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Cleaning Agents and Techniques for Concentrating Solar Collectors

M.B. Sheratte

McDonnell Douglas Astronautics Company

Prepared for Sandia National Laboratories under Contract No. 13-0261

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CLEANING AGENTS AND TECHNIQUES FOR CONCENTRATING SOLAR COLLECTORS

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Prepared for Sandia National Laboratories under Contract No. 79-7052

ABSTRACT

Tests were conducted to determine the nature of the soil which is irreversibly deposited on solar collectors during environmental exposure. Methods of removing this soil were investigated. The mechanism of attachment of the soil to the surface was determined as a potential aid to cleaning agent formulation. Reflector specimens were exposed at sites in Shenandoah, GA, Albuquerque, NM, and Daggett, CA. Three types of reflector surfaces were studied: second surface silvered glass, aluminized FEK 244 film on glass substrate, and RTV 670 on aluminum. Cleaning procedures were evaluated by microscopic examination of the solid surfaces before and after cleaning and by measurement of specular reflectance. The potential effectiveness of environmental cleaning agents, such as rain, frost and snow, is discussed.

PREFACE

This report was prepared by McDonnell Douglas Astronautics Company - Huntington Beach (MDAC) for Sandia Laboratories, Albuquerque, New Mexico. It presents the results of developing a cleaning procedure for solar reflectors. The effort described herein was performed in accordance with Contract 13-0261.

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Section 1
INTRODUCTION

A major maintenance consideration for solar energy collector systems is the energy loss associated with deposition of "soil" on the collector surface. Any object which is continually exposed to the environment rapidly acquires a coat of grime which, in the case of solar collectors, interferes to a considerable extent with the energy gathering function. This loss of function results both from transmission losses and from scattering losses. Cost implications, and also environmental requirements, demand that cleaning of collectors be as infrequent as is consistent with good maintenance practices; and the requirement for extended-use life demands a cleaning agent which is compatible with the support structure materials.

The objectives of this program were: (1) to identify the nature of the soil which adheres to solar reflectors after outdoor exposure; (2) to determine the mechanism(s) which hold this soil onto the surface; and (3) to develop methods for removing the soil and optimize them with respect to cost, compatibility with the support structure, and environmental impact.

The basic philosophy of the approach was to avoid any cleaning method based on scrubbing the surface, since the cost of such activity would be prohibitive. Sample mirrors were deployed on exposure racks at Shenandoah, GA, Albuquerque, NM and Daggett, CA. The sample orientation was 45° face up toward the south. Samples were removed periodically and the soil was identified using optical and scanning electron microscopy. Soil deposited naturally over a period of months was compared with soil deposited in minutes by stirring up the environment. Attempts were made to formulate cleaning agents based on the known nature of the soil, and many commercial glass and acrylic cleaners were also evaluated empirically.

The observations to date suggest: (1) most of the surface contamination on a reflective surface can be removed very simply - either by a mild detergent spray followed by a DI water rinse, or more simply by a spray of ordinary tap water at approximately 1000 psi; (2) after such treatments, a layer of contaminant is left which can not be removed by any except the most aggressive cleaning agents; (3) this tenacious layer is composed mainly of clays, micas and barium or calcium carbonates; (4) this tenaciously held dirt causes approximately a 2% loss of specular reflectance; (5) after many soiling and rinsing cycles, the specular reflectance remains only 2% below that of the original surface; and (6) this tenacious layer can be removed at any time using highly aggressive methods and agents.

The information obtained in this study suggests that the most cost effective method for solar collector cleaning may well be a regular spray with ordinary tap water at 1000 psi, combined with an occasional (once every year or two) thorough cleaning either by scrubbing or using a hydrofluoric acid-containing cleaning agent.

Section 2
TECHNICAL APPROACH

2.1 SITE SELECTION

The Shenandoah and Daggett sites were chosen for this study because they represent two widely different geographical regions. They are also being considered as Solar Power Plant demonstration sites. Albuquerque was chosen for convenience in sample monitoring.

2.2 TEST EQUIPMENT AND SPECIMENS

Test specimens were 5" x 5" x 1/8" glass, attached to 1" x 6" x 1/8" aluminum tags; or 6" x 6" x 1/8" glass supporting a 5" x 5" x .003" square of FEK 244* aluminized acrylic. Included at a late date in the test plan were a number of 6" x 6" aluminum squares coated with RTV 670 silicone elastomer, provided by General Electric. A total of 350 test specimens were deployed at three sites for this work.

Samples were soiled naturally and artificially. Artificial soiling was done by sprinkling material collected from the three sites onto a wet mirror surface and allowing it to dry in the sun. Repeated exposure to moisture between soil dusting was not done on the artificial soiling since adequate soil was retained after one cycle for cleaning experiments.

Natural soiling was done on exposure racks as shown in Figures 1 and 2. The sheet on which samples were mounted was inclined at a fixed angle of 45° and faced the south. This represents an average position for exposure to sun and the elements in a given location. The entire exposure rack was braced against heavy wind gusts and held down using concrete blocks.

The majority of the cleaning experiments was done using 1 quart plastic spray bottles filled with the materials to be sprayed. One series of tests was made

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*FEK 244 is a trade name of 3M Core Decorative Products Div. for an 0.004 inch aluminized acrylic sheet with 0.001 inch layer of adhesive backing.

