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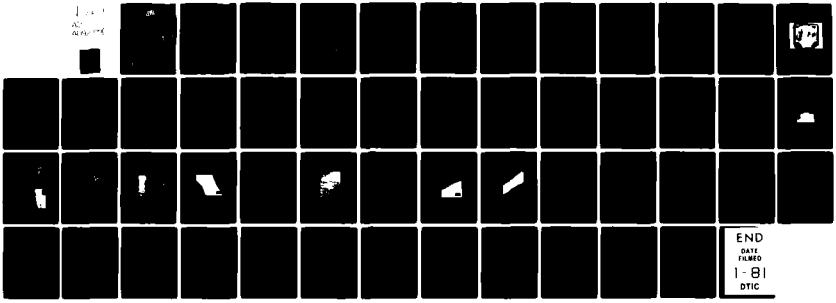

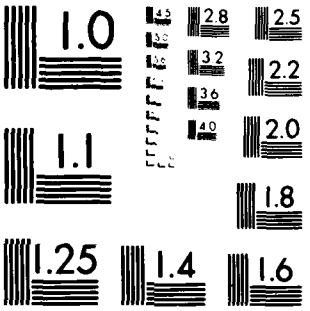

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Deterioration of Superpolished Metal Mirrors by Blue Haze

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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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Superpolished mirrors lose their low-scatter finish in industrial atmospheres because of a corrosion process. This degradation is investigated by exposing mirrors in controlled gaseous environments, monitoring changes with scatter measurements, microscopically and elementally analyzing the surface films. Blue haze results when nickel from the mirror combines with airborne pollutants and water to form an amorphous salt, which can coat the nickel and etch it. Preventive techniques to keep the metal clean and free of water films are also discussed.

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PREFACE

The diligent assistance of W. C. Burns is gratefully acknowledged, as is the most competent support we have received from the operators of surface analysis machines, N. Marquez, T. B. Stewart, R. A. Brose, E. S. Watts, and P. A. Bertrand. A special thanks is due to H. S. Judeikis, who made his chemical reaction cell available.

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I. INTRODUCTION

"Blue haze" is the name commonly used to describe the tarnishing of the surface of superpolished electroless nickel mirrors in ordinary laboratory air, which results in a considerable increase in visible and infrared scatter. This problem has plagued the development of infrared sensors for space during the 1970s and has eluded explanation or cure. We undertook the present study with the objective of identifying causes and finding ways to avert blue haze formation. We describe the phenomenology of the corrosion process and its effects on scatter. We also identify the constituents and relate blue haze to exposure in humid industrial atmospheres. Preventive techniques are discussed as well.

II. BACKGROUND

Since the invention in 1946 of electroless metal plating,[1] much has been published concerning the deposition processes and the resultant deposits, particularly nickel phosphorus alloys.[2-10] The advantages of electroless coatings over electrodeposits include uniformity of thickness, low porosity, and, consequently, better corrosion protection for steels and other metals. The use of electroless nickel coatings on lightweight beryllium and aluminum mirrors for spacecraft intensified in the late 1960s and 1970s because of the superior polish and lower scatter that could be achieved, in comparison to the substrate metals. In most of the spaceborne infrared telescopes designed for strong rejection of off-field bright sources, such as when viewing the earth's limb, so-called *superpolished electroless* nickel mirrors are used. The word "superpolished" in this context is poorly defined in terms of added performance and refers to final polishing processes that are proprietary to the vendors and which result in very-low-scatter metal mirrors. Again, "very low scatter" is poorly defined, as the surface finish of a mirror depends on many variables, including the age, plating history, and operating techniques of the electroless bath; the complexity of the mirror shape and associated tolerances, i.e., how much figuring is required; and even propitious talent and luck. Resultant mirror scatter at a wavelength of 10.6 μm can range from matching that of the smoothest fused-silica mirrors made (less than 6 Å rms roughness) to some two orders of magnitude greater scatter sometimes observed on aspherics. The bidirectional reflectance distribution function (BRDF) of some superpolished electroless nickel and two other mirrors is shown in Fig. 1.

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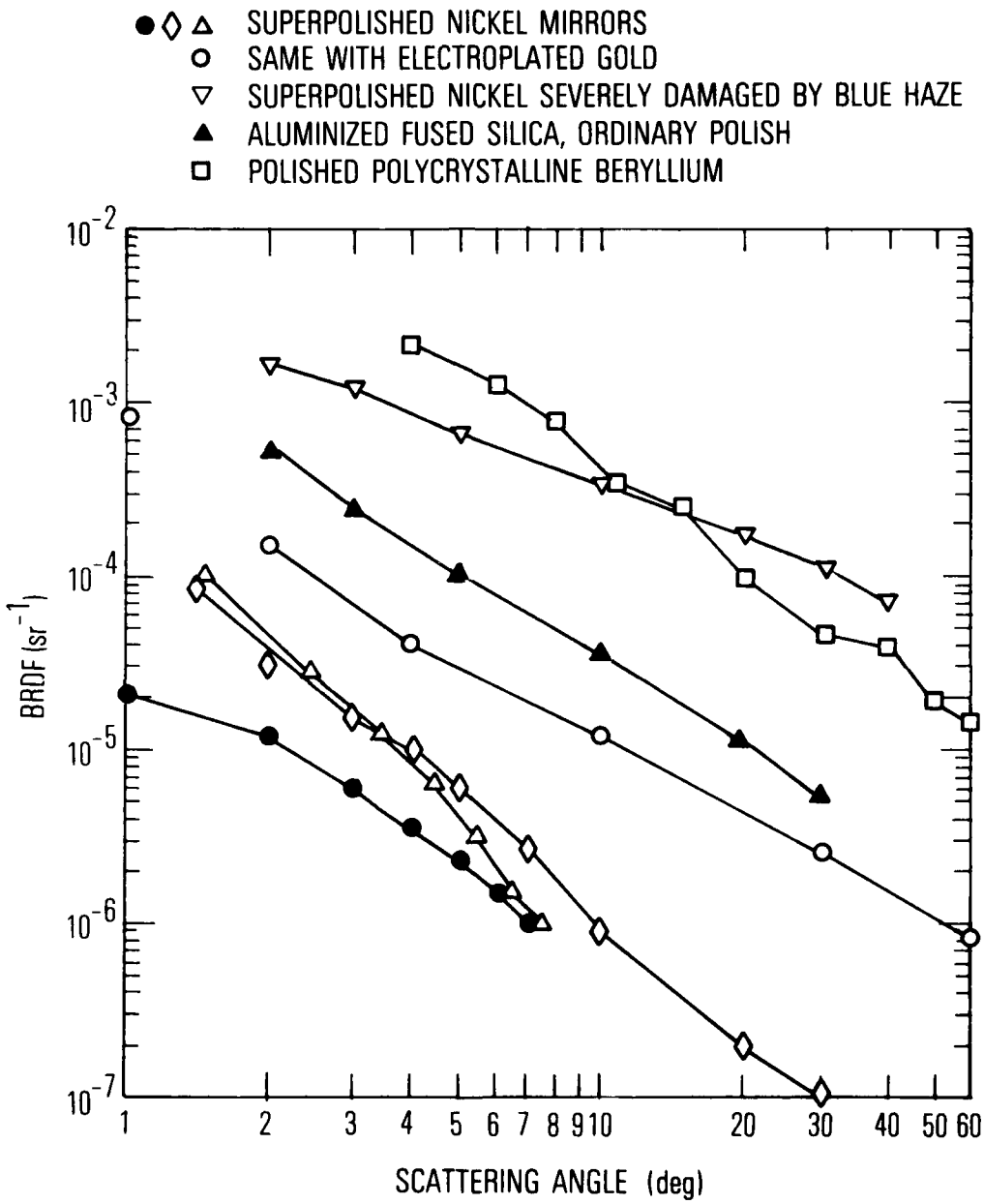

Fig. 1. BRDF of Several Mirrors at 10.6μm and Near Normal Incidence

Figure 2 is a dark-field or scatter photograph of a 12-in.-diameter superpolished nickel mirror in which are evident the irregular patterns typical of blue haze that formed over a period of several months. The lighter areas on the photograph are affected the most and are of a characteristic pale blue color. The same type of surface deterioration has been observed in laboratories near Boston, in Philadelphia, and in Los Angeles. In each case,

1. Mirrors exposed to ordinary laboratory or even clean room environments were affected within 6 months.
2. No solvent or washing solution was found that could remove the blue haze and completely recover the original scatter levels although the mirror recovered partially if washed and rubbed laboriously with soft wet cloths.
3. An increase in visible and infrared scatter resulted.

