp.

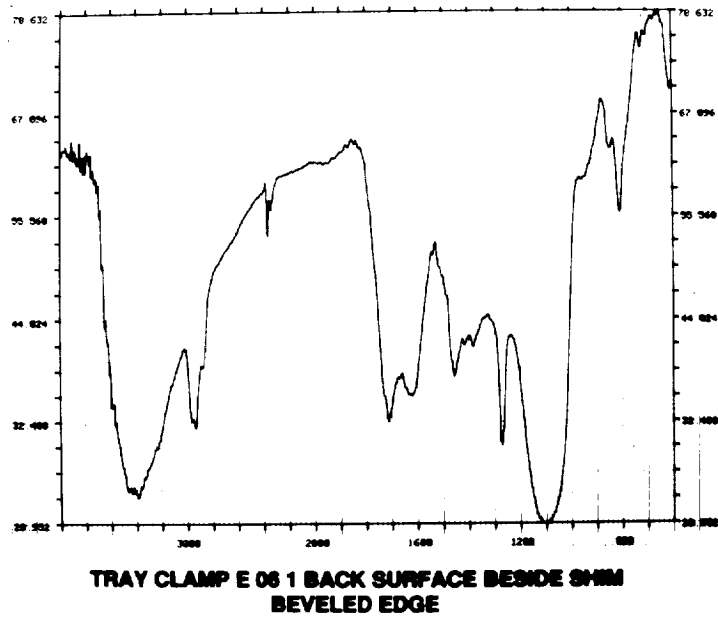


Figure 19: Tray E-06, clamp 1, deposit on beveled edge of clamp.

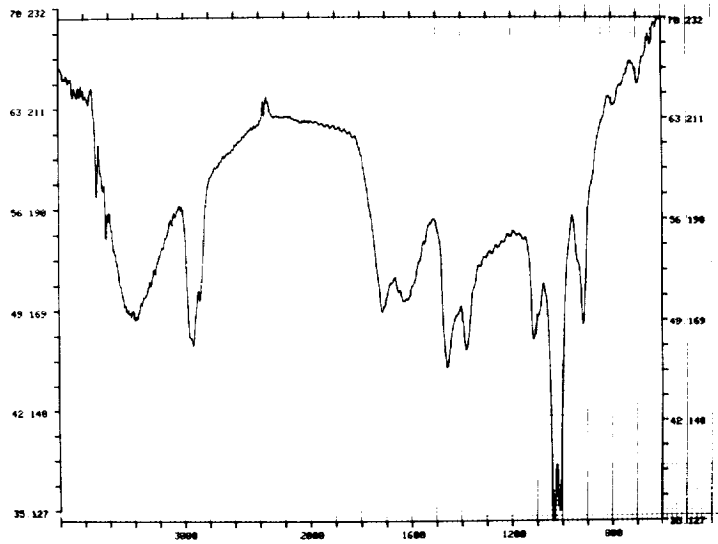


Figure 20: Tray F-09, clamp 8, brown spot.

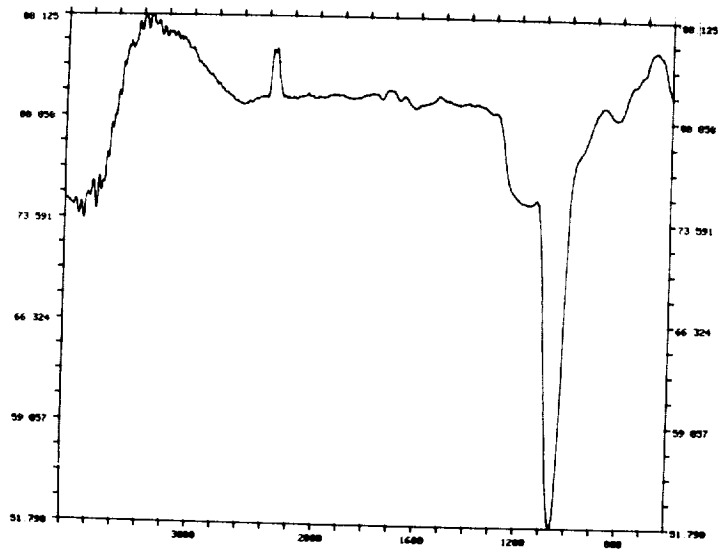


Figure 21: Tray F-09, clamp 4, surface with change in interference color.