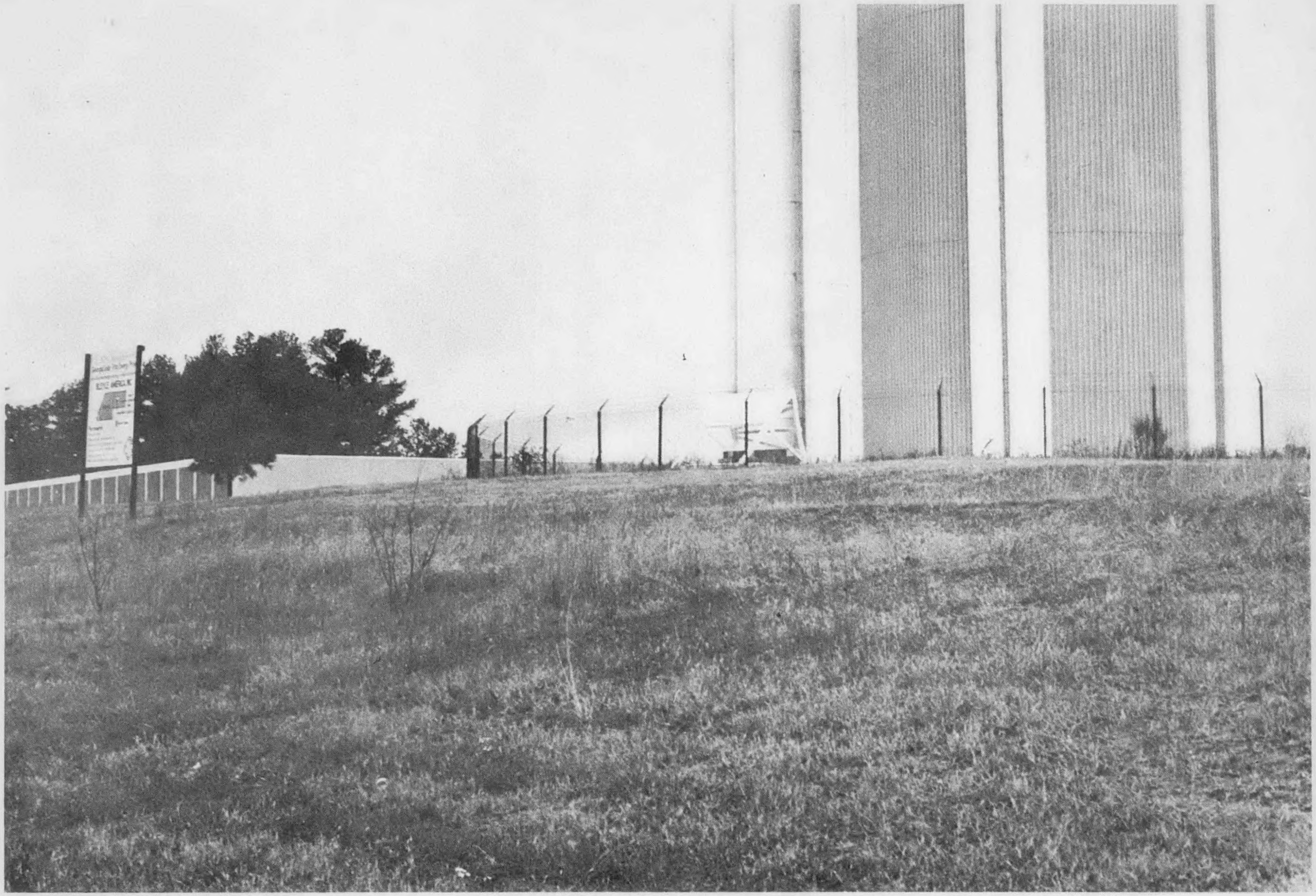
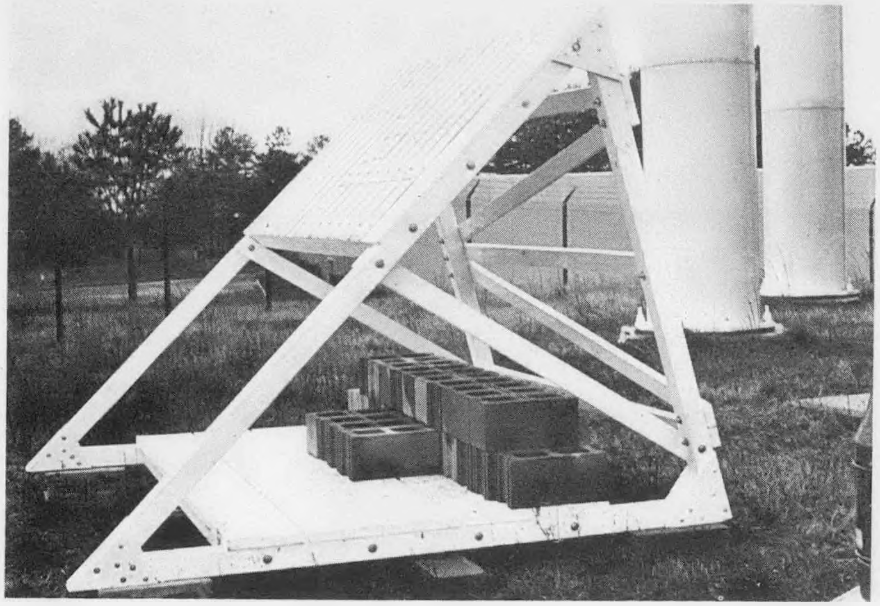
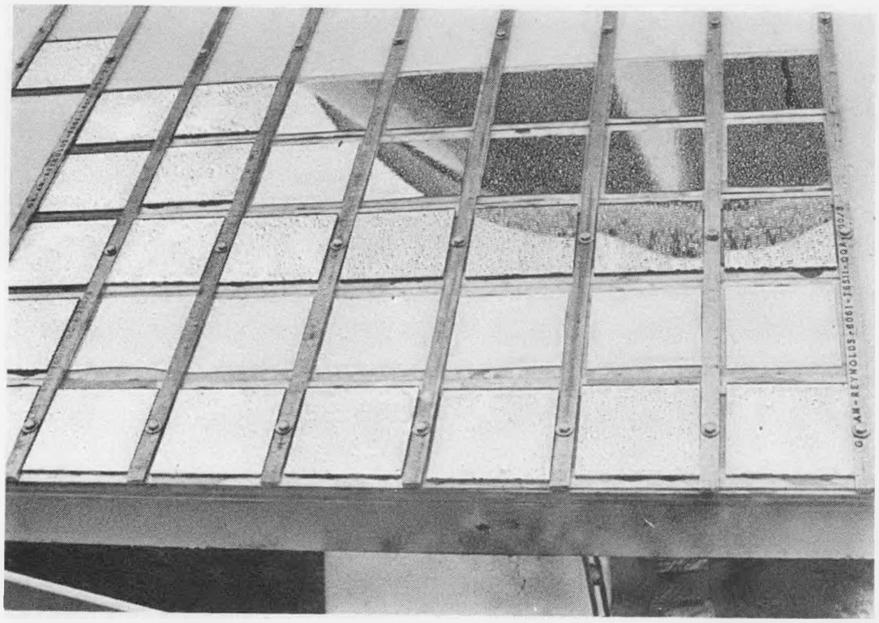