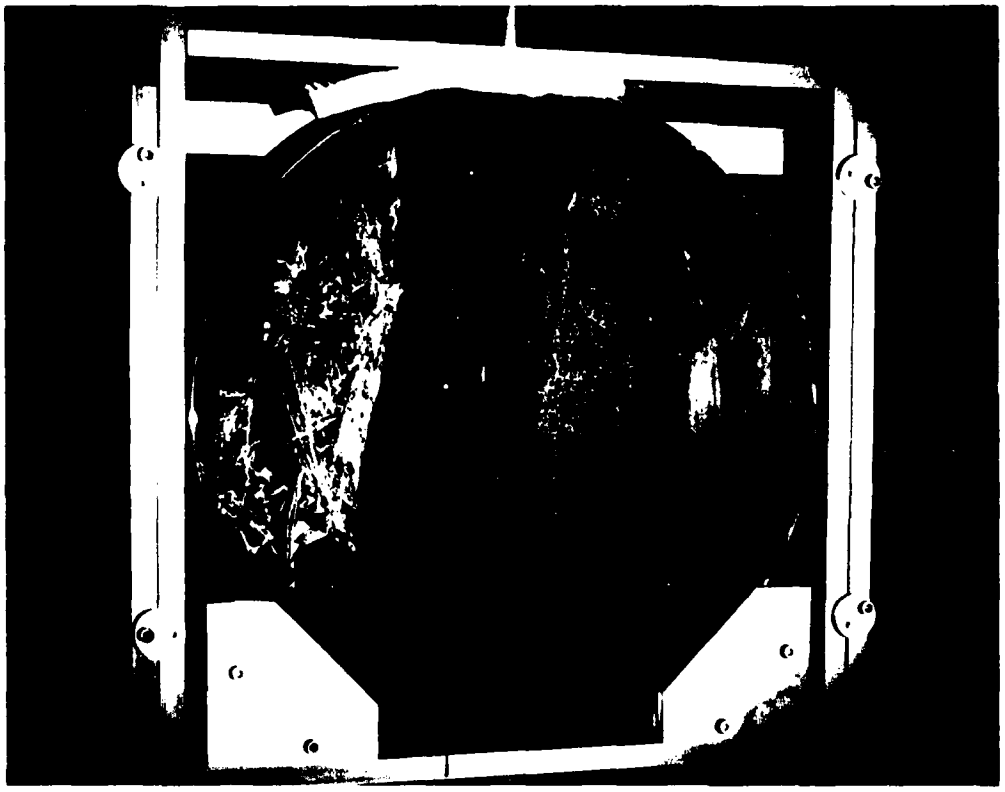

Fig. 2. Scatter Photograph of 12-in. Mirror Affected by Blue Haze

III. APPROACH

Our investigation was conducted to: (1) Determine that blue haze occurs in our laboratory and compare effects with those observed at other locations. (2) Section individual mirrors into sets of several pieces to eliminate production variables within a set and expose each piece in a predetermined manner in order to systematically alter the environment. (3) Monitor the growth of blue haze with noncontact, nondestructive methods such as visual observations, scatter measurements, scatter photographs, and microscopy. (4) Characterize the surface morphology and its elemental compositions with ion microprobe mass analysis (IMMA), Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), scanning electron microscopy (SEM) combined with energy dispersive analysis of x-rays (EDAX), and transmission electron microscopy (TEM), along with high-energy electron diffraction (HEED) and optical microscopy. (5) Devise preventive techniques and test them.

IV. EXPERIMENTAL

A. SAMPLE MIRRORS

Most of our small test samples originated from two mirrors made in 1974 by Applied Optics Center Corporation, Burlington, Massachusetts. Each consisted of a 125-μm-thick electroless nickel layer over an aluminum substrate, measured to be 5-cm in diameter with a superpolished concave reflective surface with a 122 cm radius of curvature. These mirrors were part of a set purchased for a systematic comparison of BRDF measurements at several facilities[11] and had been used and washed numerous times with no apparent surface deterioration for three years. For the present work, each mirror was sliced with a motorized saw with the use of diamond impregnated wire and a water lubricant in one case and oil in the other. The cut pattern was a square grid 1.25 cm per side, producing 16 pieces, of which four were small triangles. The remainder of the electroless nickel mirrors were made by Speedring Systems, Warren, Michigan, and The Perkin Elmer Corporation, Costa Mesa, California. We prepared some mirrors by polishing 99.99% pure nickel ribbon (Alfa Products, Danvers, Massachusetts) and also by vapor depositing 500 Å of chromium over an Applied Optics Center nickel mirror. Some mirrors consisting of evaporated chromium over fused silica had been purchased in 1972 from The Perkin Elmer Corporation, Norwalk, Connecticut. In addition, several mirrors, which had been damaged by blue haze in laboratories in Los Angeles and Philadelphia, were made available to us for study.

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B. CLEANING AND HANDLING PROCEDURES

Freshly sliced mirrors were carefully washed free of debris and abrasives by dousing and submerging the pieces repeatedly in acetone, as well as liquid detergent and water baths. The samples were washed a number of times by means of our low-scatter cleaning procedure. This technique is analogous to that in use in other laboratories and is more convenient than the tissue drag technique when working with large metal mirrors. The mirror, if visibly contaminated with dust, is first submerged in our washing mix, which consists of approximately 50 ml of liquid detergent and 100 ml of ethanol in 1 liter of H_2O. Detergents free of aromatic additives, such as Liquinox, are satisfactory. (Liquinox is made by Alconox, Inc., New York, New York. The manufacturer describes its formulation as a blend of anionic and nonionic detergents and wetting agents.) Particles are loosened by lightly brushing the immersed surface with cotton balls so as not to cause scraping, and rinsing in tap water. The procedure is repeated with fresh solution until no particles are seen on the surface. For the next wash, the cotton is held firmly with fingers and rubbed hard on the surface. Usually, after rubbing less than 1 min on the same spot, nickel mirrors suddenly become hard to rub because of a rise in friction coefficient. Mirrors affected by blue haze are washed instead in hot water (~ 50°C) and Liquinox detergent, which rapidly removes all but the most tenacious film. The mirror is then rinsed thoroughly with distilled deionized water. Any remaining film or droplets of water are then blown off with a filtered dry nitrogen jet. The object is to minimize the amount of water, ethanol, or other solvent that might evaporate off the mirror, and to ensure that the residue content of any liquid film is negligible. For

optimum results, the final steps should be performed in a laminar flow clean air bench with a bright beam of light illuminating the mirror, which is viewed away from the specular reflection. Gloves, finger cots, or holding devices are helpful to avoid contamination by the experimenter.

C. DIAGNOSTIC APPARATUS

In most of our routine monitoring, the diffuse reflectance sphere for measuring total integrated scatter (TIS) at 0.633 μm and a metallographic microscope adapted with oblique illumination for dark-field photographs are used.

1. TIS SPHERE

We have modified an integrating sphere directional reflectometer for measuring scatter with an He-Ne laser (Fig. 3), in a manner similar to that of a device in use at Perkin Elmer for the same purpose. Our sphere is 20 cm in diameter and is coated on the inside with Eastman white paint, a high-purity $BaSO_4$ diffuse reflector. The laser beam passes a small external aperture and enters the sphere through a 6-mm opening, is reflected at normal incidence by the specimen mirror positioned at a diametrically opposite opening, and retraces its path to exit the sphere. Nonspecular reflection, i.e., scattered power, illuminates the inside face of the sphere and is measured by a detector mounted externally flush with the inner wall at a point equidistant from the other two openings. The detector is a photomultiplier tube rendered approximately diffuse with a thin coating of $BaSO_4$ paint on its cathode face. Careful beam alignment is required to reduce the background signal with no sample to a level well below that of any measurements. In addition to the necessary tilt adjustment, the specimen mount provides three-axis linear positioning,

