ORGANIC CONTAMINATION OF LDEF

N92-23290

Gale A. Harvey
NASA Langley Research Center
Hampton, VA 23665-5225
Phone: 804-864-6742, Fax: 804-864-7790

SUMMARY

A brown stain of varying thickness was present on most of the exterior surface of the retrieved LDEF. Tape lifts of Earth-end LDEF surfaces taken in February 1990 showed that the surface particle cleanliness immediately after retrieval was very good, but faint footprints of the tape strips on the tested surfaces indicated a very faint film was removed by the tape. Solvent wipes of these surfaces showed that the stain was not amenable to standard organic solvent removal. Infrared spectra of optical windows from tray E5 and scrapings indicate that the film is primarily of organic composition, but is not similar to the oil that seeped from tray C12. Very dark and heavy deposits of the stain are present at openings and vents to the interior of LDEF. Heavy brown and blue-green deposits are present in the interior of LDEF where sunlight penetrated through cracks and vent openings. Photographs of the deintegrated LDEF graphically show the stain distribution.

The exterior of LDEF had significant areas painted with a white polyurethane paint for thermal control, and almost all of the interior was painted with a black polyurethane paint for thermal control. The brown staining of LDEF is consistent with long-term outgassing of hydrocarbons from these paints followed by rapid solar-ultraviolet-induced polymerization of the outgassed hydrocarbons when the outgassed molecules stuck to surfaces exposed to sunlight.

INTRODUCTION

The Langley Research Center developed and manages the Halogen Occultation Experiment (HALOE, ref. 1) to measure stratospheric ozone chemistry on a global basis. The HALOE instrument is a mid-infrared optical instrument which is sensitive to organic film on optical surfaces because the two spectral bandpasses for measurement of HCL and CH4 include the 3.4μ hydrocarbon absorption band (ref. 2). The HALOE contamination control program makes extensive use of high-resolution-in-transmission Fourier Transform Infrared (FTIR) spectroscopy of the 3.4μ band to monitor HALOE organic cleanliness (ref. 3). The HALOE measurement-of-organic-film techniques have been applied to the retrieved LDEF.

TAPE LIFT DATA

Taking of tape lifts is an established procedure for measuring surface particle cleanliness. Particle cleanliness is related to MIL-STD-1246B (ref. 4) which gives the particle cleanliness level, CL, which is a standard method of specifying particle cleanliness. Specific descriptions of particles and their size distributions are used to evaluate sources of particle contamination and to evaluate cleaning procedures.

The procedure consists of preparing tape-lift kits, taking tape lifts of a test surface, and reading the tape lift strips in a clean environment.

Sixteen tape lifts of removed LDEF Flight hardware and surfaces in the SAEF 2 clean room were taken on February 14, 1990. The cleanliness levels are plotted in Figure 1. The particle cleanliness level of the retrieved LDEF end panels as seen in Figure 1 was better than 300, which is quite clean. However, observers of the tape lift operation noticed faint "footprints" of the contact area of the tape strips were visible on the tested LDEF surfaces indicating a faint film was removed by the tape. Subsequent tape lifts indicated the surface cleanliness rapidly deteriorated with deintegration activities.

SOLVENT WIPE DATA

Extracted clean room wipes (ref. 5) were used extensively in the cleanliness certification of thermal-vacuum chambers used for testing the HALOE instrument. The procedure is to wet the test surface with a cleaning solvent (ie spectroscopic grade isopropyl alcohol) which will allow transfer of some of the organic film (typically about 75 percent) to an extracted cleanroom wipe. The wipe is air dried at the field site, bagged, and transported to an analytical lab. The cleanroom wipe is soaked in a high purity transfer solvent at the lab, and the organic contamination is then extracted and transferred to an IR window for weighing and FTIR spectroscopy. The surface concentration factor from wipe to IR window is 1,000. The 3.4μ spectrum of an isopropyl alcohol wipe of 1 square foot of an LDEF Earthend thermal control panel is present in Figure 2 along with the spectrum of a control wipe. The LDEF Earthend thermal control panel wipe had about twice the NVR as the control wipe. That is, the thermal control panel had about 0.06 mg/ft^2 of organic film that would dissolve in isopropyl alcohol.

ABSORPTION SPECTRA OF E5 OPTICAL WINDOWS

Experiment S0050-1 contained several infrared transmitting windows. These optical windows were in a 1/6 compartment of tray E5 which was covered with a 50 percent transmitting/50 percent blocking sunscreen. The inside surface of the sunscreen was painted with Chemglaz Z306 black paint for thermal control.

A 3.4μ spectrum of the CaF2 window flown on LDEF is presented as Figure 3. Similar CaF2 windows are used extensively in the HALOE contamination control program (ref. 6) and a large data base of organic films on CaF2 windows exists at LaRC. The 3.4μ absorption on the LDEF window is about 7 percent.

An estimate of the organic film mass per square foot can be obtained by ratioing the NVR mass with 7 percent absorption on an IR window/weighing pan of small area (0.08 in^2) to 1 square foot of area. Numerous measurements of organic film show 0.1 mg of organic residue on a 0.08 in^2 of CaF2 corresponds to 7 percent absorption at 3.4μ. Thus, a calculated mass/ft^2 of organic film on the LDEF window is:

$$\frac{144\ \text{in}^2}{1\ \text{ft}^2} \times \frac{0.1\ \text{mg}}{0.8\ \text{in}^2} = 180\ \text{mg/ft}^2$$

This is a lot of organic film. One mg/ft^2 or less of organic film is the standard cleanliness level "A" typically required of contamination sensitive flight hardware.

The visual discoloration of this film can be seen in a photograph of a film-bracket-covered area and uncovered area in tray E5, shown in Figure 4.

ABSORPTION SPECTRA OF SEEPAGE FROM TRAY C12

Tray C12 of LDEF was observed to be leaking fluid several days after LDEF was moved to SAEF 2 for deintegration. This tray had heavy deposits at the edges of the tray cover, ranging from yellow-brown stains to a black layer of deposited material. The interior contained runs of fluid along the walls and a wet band about 6 cm wide by 60 cm long on the bottom of the tray against one end. Fluid from one of the runs was contact transferred to a clean CaF2 window. The 3.4μ spectra of this fluid is presented as Figure 5. The great strength of the methel stretch at 2860 cm^{-1} and 2960 cm^{-1} shows that the hydrocarbon composition of this fluid is much different than the hydrocarbon composition of the contamination of Tray E5.

EXTERIOR PHOTOGRAPHS

Visual inspection of the deintegrated LDEF in April of 1990 clearly revealed several characteristics of the organic stain on LDEF. Figures 6 and 7 show the stain on the trailing edge (row 3) of LDEF. Figures 8 and 9 show a much fainter stain on the leading edge (ram direction=row 9) of LDEF. But Figures 10, 11, 12, and 13 show the heaviest deposits on end plates surface near vents from the interior. At these locations the deposits were so heavy they were curling off the rough milled surfaces of the end plates. It is concluded that the stain at one time was greatest on all leading edges, but that the direct ram surfaces were effectively cleaned by atomic oxygen during the later months in orbit. Figure 14 shows light NVR on the trailing edge of an end plate.

INTERIOR PHOTOGRAPHS

Brown stains were present on unpainted diagonal braces behind cracks between two sections of micrometeoroid panels (Figure 15). Brown stains were also present on unpainted end braces. Dark blue and blue-green deposits were present on interior surfaces facing the ram direction where sunlight was incident through cracks or vent holes. Figure 16 and 16a show the undeposited shadow of a fastener surrounded by a blue-green deposit. A blue deposit is shown in Figure 17 with a rail clip and its shadow. The deposit behind a 3/4" x 3/4" tray corner vent hole is shown in Figure 18. These deposits could be scraped off to uncover the black thermal-control paint underneath.

These photographs demonstrate that the organic stain was polymerized by sunlight and that the heaviest deposits were on the ram side.

OUTGASSING MEASUREMENTS OF THE THERMAL CONTROL PAINTS

Three independent measurements of outgassing of the black thermal control paint (Z306) used on LDEF were made at LaRC following the retrieval of LDEF. Exposures in a vacuum oven gave

0.1 percent mass loss after 1 week at 24° C;
1.4 percent mass loss after 1 week at 60° C;
and 23.0 percent mass loss after 16 hours at 177° C.

The 16 hours at 177° C would correspond to 6 years at ambient (25° C) temperature if the 10° C rise in temperature produces a doubling of outgassing rule applied.

