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Active Cleaning Technique for Removing
Contamination From Optical Surfaces In Space

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Active Cleaning Technique for Removing
Contamination From Optical Surfaces In Space

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by

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1.0 SUMMARY

This report discusses work accomplished during the third quarter of NASA Contract NAS 8-26385. This program is aimed at developing an active cleaning technique (ACT) for removing contaminants from optical surfaces in space. During this reporting period plasma cleaning experiments were completed on hydrocarbon contaminant films, experiments were initiated to determine a satisfactory technique for depositing silicone contaminant films, and an experiment was conducted to determine whether specimens are being "thermally cleaned" rather than "plasma cleaned". Results of plasma cleaning experiments on hydrocarbon contaminant films showed that the optical properties of mirrors and gratings could be satisfactorily restored. Results on fused silica optical flats were inconclusive because of the insensitivity of measurement techniques to the contaminant films. White thermal control surfaces (S-13G and Z-93 paints), degraded by the hydrocarbon contaminant film, could not be restored by oxygen plasma exposure. On the other hand, the reflectance of silvered FEP Teflon thermal control surfaces could be restored by plasma cleaning. Preliminary experiments with a silicone contaminant indicated that it could not be easily polymerized onto surfaces with ultraviolet radiation. Additional experiments need to be performed to determine a satisfactory deposition technique. Results of the "thermal cleaning" experiment showed that the polymerized hydrocarbon contaminant film could not be removed by heating in vacuum to a temperature in excess of that expected during plasma cleaning.

2.0 INTRODUCTION

The need for developing an in-situ or active cleaning technique (ACT) for use in both space and vacuum chambers has recently become apparent. Manned spacecraft have experienced numerous contamination problems including deposition of volatile organic compounds onto windows, and light scattering from particulate contaminants surrounding the spacecraft. Sources of this contamination include outgassing of organic compounds, waste and water dumps, rocket plumes, and leakage from the life support system. It is believed that contaminant film deposition has also occurred on unmanned spacecraft surfaces. Data from a reflectometer experiment on the ATS-3 spacecraft (Reference 1) has indicated rather severe degradation on reflective surfaces, which may be the result of contaminant film deposition. Also, the TV camera mirror from the Surveyor III spacecraft which resided on the moon for 2 1/2 years, was covered with a diffuse coating -- presumably the result of contaminant film deposition from surrounding surfaces. Contamination on an unmanned spacecraft has been verified with quartz-crystal thin film monitors on OGO-6 (Reference 2). A recent review of the spacecraft contamination problem has been published in Reference 3.

Contamination can also occur during spacecraft testing in high vacuum chambers. A recent example of this was the extreme-UV solar spectro-heliometer experiment for the Apollo Telescope Mount (ATM) vehicle. A film of back-streamed diffusion pump oil was apparently deposited on surfaces during thermal/vacuum testing (Reference 4). Another example of contaminant film deposition during environmental testing is discussed in Reference 5. In those experiments it was shown that an extremely stable organic film could be deposited onto telescope mirror surfaces during irradiation with low energy protons in a relatively clean vacuum environment.

Based on existing knowledge, contamination problems anticipated for future spacecraft include: (1) deposition of non-volatile substances onto optical components, sensing elements, and temperature control surfaces; (2) particulate and gaseous contamination near the spacecraft (resulting in light scattering and absorption); and (3) chemical contamination which can interfere with upper atmosphere studies, analyses of interplanetary or planetary matter, and material processing experiments. It is anticipated that contamination effects can be reduced by changes in design, materials, operating procedures, and possibly control techniques. The use of more sensitive surfaces and longer term missions will, however, offset these improvements. Thus, the need exists for developing an ACT for space use.

The specific approach being investigated in this program involves exposing surfaces to a plasma containing atomic oxygen or combinations of other reactive gases. Experiments in Reference 5 have shown that this cleaning technique is very effective for removing contaminant films from optical surfaces in vacuum. Although detailed mechanisms of this process have not yet been studied, it is believed that oxidizable organic contaminant films are converted to volatile products such as CO_2 and H_2O which subsequently evaporate in vacuum. Recognizing that some contaminants will not be oxidizable into volatile compounds, cleaning by rf-sputtering will be evaluated on these materials.

In this research program, four different types of contaminant films are being applied to various types of mirrors, thermal control surfaces, and optical windows. Two types of contaminants are being applied to gratings. Contaminants are derived from a typical hydrocarbon monomer (1, 3-Butadiene, $\text{CH}_2\text{:CHCH:CH}_2$), a typical silicone monomer (Methyl trimethoxysilane, $\text{CH}_3\text{Si}(\text{OCH}_3)_3$), ethylene glycol, and urine. Mirror coatings include Pt, Au,

and $1/2 \lambda$ and $3/4 \lambda$ MgF_2 (at 121.6 nm) over Al. Grating coatings include Pt and $1/2 \lambda$ MgF_2^* (at 121.6 nm) over Al. Thermal control surfaces are treated zinc oxide in methyl silicone (S-13G), zinc oxide in potassium silicate (Z-93), and silver-coated FEP Teflon. The optical windows are polished fused silica flats.

* The terminology " $1/2 \lambda$ " implies a MgF_2 thickness designed to produce a reflectance maximum (by interference) at 121.6 nm wavelength. " $3/4 \lambda$ " implies a MgF_2 thickness designed to produce a reflectance minimum (by interference) at 121.6 nm wavelength.

3.0 EXPERIMENTAL RESULTS

A summary of contamination and plasma cleaning experiments conducted thus far in the program is given in Table I. Data are listed chronologically by the specimen type and code number. The numbers of the Quartz Crystal Monitor (QCM) and Interferometer Reference Mirror (IFM) included with each specimen are recorded in adjacent columns. Other data are recorded as contamination test conditions, plasma test conditions, and contaminant film thickness. The following discussion contains results of contaminant film deposition and plasma cleaning experiments on various types of surfaces.

3.1 Contaminant Film Deposition

3.1.1 Rate of Deposition

During the third reporting period, the hydrocarbon contaminant film deposition experiments on optical and thermal control surfaces were completed, and the silicone contaminant film deposition experiments were begun.

The hydrocarbon 1, 3-Butadiene ($\text{CH}_2\text{:CHCH:CH}_2$ or C_4H_6) monomer was successfully polymerized on all the specimen types. A QCM and an IFM were contaminated along with each test sample. The QCM's purpose was to provide the change of frequency vs time during contaminant film deposition and during O_2 plasma cleaning. This change of frequency of the crystal was then to be converted into a time history of the thickness of the contaminant film by using as a calibration, the absolute thickness data available from interferometry measurements of the IFM.

Figure 2 of the second quarterly report presented the change of frequency for a MgF_2/Al -coated quartz crystal during butadiene contamination. The linearity of this curve is fairly typical for UV radiation exposure times of about

Specimen Type	Specimen No.	QCM No.	IFM No.	Contamination Data			Plasma Cleaning Data				Comments	
				Type	Time (min)	Pressure (torr)	Radiation	Film Thickness (Å)	Chamber Pressure (torr)	Manifold Pressure (torr)		Exposure Time (min)
UV Mirror	MgF-1			styrene	216	1×10^{-4} to 2×10^{-3}	UV + Protons*	—	—	—	—	Coating was very non-uniform and unsatisfactory
UV Mirror	MgF-2			styrene	27	$\sim 10^{-3}$	UV + Protons	—	—	—	—	Coating was very non-uniform and unsatisfactory
UV Mirror	MgF-3			methane	31	5×10^{-3}	UV + Protons	—	2×10^{-3} to 3.5×10^{-3}	4	4	Specimen destroyed by failure of plasma generator tube
UV Mirror	MgF-33			none	—	—	—	—	$\sim 2 \times 10^{-3}$	4	15	No degradation observed
				methane	30	5×10^{-3}	UV + Protons	—	—	—	—	Small degradation produced
				methane	82	5×10^{-3} to 1×10^{-2}	UV + Protons	—	$\sim 2 \times 10^{-3}$	4	3	More degradation produced, all removed with plasma
UV Mirror	MgF-5A			methane	141	4.2	UV	—	—	—	—	Only 1-2% degradation in 250-650 nm wavelength region.
				methane	61	$< 1 \times 10^{-3}$	UV + Protons	n.m.**	—	—	—	Contaminant film too rough to measure with interferometer
UV Mirror	MgF-5B			styrene	160	2.5 to 9.5	UV	n.m.	—	—	—	Thin contaminant film produced, no cleaning attempted
UV Mirror	MgF-6A			butadiene	60	8×10^{-5}	UV + Protons	n.m.	—	—	—	Uniform thick film produced, no cleaning attempted
UV Mirror	MgF-6B			butadiene	65	1.5 to 2.5×10^{-2}	UV	—	—	—	—	
				butadiene	975	1 to 4	UV	5540	—	—	—	
UV Mirror	MgF-7A			butadiene	120	4	UV	n.m.	—	—	—	
UV Mirror	MgF-7B			butadiene	240	4	UV	125	—	—	—	
UV Mirror	MgF-8A			butadiene	480	4	UV	242	—	—	—	
Thermal Surface (silvered FEP Teflon)	FEP-1			butadiene	860	4-760	UV	—	—	—	—	Test abandoned because pressure rose to atmospheric
Thermal Surface	FEP-2			butadiene	1050	4	UV	6100	$\sim 2 \times 10^{-3}$	4	65	2060
									$\sim 2 \times 10^{-3}$	3.5	64	0
Thermal Surface	FEP-3			butadiene	939	4	UV	1260	—	—	—	No contaminant deposited on specimen because of cooling problem
				butadiene	964	4	UV	680	$\sim 2 \times 10^{-3}$	4	30	()**
UV Mirror	MgF-35			butadiene	939	4	UV	1260	$\sim 2 \times 10^{-3}$	4	42	20
UV Mirror	MgF-43			butadiene	833	4	None	—	—	—	—	Contaminant film deposited and cleaned successfully
												Contaminant film deposited and cleaned successfully
UV Mirror	MgF-43			butadiene	142	4	UV	1060	$\sim 2 \times 10^{-3}$	4	112	540
UV Mirror	MgF-36			butadiene	951	4 to 7	UV	320	—	—	—	Contaminant film deposited and partially removed
				none	494	2×10^{-5}	UV	—	$\sim 3 \times 10^{-3}$	4	5	—
UV Mirror (gold coated glass)	Au-1			butadiene	98	4	UV	()**	$\sim 3 \times 10^{-3}$	4	15	()**
UV Mirror (platinum coated glass)	Pt-11			butadiene	38	4	UV	()**	$\sim 3 \times 10^{-3}$	4	16	()**
												Negligible contamination, and negligible effects of plasma cleaning in UV wavelengths. Specimen visibly darkened during cleaning.

***data still being processed

**not measurable

*10 keV energy, about 6×10^{17} protons/cm²-sec

Δ residual film thickness

TABLE I - TEST SUMMARY

Specimen Type	Specimen No.	QCM No.	IFM No.	Contamination Data			Plasma Cleaning Data				Comments		
				Type	Time (min)	Pressure (torr)	Radiation	Film Thickness (Å)	Chamber Pressure (torr)	O ₂ Flow ⁽¹⁾ (std cm ³ /min)		Exposure Time (min)	Film Thickness ^Δ (Å)
Grating (MgF ₂ /Al Coated, Blaze = 1500 Å)	GAI-1	MgF-67	MgF-13	Butadiene	41	4	UV	()***	~2 x 10 ⁻³ ~2 x 10 ⁻³	30 30	15 15	()*** ()***	Contaminant film deposited and cleaned successfully
	GPI-1	Pt-22	Pt-2	Butadiene	89	4	UV	()***	~2 x 10 ⁻³ ~2 x 10 ⁻³	30 30	15 15	()*** ()***	Contaminant film deposited and cleaned successfully
Thermal Surface	FEP-4	Au-43	Au-12	Butadiene	248	4	UV	430	~2 x 10 ⁻³	30	16	120	Noticeable degradation and cleaning on IFM
UV Mirror	Pt-12	Pt-23	Pt-3	Butadiene	224	4	UV	330	~2 x 10 ⁻³	30	30	35	Contaminant film deposited and cleaned successfully. Specimen was not darkened during cleaning as was Pt-11
UV Mirror	MgF-44 MgF-44	MgF-68	MgF-14 MgF-14	Butadiene None	62 —	4 —	UV —	98 —	~2 x 10 ⁻³ ~2 x 10 ⁻³	30 30	62 60	()** ()**	QCM acted strangely
Thermal Surface (S-13g Paint)	S-1	Au-44	Au-13	Butadiene	1020	4-20	UV	2,540	~2 x 10 ⁻³	70	234	746	Reflectance degraded after cleaning
Thermal Surface (Z-93 Paint)	Z-1	Au-45	Au-14	Butadiene	936	4-20	UV	>10,150(2)	~2 x 10 ⁻³	70	291	()***	Reflectance degraded after cleaning
Thermal Surface	FEP-5	Au-46	Au-15	Butadiene	1009	4-6	UV	10,150	~2 x 10 ⁻³	70	263	1800	QCM acted strangely
Thermal Surfaces Z-2 & S-2	Z-2 & S-2	Au-47	None	None	—	—	—	—	~2 x 10 ⁻³	70	198	—	No reflectance change
Lens (Fused Silica Optical Flats)	L-1	Au-50	Au-19	Butadiene —	1397 1016	4-760 760	UV UV	()*** ()***	—	—	—	—	Chamber began leaking to atm. Effect of additional UV radiation on film
Lens	L-2	Au-51	Au-20	Butadiene	1010	4-270	UV	()***	—	—	—	—	Chamber leaking
UV Mirror	MgF-46	MgF-69	MgF-15	Silane [CH ₃ Si(OCH ₃) ₃]	1039	4	UV	()***	~2 x 10 ⁻³ ~2 x 10 ⁻³	70 70	73 55	()*** ()***	Found and repaired leak, initial silane deposition, small reflectance change
UV Mirror	MgF-37	MgF-70	MgF-16	Silane	1287	1-2.5	UV	()***	~2 x 10 ⁻³	70	180	()***	Thick spots of contaminant formed
UV Mirror	MgF-48	MgF-72	MgF-18	Butadiene	1096	4	UV	()***	Thermal Cleaning Test	—	—	—	No Reflectance Restoration

***Data still being processed

**Not measurable

Δ Residual film thickness

(1) Changed to record O₂ flow instead of manifold pressure

(2) Thickness at least as large as for FEP-5

TABLE I - TEST SUMMARY, CONT.

180 minutes or less. From the test summary given in Table I it can be seen that the UV mirror samples usually had radiation exposures of about 180 minutes or less. However, for samples with much longer UV exposures, e.g., thermal control surfaces, the QCM change of frequency did not remain linear. Figure 1 shows the change of frequency for two gold-coated quartz crystals during the first 600 minutes of UV radiation exposure. As can be seen, the rate of change of frequency decreases as deposition proceeds. This effect is believed to be caused by contamination of the quartz window through which the UV enters the test chamber. The contaminant film presumably absorbs a portion of the UV radiation from the mercury-arc lamp, and reduces the rate of deposition on the test samples.

Figure 1 also shows the effect of chamber (butadiene) pressure on the deposition rate. During contamination of Au-45 the pressure varied from 4 to 20 torr over the total UV exposure time of 936 minutes. For Au-46, the pressure variation was 4-6 torr over a total UV exposure time of 1009 minutes. This data indicates that the deposition rate proceeds more rapidly at higher chamber pressures, and that absorption of UV in the butadiene gas at these pressures is apparently negligible. The increased rate of deposition at higher pressure is expected because of the higher arrival rate of monomer molecules on surfaces. Since the deposition rate was sufficient at a pressure of about 4 torr, no further experiments of this type were performed.