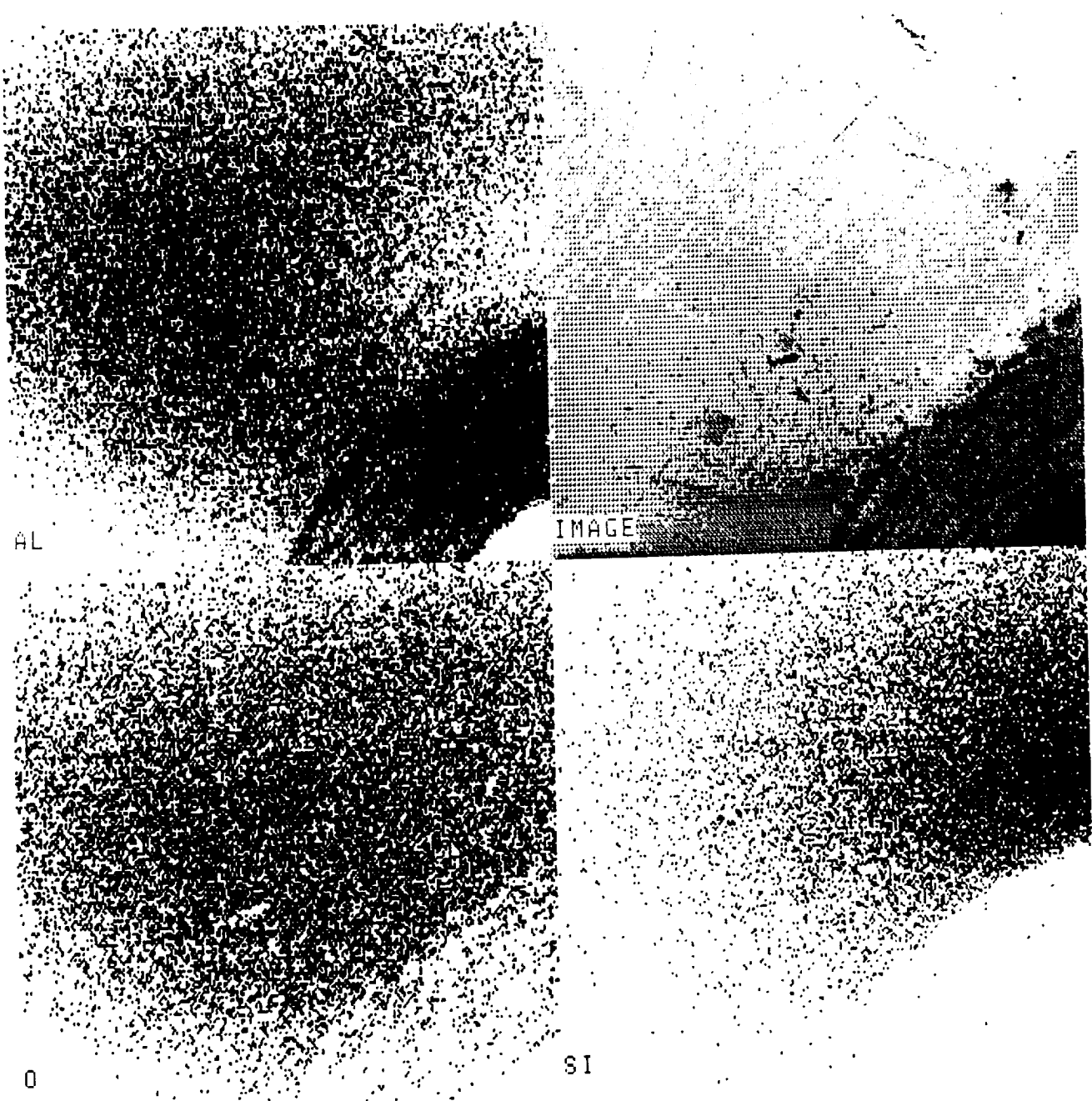
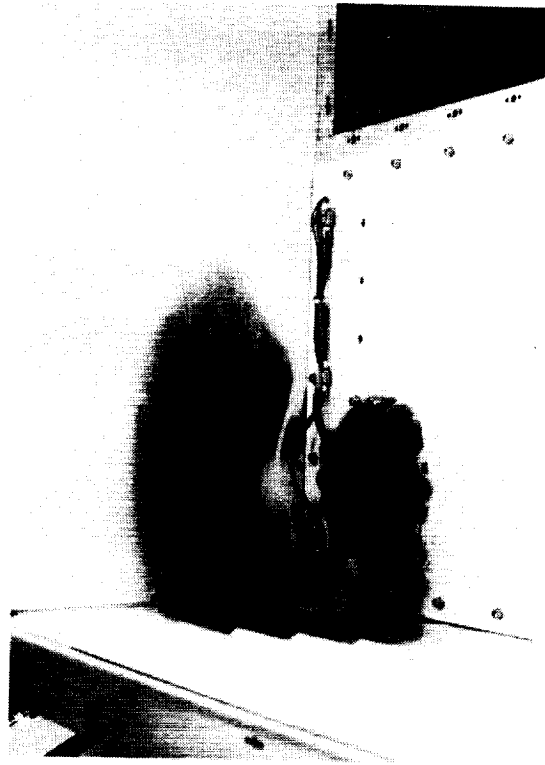