High resolution FTIR spectra (Figures 19 and 20) of Z306 heated in an evacuated gas cell show considerable CO_2 and CO, and some CH_4 and H_2O outgassing during the first few hours at approximately 120° C. Heavier hydrocarbon absorption is also present at 2960 cm^{-1} (CH_3 stretch) in Figure 21. The mass loss during heating was 2.8 percent. A brown film coated the gas cell walls after heating of the 16 mg paint sample. Also shown in Figure 20 is a spectrum of scraped film from an LDEF end plate. The 3.4μ spectrum of the end plate scraping is almost identical to the gas cell film, but very unlike the spectrum from Tray E5 (Figure 3) and Tray C12 (Figure 5). The LDEF end plate scraping has 2 gm/ft^2 of mass per unit area.

Time-sequence FTIR spectra were obtained of outgassing of the white Chemglaz paint (A276) in an evacuated gas cell heated to 115°C. Spectra were obtained after 5, 10, 25, 40, 65, and 155 minutes of heating. Spectra of the unheated cell were also obtained 1 and 2 days later. These spectra are presented in figures 21-24. The 3.4 m absorption is the same as that of Chemglaz Z306. This absorption is the strongest feature in the 5 minute spectrum, but is surpassed in strength by CO_2 after 25 minutes of heating at 115°C. The mass loss after 155 minutes at 115°C was 2.7 percent.

Atomic mass spectra (figure 25) of outgassing at room temperature from a 5 month cured sample of Chemglaz Z306 was obtained with a residual gas analyser. A mass fragment of 113 amu is the most abundant paint outgassing heavy-mass-fragment. Additional mass-spectral data are reported in references 6 and 7.

CONCLUSIONS

The major conclusions drawn from studies of LDEF relating to organic film contamination are:

1. The primary source of the ubiquitous brown stain was outgassing of the black thermal control paint (Chemglaz Z306). The stain is a different hydrocarbon composition at the vent openings than on tray surfaces.

2. The paint outgassing and redeposition was temperature driven and retention on surfaces was strongly affected by solar ultraviolet induced polymerization of outgassed molecules.

3. Atomic oxygen severely eroded the stain on the leading edge (row 9) late in the mission.

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1. UARS Project Data Book, General Electric Astrospace Division, April 1987.

2. Harvey, G. A., J. L. Raper, and R. N. Messier, "Microcontamination of IR Spacecraft Optics," in Proceedings of Microcontamination Conference and Exposition, Anaheim, CA, pp. 237-259, October 1989.

3. Harvey, G. A. and J. L. Raper, "Halogen Occultation Experiment (HALOE) Optical Witness-Plate Program," NASA TM 4081, February 1989.

4. Military Standard Product Cleanliness Levels and Contamination Control Program, MIL-STD-1246A, August 18, 1967, Department of Defense, Washington, DC 20301.

5. Harvey, G. A., J. L. Raper, and D. C. Zellers, "Measuring Low-Level Nonvolatile Residue Contamination on Wipes, Swabs, and Gloves," Microcontamination, 8(11): 43-46, 69, 1990.

6. Colony, J. A., "Mass Spectrometry of Aerospace Materials," NASA TN D-8261, June 1976.

7. Glassford, A. P. M. and J. W. Garrett, "Characterization of Contamination Generation Characteristics of Satellite Materials, WRDC-TR-4114," WRDC/MLBT, WPAFB, Ohio, November 1989.

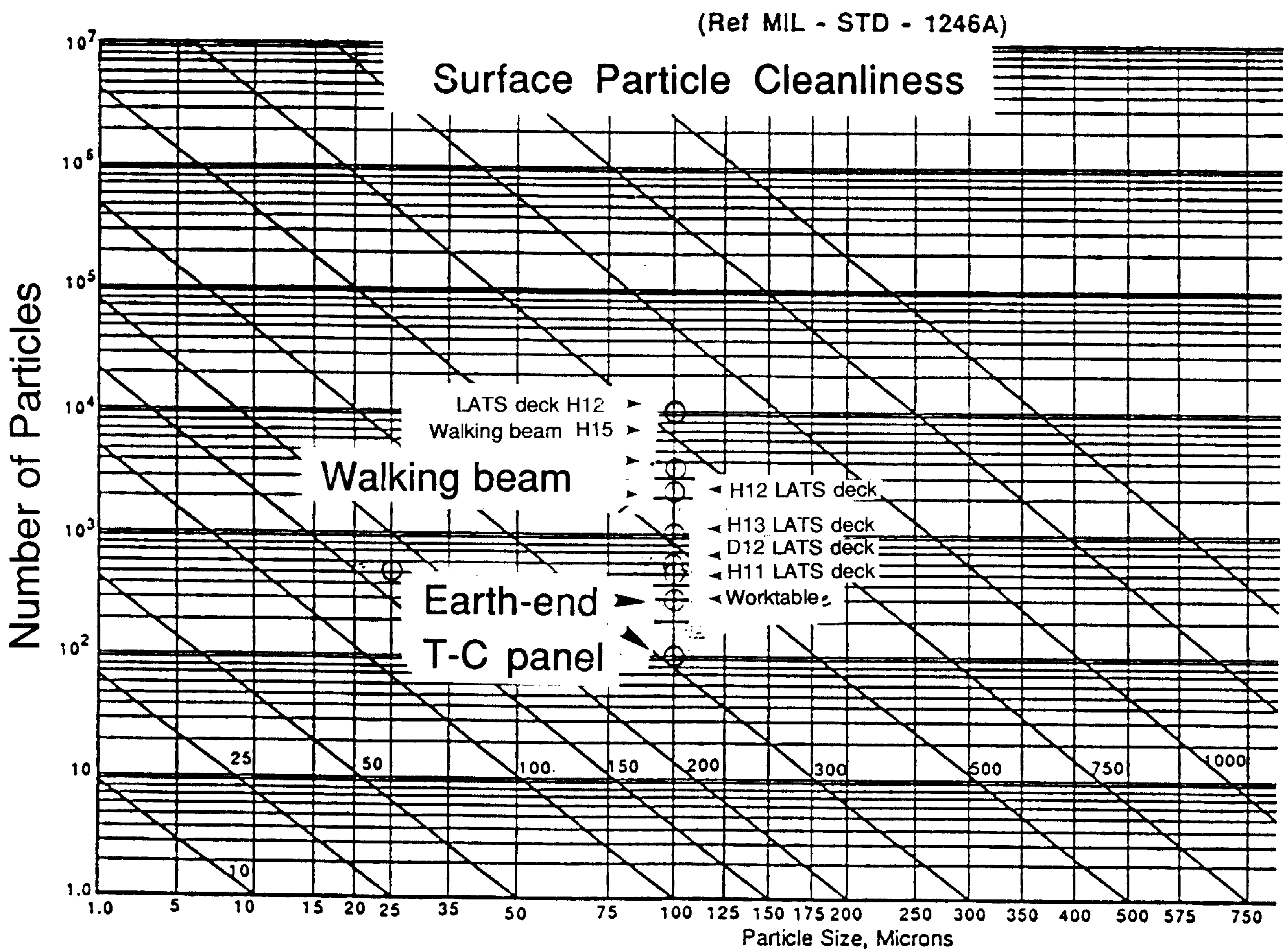

Figure 1. Surface particle cleanliness of LDEF Earth-end panel and walking beam.

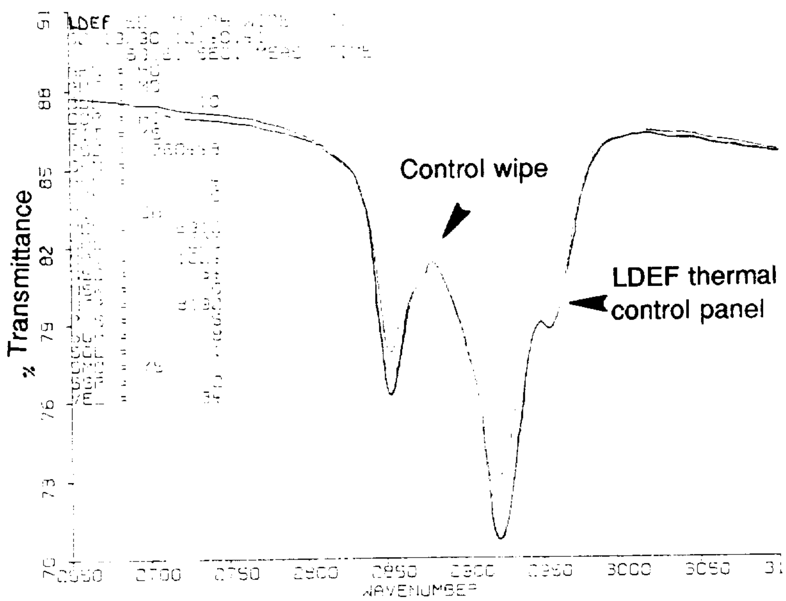

Figure 2. 3.4 μ spectra of Earth-end-panel NVR.