3.1.2 Correlation of QCM and IFM Data

As was stated before, the absolute thickness data from the IFM's were to be used to calibrate the change of frequency of the QCM's to give a time history of the contaminant film thickness during deposition and plasma cleaning. However, the following data shows that the correlation is not possible at the present time:

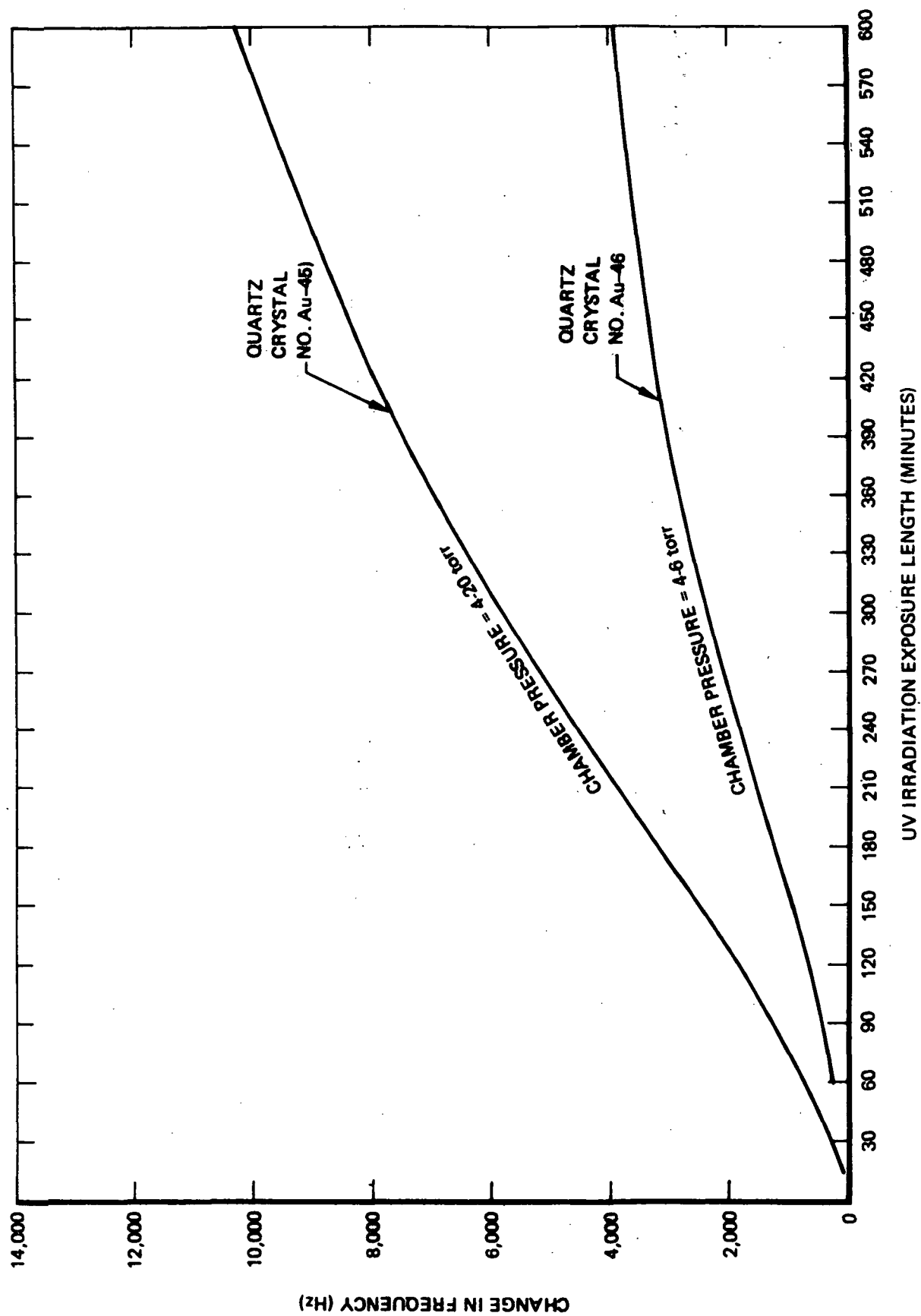


Figure 1: QCM Δf VS UV IRRADIATION EXPOSURE LENGTH FOR BUTADIENE CONTAMINANT

Table 2: Comparison of QCM and IFM Thickness Data

QCM NO.	UV Exposure Time (Min)	O ₂ Plasma Time (Min)	QCM Rdg (Hz)		IFM Rdg (Å)	
			After Contam- ination	After Plasma	After Contam- ination	After Plasma
MgF66	142	112	1140	-	1050	540
MgF68	62	62	350	(1)	100	(2)
Pt-23	224	30	280	(1)	330	40
Au-44	1020	234	12400	4800	2540	750
Au-45	936	291	12500	(1)	> 10000 ⁽³⁾	-
Au-46	1009	263	4900	(1)	10,150	1800

(1) QCM Reading was not possible because of erratic behavior of QCM

(2) Film was too thin to be measurable with interferometer

(3) Film was too thick to be measurable with interferometer

The erratic behavior of the QCM's mentioned in Table II is shown in Figures 2, 3 and 4. These three figures show the change of frequency for 4 quartz crystals. As can be seen from these curves and the data in Table II, the type of coating of the crystal was apparently not a factor in the erratic behavior, since all coating types were affected. The MgF₂/Al-coating, however, was affected to a lesser degree.

The cause of the QCM problem is not yet known, however, it is believed to be related to a discoloration phenomenon observed on the QCM's during cleaning. Areas of the crystal surface which have either not been contaminant coated or have been cleaned, turn black. It is speculated that this black appearance is attributable to silver oxide formation. During the manufacture of crystals by Sloan Instruments Inc., a silver coating was applied to the

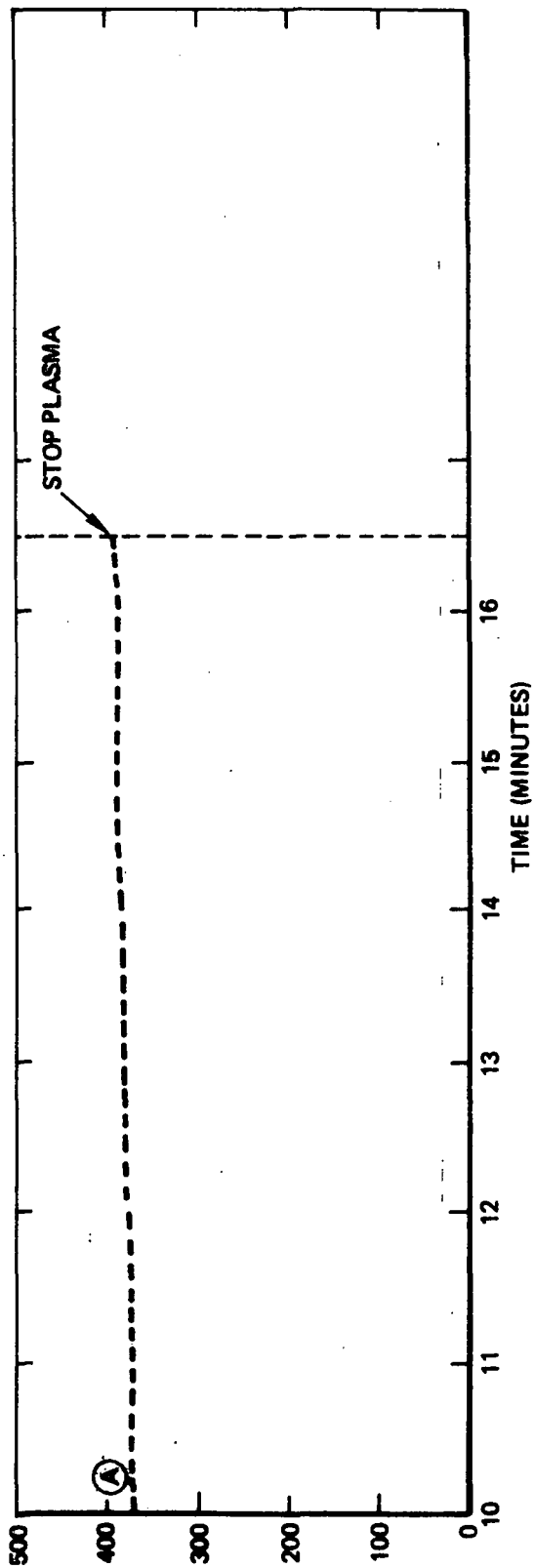
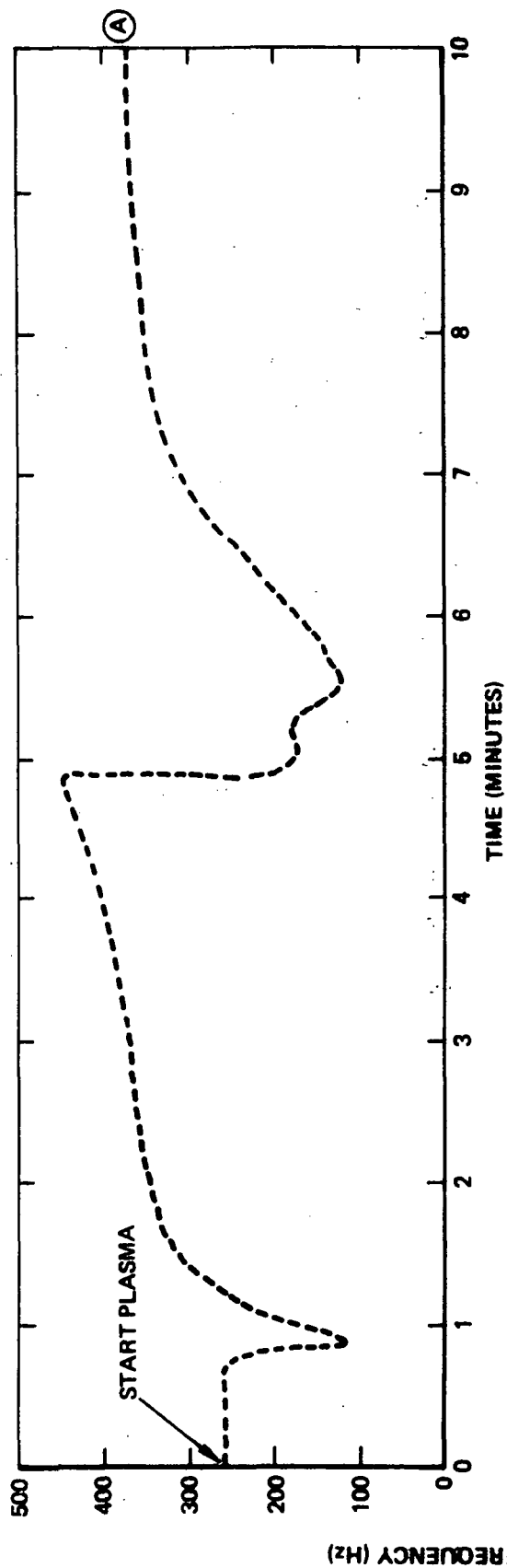


Figure 2: QCM CHANGE IN FREQUENCY VS O₂ PLASMA EXPOSURE TIME FOR A BUTADIENE CONTAMINANT FILM ON A PLATINUM-COATED QUARTZ CRYSTAL (NO. Pt-21)

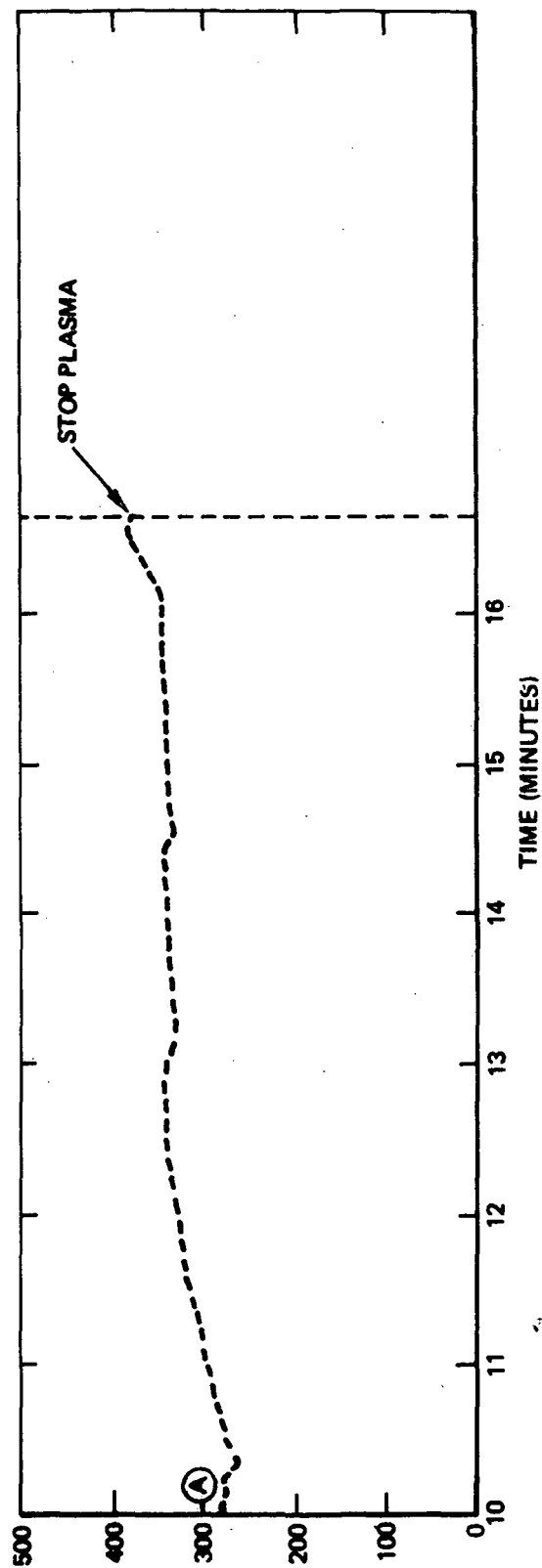
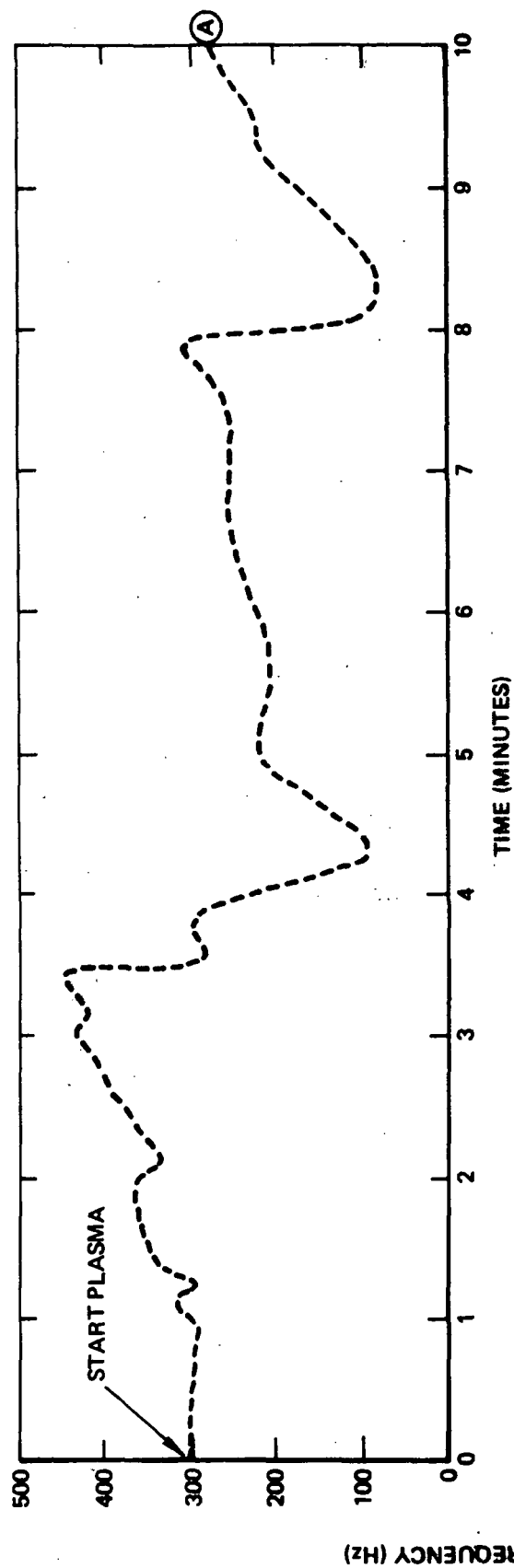