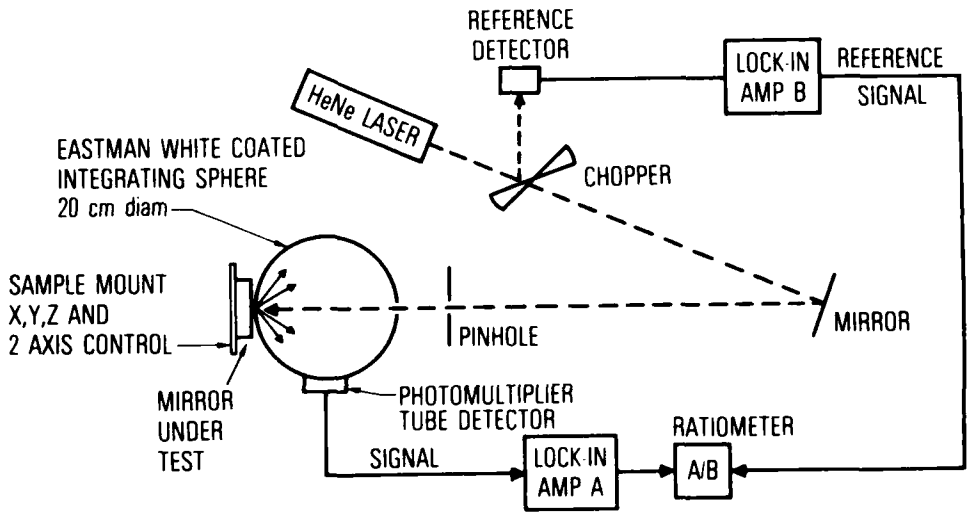

Fig. 3. TIS Integrating Sphere

which permits scans of a mirror surface or surveys of predetermined spots. Phase-lock amplifiers are used in the signal channel and in a reference channel that monitors laser power after reflection off the chopper. The signals are ratioed to eliminate errors resulting from laser drift. Calibration is easily accomplished by (1) tilting a sample with known reflectance so the specular beam impinges on the sphere wall or (2) rotating the sphere about an axis normal to the beam and passing through the center of the entrance port, thus causing the laser beam to impinge directly on the wall. Routine verification is also accomplished with reference samples. The wide dynamic range in signals, i.e., approximately seven orders of magnitude, is accommodated by optimizing photomultiplier-tube voltage to avoid nonlinearity and is verified by placing neutral density filters in the beam, both singly and in additive combinations. The precision of the scatter measurements for clean mirrors is mostly affected by the positional repeatability of the laser beam on a given spot and can range from approximately 20% to as little as 1% under optimum conditions. Samples of 1.25 cm by 1.25 cm were indexed and positioned with micrometers, and either six or ten locations were routinely checked and averaged. However, our experimental plan required that most of the specimens not be washed prior to each measurement. A dry nitrogen jet was then used to blow off most of the dust, but some usually remained, affecting the precision of TIS data.

2. BRDF APPARATUS

The BRDF apparatus consists of interchangeable laser sources, a sample held in a laminar flow clean air bench, a photometer on an arm rotating about the sample, and signal electronics. For carbon dioxide operation (Fig. 4), the 10.6 μm wavelength is selected with a grating, the laser cavity length is controlled with a feedback system, and a pyro-electric or a HgCdTe detector is used in the photometer. The beam is focused so as to place the waist at the sample position. Calibration is accomplished with a very diffuse sample of known reflectance.

3. REFLECTOMETER

The measurements were made with a Cary 14 spectrophotometer (Varian Instrument Division, Palo Alto, California) equipped with a Cary semi-microspecular reflectance accessory (special products No. 50-502-000), which collects only a measured 5% of the power reflected by a nearly perfect diffuser such as a thick Eastman white paint coating. Since the TIS values for the most damaged mirrors were 10 to 20% at 0.633 μm, the diffuse contributions to specular reflectances are at most approximately 0.01. Extension of these measurements to the 2- to 25-μm range was accomplished with Beckman IR-5 and Perkin-Elmer 467 spectrophotometers with a relative specular reflectance accessory.

D. EXPOSURE CONDITIONS

Several of the exposures consisted of simply placing samples face up or face vertical, on a shelf in our laboratory, which is located in the Los Angeles basin approximately 3 km from the ocean and 2 km from an oil refinery. The indoor relative humidity is typically in the 40 to 60% range, and the air

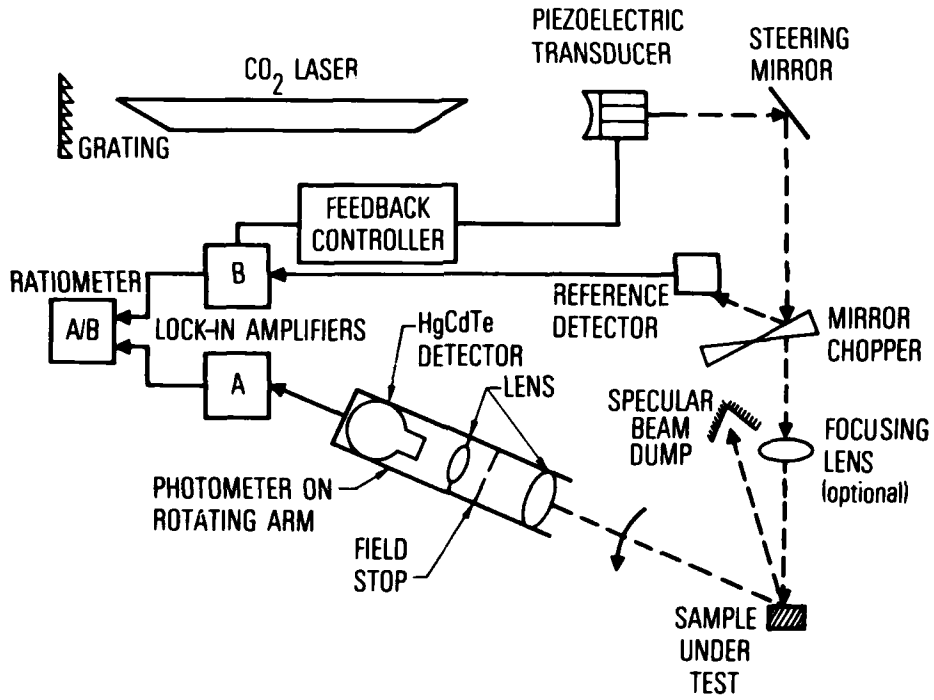

Fig. 4. BRDF Apparatus for CO_2 Laser Operation

pollutant concentrations vary with wind conditions. Reference samples were stored in machined-aluminum containers and also in cleaned clear plastic boxes (polymethylmethacrylate). Before and after scheduled exposures, all other samples were kept in plastic boxes. Mirrors were exposed under one of the conditions listed in Table 1 to gage the importance of various environmental factors.

Most of our test mirrors were subjected to a 55-day exposure followed by up to 12 months of storage to simulate the history of some space hardware through assembly, alignment, and subsequent functional tests and storage prior to launch. Periodic noncontact measurements were carried out solely with the use of a filtered dry nitrogen jet for dust removal.

Table 1. Exposure Conditions[a]

Sample	Environment	Parameters Controlled			
		Air Flow	Humidity	Pollutants	Other
A,B,C,D	Laboratory shelf, no enclosure	Ambient			
E	Laboratory shelf, no enclosure	Ambient			Periodic Washing
F	Closed plastic box	None		None	
G	Sealed metal canister	None		None	
H,I	Warmed to 37°C with incandescent lamp	Ambient	Low		
J	Irradiated with 2537-Å Hg lamp	Ambient			Ultraviolet photons, slight warming
K	In metal box with jar of water	None	High	None	
L	In unoccupied mountain cabin	Low	Low	Low	
M	In laminar flow clean air bench	Medium	Ambient	Ambient	Reduced dust fall-out
N	In glass cell with flow of clean air bubbled through water	Medium	High	None	
O,P,Q,R,S	In chemical reactor	Medium	High		Controlled concentrations of NO_2 and SO_2

[a]All samples were washed initially except for one set of mirrors that were never taken out of plastic shipping containers except for final measurements and surface chemical analysis.

V. OBSERVATIONS AND RESULTS

After describing blue-haze phenomenology, we present our observations grouped under each type of environmental factor investigated. Chemical analyses follow.

A. BLUE-HAZE EFFECTS AND CHARACTERIZATION

We first determined that blue haze occurs in our geographical area. We found that any electroless nickel mirror left out of its container and exposed to the laboratory environment always degrades with visible effects within ten days. The resultant hazy appearance is barely discernible at first but becomes increasingly obvious with the passage of time. The original condition free of haze can be recovered by simply washing the surface, but permanent damage results if the haze is permitted to remain or build up for more than 1 month in our location.

Losses in specular reflectance for severely affected and unwashed surfaces (Fig. 5) are large in the ultraviolet and visible and very slight at longer wavelengths where such mirrors are normally used.