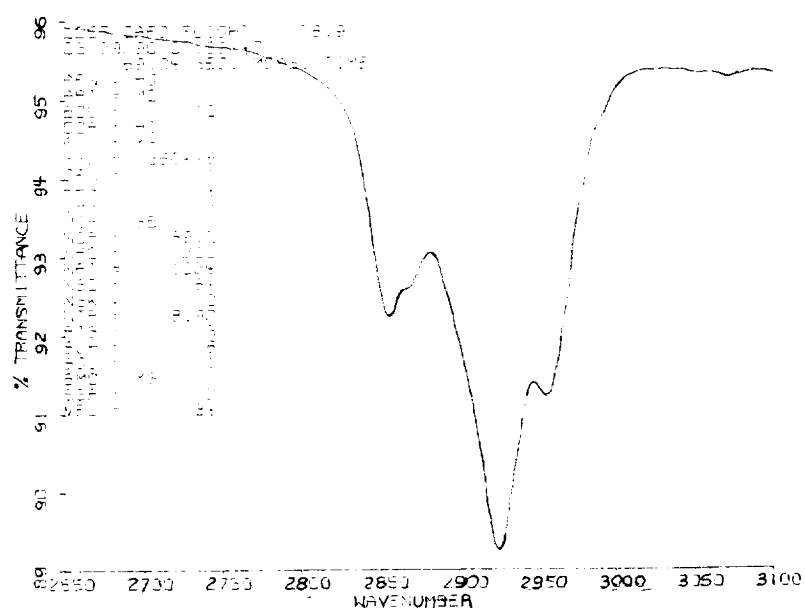

Figure 3. 3.4 μ spectrum of CaF_2 window from Tray E5.

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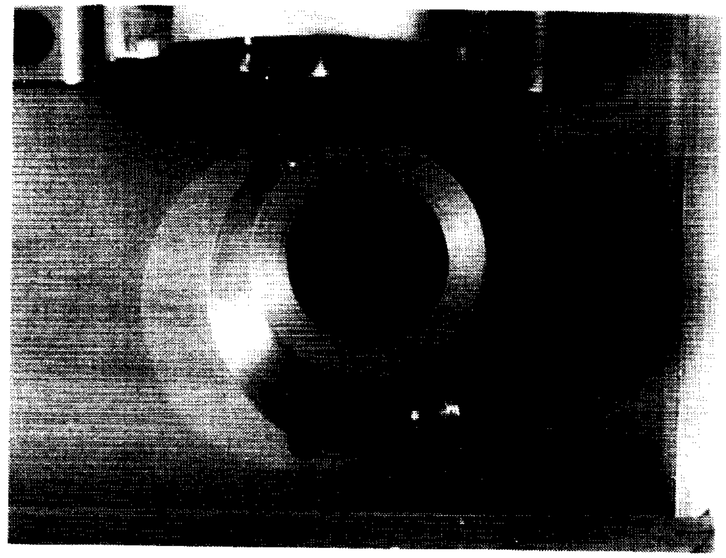

Figure 4. NVR stain in Tray E5.

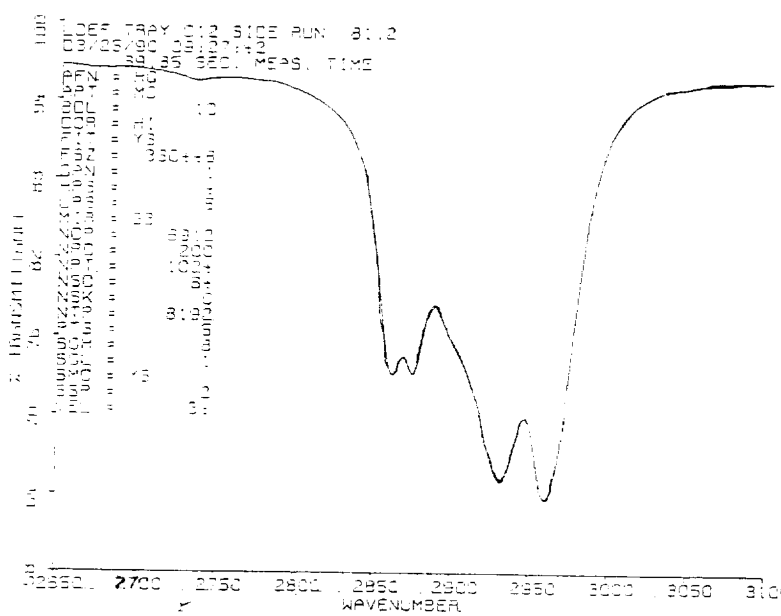

Figure 5. 3.4 μ spectrum of NVR from Tray C12.

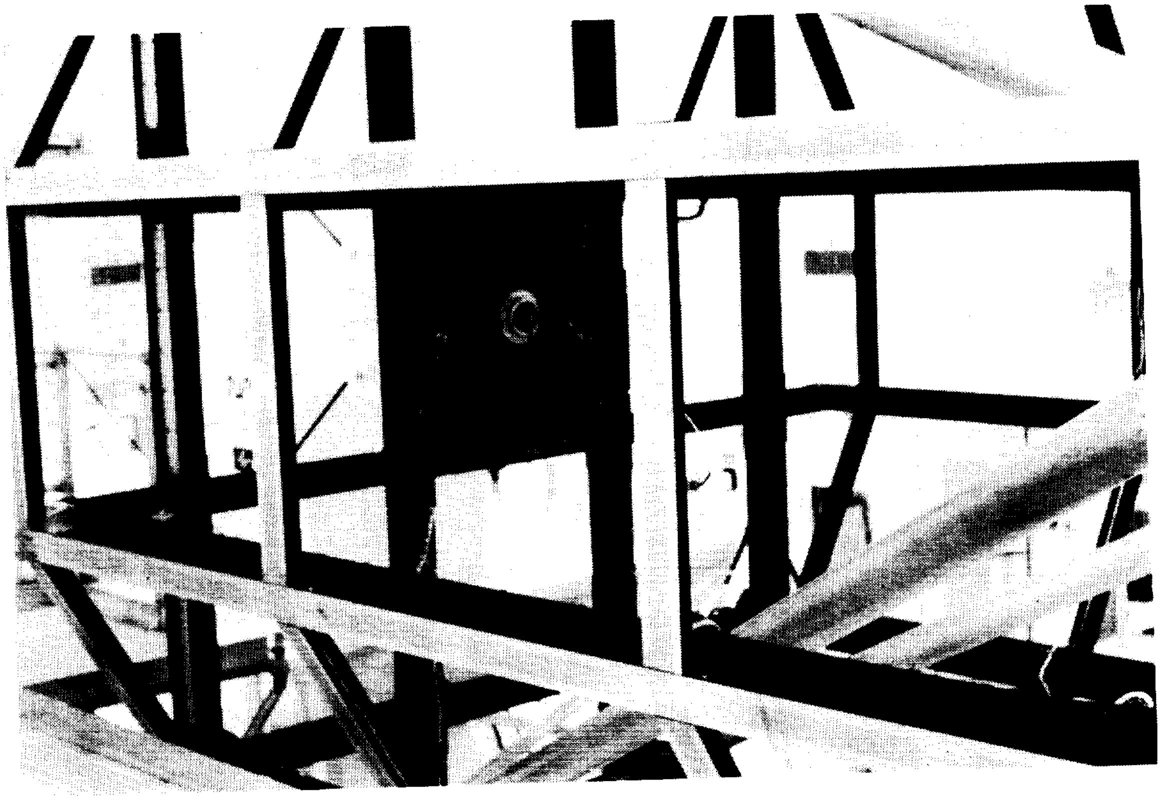

Figure 6. NVR on Earth-end Row 3.