Figure 3: QCM CHANGE IN FREQUENCY VS O₂ PLASMA EXPOSURE TIME FOR A BUTADIENE CONTAMINANT FILM ON A GOLD-COATED QUARTZ CRYSTAL (NO. AU-42)

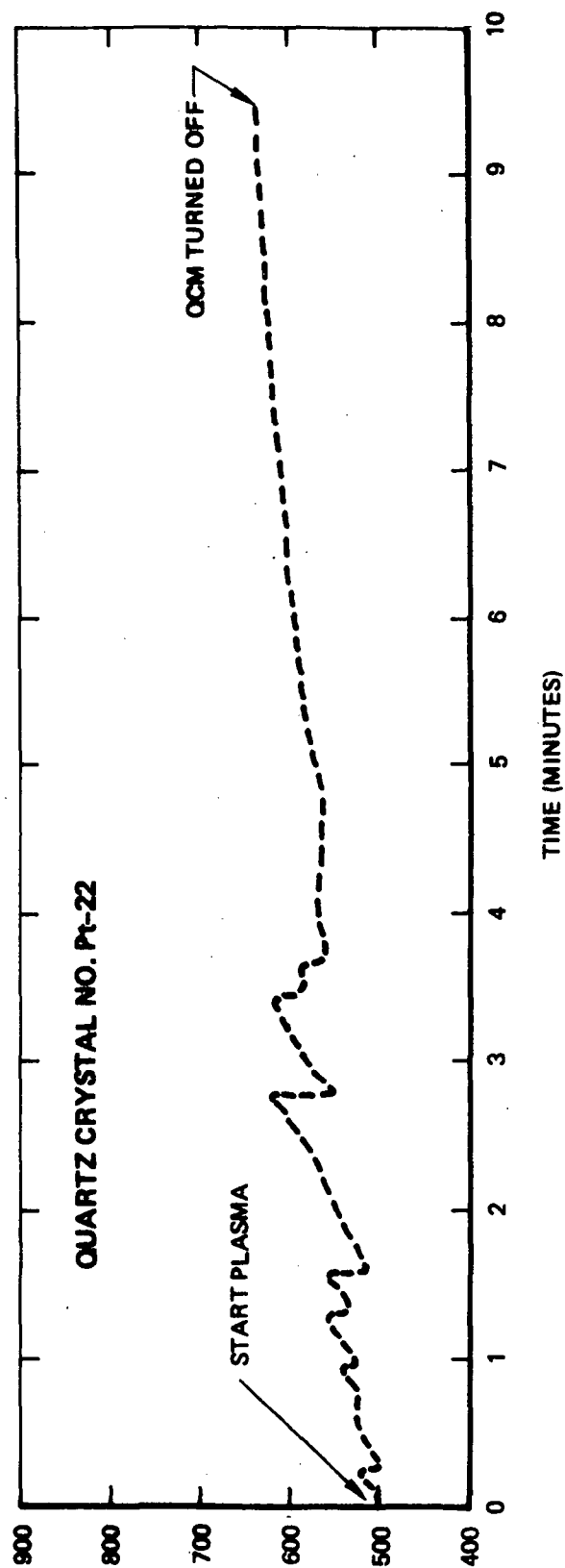
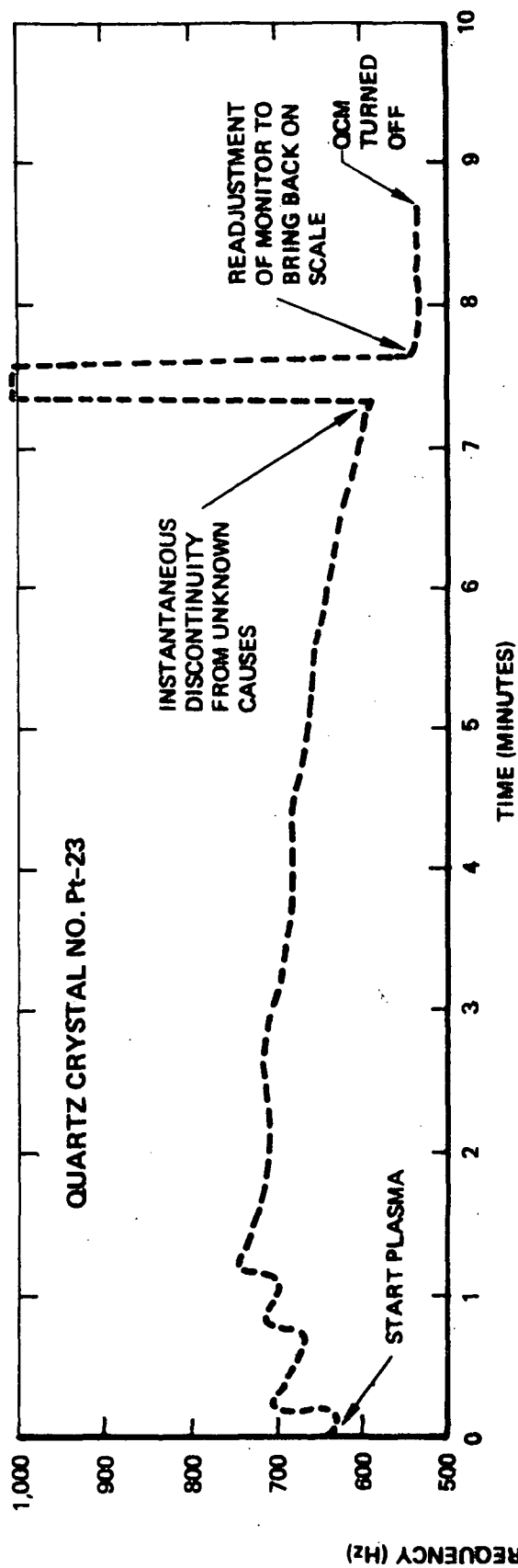


Figure 4 : OCM CHANGE IN FREQUENCY VS O₂ PLASMA EXPOSURE TIME FOR A BUTADIENE FILM ON TWO PLATINUM-COATED QUARTZ CRYSTALS (Pt-22 AND Pt-23)

bare crystal. These crystals were subsequently overcoated with either gold, platinum or MgF_2/Al . It is quite possible that diffusion and/or oxidation of the silver sub-layer through pinholes is taking place. Figure 5 is a photograph of three gold overcoated quartz crystals (Au-52, Au-42, and Au-49). Au-52 has had no contamination or plasma treatment. Au-42 was contaminated with butadiene and plasma cleaned for 15 minutes. Au-49 was contaminated with butadiene and plasma cleaned for about 30 minutes. Au-49 had very little contaminant when exposed to the plasma, and as can be seen began to turn dark all over the surface. The contaminant film was not completely removed from Au-42 as can be seen by the lighter portion in the center (unmasked area) of the crystal. All three crystals were coated with gold at the same time and were held in place during coating by a small spring. Consequently, the crystal surface beneath these hold down springs was not coated with gold, leaving the silver sublayer exposed. This sublayer as can be seen in Au-52 appears white before plasma exposure. Subsequently, the area turns black when exposed to the oxygen plasma as Au-42 and Au-49 show. Figure 6 shows a 120X photomicrograph of the edge of the spring "shadow" on Au-49. More experiments would be necessary to prove that the silver sublayer was actually diffusing through the surface coatings and that the presence of the silver would cause the erratic behavior of the QCM's. However, the evidence of the darkening of the crystals with plasma treatment tends to give support to this possibility. Based on the above observations, it is recommended that a new batch of crystals be prepared for future experiments which do not have the silver sublayer.

Another possible explanation for the lack of correlation between QCM and IFM data is their geometric relationship with respect to the plasma generation tubes. It is expected that a variation in oxygen atom flux exists across the specimen mounting plate, which results in different cleaning rates at different locations.

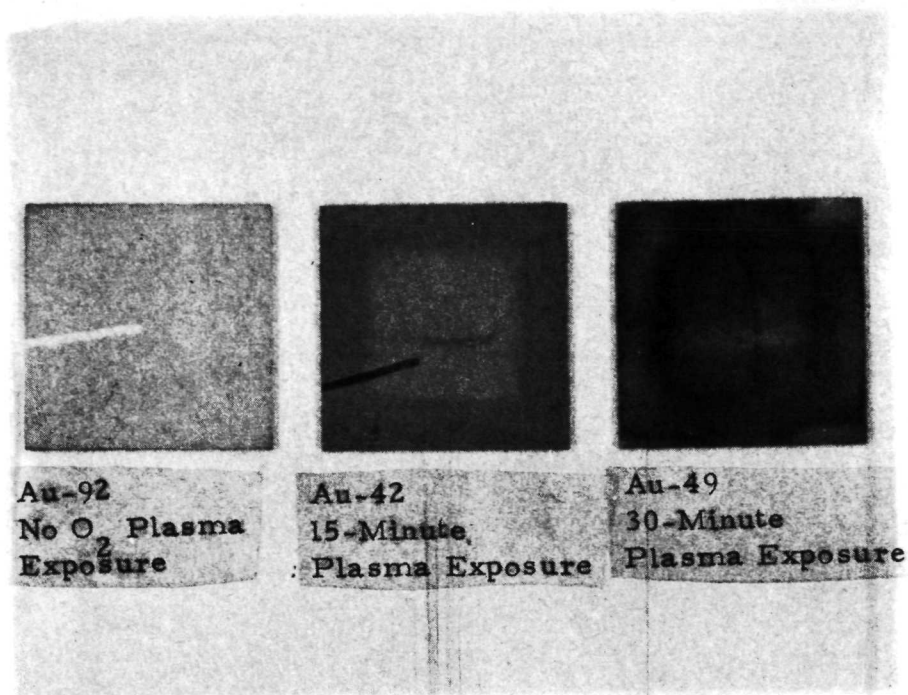


Figure 5: CHANGE OF QUARTZ CRYSTAL SURFACE WITH O₂-PLASMA EXPOSURE

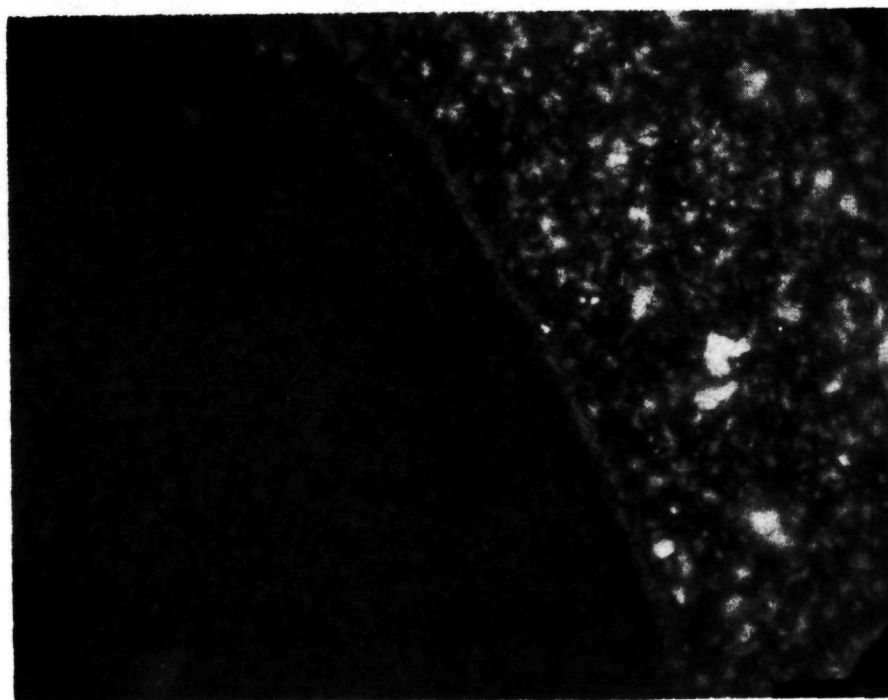


Figure 6: EDGE OF SPRING "SHADOW" ON Au-49 (120X MAGNIFICATION)

This also implies that residual contaminant film thicknesses for IFM's after cleaning quoted in this and prior reports, may not be representative of film thicknesses on optical test specimens. To eliminate this data uncertainty, it is proposed to perform an experiment during the next quarter to measure the variation in cleaning rate across the specimen holding plate.

3.1.3 Contaminant Film Surface Roughness

To determine the surface characteristics of the butadiene film after deposition and after O_2 plasma exposure, a series of photomicrographs were made on an IFM (MgF₂-9) with an electron scanning microscope. Figures 7-12 are photomicrographs of two of the interference steps used to calculate the film thicknesses. Figures 7 and 8 are low-power magnification photos of two portions of the steps formed during contamination. The dark area at the top of the photos is the MgF₂/Al surface, whereas the lighter surface is the butadiene film. Interferometer data indicated that the step between the two areas was $6100 \pm 100 \text{ \AA}$ thick. Figures 9 and 10 are higher magnifications of the step pictured in Figure 8. Even at low magnification, it is easily seen that the butadiene film is not uniform. Figures 11 and 12 are photomicrographs of the interference step caused by the second O_2 plasma exposure of MgF-9. In Figure 11, the dark area at the top of the photo is the thicker butadiene film, whereas the lighter portion has had most or all of the butadiene film removed. The interferometer data for this step indicates that the step is $2100 \pm 100 \text{ \AA}$ thick. Figure 12 is a higher-power magnification than Figure 11. Both of these photos indicate that the O_2 plasma roughens the contaminant film surface. The diagonal stripes in the photo were believed to be caused by the movement of the mask used to obtain the step.