Figure 1. Exposure Rack in Place at Base of Water Tower, Shenandoah, GA.



a. Overall View of Rack



b. View of Samples on Rack

Figure 2. Exposure Rack With Samples Mounted On It.

with the high pressure spray system shown in Figure 3. The regulator was set to control at 1000 psi which was the pressure at the nozzle. A Gunjet S-8010 nozzle was used. It produced a flat fan shaped spray delivery 5 gpm at 1000 psi over an included angle of 80 degrees. Cleanliness was measured by its effect on specular reflectivity of the specimens. Measurements were made on a Scheldahl Model PBDRF reflectometer. Figure 4 shows the reflectometer with a sample on it.

Measurements were made by adjusting the instrument with a standard of known reflectivity. The standard used was a front surface silver mirror which was stored in a dessicator between measurements.

Materials were identified by optical microscopy and with the scanning Electron Microscope. For the SEM, approximately one inch square specimens were cut from soiled as well as cleaned mirrors. Examination was done in a Cambridge Mk IIA scanning electron microscope. In order to eliminate static buildup ("charging"), the specimens were carbon-coated using an Edwards vacuum evaporator. Typical debris was photographed, and qualitative chemistry of individual particles was determined by energy dispersive x-ray analysis (Kevex Subsystem 4001 and Nuclear Data NDP 812 Computer). The x-ray analysis system can detect all elements with an atomic number of 9 (Fluorine) and higher.

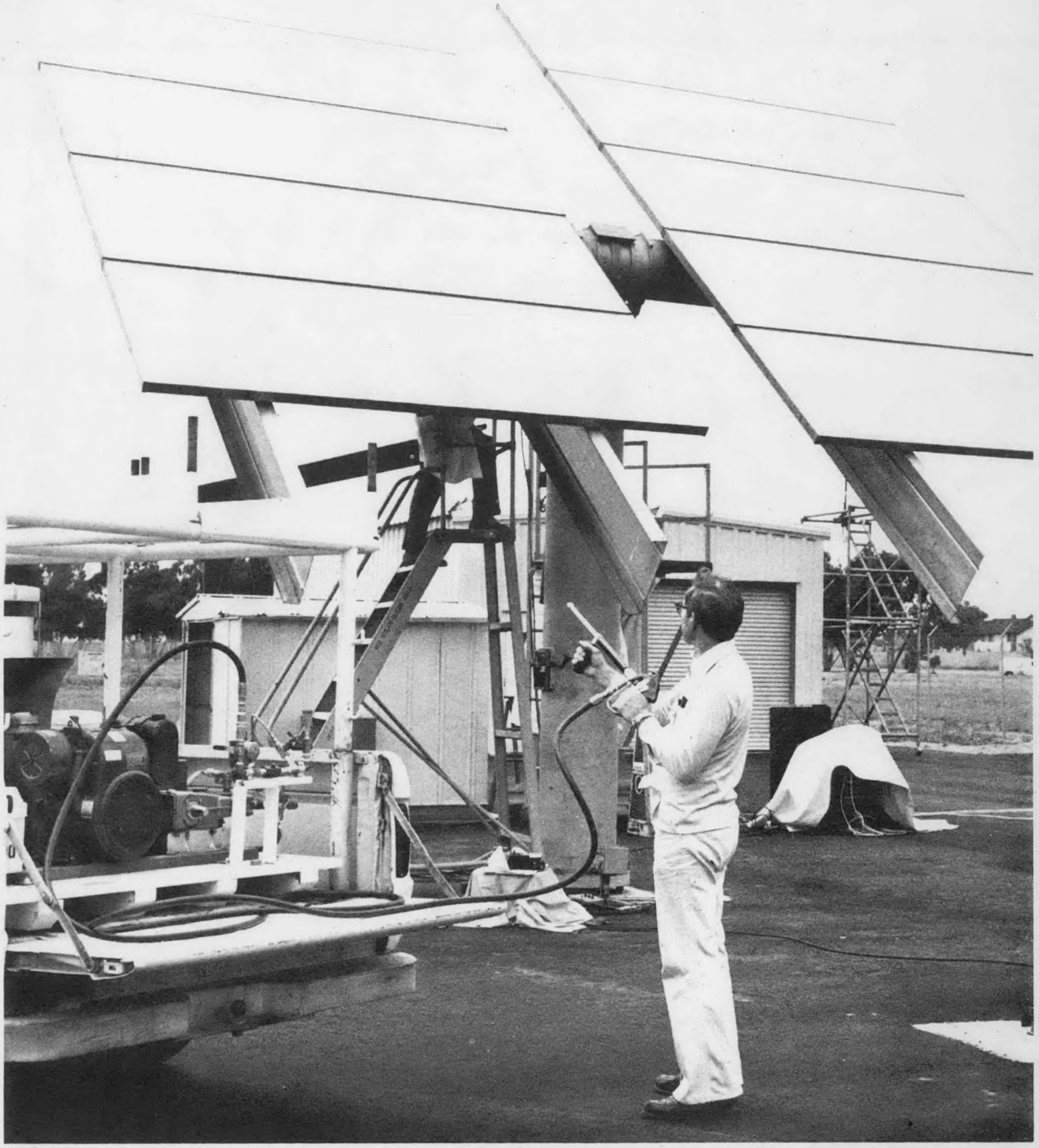


Figure 3. High Pressure Spray System in Back of Truck.