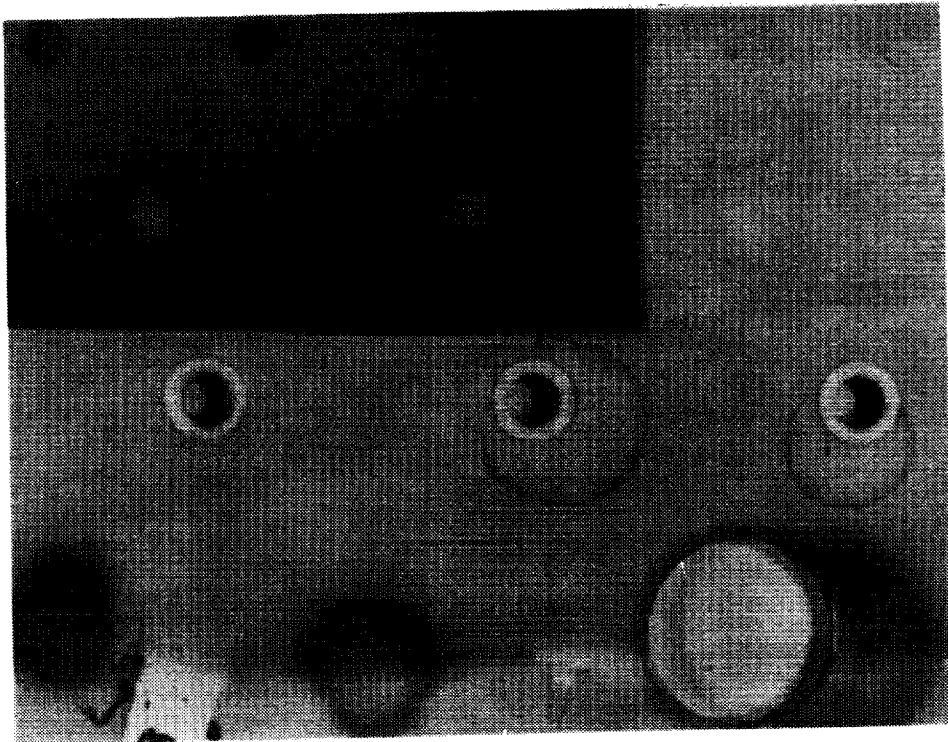
Figure 22: Tray F-09, clamp 4, elemental map of area with different interference color.
(Original figure not available at time of publication.)