3.1.4 Silicone Deposition Experiments

During the third reporting period, silicone deposition experiments were begun. The silane monomer, methyl trimethoxysilane ($CH_3Si(OCH_3)_3$), was

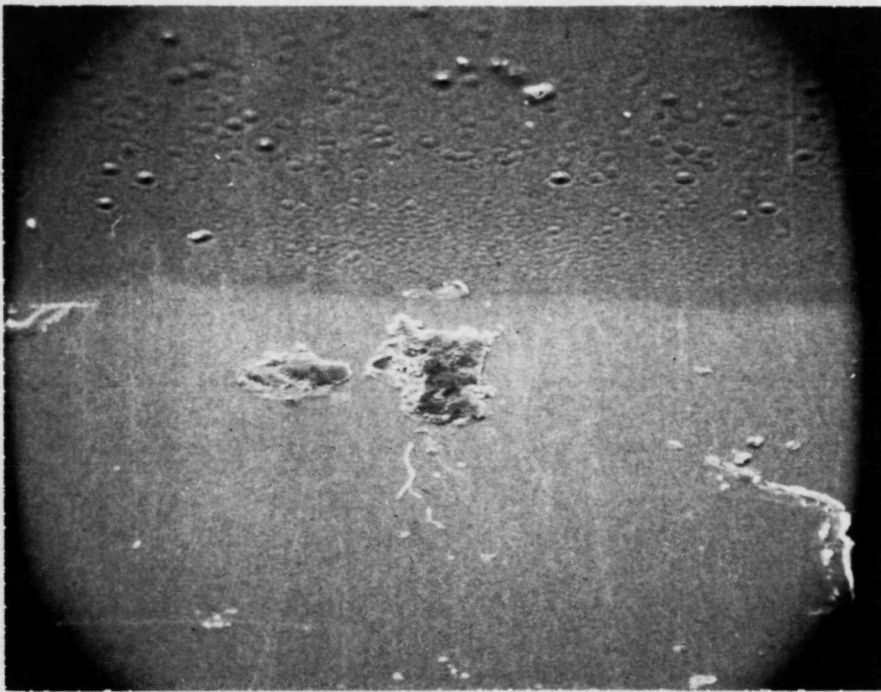


Figure 7: INTERFEROMETER STEP FORMED DURING BUTADIENE CONTAMINATION (180X MAGNIFICATION)

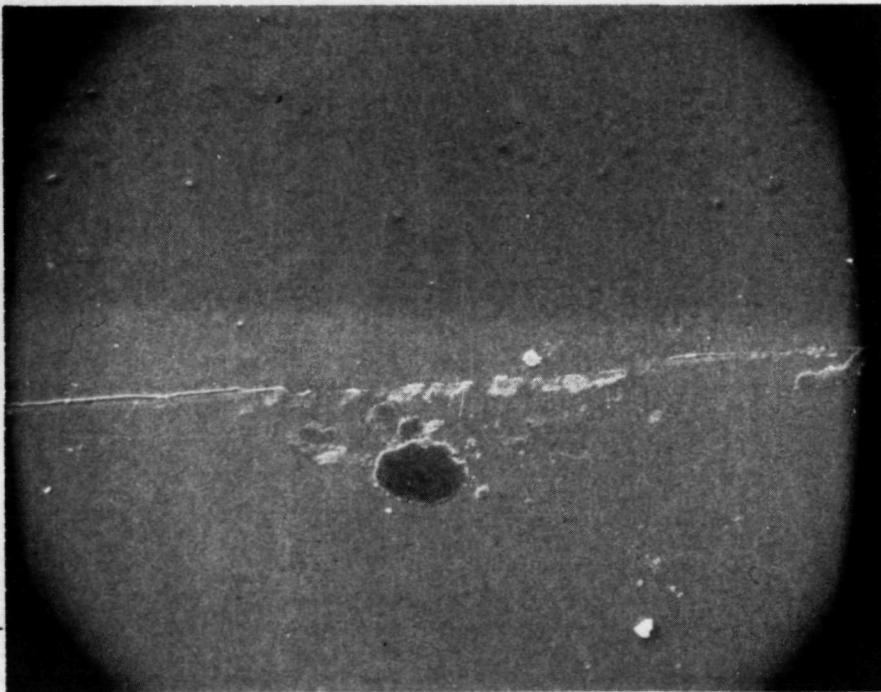


Figure 8: INTERFEROMETER STEP FORMED DURING BUTADIENE CONTAMINATION (140X MAGNIFICATION)

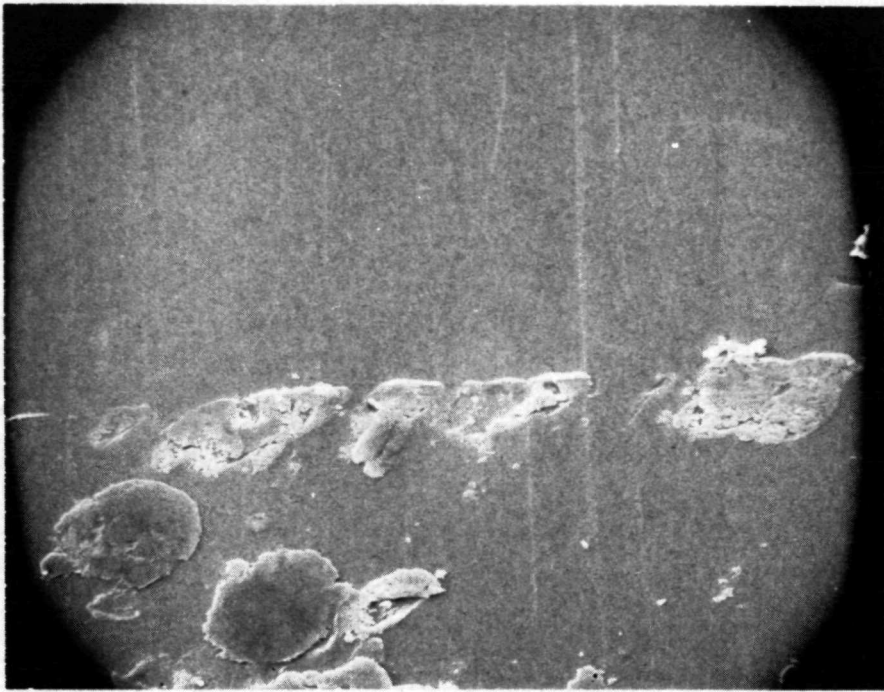


Figure 9: INTERFEROMETER STEP FORMED DURING BUTADIENE CONTAMINATION (700X MAGNIFICATION)

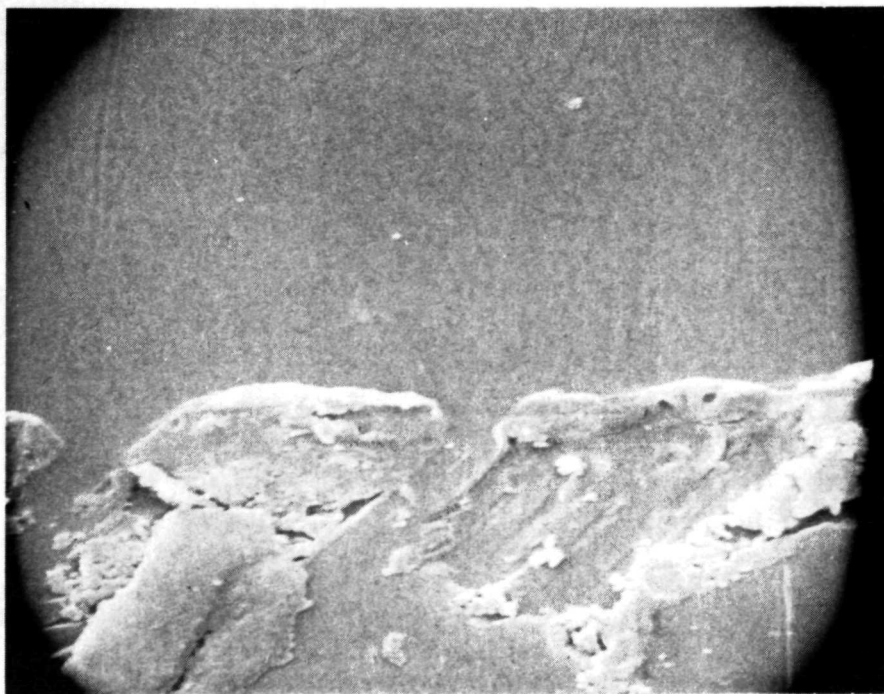


Figure 10: INTERFEROMETER STEP FORMED DURING BUTADIENE CONTAMINATION (2800X MAGNIFICATION)

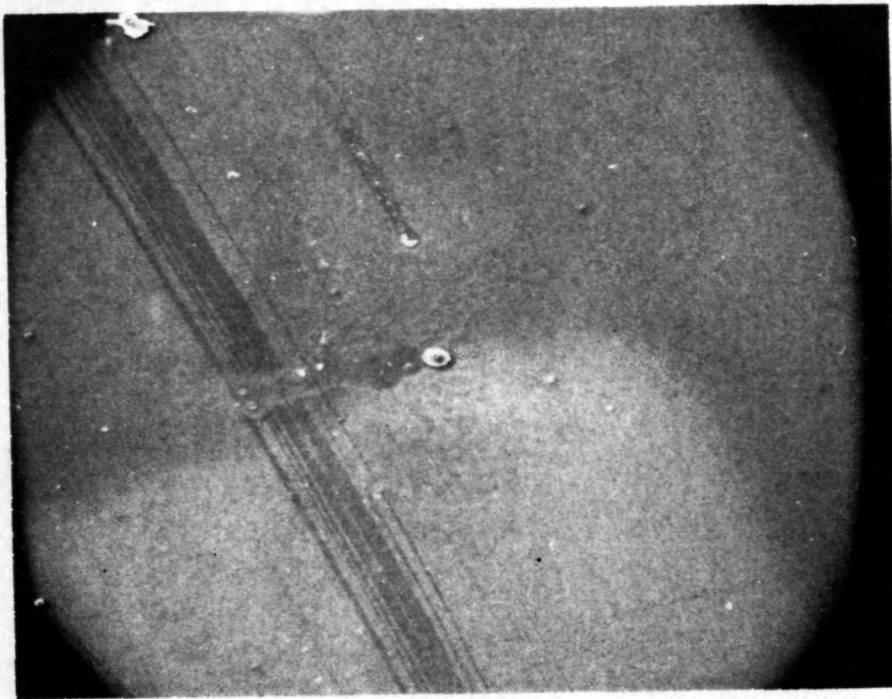


Figure 11: INTERFEROMETER STEP FORMED BY O₂ PLASMA EXPOSURE
(140X MAGNIFICATION)

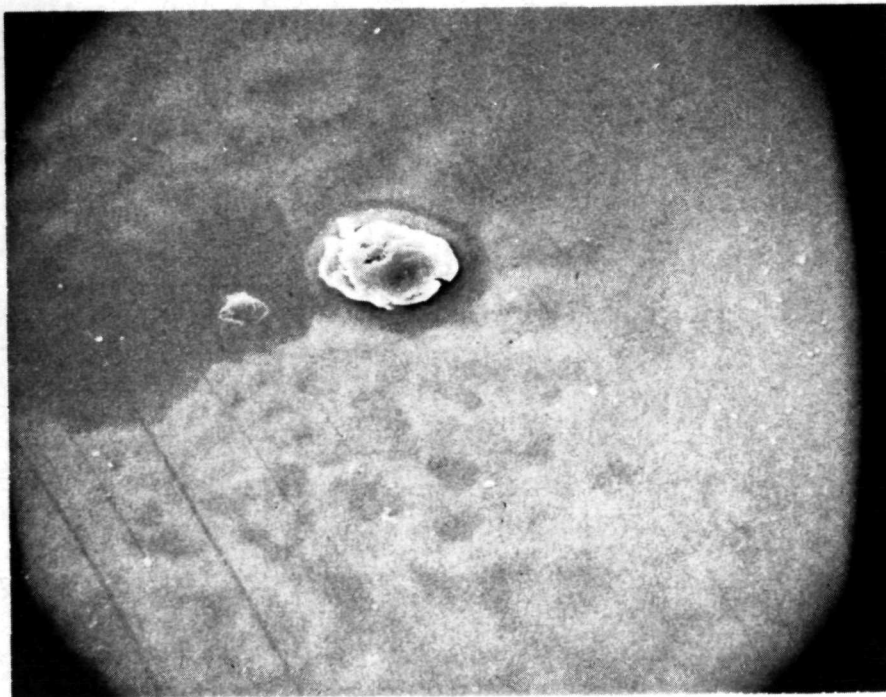


Figure 12: INTERFEROMETER STEP FORMED BY O₂-PLASMA EXPOSURE
(700X MAGNIFICATION)

vaporized in a heated flask and allowed to backfill the chamber to a pressure of 4 torr. Figure 13 presents the QCM change in frequency during the deposition of MgF-46. As can be seen by comparing Figures 1 and 13, the silicone was deposited very slowly compared to the butadiene deposition. Because of the long period of time involved, a portion of the erratic behavior shown in Figure 13 could be caused by drift in the QCM electronics. The reflectance changes caused by this silicone contaminant film were very small. Another attempt was made to deposit a film at a lower chamber pressure (1-2.5 torr), however, this test was aborted because droplets of silane impinged on the mirror during the backfilling operation. Deposition was also attempted by placing a small amount of silane in a beaker inside the chamber. This resulted in deposition of a visible film on the sample at 3 torr. However, the film evaporated when the sample was let up to atmospheric pressure, indicating that the silane had not been polymerized by the UV radiation. Because of these unsatisfactory results, other methods of silicone film deposition are being explored.

3.2 Cleaning Experiments

3.2.1 Ultraviolet Reflecting Mirrors

Results of a contamination/plasma cleaning test on a $\lambda/2$ MgF₂/Al-coated mirror (No MgF-44) are shown in Figure 14. The mirror was contaminated during an exposure of 62 minutes using UV and butadiene. Interferometry data from this test indicates that the film thickness on the IFM was about 100 Å after contamination. (This compares with the 1050 Å film that was determined to be on MgF-43. Reflectance data for MgF-43 was presented in Figure 8 of the second quarterly report.) As can be seen, in Figure 14, the reflectance was reduced by as much as 70 percent at a wavelength of about 130 nm. After a total O₂ plasma exposure time of 122 minutes, the

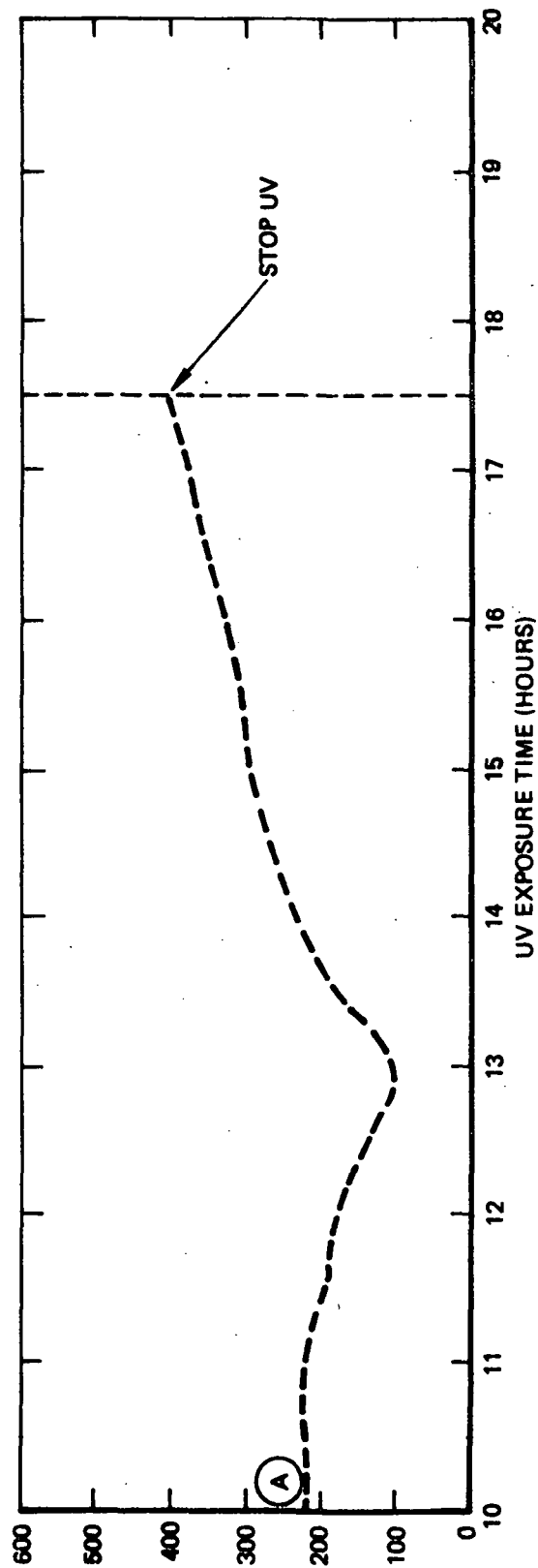
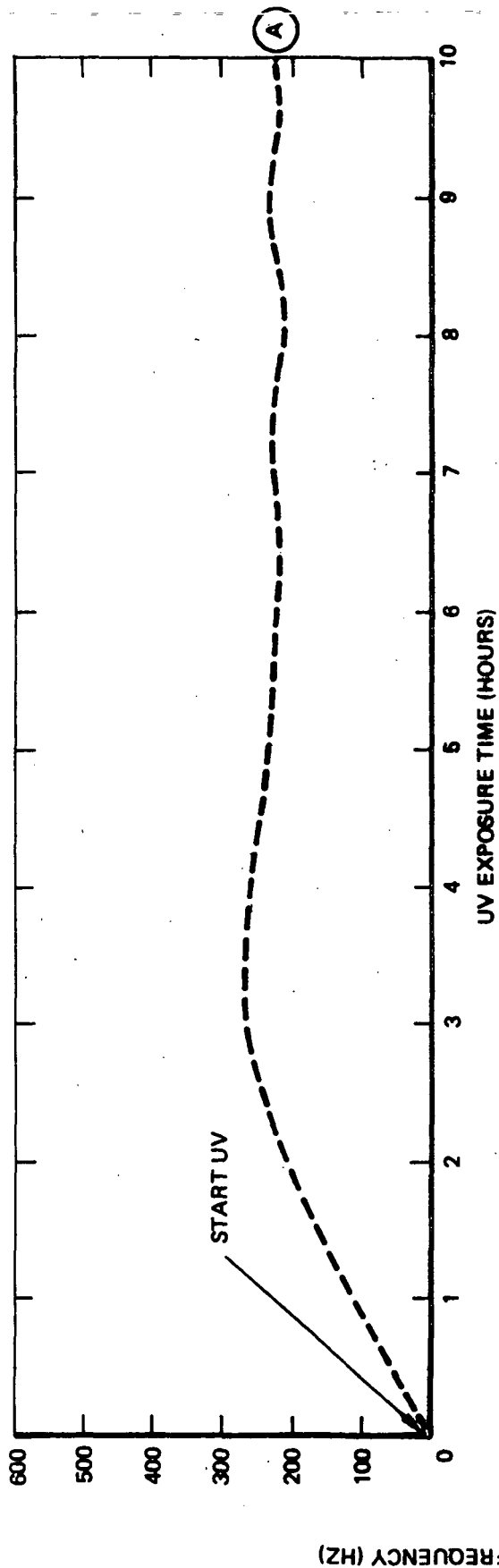