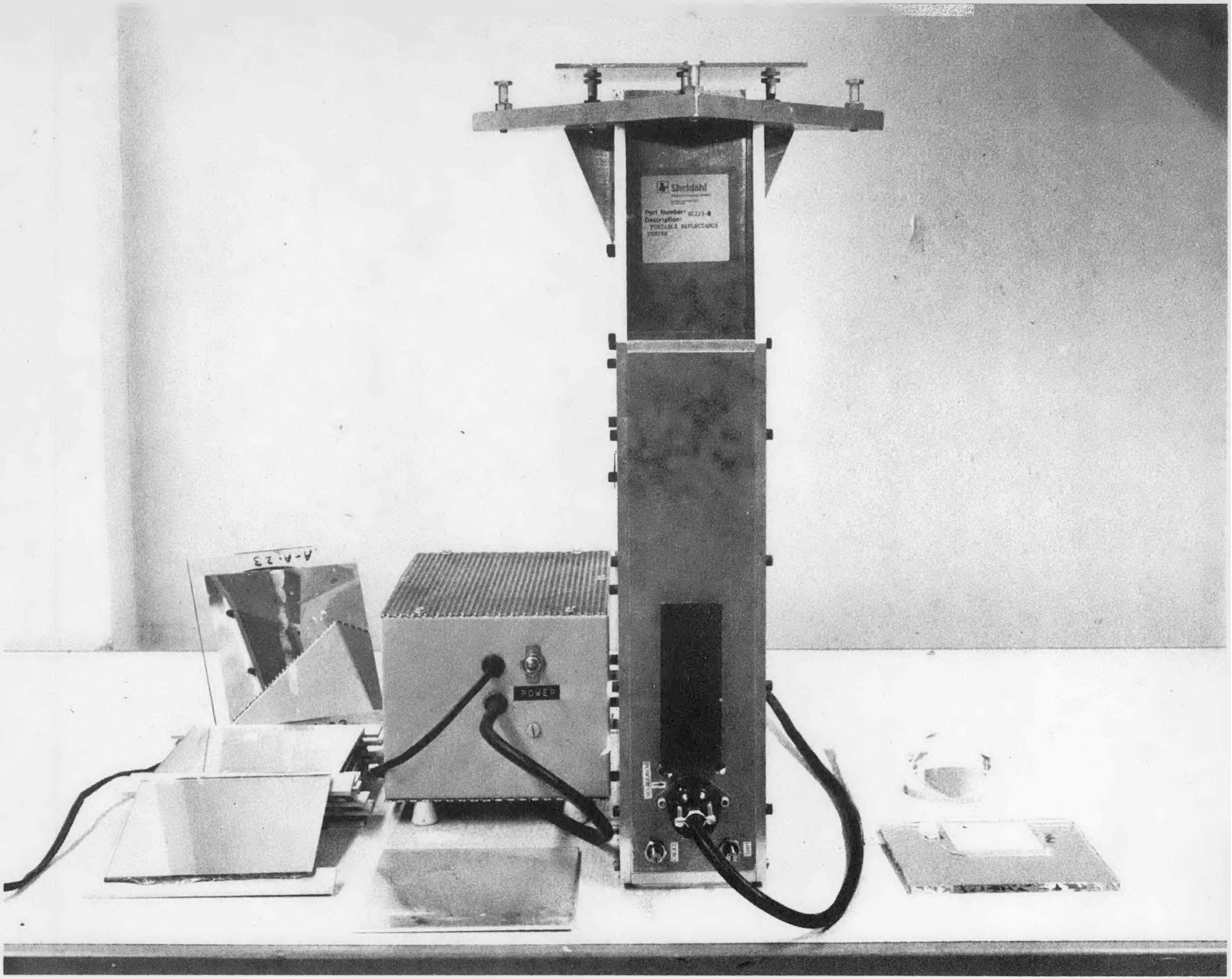


Figure 4. Scheldahl Reflectometer With Samples at Left and Standards on Right.

Section 3
RESULTS AND DISCUSSION

3.1 NATURE OF THE SOIL

Investigations done by California State University, Fullerton, personnel showed that artificially and naturally soiled surfaces carried a very large variety of mineral contaminants. All varieties of minerals which were typical of the immediate surroundings were found on the surface of the reflectors. There was a greater profusion of larger paricles (>50μ) on the acrylic and silicone surfaces than on the glass, but the differences were scarcely significant. What was significant was the observation that most of the soil was rather easily removed, and that the soil that remained tenaciously held to the surface was restricted to three basic types. These tenacious materials were montmorillonoid clays, micas and carbonates. This was true for both glass and acrylic. (Silicone remains to be studied for this.) The clay predominated on the artificially soiled specimens and on samples in the early months of environmental exposure. Samples which were exposed for longer periods of time showed more carbonate and mica on their surfaces. Refer to Appendix B fur further details on this work.

3.2 ADHESION MECHANISM

There was no evidence for any chemical attack by the contaminants on the substrate. In fact, when the soil was removed by scrubbing in the presence of detergent, or by treatment with CB 120, no evidence of a "scar" on the substrate could be detected. The soil could also be removed by running the specimens through the normal cycle of a household dishwashing machine, and in the case of glass reflectors, a return to 100% of the original specular reflectance was obtained.

The absence of any chemical interaction between the soil and the substrate should not be taken as an indication that the energy of interaction is low. It should be remembered that the vast majority of adhesives and paints cling to their substrates because of physical forces only. The only prerequisite to very strong adhesion is that the two adherends be brought into intimate contact on a molecular scale. Once this has been accomplished, the ordinary intermolecular forces are powerful enough to hold even quite massive adherends together. If two molecularly flat solid surfaces could be placed together, the theoretical interfacial tensile strength of such a joint would be greater than 100,000 psi (Reference 1). In practice, of course, such joint strengths are not seen because of many flaws which interfere with extensive intimate contact at the molecular level, and which also provide stress risers to concentrate externally applied stress. The soil particles which adhere most strongly to the reflector surfaces are generally less than 5μ in diameter, and it is easy to appreciate that close molecular intimacy is more likely to extend over a 5μ size particle than over one which may be 10 or 100 times larger. In the case of the montmorillonoids, this intimate surface contact is enhanced by their property of absorbing water and swelling. The swelling is accompanied by a softening of the particle, so that it can in effect "flow" until the surface in contact with the glass extends over the entire horizontal dimension of the particle. Mica particles do not swell, but they occur in very thin plates with optically flat surfaces. The surface of a large mica flake is composed of a series of steps, but many particles with sizes in the range of 4 - 10μ are flat over their entire dimension and would be expected to adhere very strongly to the optically flat reflector substrates. The carbonates are found mainly in conjunction with mica, and it appears likely that they are trapped between the mica and the reflector surface forming a semi-soluble "cement" which can not be leached out because the high interfacial energies prevent solvent penetration. (See Section 3.5 for a discussion of time-dependent interfacial penetration.)