Microscopic examination of mirrors exposed in the various environments, reveals that one of two types of damage can occur, depending on the ambient humidity levels and on the impurity content of the air and the electroless nickel surface itself. One type, benign compared to the other, results in shallow pits typically 1 to 5 μm across, somewhat spherical in shape, and usually separated from each other by at least several diameters. The other is a more severe case of the first and takes the form of a film that can sometimes cover large portions of the surface and, if left on long enough, leaves

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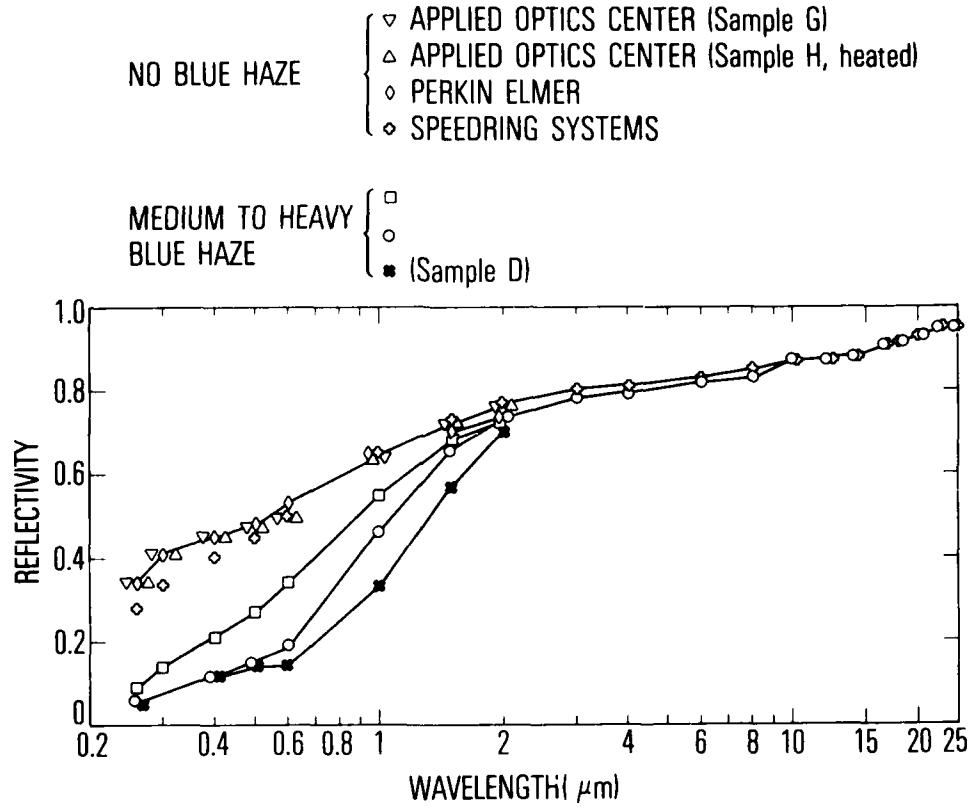


Fig. 5. Specular Reflectance of Electroless Nickel Mirrors. Effect of blue haze is evident.

a permanently corroded finish. A film resulting from several weeks of exposure is readily noticeable, as it gives the covered portions of the mirror a finely frosted, higher scatter appearance with the typically bluish hue. There seems to be no consistent pattern with existing surface imperfections such as polishing marks, pits, and circular spots.

After several months, a mirror becomes obviously hazy (Fig. 6), may have stains, and may be various shades of light brown, as would be expected from the specular reflectance spectra. The usual practice with spacecraft contractors has been to wash and laboriously rub a mirror so affected in detergent and ethanol or similar aqueous baths to "remove" as much of the blue haze as possible. We have found it necessary to completely clean away the film in order to minimize scatter and prevent further corrosion of the metal. Immersion in a hot water and Liquinox bath at about 50°C for a few minutes is very effective, and no rubbing is necessary. A camel's hair brush can be used to remove dust particles. Films that have existed for several years on electroless nickel are more tenacious and partially solidified, so that abrasion with cotton may be required as well.

We observed that following a two-month exposure, the film and the TIS grew considerably during the storage period in boxes containing only air. Figure 7 is a photomicrograph of the unwashed surface of a mirror taken at the end of the storage period with Nomarski interference phase contrast; in Fig. 8, the same sample at higher magnification with replicas shadowed approximately 10 deg from the surface for TEM is shown. In the Nomarski views of the same area of a mirror before washing (Fig. 9) and after (Fig. 10), the etching that occurred where the film (dark areas in Fig. 9) covered only part of the sur-

Fig. 6. Mirror B After Exposure (Top) and Unexposed (Bottom). Viewed along surface normal, 45-deg illumination. Bottom sample is 1.25 by 1.25 cm.

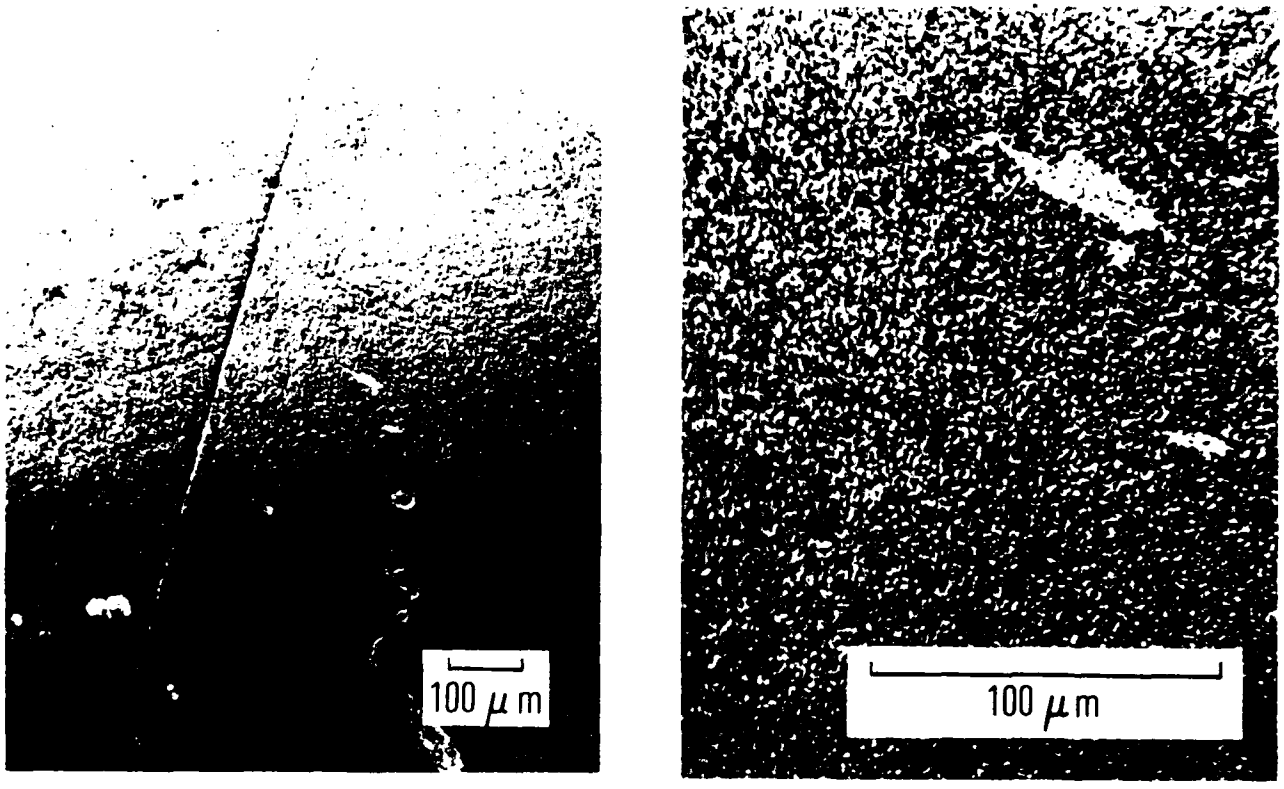


Fig. 7. Nomarski Views of Sample A Covered with Blue Haze

Fig. 8. Electron Micrograph of Sample A. Replica of surface is shadowed at 80-deg angle of incidence