Figure 13: OCM CHANGE IN FREQUENCY VS UV IRRADIATION EXPOSURE TIME FOR METHYL TRIMETHOXYLANE ($\text{CH}_3\text{Si}(\text{OCH}_3)_3$) CONTAMINATION ON $\frac{1}{2}\lambda$ MgF_2/Al -COATED QUARTZ CRYSTAL (NO MgF-69)

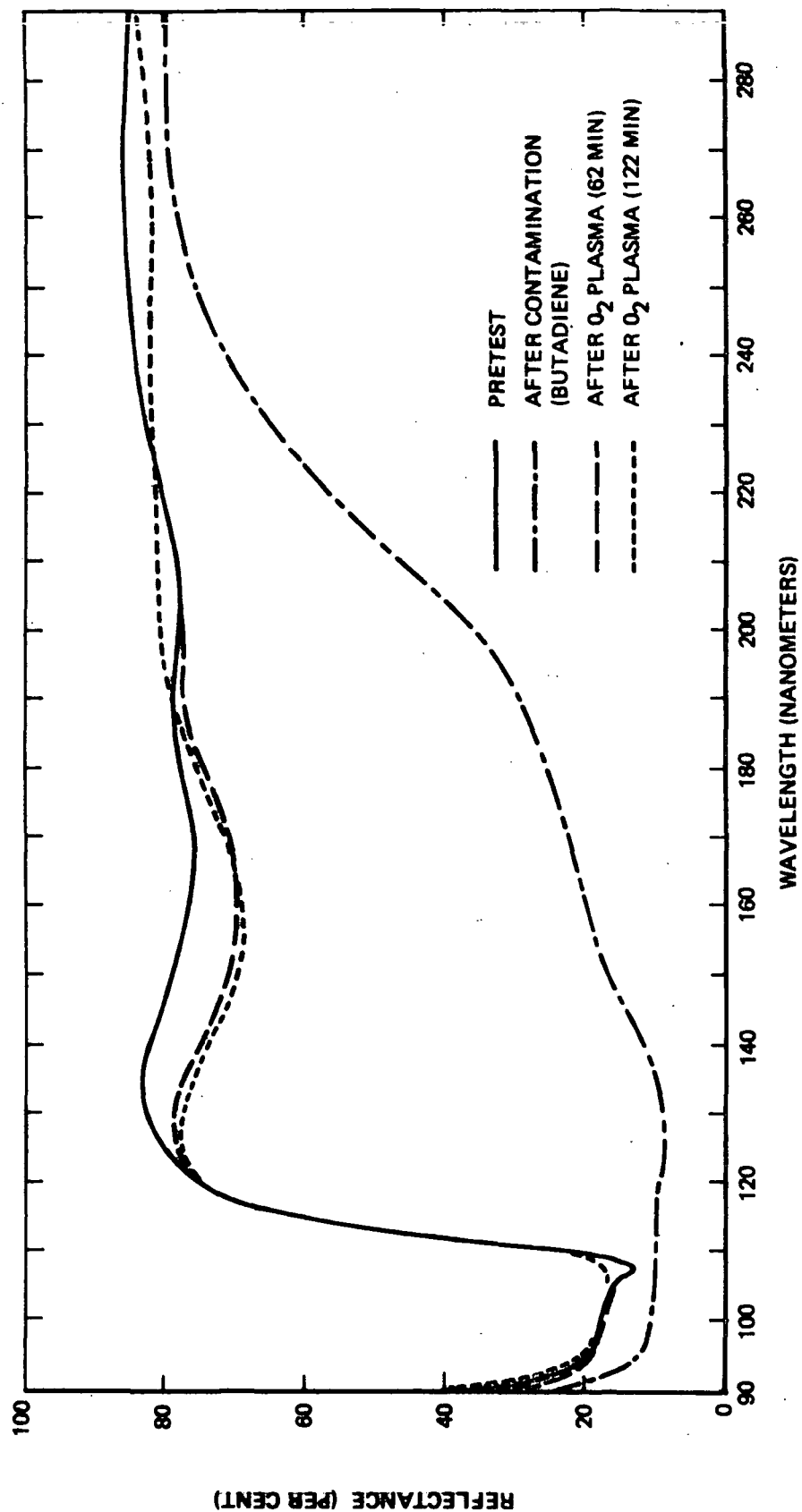


Figure 14: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF $\frac{1}{2}\lambda$ MgF_2/Al -COATED MIRROR (NO. MgF-44)

reflectance was completely restored in the wavelength region below 117 nm. Comparison of data for MgF-44 and MgF-43 shows that both samples had some residual degradation, although interferometric measurements on the IFM adjacent to MgF-44 could not detect any film after plasma treatment.

In response to a request by the NASA contract technical monitor, a thermal cleaning experiment was conducted on a $\lambda/2$ MgF₂/Al coated mirror. The basis for this request is that when atomic oxygen O(³P) recombines on a surface to form O₂, thermal energy is transferred to the surface. In the case of a contaminated surface, it may be possible that the plasma thermal energy alone is the mechanism of contaminant film removal. Thus, the approach used was to heat a contaminated sample to a temperature representative of that achieved during plasma cleaning, and determine whether the contaminant film sublimates in vacuum. The temperature that would be representative was inferred from an exploratory test reported in the first quarterly report. Figure 9 of that report showed the test setup used in which a stainless steel disc was placed within about 1 cm from the end of a plasma-generation quartz tube. Figure 10 in that report showed the variation of disc temperature as a function of pressure at the inlet of the quartz plasma generation tube for RF power settings of 30 and 50 watts. It is noted that the maximum temperature obtained was about 250°F at about 70 torr and 50 watts. Since the recent plasma exposure tests have been run at 40 watts RF power (20 watts/tube), plasma generation tube inlet pressures less than 10 torr, with specimens clamped to a water-cooled copper plate, and with a 10 cm spacing between the plasma tube and the test specimen, it was decided that a temperature of 200°F would be pessimistically high.

In the thermal cleaning test, mirror No. MgF-48 was contaminated with butadiene during exposure to UV radiation for 1096 minutes. The test

facility was modified to allow hot mineral oil to be circulated through the cooling coils of the specimen holding plate (see Figure 4 of second quarterly report for a photograph of the specimen holding plate). The plate temperature was maintained at 200° - 220°F for 300 minutes at a chamber pressure of $1-4 \times 10^{-4}$ torr. Figure 15 shows the effect of the thermal cleaning test on the sample reflectance. As can be seen, no significant change in reflectance occurred during the 300 minute period. A minor decrease of reflectance occurred at wavelengths longer than 260 nm.

As discussed previously, the specimen temperature used in the thermal cleaning was much higher than that anticipated during plasma cleaning. Also, Table I shows that the longest plasma exposure for any mirror sample was 112 minutes for MgF-43 (see Figure 8 of second quarterly report for reflectance data). The reflectance of MgF-43 was significantly restored during the plasma exposure. This data strongly indicates that the mechanism of contaminant film removal is definitely related to the reaction of the plasma with the contaminant film.

Contamination/plasma cleaning data for a platinum-coated mirror (No. Pt-12) are shown in Figure 16. This mirror was contaminated during an exposure of 224 minutes using UV and butadiene. The thickness of the film on the IFM after contamination was determined to be about 330 Å. As can be seen, the reflectance was substantially reduced by the presence of the contaminant film. This is contrasted to the small amount of degradation noted in the data for Pt-11 in Figure 10 of the second quarterly report. It was determined that the film thickness on Pt-11 was too thin ($< 50 \text{ Å}$) to be measured by the interferometer. The curves for Pt-12 show that a 30 minute O_2 plasma treatment essentially restored the reflectance of the sample. Visual observations of this sample did not show any discolorations as were observed on Pt-11.

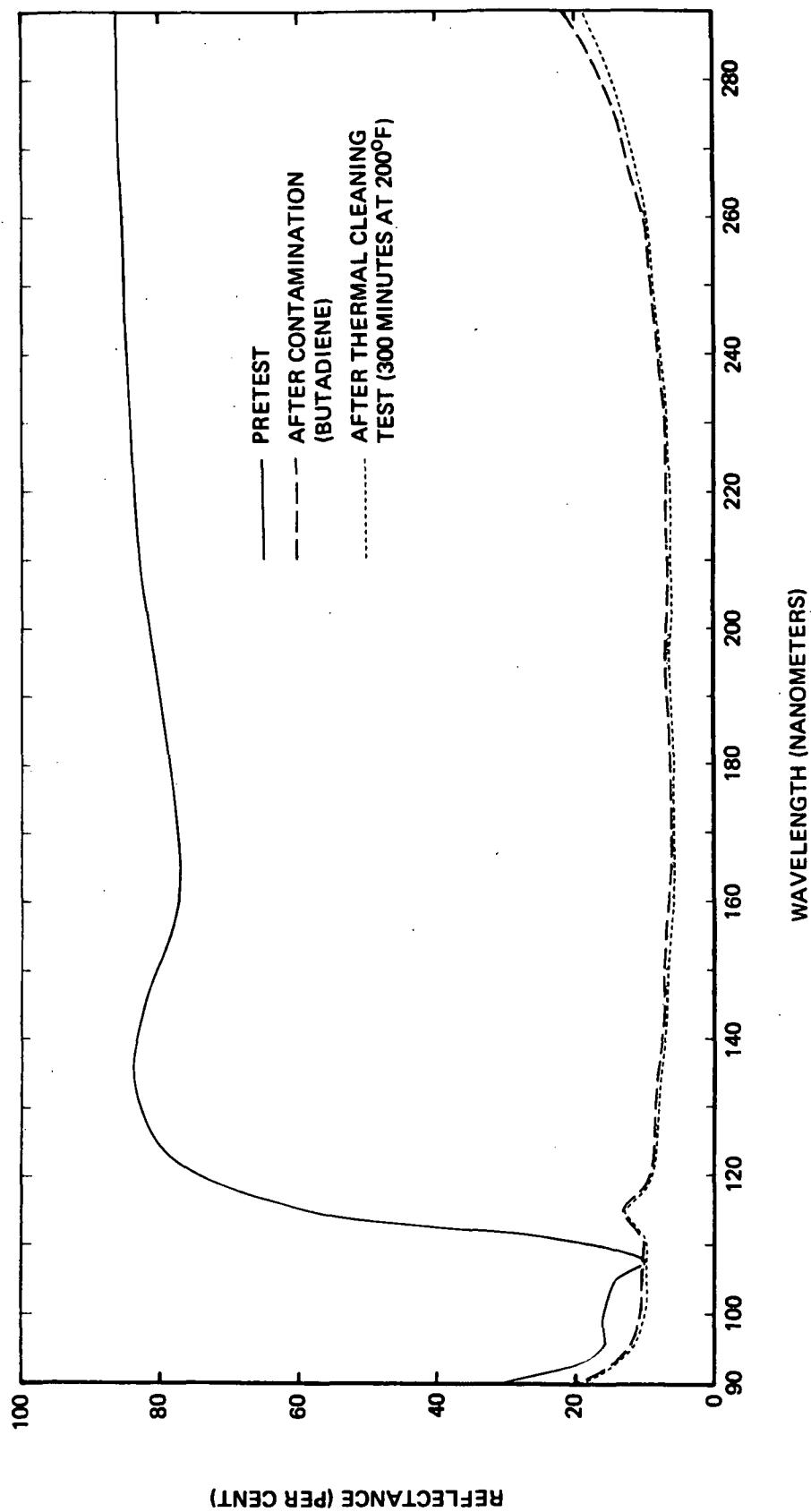


Figure 15: EFFECT OF BUTADIENE CONTAMINATION AND THERMAL CLEANING TEST ON $\frac{1}{2}\lambda$ MgF_2/Al COATED MIRROR (NO. MgF48)

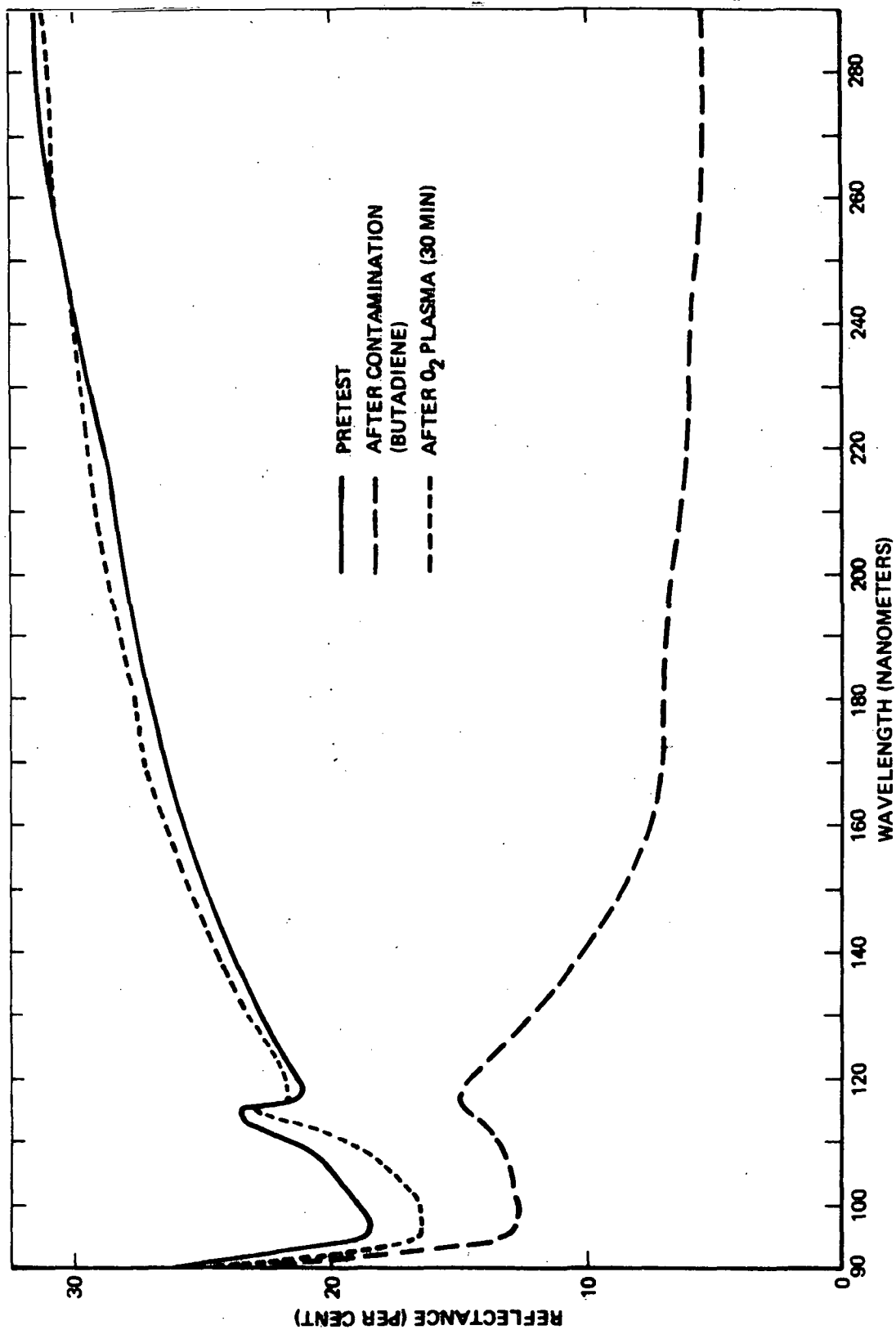


Figure 16: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF PLATINUM-COATED MIRROR (NO. Pt-12)

3.2.2 Gratings

Figures 17 and 18 present the first-order reflectance data on gratings GAl-1 and GPt-1 respectively. The GAl-1 was blazed at 150 nm and coated with $\lambda/2$ MgF_2/Al . As can be seen from Figure 17, there is a maximum reflectance in the pretest data near 150 nm which correlates well with the blaze wavelength. After contamination with butadiene, there was a significant drop in reflectance in the region below 250 nm, and an increase for longer wavelengths. The plasma exposure substantially restored the reflectance near the blaze wavelength, but induced a small degradation in the long wavelength region.