3.3 COMMERCIAL CLEANING AGENT EVALUATION

A number of manufacturers of commercial cleaning products agreed to provide samples for evaluation of their effectiveness in cleaning solar reflectors. These manufacturers and their products are listed in Table 1. Many of the products were able to produce clean mirrors with 100% of the original specular reflectance, but only if a soft cloth wipe was used in conjunction with the wash. It was observed that wiping is effective only when the surface is wet with the detergent solution. Wiping in the presence of the rinse water left streaks, and wiping the dry surface before or after a spray and rinse

Table 1

MATERIALS SUBMITTED FOR EVALUATION AS MIRROR CLEANERS

Company	Materials
Cee Bee Chemical Div. McGean Chemical Forp. Buena Park, California	C-120 C-120 D
Judi Goose Anaheim, California	Judi Goose Oven Cleaner
Oxford Chemicals Atlanta, Georgia	Crystal Clear Concentrated Glass Cleaner
Puritan Churchill Chemical Co Houston, Texas	Float Glint Orion II Sanogen Super Starlite
Van Straaten Chemical Co. Chicago, Illinois	21-200-A 51-155-B Liftoff
Vestal Laboratories Div. Chemed Corp. St. Louis, Missouri	Lime Brite

left scratches. When used without wiping, many of these cleaners were able to produce a surface with 98% of its original specular reflectance, but none of them could get the mirrors any cleaner than that. In view of the adhesion mechanism, it was felt that applying more energy at the surface, such as by wiping, might improve reflectivity. Consequently, application of hot detergent solutions and application of detergents under high pressure were also studied, but the 98% barrier could not be passed by any of the commercial cleaners.

3.4 NON-DETERGENT CLEANING METHODS

A number of cleaning procedures were studied in the hope that their relative success or lack of success might yield further insight into the mechanism of adhesion and perhaps suggest alternative approaches to removal of soil.

3.4.1 Ice and Snow

Previous investigators (Reference 2) had observed that formation of frost on full-scale heliostats was beneficial. It was of interest to discover if this was an effect of water freezing in contact with the soiled reflector surface, or simply a cooling or abrading effect of already frozen water impacting the reflector surface. Water was allowed to freeze in contact with the soiled surface by wetting the surface and placing the wet reflectors in the freezing compartment of a lab refrigerator. This method of cleaning restored about 95% of the reflectivity of the glass and acrylic surfaces, although the RTV 670 was scarcely affected (visual evaluation only - no reflectivity measurements possible with these samples because of poor substrate quality). On the other hand, sprinkling crushed ice onto the surface and then allowing it to melt and drain off produced practically no improvement in reflectivity (see Table 2).

3.4.2 Ultrasonic Cleaning

Application of ultrasonic vibration was studied as another means of supplying extra energy to the surface. It was found that ordinary water is as effective as the best detergents under these conditions, but even the best detergents could not clean the surfaces beyond the 2% loss associated with what now appears to be the result of a normal irreversible soiling process.

3.4.3 High Pressure Water Spray

A spray of water under 1000 psi proved to be as effective in removing soil as any other non-scrubbing technique. Spraying with deionized water at 1000 psi left the reflectors with the usual 2% loss of reflectivity. Using ordinary tap water followed by a rinse at low pressure with deionized water had the same effect, but ordinary tap water without a subsequent rinse left hard water spots. These spots were difficult to remove on subsequent washings, requiring longer applications of the high pressure spray. Such spots could be avoided without the added expense of deionized water, by adding a sheeting agent to the tap water. These materials are in common use in household dishwashers to prevent spotting of glassware, and they appear to work as well under laboratory conditions as they do in the home. A typical concentration for solar reflector cleaning is 200 ppm sheeting agent. The results of this study are shown in Table 3.

In connection with the high pressure spray cleaning technique, it was necessary to know if the films of acrylic or silicone would remain adherent to

Table 2
EFFECT OF ICE FREEZING VS SPRINKLING

Surface	Ice Formed On Surface	Ice Sprinkled Onto Surface	Specular Reflectivity (%) Initial	Soiled	Cleaned
Glass	Yes	No	89	78	87
Glass	No	Yes	89	77	81
Acrylic	Yes	No	87	72	79
Acrylic	No	Yes	87	70	72

Table 3
CLEANING BY HIGH PRESSURE WATER

	Specular Reflectivity (%)			
Surface	Initial	Soiled*	Cleaned (A)	Cleaned (B)
Glass	89	79	87	86
(3 Specimens)	89	77	88	88
	90	79	88	88
Acrylic	86	71	79	80
(3 Specimens)	86	70	80	78
	87	70	80	80

*Naturally soiled at Daggett for 2 months.

(A) DI water.

(B) Tap water with sheeting agent.

their substrates under the water bombardment. It was observed that undamaged films did remain in place, even after as much as 1 minute continual spray at 1000 psi. However, a spray which was directed inward toward the edge of one acrylic film caused a peel-back of about 1/4 inch after about 15 seconds continual spraying on one occasion. Further application of the spray caused no further damage - even spraying directly under the damaged strip failed to peel back any more film. The initial peel-back at the edge may have been caused by incomplete adhesion at that point, particularly since it could not be repeated.

In contrast to the above behavior, the RTV 670 film was easy to remove when damaged. The film was cut with a razor blade, since it had no edges, and the spray was directed at right angles to the cut. Most of the silicone film peeled away within 15 seconds after first application of the spray. Apparently the adhesion between the silicone and the aluminum was unable to withstand the force of the water impingement.

3.5 FORMULATION STUDIES

This investigation of generic cleaning agents was performed under subcontract by McGean Cee Bee Chemical Company with technical supervision by MDAC. Representative samples of the four major types of detergent were studied: cationic, anionic, amphoteric, and non-ionic. Molecular size and charge separation were varied to try to correlate with the known distances between charges of the contaminant particles, and a number of molecular types not normally used in detergent formulations were also studied. In particular, some materials used in ore benefication were evaluated. These substances have the ability to absorb onto the surfaces of small particles, and hence to interfere with their ability to interact normally with their surroundings.