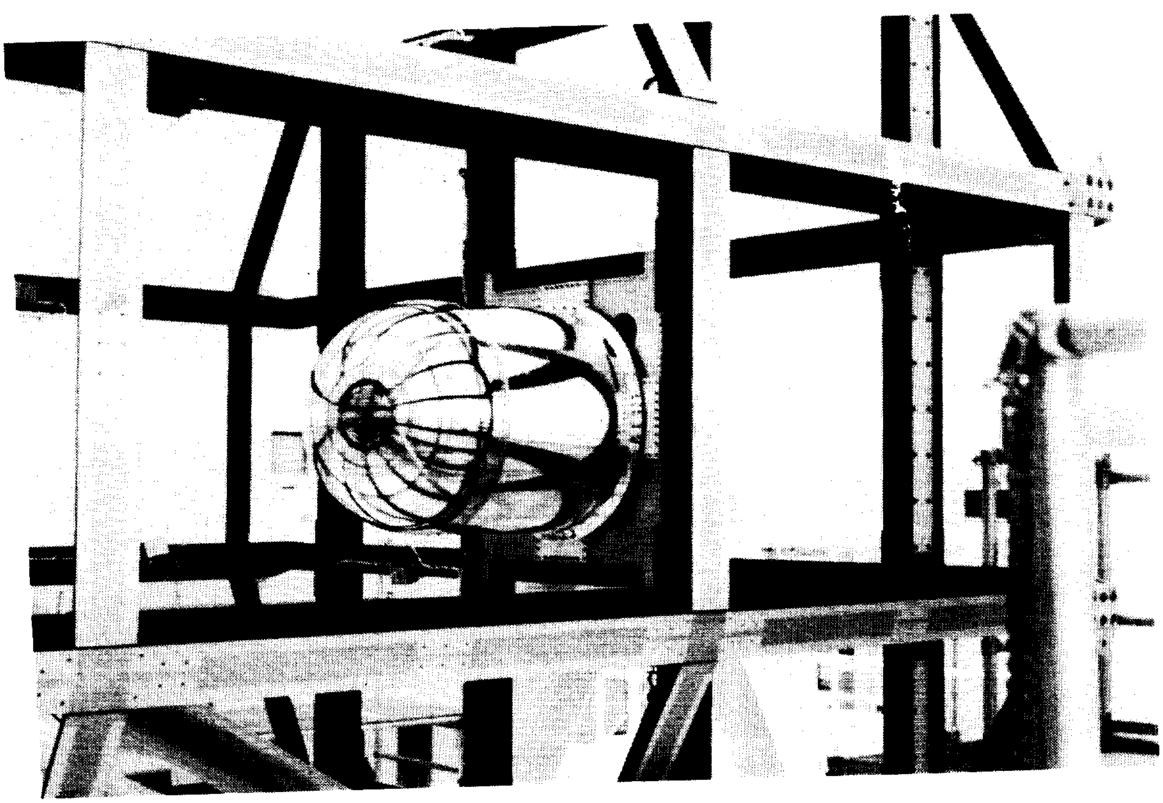

Figure 7. NVR on Space-end Row 3.

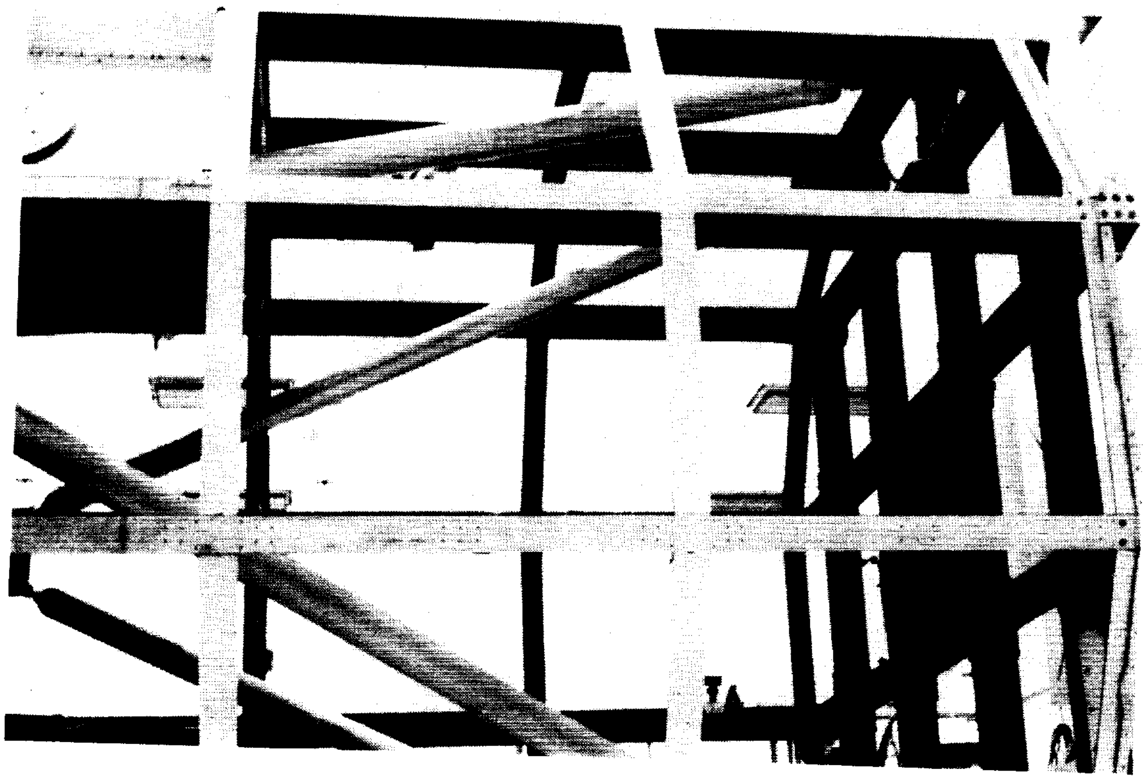

Figure 8. NVR on Earth-end Row 9.

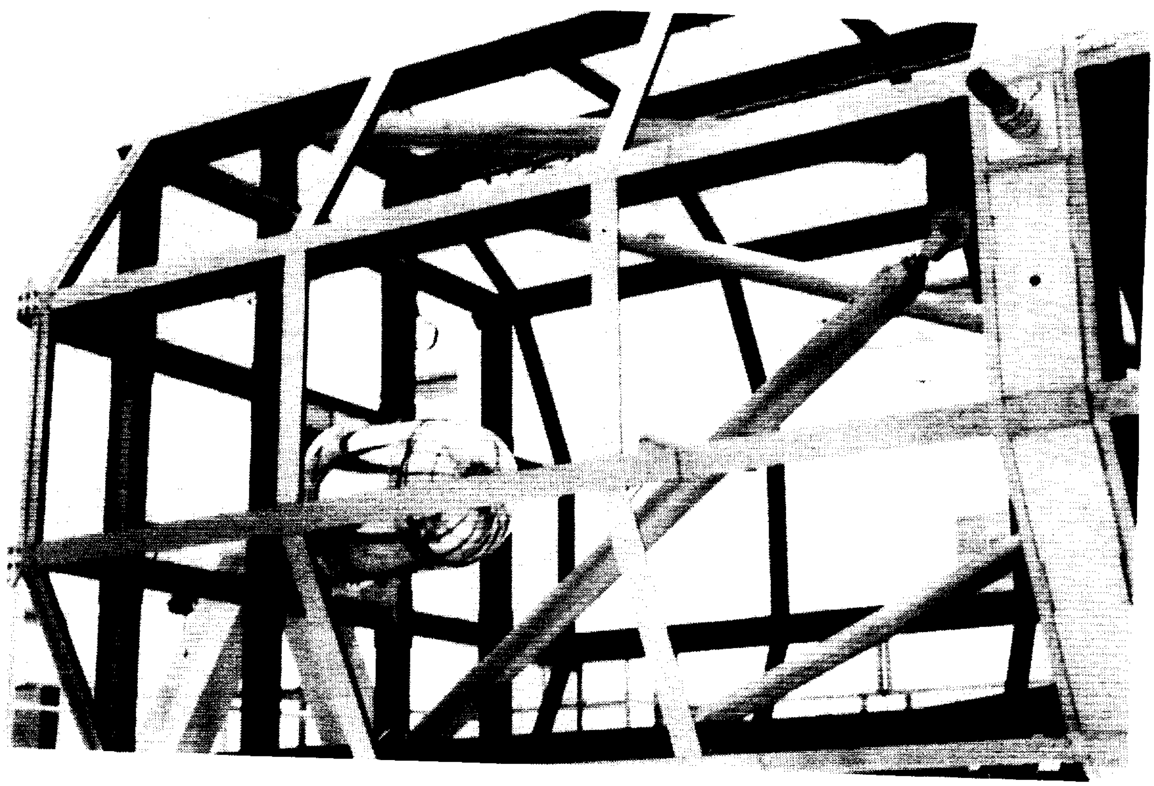

Figure 9. NVR on Space-end Row 9.