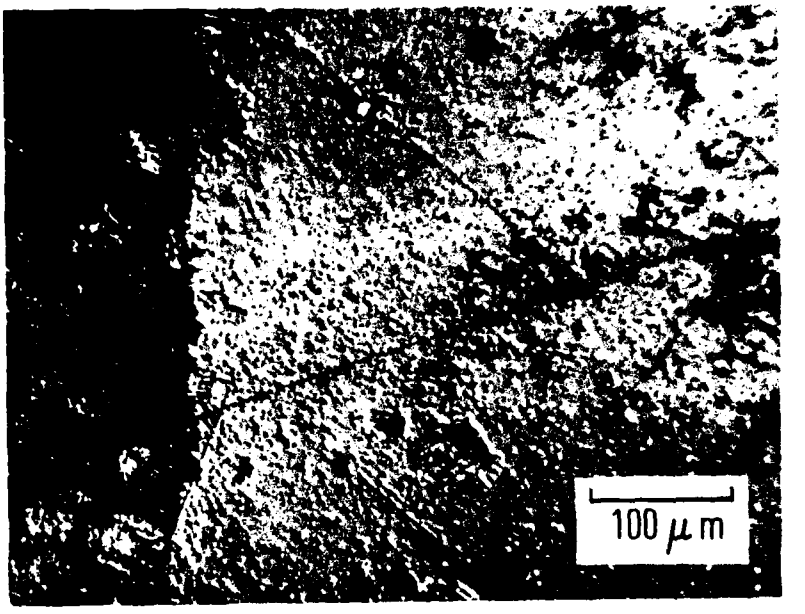


Fig. 9. Nomarski View of Mirror Partially Covered with Blue Haze

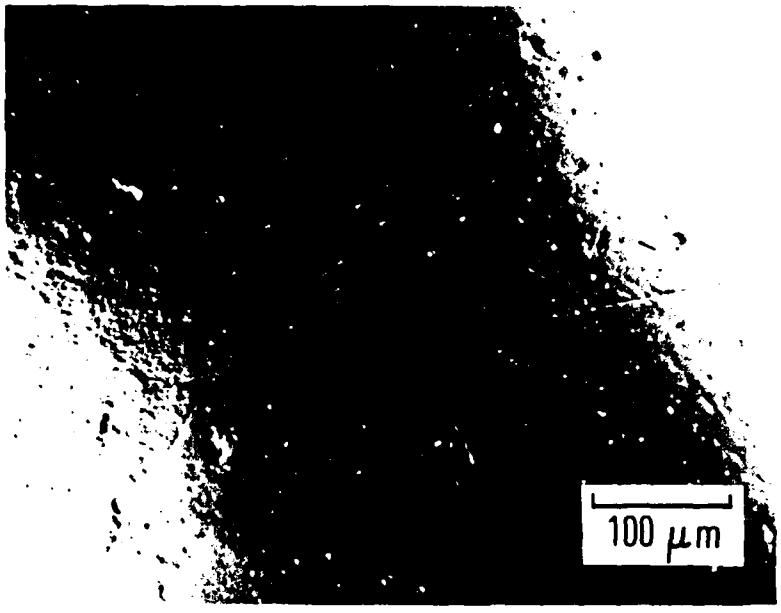


Fig. 10. Nomarski View of Same Area as Shown in Fig. 9 After Washing

face is readily seen. Pitting damage in areas free of film is also evident, as is film growth, which sometimes occurs preferentially along sleek marks. Incomplete film removal such as can occur with insufficient rubbing in cold water is demonstrated in Fig. 11; microscopic gouge marks into the film have resulted. Figure 12 is a photograph of the same mirror following a hot wash. The etching of nickel beneath the film sometimes results in a striated pattern probably related to the polishing process as in Fig. 12 or in a more random pitting as in Fig. 13. Circular spot-like features as seen in the latter photograph are sometimes not covered with film, leaving islands with a less severe etching pattern. The photograph of the undamaged mirror (Fig. 14) is provided for comparison.

B. FACTORS INFLUENCING BLUE-HAZE FORMATION

Our principal means of gaging the importance of environmental factors tested were the time histories of TIS data for exposed samples (Fig. 15).

1. HUMIDITY

The accumulation of water on surfaces, as a function of relative humidity has been reviewed by Curcio.[12] Several investigators indicate generally that a water film does not exceed more than a few nanometers of equivalent thickness on clean surfaces. The deposition of airborne hygroscopic contaminants is needed for films to grow further. These are normally more abundant near the ocean than in continental air. Water film thicknesses as great as 100 nm thick have been detected by weight measurements in ordinary indoor environments from a near saturated vapor.[13]

We exposed mirrors while warming them continuously to 37°C, or 13 to 16°C above ambient to reduce the thickness of water films in a laboratory with

Fig. 11. Nomarski View of Mirror with Heavy Blue Haze After Incomplete Film Removal by Rubbing in Cold Water

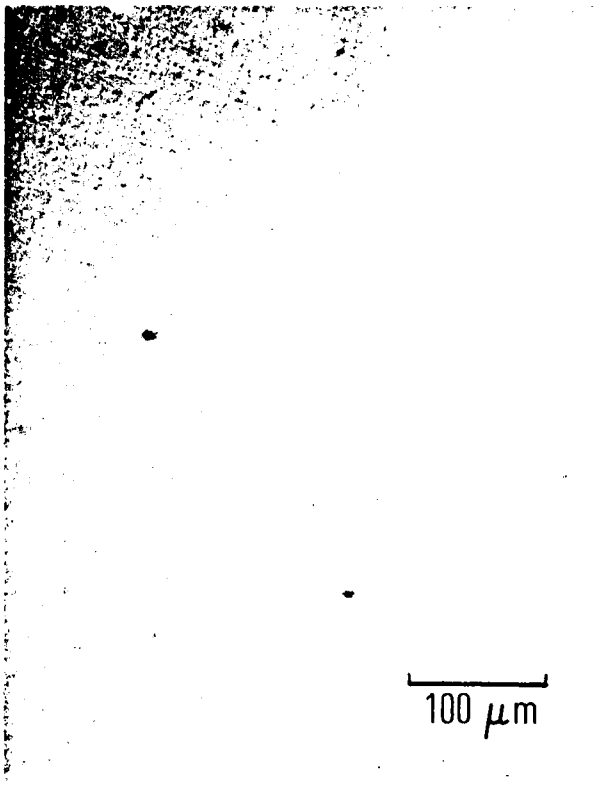


Fig. 12. Nomarski View of Mirror Shown in Fig. 11 After Complete Film Removal in Hot-Water

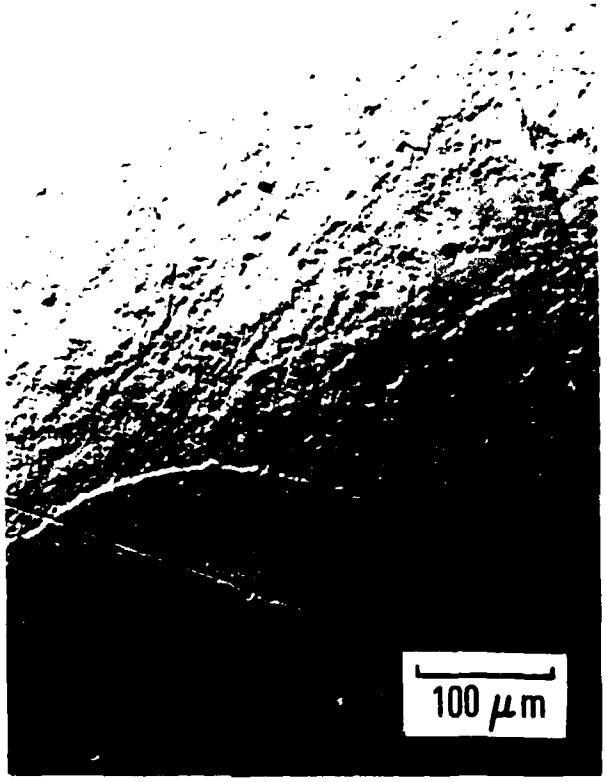
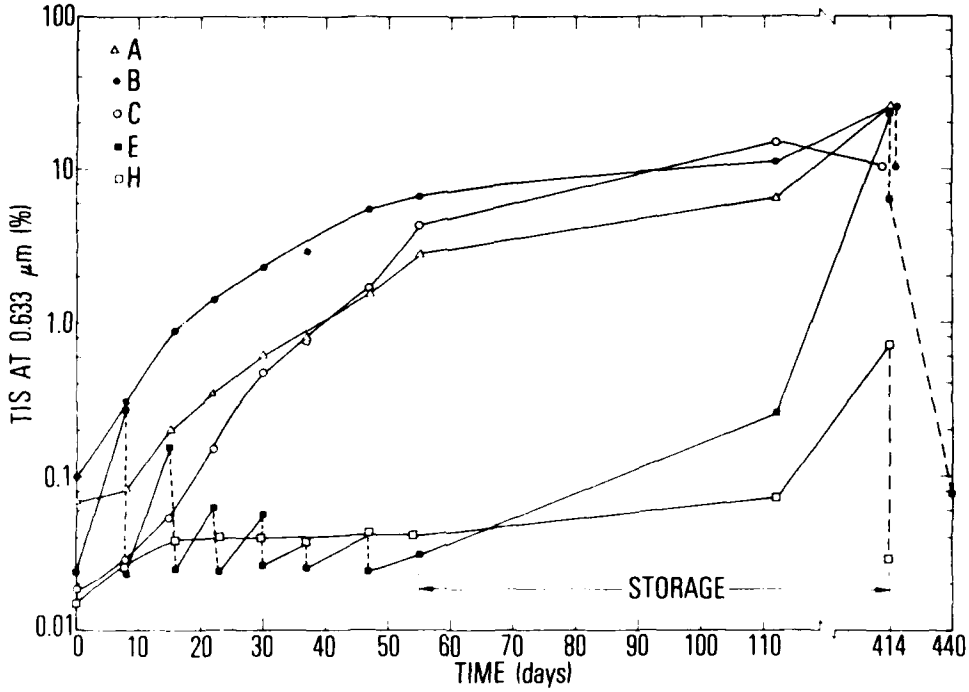