An evaluation of reflector surface pretreatment was conducted as an alternative to aggressive chemical cleaning to remove tough mineral deposits. The pretreatment method that showed promise was creating a barrier layer on the reflector surface. On an annual basis the barrier layer would be removed, thus removing the mineral deposits without affecting the reflector surface. Double- and single-layer barrier coatings were evaluated, and two single-layer barrier coatings showed promise. However, the cost of the surface pretreatment was considered prohibitive and was not considered viable as a cleaning alternative.

These investigations by McGean Cee Bee showed that a return to 98% of the original specular reflectance values was easy to achieve, but any further cleaning without scrubbing or the application of HF was impossible.

McGean Cee Bee was unable to develop a new formulation for a cleaning agent that performed better than those already commercially available. Formulations developed outside the contract are proprietary and can only be classified by their generic or commercial name.

3.6 EXTENDED SOILING AND CLEANING CYCLES

Solar reflectors are expected to be in place for up to 30 years, and will experience many cleaning and soiling cycles in that time. There are three important questions concerning long-term maintenance of reflectivity: Is there a continual buildup of irreversibly adsorbed soil? Does soil which would be removable become irreversibly attached if left on the reflector surface long enough, and if so, how long is "long enough"? Do any of the better cleaning methods produce harmful effects on the reflecting surfaces?

The question of whether there is a continual buildup of irreversibly adsorbed soil is important in view of the observed retention of that soil which caused the 2% reflectivity loss. Reflective surfaces were subjected to up to 30 artificial soiling/cleaning cycles, and the reflectivity was monitored every 5 cycles. The artificial soiling was performed in the laboratory by sifting authentic desert soil directly onto the wet reflector surface, and then allowing the surface to dry in the sun. This soiling procedure does not take into account the observed difference between short-term dirt, which is mainly montmorillonoid in nature, and the long-term soil, which is chiefly mica and carbonate. This is because this latter piece of information was available only towards the end of the investigation, when there was no longer time to study the real-life situation.

Nevertheless, the results of this initial study (Table 4) are worthy of note. The glass surface rapidly reached a "saturation" condition with soil irreversibly adsorbed up to the well-known 2% specularity loss. Further soiling and cleaning cycles failed to make the reflector any "dirtier," as measured by specular reflectance. The acrylic (FEK 244) surface also appeared to achieve saturation, although the reflectivity loss after 30 cycles was somewhat greater - closer to 8%. The reflectivity loss of the silicone/aluminum surface could not be determined, but this surface appeared to be visually the dirtiest of the three after the 30 cleaning/soiling cycles.

There has not been enough investigation done to decide if the passage of time causes reversibly adsorbed soil to become irreversibly attached to the reflector surfaces. If this change does occur, there is some indication that it takes longer than eight months for glass surfaces, although the time may be shorter for acrylic and especially RTV 670 films. Three reflectors which had been exposed for eight months (one for each surface) were retrieved from the Albuquerque test rack, and attempts were made to clean them using the 1000 psi spraying technique. The glass mirror recovered 98% of its original specular reflectance, while the acrylic surface showed only a 90% recovery. Visually, the RTV 670 surface could only be described as filthy, and even up to one minute under the high pressure spray did little to restore it to an acceptable level of cleanliness. It should be noted that all three reflectors had been exposed continually for eight months, and consequently they had been exposed to the cleaning action of the rain, as well as to the soiling activity in the environment. It has been observed that the heliostats in the STTF at Albuquerque appeared to recover 100% of their original reflectivity if exposed to a good rain for two or more hours (Reference 3). Such a rain had occurred shortly before the three mirrors were removed from the racks; thus, it appears that the organic coatings are less responsive to natural cleaning occurrences than are the glass surfaces.

Table 4

REPEATED SOILING AND CLEANING CYCLES
SHORT TERM

Cleaning Method	Surface	Number of Cycles*	% Original Specularity Retained
Lime Brite spray and rinse with DI water. Drain dry.	Glass	1	99
		5	98
		10	98
		20	97
		30	98
	Acrylic	1	98
		5	95
		10	93
		20	92
		30	93
Tap water plus sheeting agent at 1000 psi. Drain dry.	Glass	1	98
		10	97
		30	97
	Acrylic	1	98
		10	94
		30	92

*A cycle comprised:

a. Wet the surface.

b. Sprinkle soil onto surface.

c. Allow to dry.

d. Apply cleaning method.

These observations provided some insight into the mechanism(s) of soil adhesion. It is easy to understand how long-term soaking would remove the montmorillonoid soil, since it would eventually absorb water and swell, thus losing structural integrity and strength and becoming susceptible to removal by relatively low energy water impingement. The removal of the carbonate "cements" from glass surfaces can be understood in terms of the kinetic phenomena associated with wetting. Figure 5 shows a cross section of an interface between a particle of carbonate cement and a reflector surface, with liquid water adjacent to the carbonate particle. In Figure 5A no penetration has yet occurred, while Figure 5B shows the condition of the interface with some water penetration. The penetration of water has created a certain area of new interface - water/glass and water/carbonate. Creation of new interfacial regions requires energy, which is supplied by molecules in the water which have higher kinetic energy than the average. The rate at which water penetration of the interface occurs is a function of the average kinetic energy of the water molecules (i.e., the temperature of the water), of the duration of exposure, and of the "wettability" of each of the surfaces. Since glass is known to be much more wettable than organic materials, it is not surprising that tightly bound soil is more readily removed from glass surfaces. The implication here is that there is no chemical interaction between the soil particle and the glass substrate, for if there were, much more energy would be needed to separate the two materials.