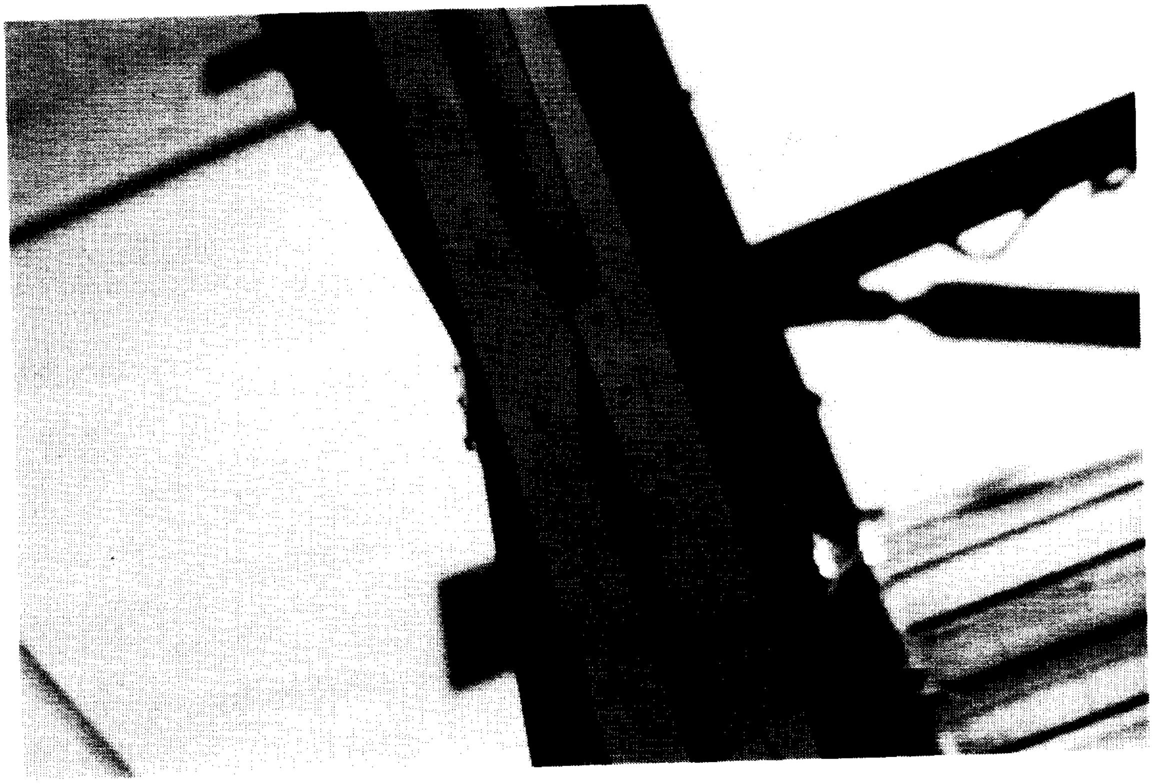

Figure 10. NVR on Space-end intercostal.

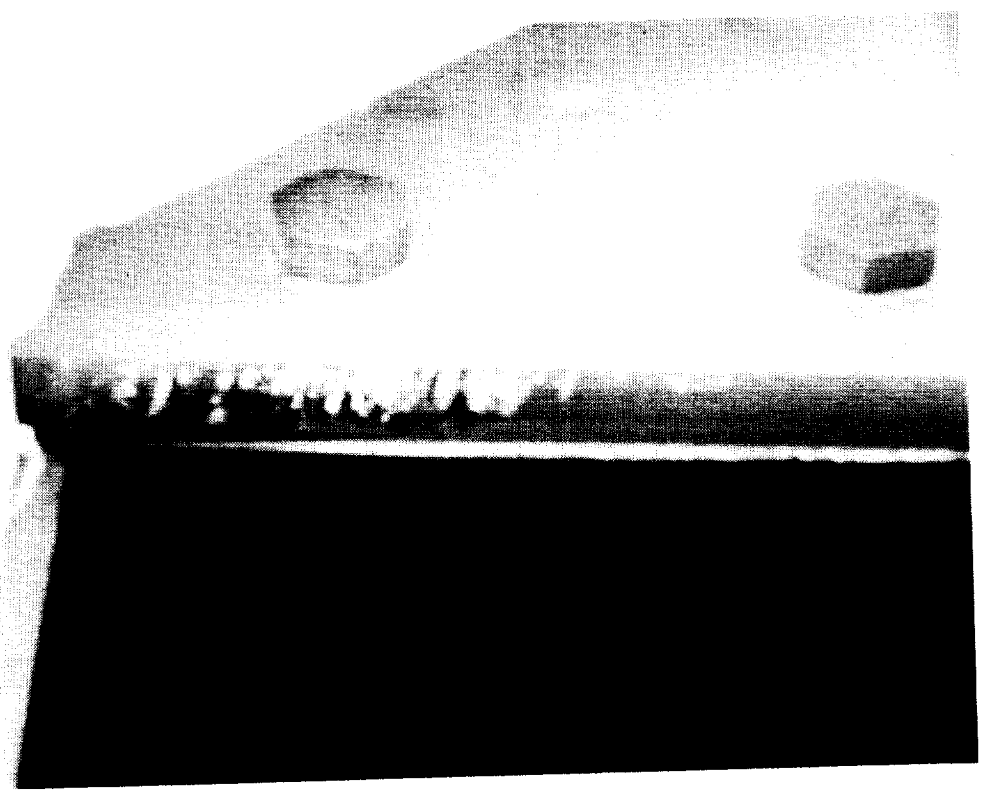

Figure 11. Peeling NVR on Earth-end plate.

Figure 12. Peeling NVR on Space-end plate.

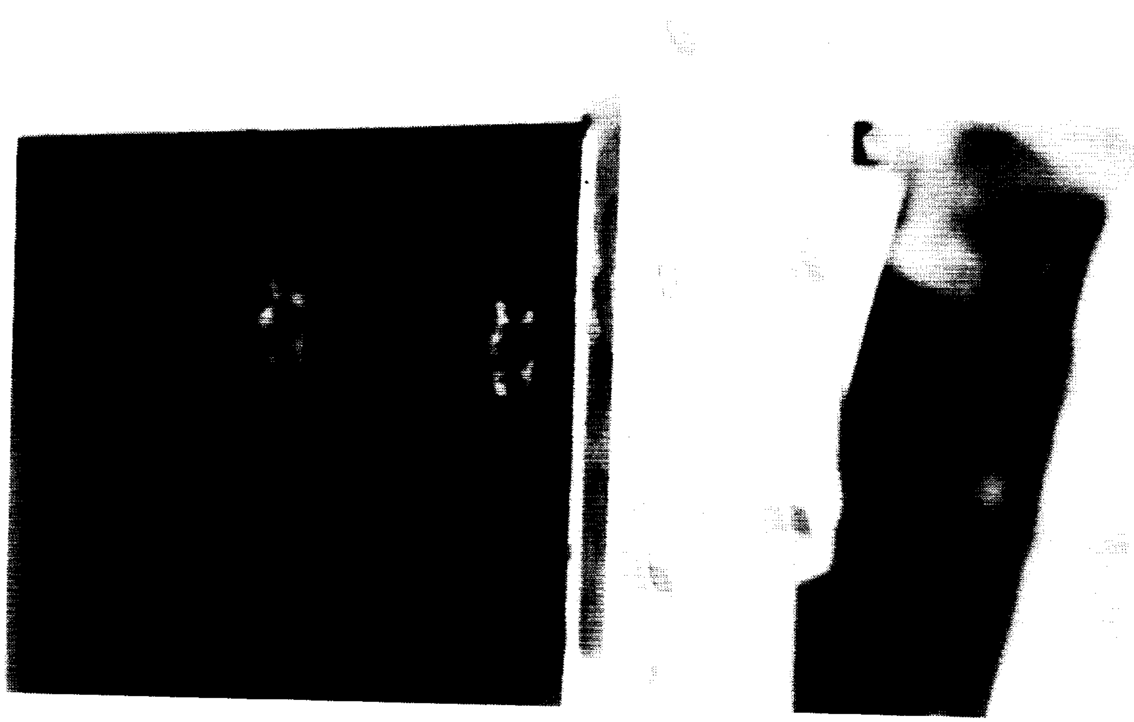

Figure 13. NVR on Space-end plate (ram direction).