Fig. 13. Nomarski View of Mirror Partially Covered with Blue Haze and Subsequently Washed Clean

Fig. 14. Nomarski View of Unexposed Mirror of Sample with Lowest Scatter Shown in Fig. 1



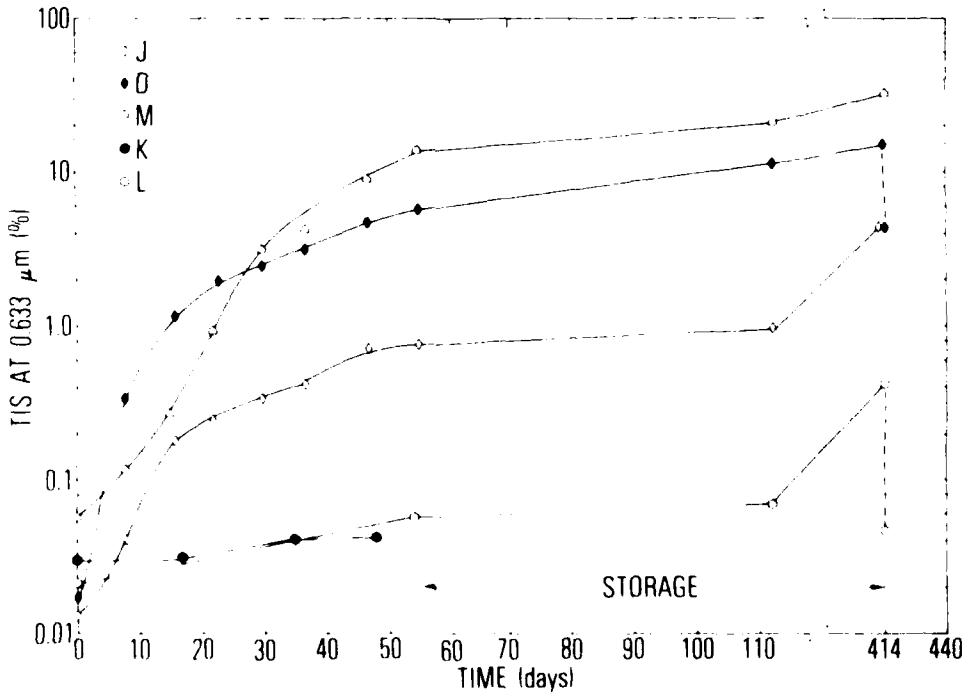


Fig. 15. Time dependence of TIS at 0.633μm for Mirrors Subjected to Various Exposures (Table 1)

humidity usually ranging from 40 to 60%. In sample H in Fig. 15, there is a slight TIS increase from 0.15 to 0.29% after a gentle wash to remove dust and organic contaminants, following a 13 month exposure. Sample J was used to test the effect of weak ultraviolet exposure on organic contaminants by locating it under a low-pressure mercury lamp emitting at 2537 Å. We saw instead a markedly lower TIS increase compared to ordinary exposure (samples A, B, C, and D) because of the slight heating effect of the lamp.

We tested the influence of high humidity on a clean surface by placing mirror K in a large sealed box along with a beaker of water and saw none of the rapid initial TIS rise. This exposure was accidently aborted after 47 days. Another mirror used periodically but stored in perfect condition for two years was then washed and stored partially wet on its backside for another two years in a plastic box. When taken out and examined, the water had dried up, and very slight traces of blue haze were evident. The haze was readily washed and rubbed off.

In yet another test, three mirrors were placed in a glass tube and exposed to a steady flow of air from a pressurized gas bottle. The gas was bubbled through a column of deionized water upstream of the samples to maximize relative humdity and minimize air pollutants such as SO_2. After 14 days, no change was evident whereas control samples in ambient air showed blue haze starting within 2 days.

Sample L was stored indoors in a mountainous environment, 1700-m altitude and 80 km north of the Los Angeles basin, with considerably cleaner air and varying humidity, from a low of about 10% to high values during periodic rain. After 60 days, the TIS of the sample was measured, and it was placed in a box.

Very minor damage was evident a year later. The damage was primarily some pitting, which is discernible only by comparison to an unexposed reference sample.

2. AIR FLOW AND POLLUTANTS

At medium-to-high humidity, we found blue-haze formation to be strongly dependent on the circulation of air at the surface. Our usual practice of storing mirrors in sealed aluminum cans or clean plastic boxes with a small air volume for time spans sometimes exceeding two years had never resulted in damage, with only two exceptions: the mirror that was stored wet and a whole set of mirrors intended for a space experiment that were left for 11 months as received in unopened plastic boxes. Most of the latter developed a difficult-to-remove haze in the form of isolated lumps of dielectric material, which did not recur after cleaning and storage. All purchased mirrors are usually washed and used when delivered.

Whereas carefully cleaned mirrors deprived of air flow do not suffer from a TIS increase, those purposely placed in an air stream, such as near a fan or in a laminar flow clean air bench, degrade faster than the rest. Sample M (Fig. 15) was degraded slower than B and D, but another mirror (not shown) in a clean air bench matched the higher rates plotted. The mirrors in an air flow formed blue haze uniformly over their surfaces, unlike the irregular coverage evident in Fig. 2.

C. CHEMICAL VAPORS

Typical sulfur dioxide and nitrogen dioxide concentrations in daytime polluted urban atmospheres are approximately 0.1 ppm. A vapor reaction cell was used at much higher concentrations of those gases and at high humidity to

demonstrate their potentially corrosive action. In this flowing gas cell, air pollutants were diluted in a 90 to 10% nitrogen-oxygen mixture bubbled through a concentrated NaCl solution. Reactor effluents were trapped in water cells filled with 0.1 N NaOH solutions to determine concentrations. The system is not designed for simultaneous exposure to two reactive gases. Consequently, the mirrors were first exposed to SO_2, then NO_2 and SO_2 again with parameters shown in Table 2. The NaCl was probably in the form of an aerosol with an estimated approximately 4 ppm average chloride exposure based on trap contents.

If the uptake of SO_2 and NO_2 by the surfaces were proportional to the gas phase concentrations, as is the case with large-area substances in particulate form such as metal oxides, salts, and soils, accelerated exposures would be reasonably valid while holding constant the product of exposure time and concentration, at least for low pollutant levels (e.g., 1 to 100 ppm). On this basis, our combined SO_2 exposure would be equivalent to three months of outdoor urban exposure, and that for NO_2 would be 25 months. We observed (Table 3) severe damage on pure and electroless nickel (samples O and P), and none on a previously blue hazed mirror that had been washed clean (sample Q). This resistance to corrosion differs markedly from what we observed on similar restored mirrors, which grew blue haze just as new ones did when placed on a shelf. A 500-Å-thick vapor-deposited chromium film over mirror R was ineffective in protecting the nickel against the corrosive vapors, whereas a 1000-Å gold layer on mirror S prevented severe etching. We separately observed that pure nickel is noticeably etched when immersed for 10 min in a $CaSO_4 \cdot 2H_2O$ solution containing 1000 ppm sulfate.

Table 2. Exposure Conditions in Vapor Reaction Cell

	Exposure		
	1	2	3
Gas[a]	SO_2	NO_2	SO_2
Concentration, ppm[b]	150	4300	150
Relative humidity, %	95	57	95
Duration, min	30	25	55

[a]In all cases, the samples were also exposed to an estimated 4 ppm chloride, probably in the form of NaCl aerosol.