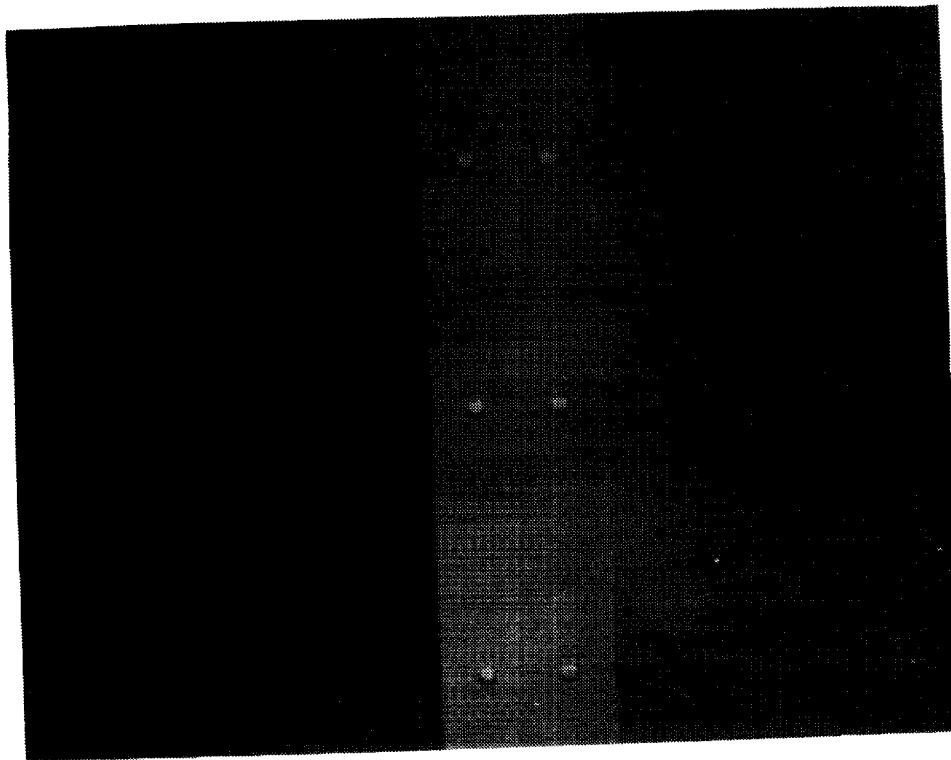
Photograph 1: Tray H-06, brown deposit in AO exposed corner.
(See color photograph, p.599.)



Photograph 2: Tray H-06, brown deposit and tie wrap deposit in other corner.
(See color photograph, p. 599.)



Photograph 3: Tray H-06, visible and UV illumination view of the tie wrap deposit.

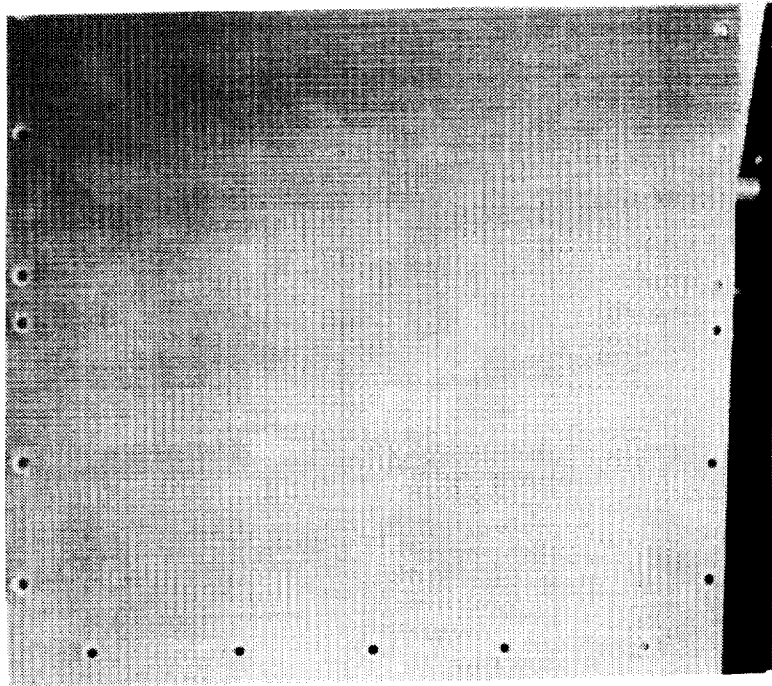


Photograph 4: Tray F-06, back of bottom panel showing shadow only visible with UV illumination.