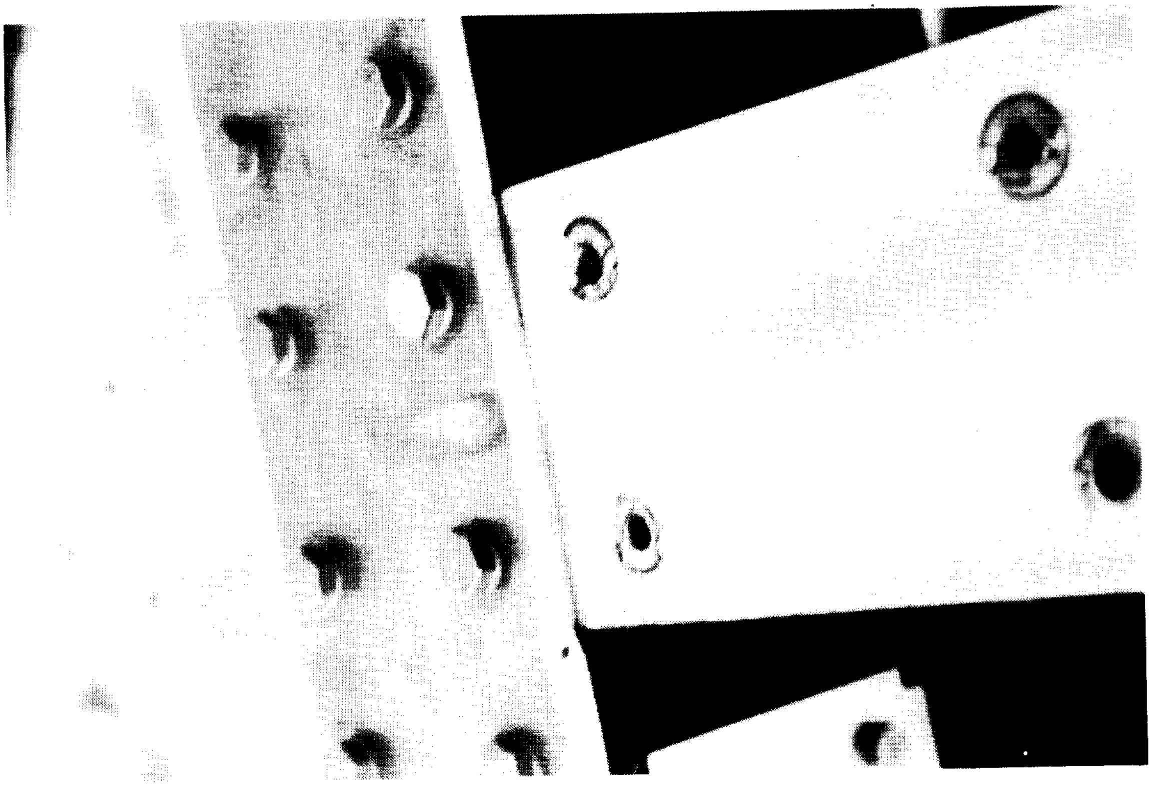

Figure 14. NVR on Space-end plate (trailing edge).

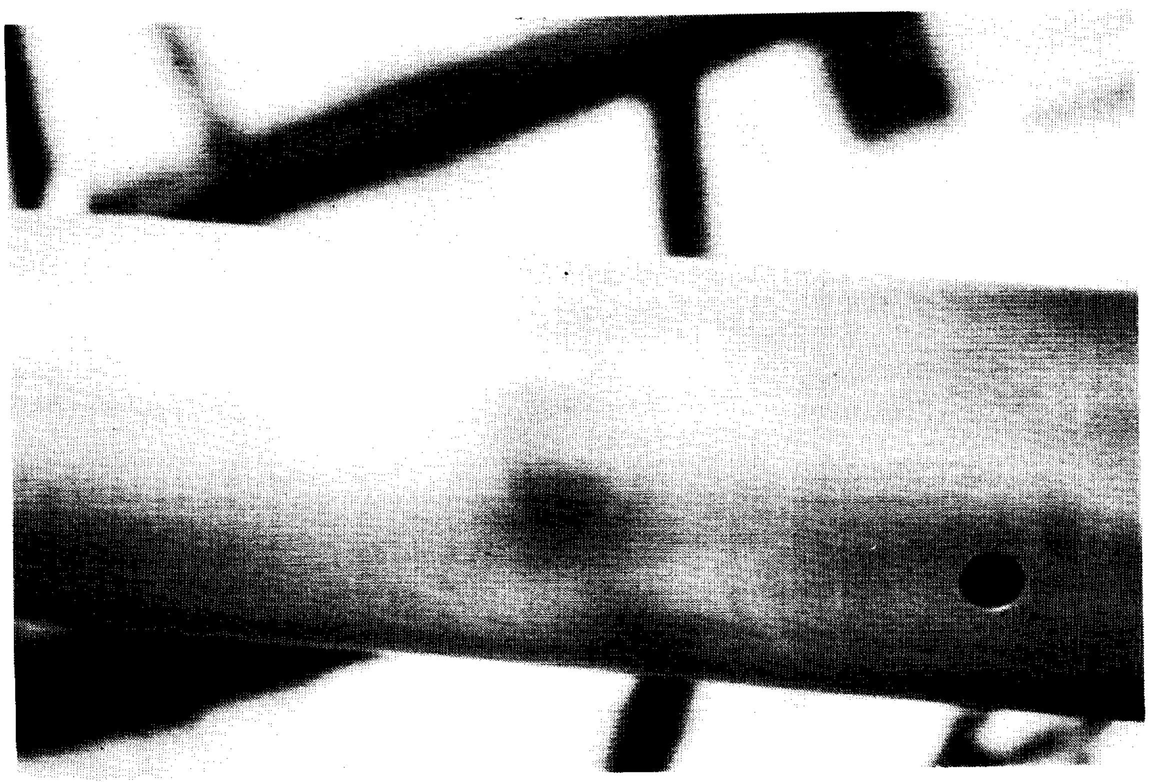

Figure 15. Diagonal brace with NVR stain.

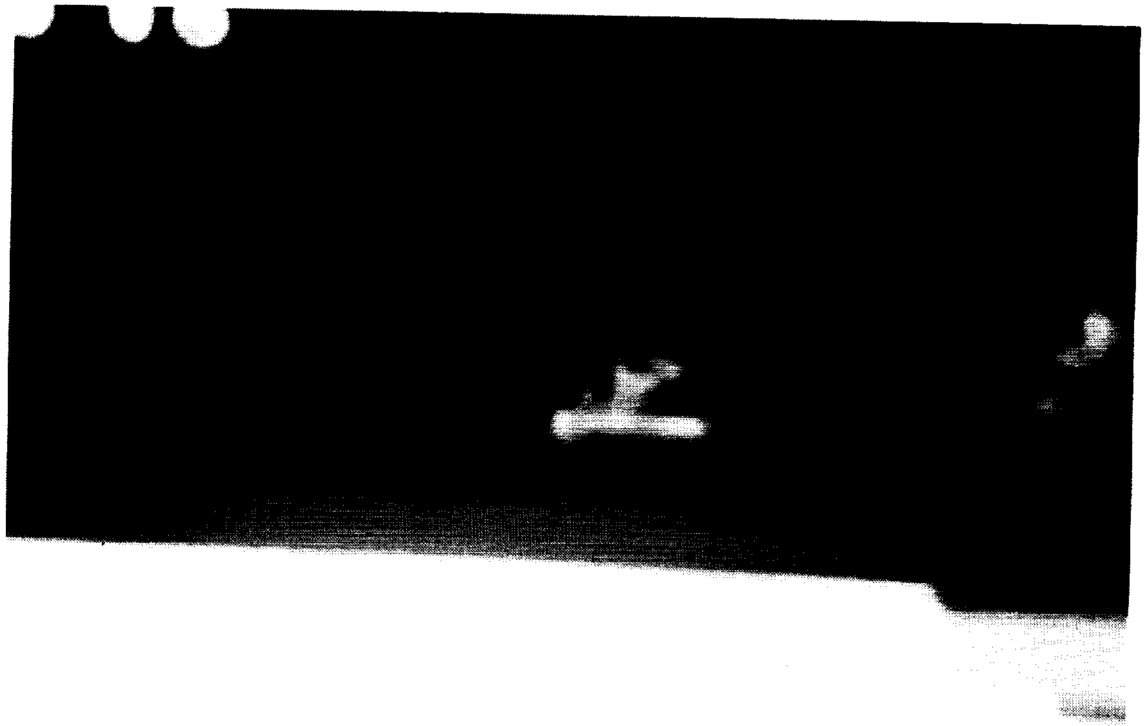

Figure 16. Earth-end interior fastener.