[b]Diluted in nitrogen-oxygen (90:10).

Table 3. Effects of Corrosive Vapors on Mirrors

Sample	Type of Mirror	TIS		Observations
		Before, %	After, %	
O	Pure nickel 99.9 + %	0.48	18	Severe etch
P	Electroless nickel	0.017	19	Severe etch
Q	Heavily blue hazed electroless nickel washed clean	0.36	0.36	No evidence of damage
R	500 Å chromium over electroless nickel	0.059	13	Etched surface, metal shavings (probably chromium)
S	1000 Å gold over electroless nickel	0.05	22	Frosted deposit, readily washed off, leaving specular gold

D. OTHER FACTORS

We initially tested the effects of other environments and found no relationship to blue-haze formation. Weak ultraviolet exposure from a 2537-Å mercury lamp did not promote growth, and, instead, retarded the haze probably because of a slight warming effect; ionizing the air in the vicinity of the mirror with an alpha-particle source had no effect on growth rate; even rinsing with tap water rather than distilled deionized water produced no appreciable difference. Poorly rinsed samples may have surface residues that serve as initial growth sites, resulting in characteristically patterned haze. However, subsequent TIS increases did not appear to differ significantly.

The impurity content of the nickel surface was not a controllable variable, as the mirrors were not made at our facility. However, mirrors made by polishing nickel greater than 99.9% pure were exposed and also found to deteriorate as did the electroless nickel.

E. COMPOSITION OF BLUE HAZE

We used several methods to determine the elemental constituents of the dielectric compound that forms over the surface of electroless nickel, and which we refer to as blue haze. A mirror that was completely covered with haze for several years was first washed with ethanol and then scraped with a small blade under a microscope. On a spot measuring 4 cm^2, 8 $\mu g/cm^2$ were removed and weighed. For an estimate of only 80% collected with the blade, the original film was in the range of 10 $\mu g/cm^2$. A density of 2, reasonable for the expected film composition, results in a film thickness of approximately 500 Å. The material accumulated on the blade had a pasty consistency and a frosty appearance. By means of an SEM with EDAX spectrometer, we

identified the primary constituents as nickel, sulfur, and chlorine (elements with $Z < 11$ such as oxygen are not detectable with this apparatus). The x-ray diffraction of the scrapings, recorded with a Debye-Scherrer camera, indicated no crystallinity, even following a 5-hr vacuum bake at 100°C, which drove off some of the water, leaving a powdery residue. Electron diffraction (HEED) of scrapings vacuum heated to 100°C revealed a spot pattern of a material not listed in the ASTM x-ray diffraction data files, but which follows an arrangement analogous to that of hydrated nickel chlorides. Some of the scraped material was pressed, by means of using a glass plate, into pure indium wire for IMMA spectroscopy. The principal constituents detected were nickel, chlorine, sulfur, oxygen, and hydrogen. Silicon and hydrocarbon fragments were also significant but are thought to be impurities collected during exposure and to be independent of the formation process. The isotope ^{18}O, used to bombard surfaces in the IMMA, does not interfere with the detection of naturally occurring oxides.

An infrared absorption spectrum of the scrapings (Fig. 16) reveals some bands consistent with the presence of a metal sulfate and water but is a poor match for $NiSO_4$ powder. An electroless mirror that formed blue haze in a clean air bench (sample M, Fig. 15) was subsequently analyzed with ESCA. The elements detected were nickel, appearing to be compounded either as a chloride or hydrated oxide, chlorine, as a chloride of a transition metal, and sulfur, as a sulfate. No $NiSO_4$ was seen directly, but the sensitivity was low. No phosphate or nitrate was detected.

An Auger comparison of features on very slightly damaged samples exposed in low-humidity environments indicates a higher concentration of sulfur,

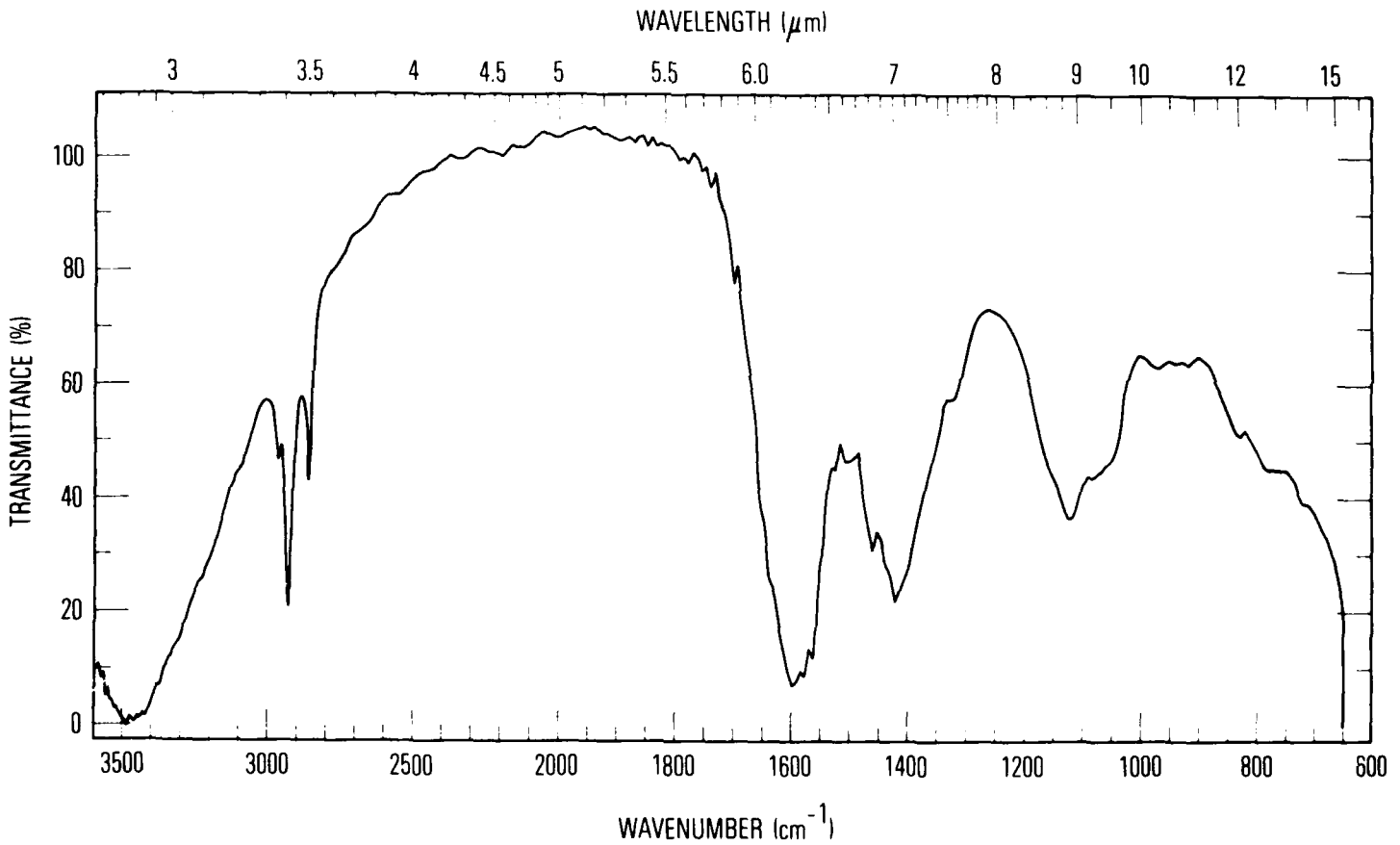


Fig. 16. Infrared Transmittance of Microquantity of Blue-Haze Scrapings

approximately 6% where the dielectric salt grows into a bump, than in nearby smooth areas with approximately 1%. The elements copper, silicon, iron, and chromium were also observed on some of the bumps. In contrast, there was no apparent correlation of nickel, phosphorus, chlorine, carbon, and oxygen surface concentrations with the location of spots or bumps on the surface. The concentrations of sodium were inconsistent and sometimes small in comparison to chlorine, indicating that the source of halogen on this sample was not necessarily sea salt, which we regard as a possible contaminant in our location.