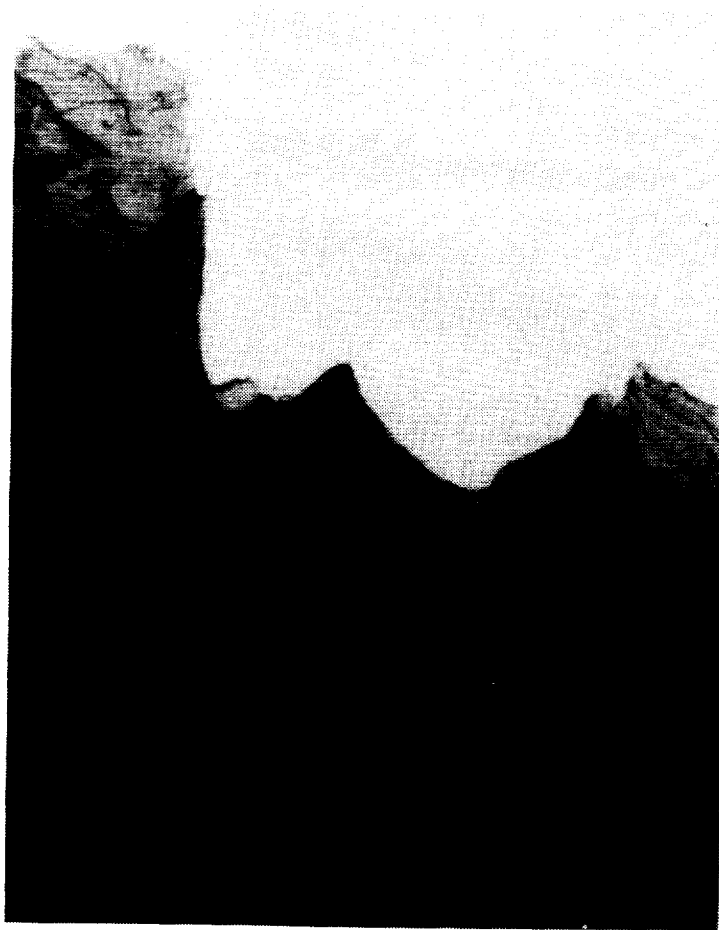
Photograph 5: Tray F-02, clamp 6, brown droplet deposit.

(See color photograph, p. 600.)



Photograph 6: Tray F-06, handprint on bottom panel.

ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH



Photograph 7: Tray C-12, layered brown film.

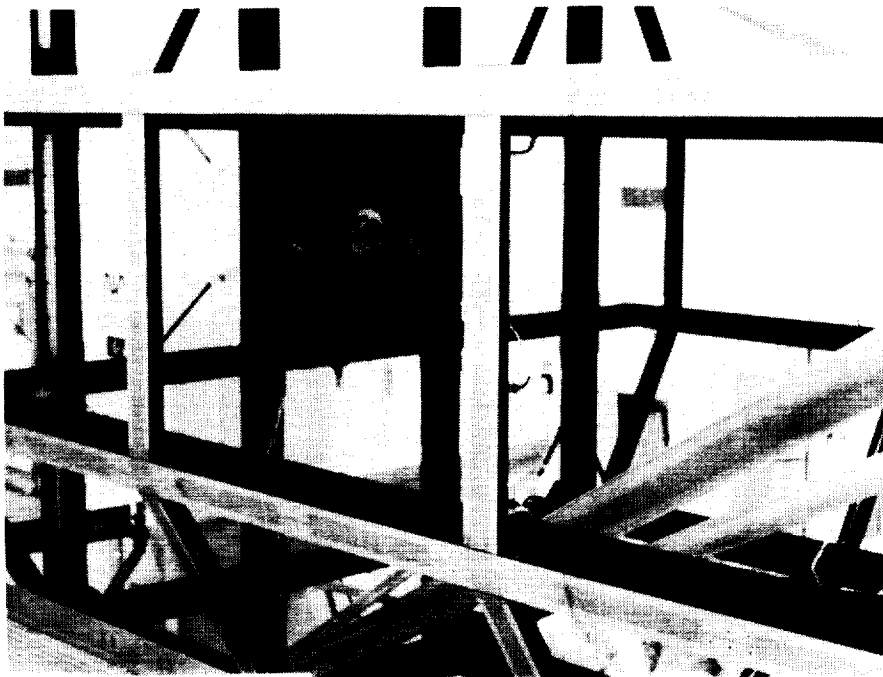
(See color photograph, p. 600.)

ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH



LDEF Leading edge (ram direction)

Photograph 8: Leading edge view of LDEF structure.



NVR stain LDEF trailing edge Earth end

Photograph 9: Trailing edge view of LDEF structure.