Figure 16a. NVR around interior fastener.

Figure 17. Blue NVR at cable clamp.

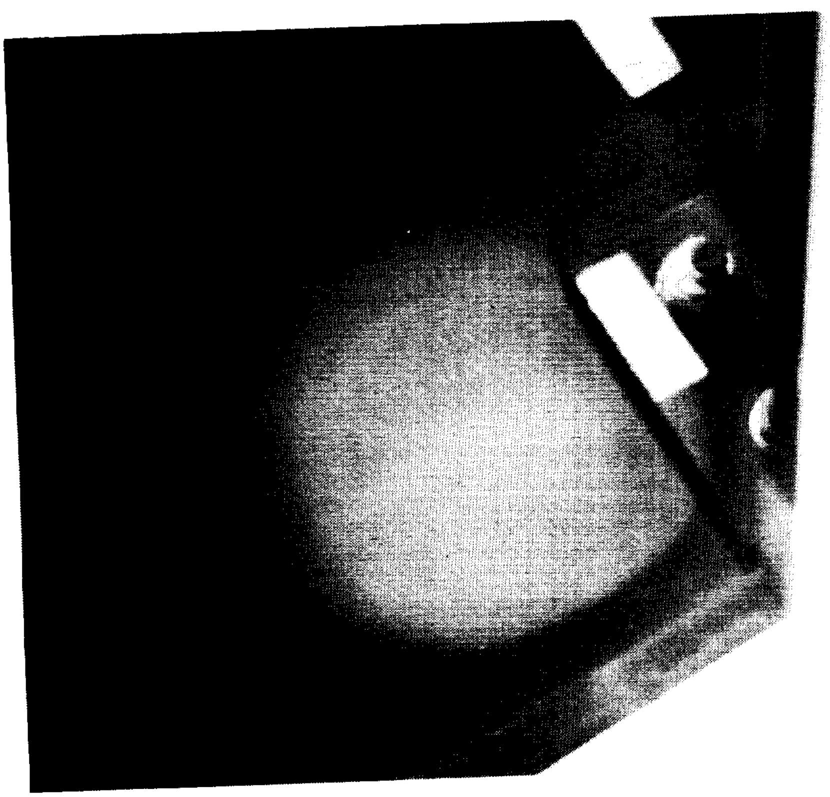

Figure 18. NVR behind tray-corner hole.

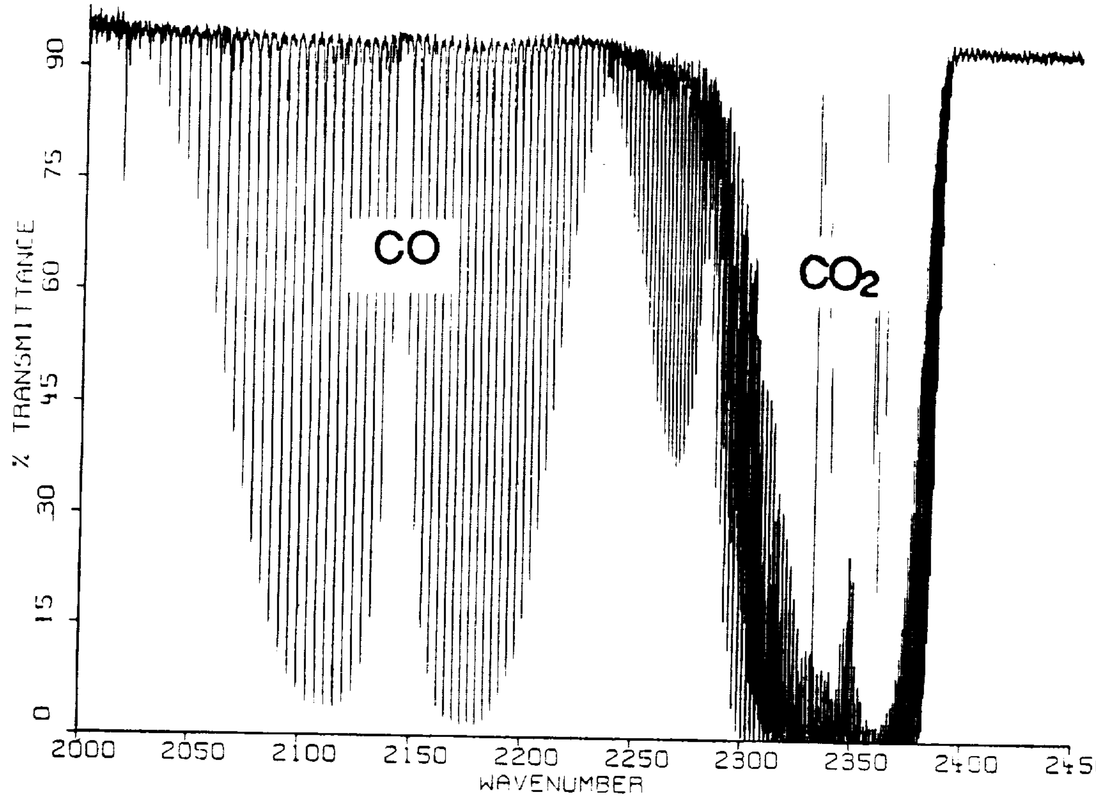

Figure 19. Outgassing of Chemglaz Z306 at 120°C.

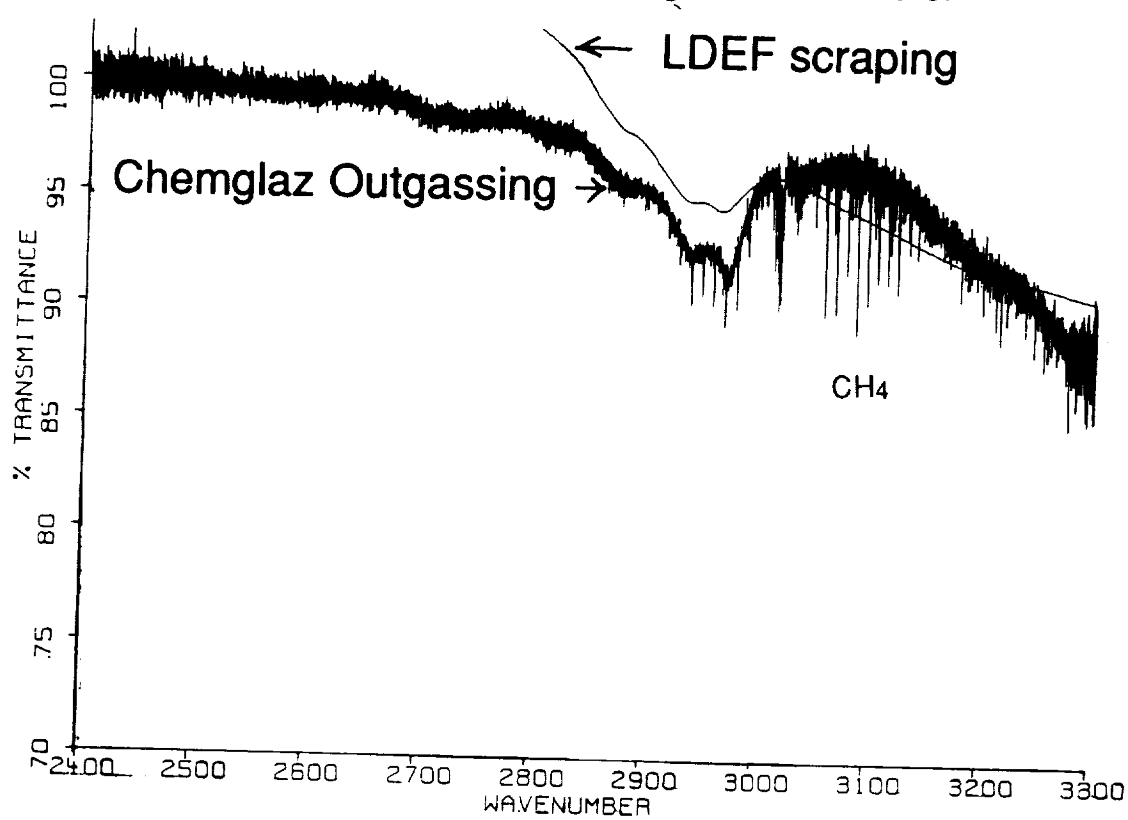

Figure 20. 3.4 μ outgassing of Chemglaz Z306 and LDEF scraping.