The data shown in Figure 18 for grating GPt-1 shows behavior similar to that of GAl-1. The blaze wavelength for this platinum-coated grating was 60 nm. Although the data does not include wavelengths shorter than 100 nm, the reflectance increases as expected near the short wavelength limit. The effect of the contaminant film was to reduce the reflectance at wavelengths below about 270 nm, and increase the reflectance at wavelengths above this point. The reflectance was substantially restored after the first plasma treatment especially at the lower wavelengths. The effect of the second plasma treatment was small, increasing at some wavelengths, decreasing at others.

The data on GAl-1 and GPt-1 indicate that the contaminant film can be successfully deposited, and its effect on the first-order reflectance measured. The plasma treatment was shown to be effective in restoring the reflectance near the blaze wavelength to the original values. At the present time, however, the cause of residual reflectance changes at longer wavelengths after plasma treatment is not known.

3.2.3 Thermal Control Surfaces

The effects on reflectance of butadiene contaminant and plasma exposure were determined for three types of thermal control surfaces: silver-coated

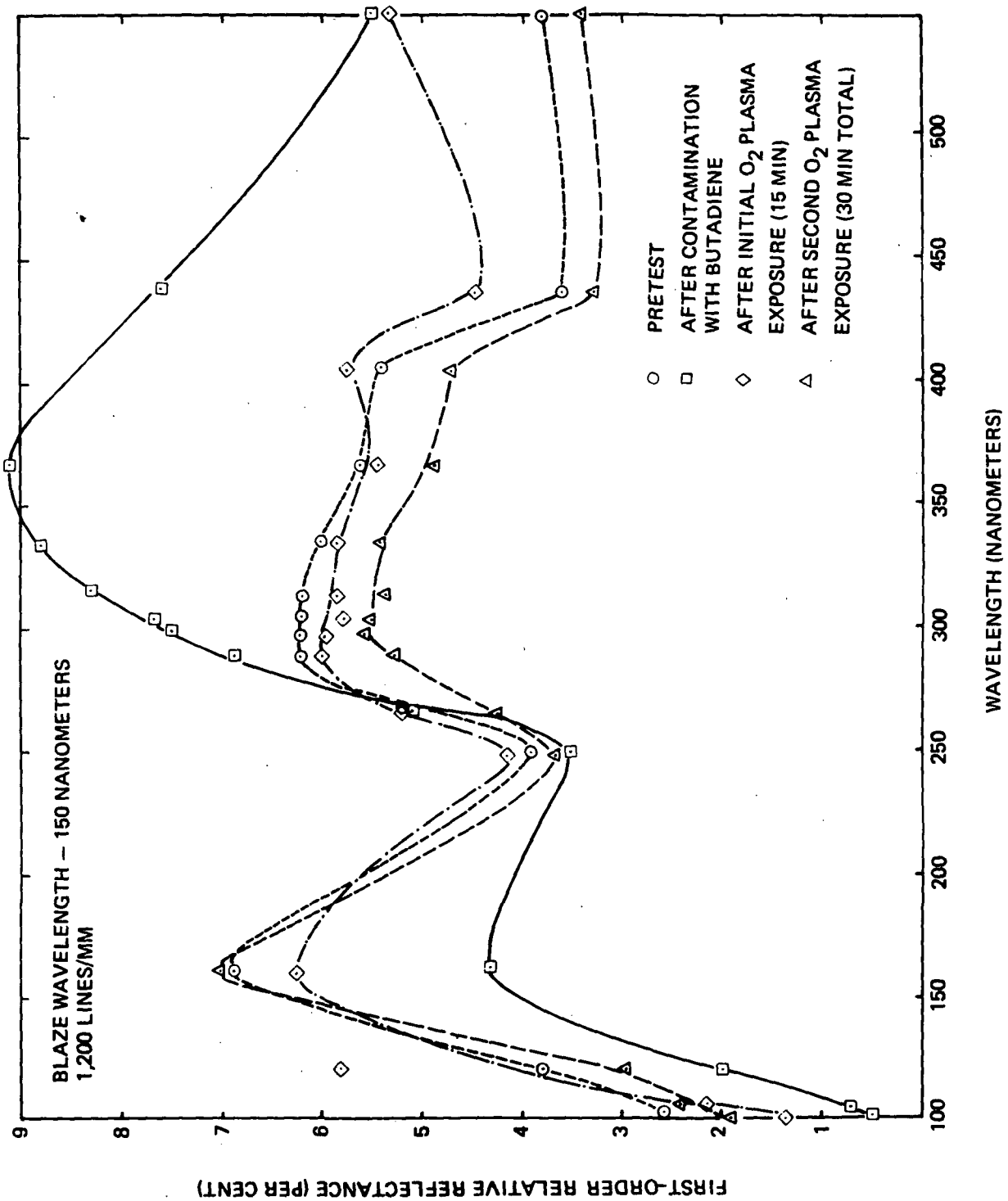


Figure 17: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON FIRST-ORDER REFLECTANCE OF MgF₂/Al-COATED GRATING (NO. GAL-1)

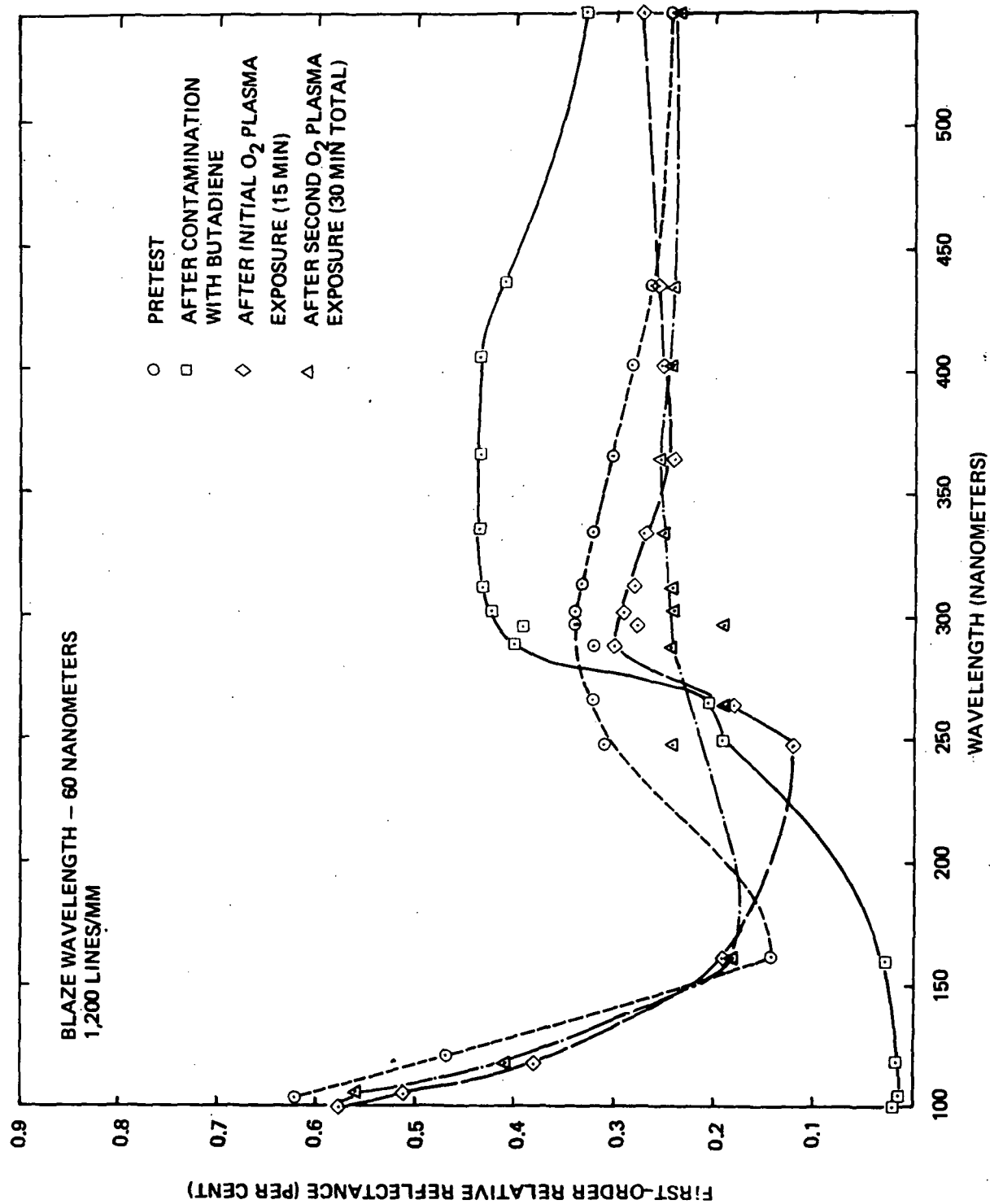


Figure 18: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON FIRST-ORDER REFLECTANCE OF PLATINUM-COATED GRATING (NO. GPT-1)

FEP Teflon, treated zinc oxide in methyl silicone (S-13 G paint), and zinc oxide in potassium silicate (Z-93 paint).

Figures 19 and 20 present the data for two silver-coated FEP Teflon samples, FEP-4 and FEP-5, respectively. FEP-4 was exposed to butadiene and UV radiation for 248 minutes. Thickness measurements on the adjacent IFM indicated that a contaminant film thickness of $430 \text{ \AA}$. After a 16 minute plasma exposure, the reflectance increased to original values at wavelengths greater than 400 nm, while a small amount of residual damage remained at wavelengths less than 400 nm. Interferometer results indicated that $120 \text{ \AA}$ of film remained on the IFM after plasma treatment. Because of the small amount of reflectance change observed after contamination of FEP-4, the effect of a much thicker film was investigated. FEP-5 (see Figure 20) was exposed to butadiene and UV radiation for 1009 minutes. Subsequent interferometer measurements indicated that the film thickness was $10,100 \text{ \AA}$. The effect of this much thicker film is readily apparent in the reflectance data. After a 263 minute plasma exposure, the reflectance was essentially restored over the whole wavelength range. This indicates that very thick films can be removed by the O_2 plasma without causing damage to the Teflon surface.

Figure 21 shows the effect of contamination and plasma exposure on two S-13G paint samples (S-1 and S-2). S-1 was exposed to butadiene and UV radiation for 1020 minutes. Interferometry measurements indicated that the film thickness was $2540 \text{ \AA}$. The contaminant film reduced the reflectance of the sample substantially in the region from 400 to 600 nm. After a 234 minute plasma treatment, the reflectance of the sample was shown to decrease even below the contaminated level. This puzzling result coupled with interferometric data that indicated $1790 \text{ \AA}$ of the film had been removed from the IFM plasma exposure, suggested that the O_2 plasma alone was degrading the paint surface. Sample S-2 was given a plasma treatment of 198 minutes to evaluate

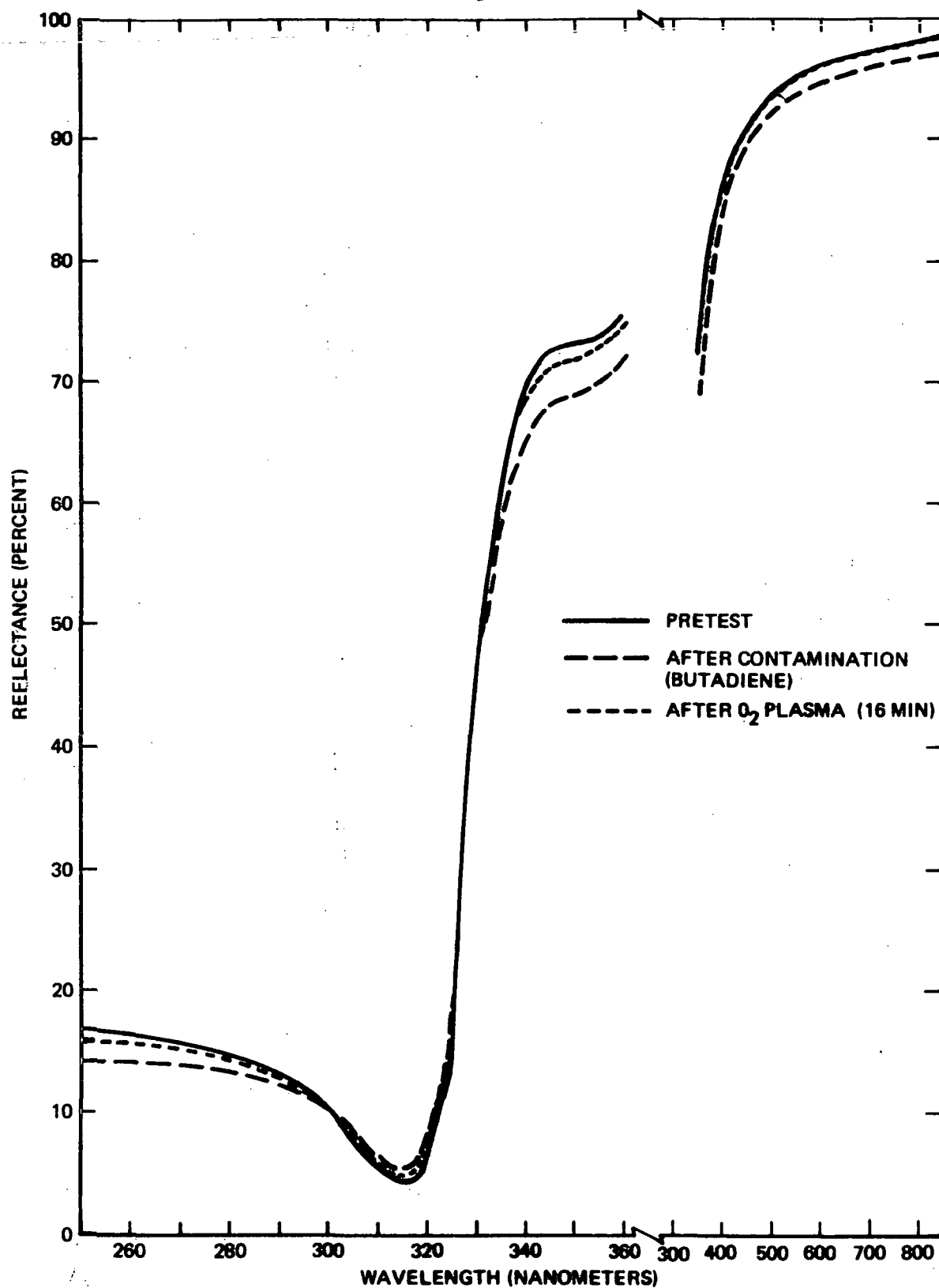


Figure 19: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF SILVER-COATED FEP TEFLON SURFACE (NO. FEP-4)