Two detergent materials were evaluated to determine whether or not they harmed reflector surfaces on repeated washing cycles. The detergents were the McGean CB 120 formulation, and a material known as Lime Brite, supplied by Vestal Labs in St. Louis. The latter material was chosen as being representative of those commercial detergent formulations which restored 98% of the original specular reflectance. The detergents were sprayed onto the reflector surface for 15 seconds, and then immediately rinsed off using DI water. The wet surface was air dried for 15 minutes, then the spray/rinse cycle was repeated. Reflectivity was measured after every 50 cleaning/rinsing/drying cycles. The results are recorded in Table 4. After 300 such cleaning cycles, the surfaces which had been exposed to Lime Brite showed no loss of specularity;

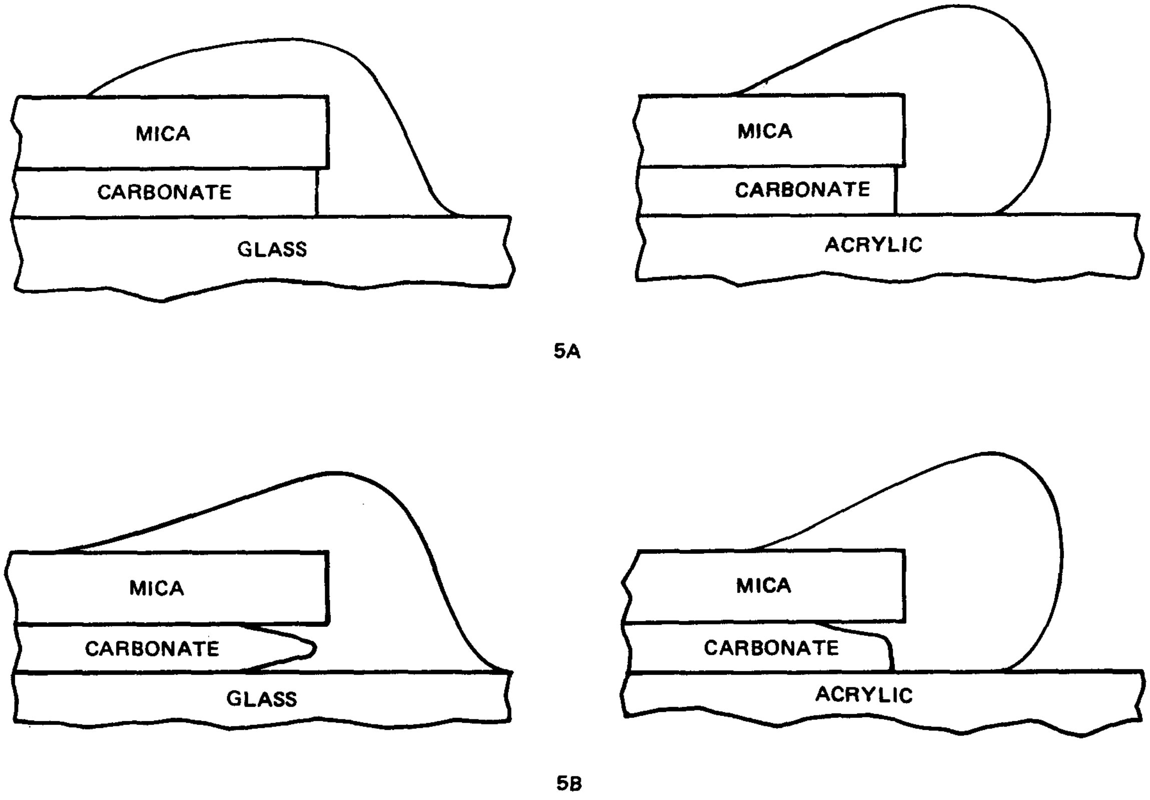


Figure 5 - Section Through Mica Crystal Cemented on Glass and Acrylic Surfaces Showing the Increased Surface Area Due to Solution

Table 5

REPEATED CLEANING CYCLES

Cleaning Agent	Number of Cycles*	% Original Specularity Retained**
CB 120	50	100
	100	100
	150	100
	200	99
	250	98
	300	97
Lime Brite	50	100
	100	100
	200	100
	300	100

*A cycle comprised:

a. A 15-second spray with cleaning agent.

b. A 30-second DI water spray rinse.

c. A 5-minute drain dry.

**Results are for glass only. The acrylic surfaces resisted attack by CB 120 and/or Lime Brite.

nor did the acrylic reflector which had been exposed to CB 120. After 150 washing cycles with CB 120 there was no detectable damage. After 300 cycles there was only a 3% loss of specular reflectivity. Visual examination of the glass after the 300 cleaning cycles revealed that damage to the glass appeared to be confined mainly to areas which had been damaged at the start of the washing period. Scratches and nicks which had not been visible before the experiment became more and more obvious as the number of washing cycles increased. To confirm this, a separate piece of glass was abraded with a Brillo pad, and then exposed to CB 120 for five minutes. Before the exposure the surface damage was not visible to the naked eye, but scratches were clearly visible after the five-minute exposure period. However, adjacent areas which had not been abraded showed no damage.

Section 4

RECOMMENDED CLEANING PROCEDURES

There are two alternative approaches to routine maintenance cleaning of solar reflectors. For planar heliostats, the application of a high-pressure spray with plain water appears to be the least costly, although in areas where the tap water is too hard, this is not certain. However, to be effective, the spray should be applied close to the reflector surface - not more than 12" away. For curved reflectors with a good deal of superstructure, this may well be impossible. For this type of surface, a spray and rinse with detergent will be as effective as the high-pressure spray. Lime Brite exemplifies the best of the commercial detergents evaluated. It is an acidic (anionic) material, and probably most commercial anionic detergents would work as well. It can be applied as a 3% solution in softened water (DI is not necessary), followed by a rinse using plain softened water or tap water containing a sheeting agent at a concentration of 200 ppm.

Both of the above procedures will leave a surface with between 92% (acrylic) and 98% (glass) of its original specular reflectivity. To bring the surface back to 100% of its starting reflectivity, more vigorous cleaning procedures are required. These can be either manual scrubbing, or exposure to a specially formulated cleaner containing HF. Routine cleaning in such an aggressive manner is definitely not recommended. Besides being either labor intensive (scrubbing) or environmentally questionable (HF), it is also a non-productive effort. After such a cleaning, the surfaces will have adsorbed enough soil to go right back to the 2% specularity loss within a few days - certainly in less than two weeks. However, it is not clear that there is not a slow buildup of nonremovable dirt, and over a period of a year or so it may be that there would be more nonrecoverable specularity loss than is acceptable. In that case, a quick wash with CB 120 would restore the reflectors to their original condition, ready to go for another year or two.