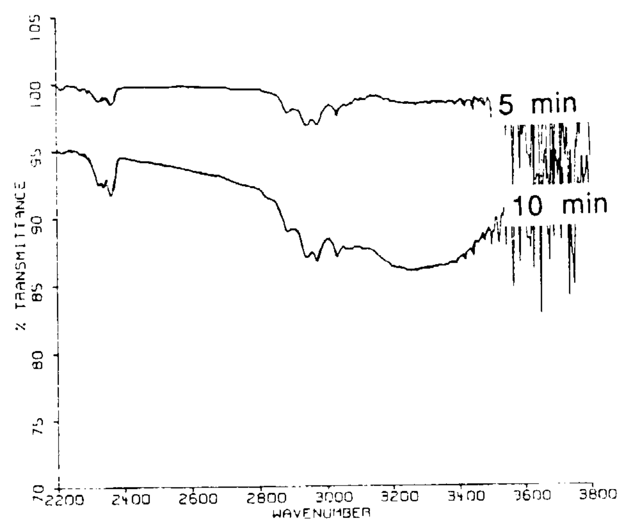

Figure 21. Outgassing of Chemglaz A276 during heating.

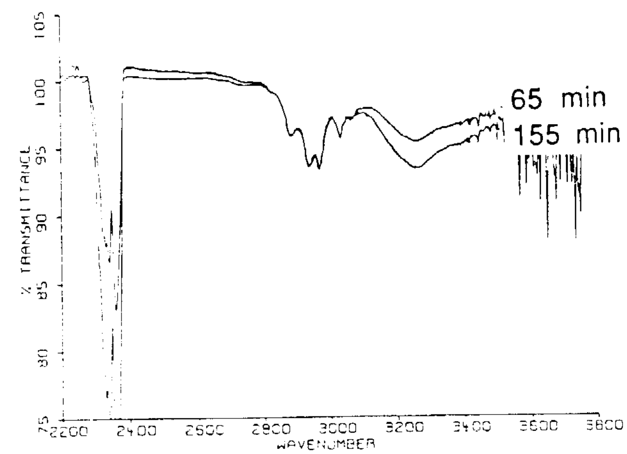

Figure 23. Outgassing of Chemglaz A276 during heating.

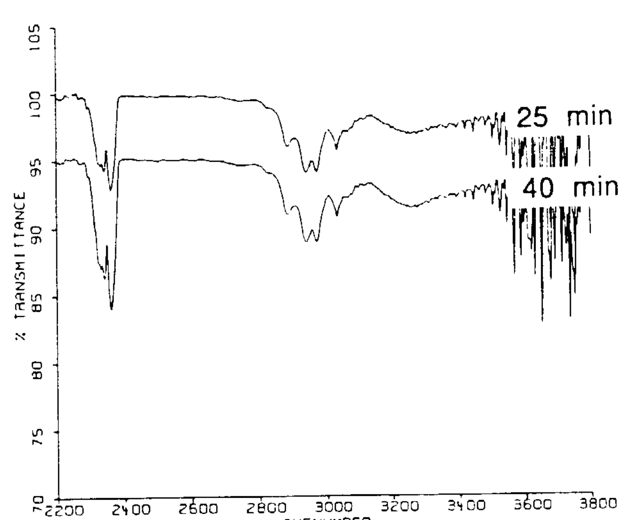

Figure 22. Outgassing of Chemglaz A276 during heating.

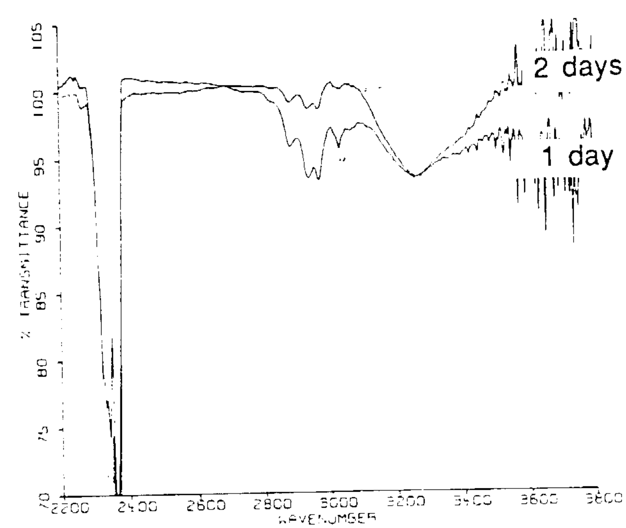

Figure 24. Chemglaz A276 residue.

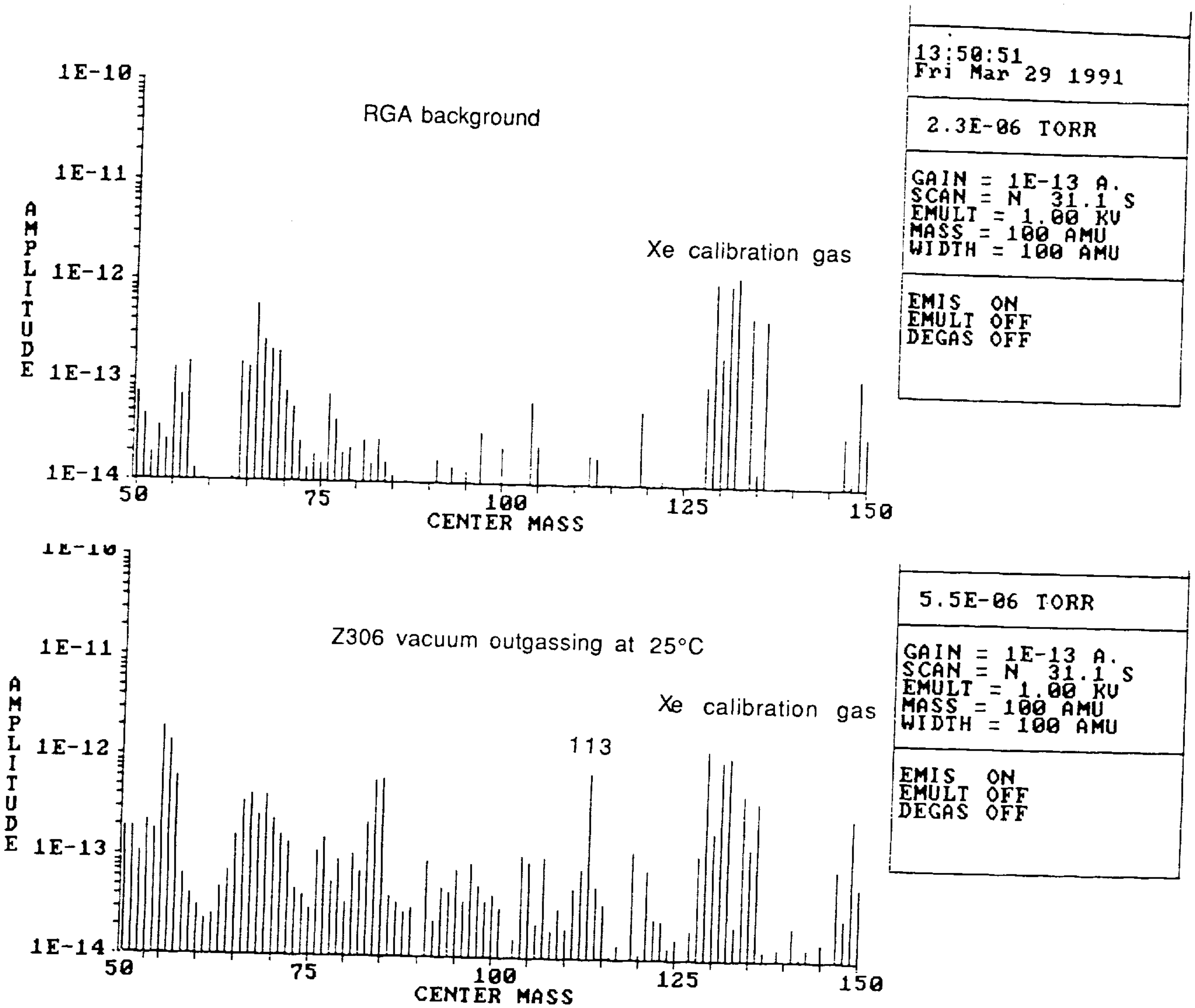

Figure 25. Atomic mass spectrum of Chemglaz Z306 outgassing.

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