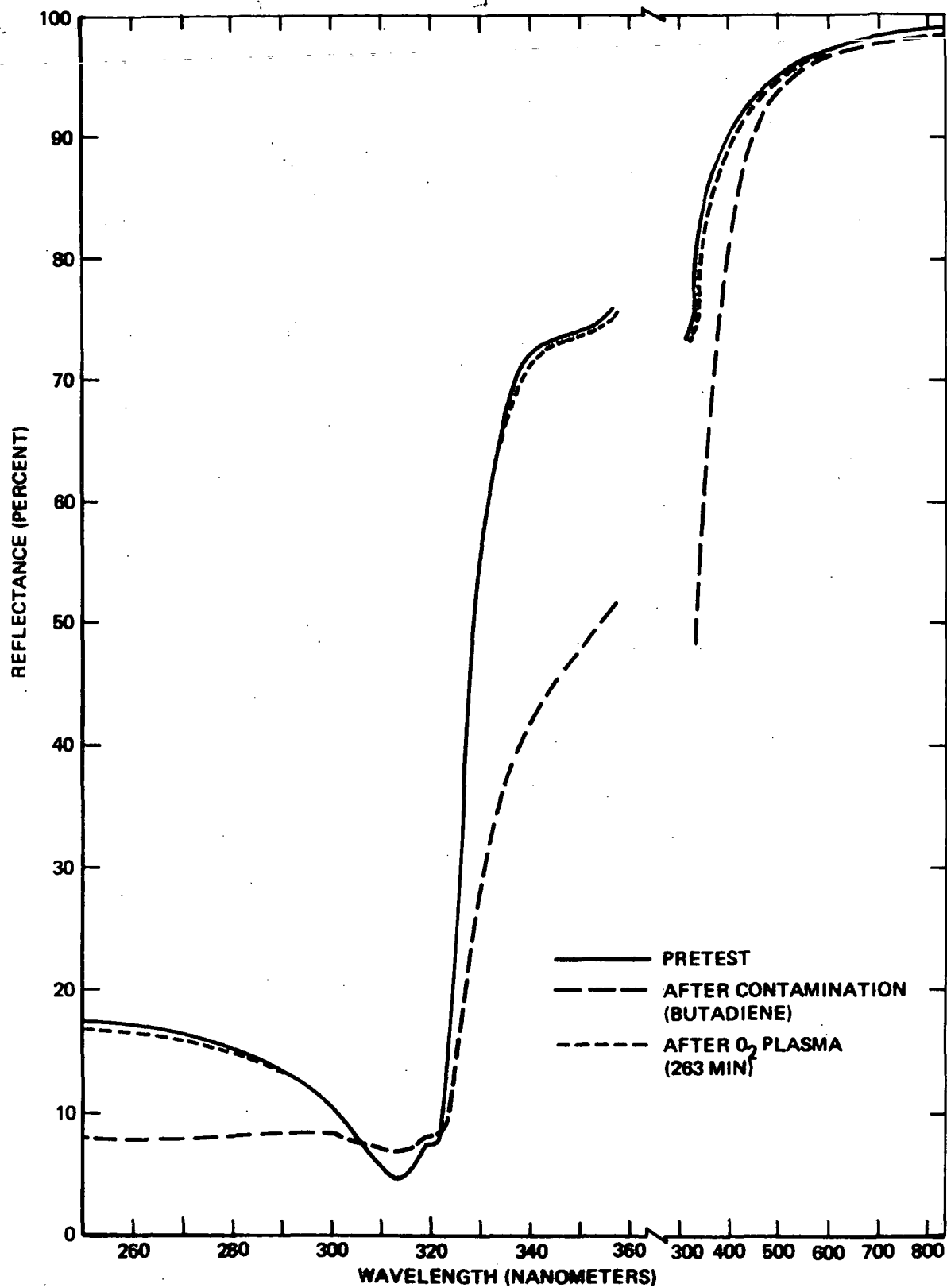


Figure 20: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF SILVER-COATED FEP TEFLON SURFACE (NO. FEP-5)

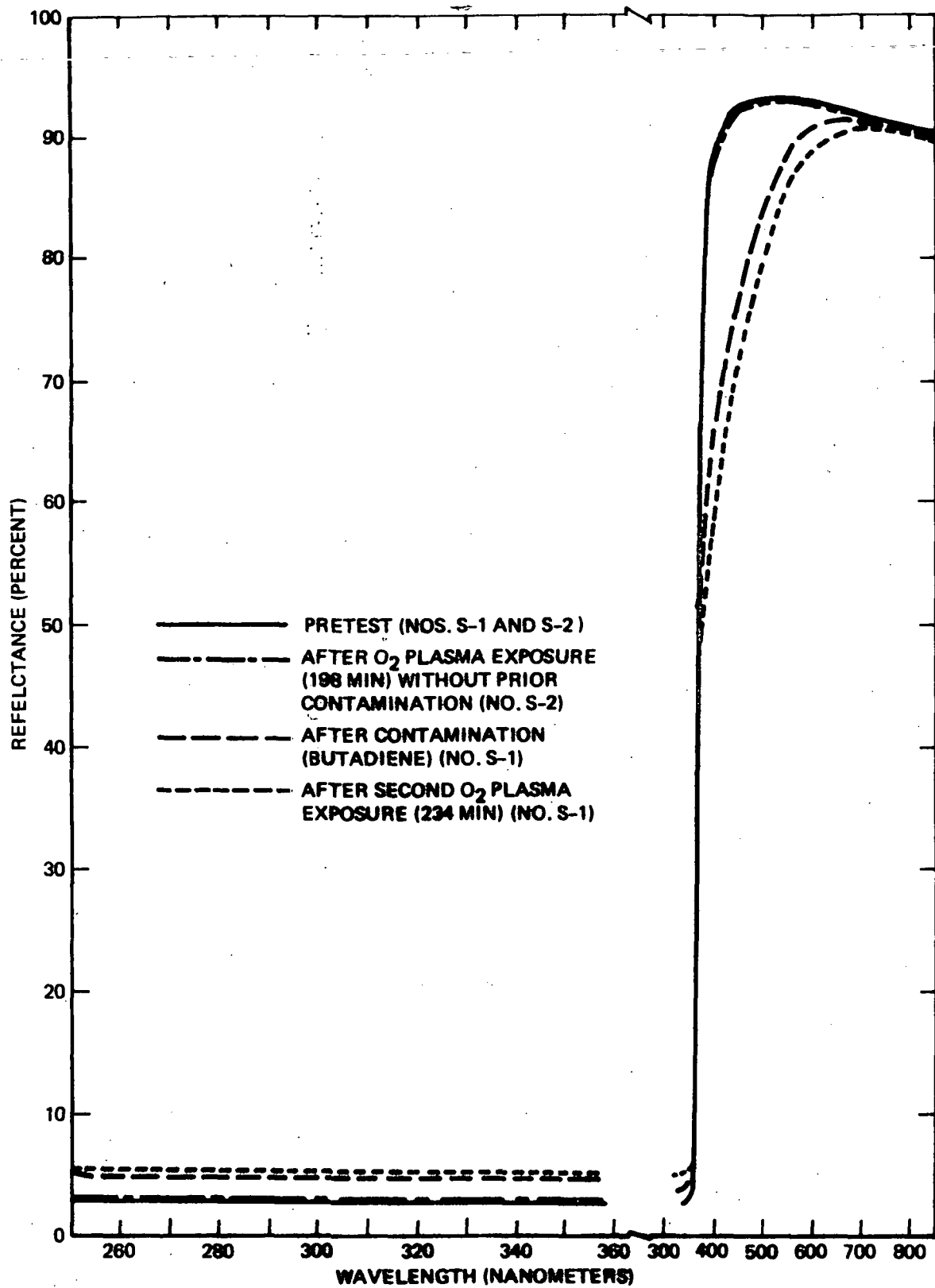


Figure 21: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF S-13_g PAINT SAMPLE (NOS. S-1 AND S-2)

this possibility. The data shown in Figure 21 shows that no reflectance change occurred.

A similar, although more pronounced, degradation was obtained with the Z-93 paint sample Z-1 (see Figure 22). Z-1 was contaminated for 936 minutes, producing a sufficiently thick film that interferometric measurements were not possible ($>10,000 \text{ \AA}$). This specimen exhibited significant damage out to the long wavelength limit of 2500 nm. After 291 minutes of plasma exposure, the reflectance increased at wavelengths greater than 900 nm, and decreased in the region from 400-900 nm. An uncontaminated specimen (Z-2) was then exposed to the plasma for 198 minutes. This test showed that plasma exposure alone would not cause degradation in reflectance.

It is recommended that further work be done to identify the cause of the white coating reflectance degradation. It may be possible that synergistic effects are taking place when both a contaminant and UV radiation are present. This type of effect may be one of the contributing causes for the lack of correlation between reflectance data taken on flight experiments and in laboratory facilities.

3.2.4 Lenses

The effects of a butadiene film on the transmittance and imaging characteristics of 2-inch diameter by 1/2-inch thick flat quartz discs, have been evaluated. Sample L-1 was contaminated by exposure to butadiene and UV for 1397 minutes*. Inspection of the sample revealed that the contaminant film was tacky. The film was hardened by an additional 1016 minutes of UV exposure at atmospheric pressure. Contaminant film effects were evaluated by modulation transfer function (MTF) analysis, visual and photographic resolution, interference and Schlieren techniques, and spectral transmittance.

* The contaminant film thickness on the companion IFM, has not yet been measured.

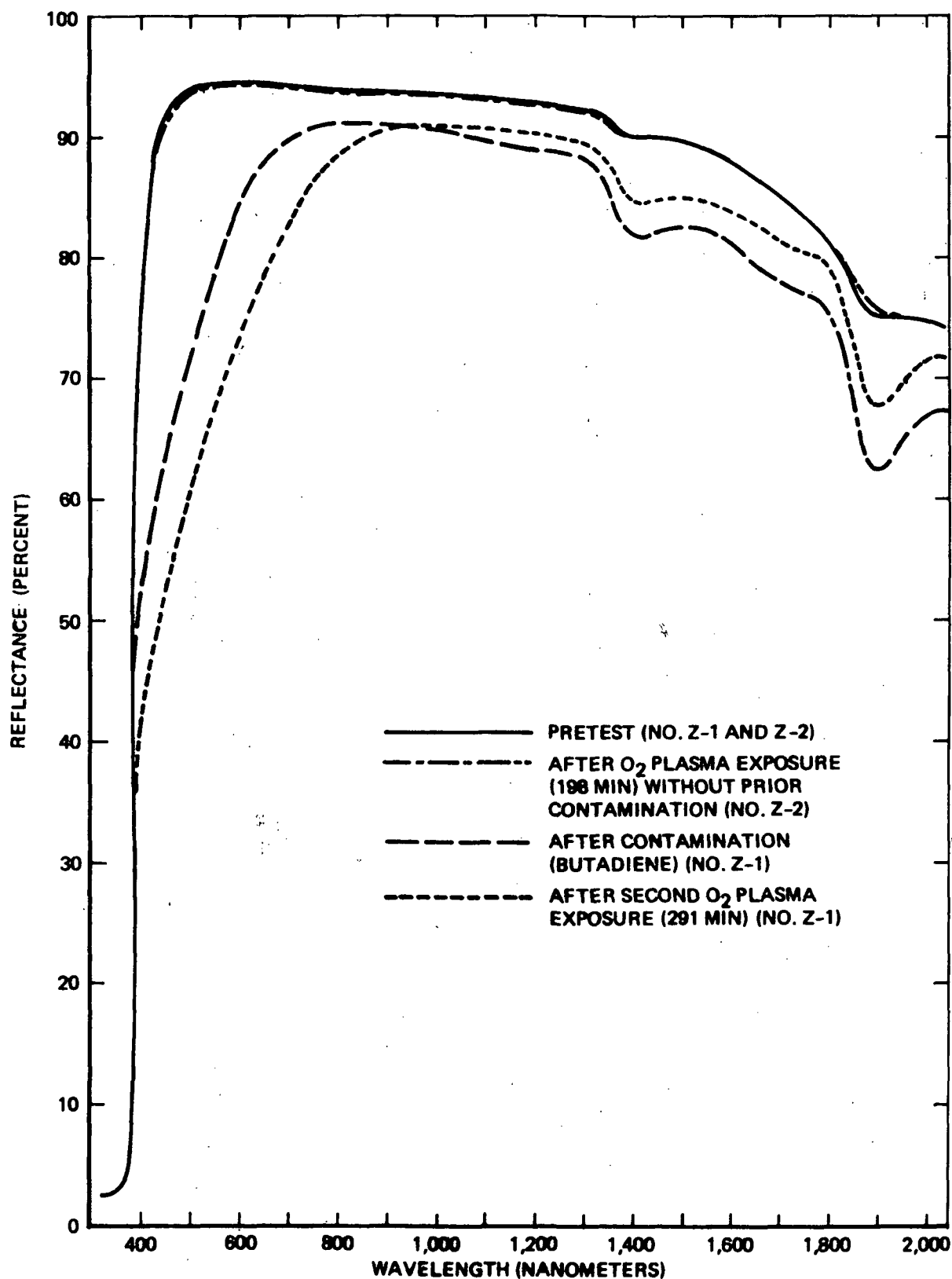


Figure 22: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF Z-93 PAINT SAMPLES (NOS. Z-1 AND Z-2)

Generally, there were no apparent changes between pristine and contaminated samples other than obvious visual differences. The exceptions were:

(1) a visual resolution test where light, scattered from intense side illumination by a contaminated specimen, reduced resolution slightly, and (2) a small amount of degradation in spectral transmittance. Transmittance measurements were made on L-1 (a contaminated specimen) and a control specimen (L-7) (See Figure 27). Then, L-1 was exposed to the O_2 plasma for 60 minutes, and the transmittance was remeasured. As can be seen from Figure 27, the contaminant film degraded the transmittance by only a small amount, mostly at shorter wavelengths. The plasma exposure restored the reflectance in the shorter wavelengths, but had little effect in the longer wavelength region.

The following is a description of the procedures used to test the lenses.

Modulation Transfer Function: A schematic of the MTF apparatus is given in Figure 23. The MTF is measured with an Ealing Eros 100 MTF Analyzer through a 20-inch input and a 3.6-inch output collimator, with a test blank placed between. Input frequency range is 0-100 cycles/mm, the output is 0-56 cycles/mm. A Corning C.S. 4-54 green filter is used at lamp output (see Figure 23). The critical region for evaluation of the fused silica flats is the central 3.8 cm diameter region. In both the MTF and resolution tests, the specimens were apertured to 37.4 mm. The diffraction limited angular frequency corresponding to this aperture at a wavelength of 555 nm is $37.4/555 \times 10^{-6} = 6.75 \times 10^4$ cycles/radian. With a 20-inch (505 mm) input collimator, this requires an input spatial frequency of 134 cycles/mm. At the output of a 36-inch collimator, the corresponding cutoff (diffraction limit) frequency is 73 cycles/mm. No significant contamination effects were observed in this test.