VI. DISCUSSION AND CONCLUSIONS

We have shown blue haze to be a corrosion process in which a substance consisting of nickel from the mirror combines with chlorine, sulfur, oxygen, and hydrogen. The amorphous mixture includes chlorides and sulfates of nickel, as well as variable quantities of H_2O. After long air exposures, impurities such as hydrocarbons were detected, as well as sodium, silicon, magnesium, and calcium from airborne contaminants. Salt formation can be limited to isolated spots in low-humidity air with little pollution and result in minor damage in the form of shallow pits. Under more adverse conditions, which include medium-to-high humidity, air pollutants such as SO_2, and probably chlorides as in coastal areas, the formation of nickel salts with the previously mentioned constituents becomes more rapid and extensive. Isolated lumps start at surface locations that may be random but could also be related to localized minute amounts of surface impurities such as copper, silicon, chromium, and iron. The lumps measure 0.5 to 5 μm and, therefore, owe their blue color to nickel compounds rather than scattering. They are not readily soluble in cold water but can be wiped off or washed off. They become more tenacious with the passage of several months, as can happen when mirrors are placed in unsealed containers. When continuously exposed to a corrosive environment, the lumps grow laterally, eventually merging into a mantle over the mirror, causing severe etching and increasing scatter.

The role of chlorine may be to turn water films into an electrolyte propitious for corrosion of the surface and should be avoided during manufacture and cleaning. As a result of extended exposure, chlorine eventually becomes a

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principal constituent of the corrosion mantle formed, probably due to sea salt aerosols present near the ocean. No growth was evident when new mirrors, contaminated with chlorine by washing in tap water, were exposed to humid air flow free of SO_2. Similarly, no growth occurs on exposed mirrors kept warm to limit water buildup. However, a pure nickel sample, once contaminated by washing in tap water, was subsequently repolished using abrasives, Liquinox, and deionized water, then washed successively in xylene, acetone, and ethanol. This procedure was devised to remove several micrometers of nickel and prepare a new surface free of chlorine. The mirror was still found to form detectable blue haze after only two days of exposure, or at about the same rate as control specimens.

There is further indication, albeit not indisputable proof, that the initiation of blue haze might be fostered by certain surface impurities. In one case, haze formed everywhere on a mirror except on the rectangular footprint left by the IMMA ion beam prior to exposure, which had sputtered several hundred angstroms off. In another case, a continually exposed mirror was washed gently on a weekly basis, causing the TIS to grow at progressively slower rates after each wash (sample E, Fig. 15a). We suggest that the mechanism that triggers the start of corrosion can be profitably investigated by studying the action of controlled impurities on pure nickel.

Our observations of a film forming on exposed nickel are consistent with reference works,[13,14,15] where it is generally described as a tarnishing in industrial sulfurous atmospheres, which eventually transforms to a tenacious film of basic nickel sulfate. Nickel is reportedly fairly stable in nonoxidizing dilute acids (HCl < 15%, H_2SO_4 < 70%), but its corrosion resistance is

impaired in the presence of oxidizing agents (e.g., $FeCl_3$, and $CuCl_2$) or by aeration.[16] The deleterious effects of chlorine in damp atmospheres is also known[14] and has been observed to occur even in continental locations on other metals.[17] A significant dependence of nickel corrosion on relative humidity has been reported recently,[18,19] as well as on temperature, pollutant concentration, particle concentration and orientation.[19]

The only noticeable evidence of passivation occurred with our previously blue-hazed mirror (sample Q, Table 3) that resisted attack by concentrated corrosive vapors, where similar mirrors degrade during ambient exposure. We found no consistent advantage to be gained by baking mirrors in air up to 200°C, the highest temperature deemed safe for large stress relieved optics on aluminum substrates. No significant oxide formation is expected unless temperatures above 277°C are used;[20,21] at which point, several monolayers of NiO form within 30 min.[21]

We believe that the formation of blue haze is not controlled by mirror processing but by the subsequent chemical environment. We have found that the strict maintenance of a clean and dry surface on nickel ensures immunity from corrosion. Mirrors should be washed meticulously prior to shipment or storage.

Where spacecraft nickel optics are necessarily exposed to industrial laboratory air during assembly and tests, we suggest the following precautions:

1. Mirror cleaning procedures should be restricted to the use of water and solvents that are free of chlorine impurity, such as monitored de-ionized water, acetone, ethyl, or isopropyl alcohol, while

excluding Freon-type compounds unless they are tested for no chlorine impurity.

2. Newly purchased mirrors should be examined visually with a very bright light source on a weekly basis until a history of no blue haze is established; at which time, longer time intervals may be applied.

3. If any blue haze starts to develop, the mirror should be washed clean and regular inspections maintained.
4. Mirrors that have a heavy blue-haze growth are effectively washed with hot water and detergent but are not immunized from recurrence.
5. When stored in air, nickel optics should be placed in clean, sealed, and desiccated containers.
6. Mirrors that have been exposed to ambient polluted air for more than a day or so should be washed and dried well prior to long-term storage.
7. Storage of an optical system should be in an enclosure provided with humidity reduction such as nitrogen backfill, evacuation, or the use of desiccants. Scatter monitoring is desirable either by visual inspection or through the use of an integral device.
8. While exposed to ambient air, heating of mirrors is effective in preventing blue haze, probably by reducing surface water films.
9. The use of small witness mirrors is helpful in the convenient monitoring of surface quality on large expensive mirrors.

Other approaches to stabilizing mirror scatter may possibly include ion-beam cleaning for which we have only one observation. We found no evidence of corrosion of evaporated chromium on glass for 10 months of indoor exposure. However, a 500-Å layer of chromium over the electroless nickel provided only partical protection, as corrosion spots were apparent beneath the chromium. Multilayer dielectric overcoats with good adhesion have been demonstrated,[22] and may provide effective long-term stability at the price of some initial scatter increase and a spectrally dependent reflectance.

Because we have been successful in maintaining bare super polished nickel mirrors free of corrsion for periods of ~1 year, we favor the use of such mirrors for very low scatter applications, rather than their gold coated versions, which we have seen suffer from considerable degradation in laboratory environments.

REFERENCES

1. A. Brenner, and G. E. Riddell, Proc. Am. Electroplat. Soc. 33, 23 (1946).
2. A. Brenner, D. E. Couch, and E. K. Williams, J. Res. Nat. Bur. Stds. 44, 109 (1950).
3. A. H. Graham, R. W. Lindsay, and H. J. Read, J. Electrochem. Soc., 112, 401 (1965).
4. R. M. Shemenski, J. G. Beach, and R. E. Maringer, J. Electrochem. Soc. 116, 402 (1969).
5. B. C. Bartlett, L. Cann, and J. L. Hayward, Plating, February 1969, p. 168.
6. J. T. Bloxsom, and J. B. Schroeder, Appl. Opt. 9, 539 (1970).
7. K. Parker, and H. Shah, J. Electrochem. Soc. 117, 1091 (1970).
8. K. Parker, and H. Shah, Plating, March 1971, p. 230.
9. G. S. Petit, R. R. Wright, C. C. Wright, and T. Kwasnoski, Plating, June 1972 p. 567.
10. F. Pearlstein, "Electroless Plating," in Modern Electroplating, ed. F. A. Lowenheim, John Wiley, 1974.
11. R. P. Young, "Mirror Scatter Measurements Facility Comparison," AEDC-TR-75-68, September 1975.
12. J. A. Curcio, "Adsorption and Condensation of Water on Mirror and Lens Surfaces," NRL Memorandum Report 3359, NRL September 1976.
13. H. H. Uhlig, ed., The Corrosion Handbook, John Wiley, 1966.
14. F. L. LaQue, and H. R. Copson, eds., Corrosion Resistance of Metals and Alloys, Reinhold, 1963.

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REFERENCES (Continued)

15. J. C. Scully, The Fundamentals of Corrosion, Pergamon, 1975.

16. N. D. Tomashov, Theory of Corrosion and Protection of Metals, MacMillan, New York, 1966.

17. Corrosion in Natural Environments, ASTM Special Technical Publication 558, ASTM, 1974.

18. P. Peterson et al., "Atmospheric Corrosion of Copper, Silver, and Nickel," Abstract No. 243, Extended Abstracts, Vol. 79-2, Electrochem. Soc.

19. D. W. Rice, R. J. Cappell, and W. Kinsolving, "Indoor Corrosion of Metals," Abstract No. 244, Extended Abstracts, Vol. 79-2, Electrochem. Soc.

20. K. Gupta, J. P. Marton, and J. J. Shewchum, Electrochem Soc., 121, 118 (1974).

21. G. C. Allen, P. M. Tucker and R. K. Wild, Oxidation of Metals, 13, 223 (1979).

22. T. T. Saito, R. R. Esposito, and F. E. Johnson, Opt. Lett. 2, 19 (1978).

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