Visual and Photographic Resolution: The apparatus used for visual and photographic resolution tests is shown schematically in Figure 24. Resolution targets used were medium and high contrast master Air Force tri-bar targets

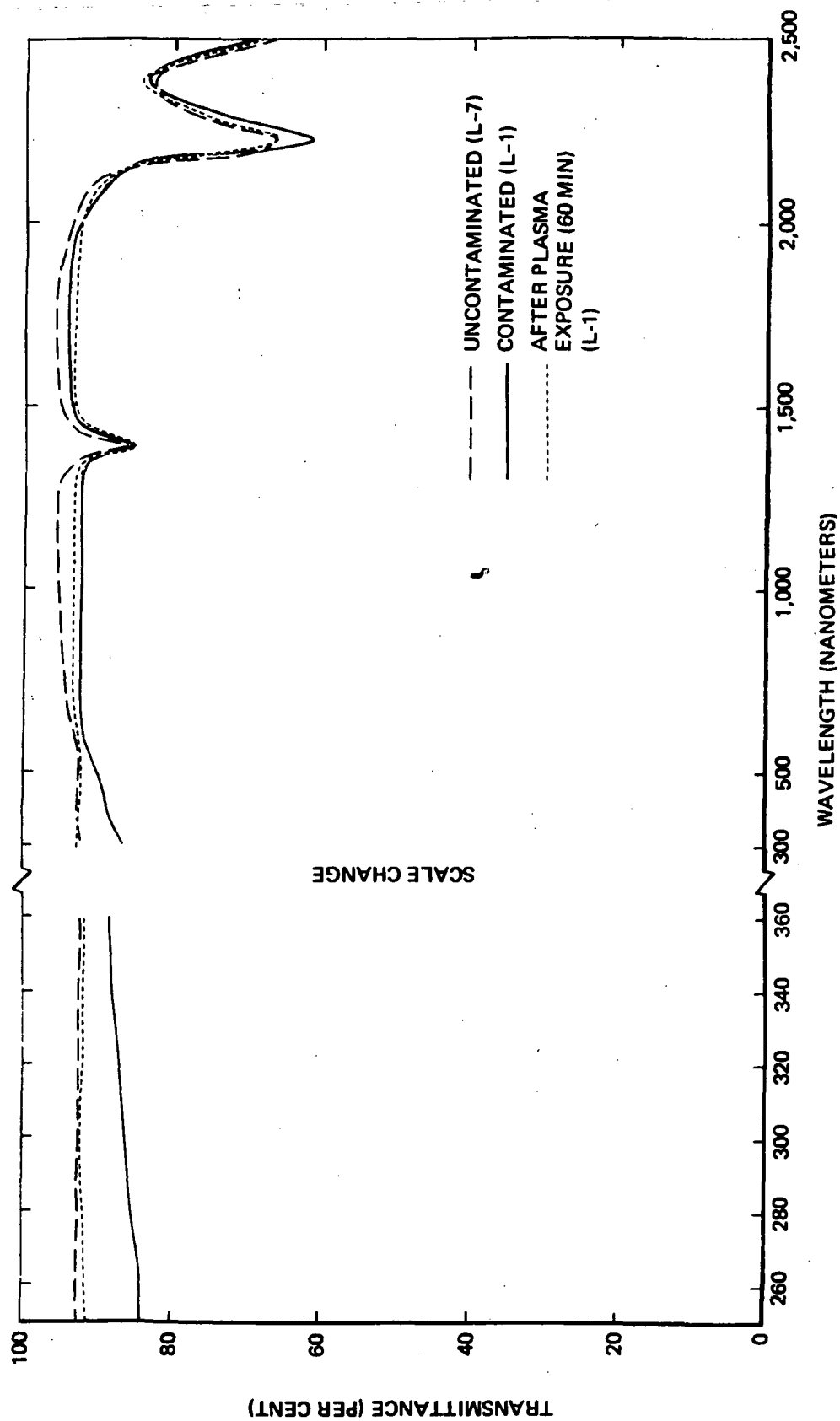


Figure 27: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA CLEANING ON TRANSMITTANCE OF FUSED SILICA OPTICAL FLAT (NOS. L-1 AND L-7)

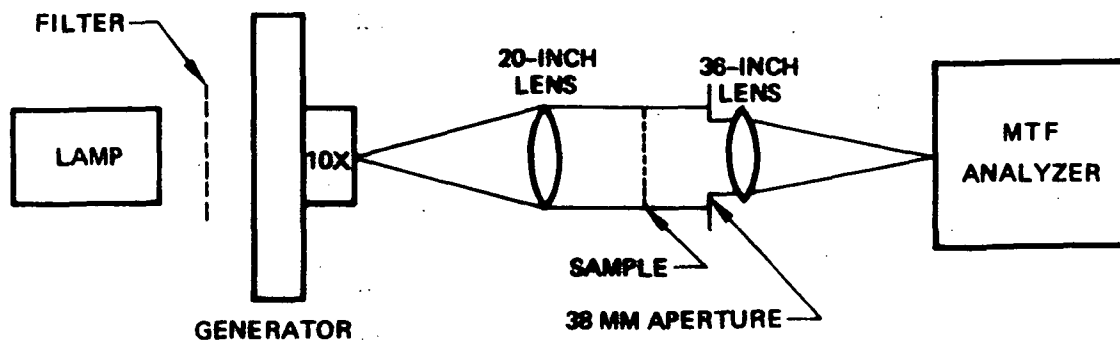


Figure 23: MODULATION TRANSFER FUNCTION TEST

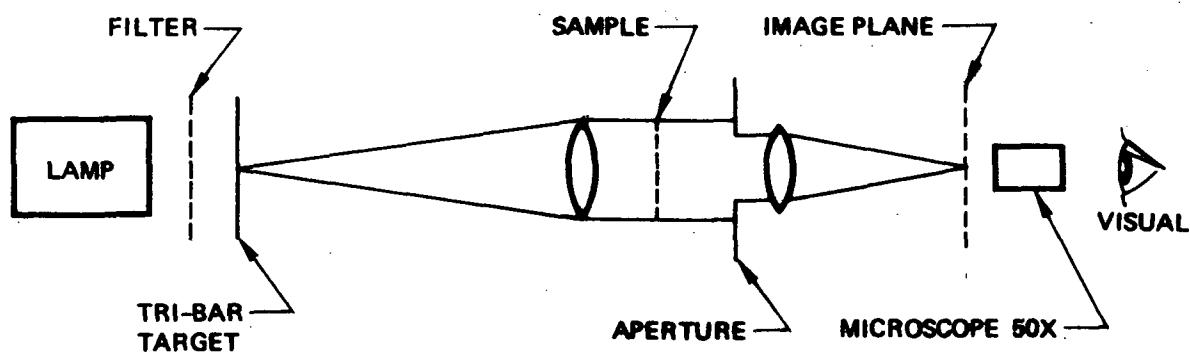


Figure 24: VISUAL AND PHOTOGRAPHIC RESOLUTION TESTS

from Buckbee-Mears. The output patterns were photographed on SO-243 film. A Wratten No. 61 green filter was used for all visual and photographic tests (see Figure 24). The same values of limiting resolution were obtained visually as by photographic test. Results of evaluation of effects of the contaminant film showed that no change in resolution occurred in the normal mode of operation. However, with the medium contrast target and flooding the contaminated sample with side illumination, one resolution group was lost visually.

Schlieren Test: A schematic of the Schlieren test apparatus is shown in Figure 25. The overall apparatus includes a Gaertner L 360 NMK Foucault knife edge attachment used as the source for an autocollimator, an 18-inch air-space collimating lens, and a 1/20 wave optical flat. No significant contamination effects were observed in this test.

Interference Pattern Test: Interference patterns were made with a helium-neon laser ($\lambda = 633 \text{ nm}$) and an 18-inch collimating lens in a beam expander as shown in Figure 26. Light, reflected from the front and back surfaces of the flat quartz discs at approximately 8° off-normal, produces interference fringes. No significant contamination effects were observed in this test.

Transmittance Tests: Transmittance measurements in the wavelength region from 250 nm to 2500 nm were made with a Gier-Dunkle integrating sphere reflectometer.

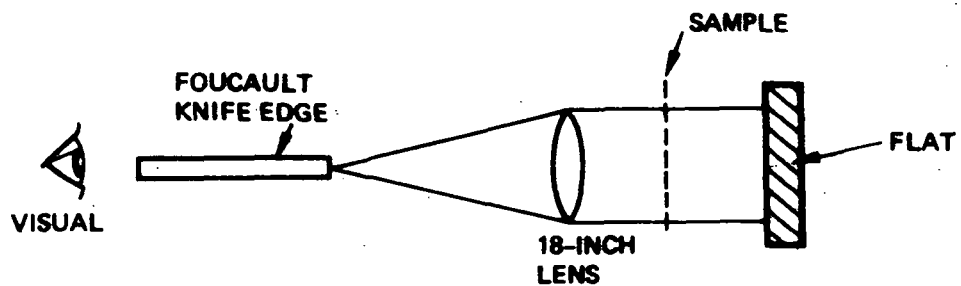


Figure25: SCHLIEREN TEST

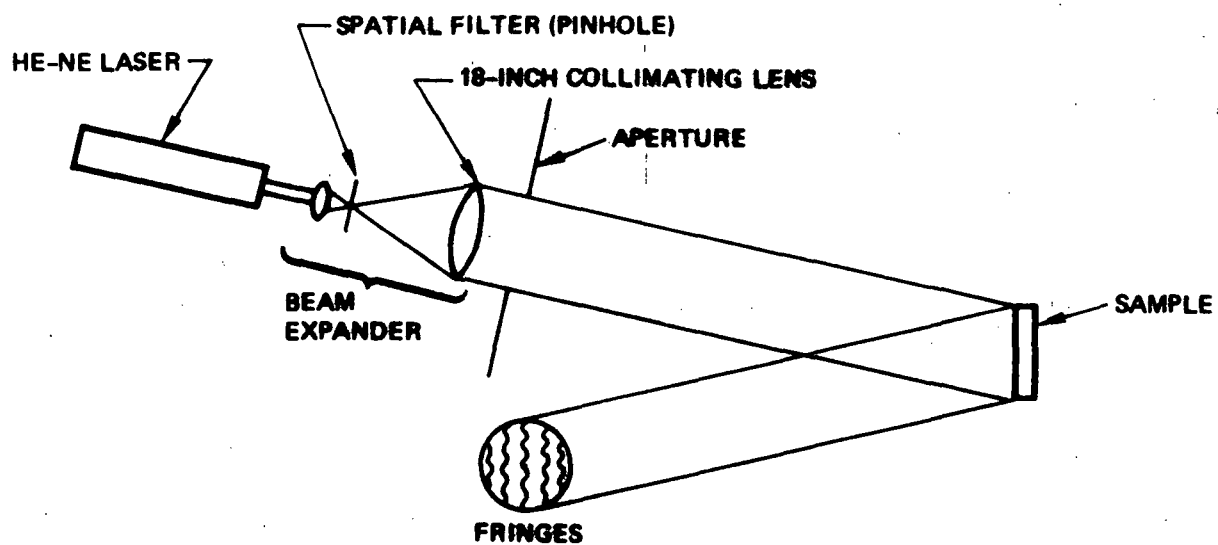


Figure26: INTERFERENCE FRINGE TEST

4.0 PROGRAM PROGRESS

4.1 Schedule

A schedule for the overall program is shown in Figure 28. Solid bars represent work completed and open bars represent work planned. As of this reporting date comprehensive experiments are in progress.

It appears at present that a 14-month time period will be required to complete the program.

4.2 Expenditures

Cumulative expenditures as of November 1 were about \$33,180. Approximately \$11,393 will be required to complete the program, including fee. No cost overrun is anticipated.

4.3 Future Work Planned

During the next reporting period the following items will be initiated or completed:

1. Comprehensive experiments will be completed;
2. Experiments with an alternative ACT will be completed if the need is demonstrated in comprehensive experiments;
3. Operational parameters of a flyable ACT will be defined;
4. A preliminary design of a laboratory model ACT will be prepared.

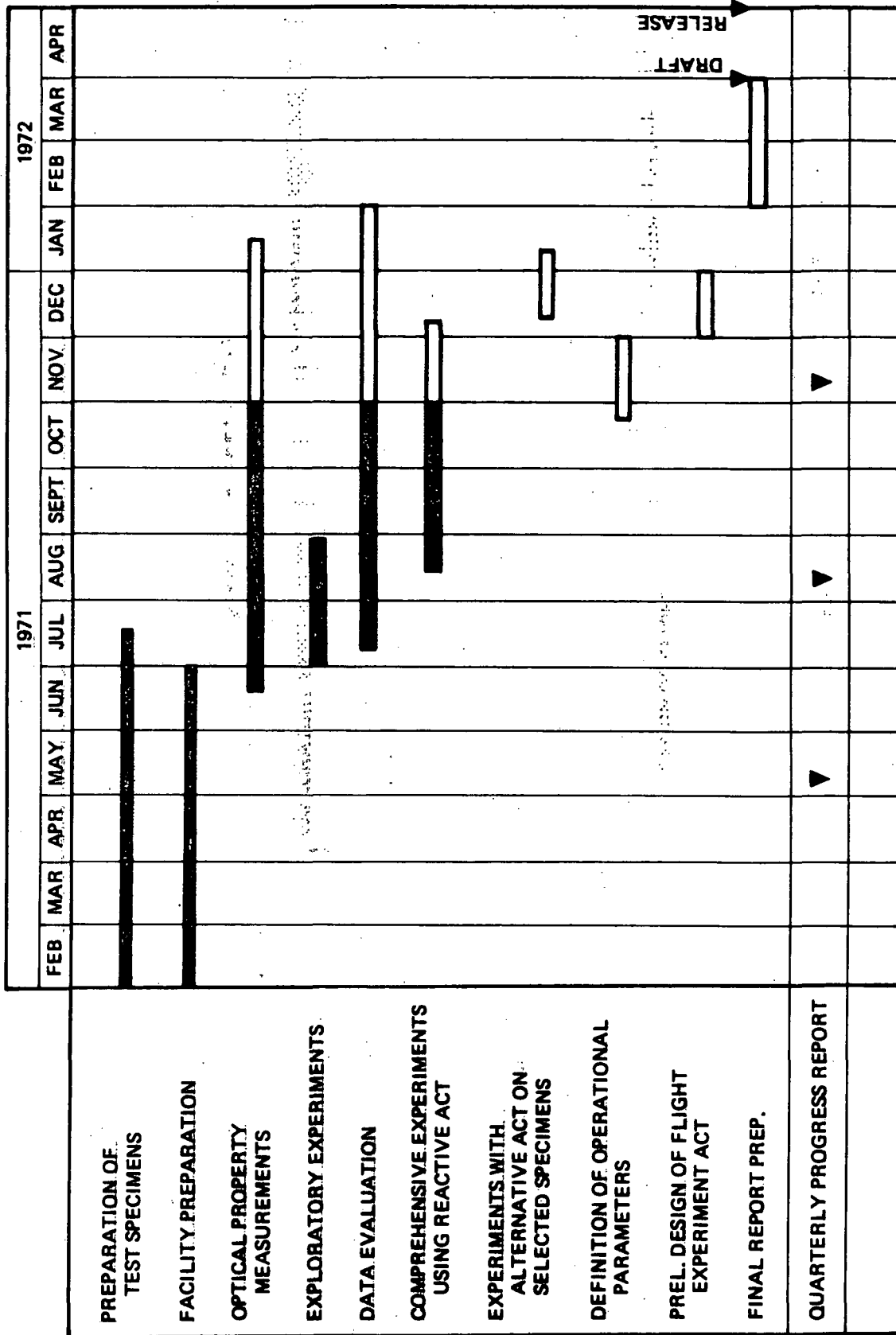


Figure 28: PROGRAM SCHEDULE

5.0 REFERENCES

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2. McKeown, D., and W. E. Corbin: "Removal of Surface Contamination by Plasma Sputtering." AIAA Paper No. 71-475 presented at the 6th Thermophysics Conference, Tullahoma, Tenn., April 1971.
3. Cothran, C. A., McCargo, M., and S. A. Greenberg: "A Survey of Contamination of Spacecraft Surfaces." AIAA Paper No. 71-457 presented at the 6th Thermophysics Conference, Tullahoma, Tenn., April 1971.
4. Private Communication with Dr. G. Timothy, Harvard College Observatory, Cambridge, Mass., April 1971.
5. Gillette, R. B. and B. A. Kenyon: Applied Optics 10, 3 (1971).