An advantage of the high pressure spray method and the detergent wash plus rinse method is that there is no requirement for protection of personnel or equipment, as all materials are passive. If the CB-120 formulation is used, protective clothing and face shields would be required for personnel. Equipment protection would involve regular flushing of all solvent reservoir and solvent transport lines to remove any precipitated fluoride salts which could occlude valves, orifices, etc. The material composition of all surfaces in contact with the solvent should be resistant to the attack of a weak acid.

The effect of temperature, wind and humidity on cleaning procedures was evaluated. The most deleterious effect would be from winds blowing dirt onto wet reflector surfaces or winds blowing with sufficient strength to deflect a portion of the water spray from the mirror surfaces. Extremely low humidity or extremely high temperatures could contribute to streaking of the reflector surfaces if the soap solution dried before the rinse was applied. It is considered extremely unlikely that conditions this extreme would be encountered.

Section 5

CLEANING COST ANALYSIS FOR MINIMUM TOTAL COST

The two recommended approaches to the routine maintenance cleaning of solar reflectors, i.e. high-pressure spray and cleaning with a 3% detergent solution with a subsequent rinse, are assessed as to cost effectiveness. The cost analysis is based on the assumption that an average field of solar reflectors consists of 1000 solar reflectors with an average surface area of 400 square feet per collector, or a total surface area to be cleaned of 400,000 square feet. The calculations contained in this report are based on actual data obtained from limited experiments on a full-scale heliostat at the MDAC Huntington Beach facility (MDAC-HB) and work done at the Naval Weapons Center (NWC) at China Lake, California (Reference 4). No provisions were made for the effect of inflation on the cost summaries. Calculations for unit costs are based upon costs which are representative of the Huntington Beach area.

Earlier work completed at NWC indicated a cleaning frequency of 12 washings per year was adequate for optimum reflector efficiency. The cost summaries for both cleaning procedures are based on the assumption that specialized equipment is employed, i.e. a truck with a 3600-gallon solvent reservoir which has high-pressure spray wands mounted on vertical columns. It is assumed four wands, mounted on two vertical levels and separated by a distance of approximately 20 feet, would be sufficient to cover the total surface area of the reflector with one pass of the equipment. If the truck moves at a steady rate of 0.5 mph, a dwell time for each vertical column of wands would be 30 sec. Assuming a 30 sec. transit time between reflectors, the total time required for each reflector would be 1.5 min. The subsequent cost summaries (Tables 6 and 7) are based on the requirement of one truck, one operator, and 1.5 min. total cleaning and transit time per reflector.

It was assumed that material costs would be a significant factor in calculating total unit costs for the cleaning procedures. Investigations into cleaning efficiency versus spray pressure of the spray wands were made. It was found that cleaning efficiency was substantially equal at spray pressures of 1000 psi (5.1 gal/min), 800 psi (4.3 gal/min), 600 psi (3.8 gal/min), 400 psi (3.0 gal/min), and 300 psi (2.7 gal/min). Subsequent calculations of cleaning material usage are based on a flow rate of 2.7 gal/min. The parameters used to choose the spray nozzle configuration on the spray wands were to find one that was commercially available and had a large spray area.

An additional consideration for the selection of a cleaning procedure for a field of solar collectors, whose life expectancy is anticipated to be 30 years, is the long-term environmental impact of the cleaning agents. The high pressure spray cleaning procedure is totally compatible with all environments. There is obviously no concern for the environmental impact of tap water. The sheeting agent which was used was chosen because it is non-foaming and biodegradable. The long-term impact of the detergent wash plus rinse also presents little concern. Again, the impact of the softened water is insignificant, and the detergent is also biodegradable and low-foaming. However, the effect of McGean CB-120 cleaner, with a 5% concentration of HF, could have a long-term effect on the environment. Although HF is a weak acid, the long-term effect of HF on vegetation, in addition to the sodium and potassium salts of HF, would be detrimental. The effect of HF or the salts of HF in natural runoff waters would probably be insignificant as they would be complexed by natural chelating agents in the water.

The cost summary for the high pressure spray cleaning procedure is calculated using tap water containing 200 ppm sheeting agent. Water cost estimates were calculated from the current Huntington Beach, CA municipal water rate of 0.0508¢/gal. The cost of the sheeting agent is based on an average cost of commercially available agents and is $5 per gallon for an 85% solution. The detergent wash with subsequent rinse cost summary is based on using softened water at 1¢/gal, and a 3 V/V% solution of the detergent, Lime Brite, at $6.25 per gal.

Table 6

UNIT COST SUMMARY USING THE HIGH PRESSURE SPRAY CLEANING PROCEDURE

Parameters

1. Total surface area to be cleaned is 400,000 square feet.
2. 1 min. wash cycle and 0.5 min. transit time for each reflector is used.
3. The cleaning solution is 200 ppm sheeting agent in tap water.
4. Fuel consumption for the truck and spray apparatus is 12 gal/hr diesel at 56¢/gal.
5. 0.5 hr per truck reload is assumed.
6. The equipment depreciates to zero value over 30 years.
7. A labor cost of $15/hr is assumed.
8. One operator is required.

Calculations

$$\frac{1000 \text{ reflectors} \times 1.5 \text{ min/reflector}}{60 \text{ min}} = 25 \text{ hrs/field}$$

A. Direct Cleaning Costs

Water

Spray Pressure (psi)	Flow Rate (gal/min)	Time Required To Clean 400,000 ft^2 (hrs)	Water Used per Surface Area (gal/ft^2)	Total Water Used (gal)	Unit Cost (¢/ft^2)
1000	5.1	25	0.019	7650	0.0097
800	4.3		0.016	6450	0.0082
600	3.8		0.014	5700	0.0072
400	3.0		0.011	4500	0.0057
300	2.7		0.010	4050	0.0051

Table 6 (Continued)

Sheeting Agent: 200 ppm agent = 0.00037 gal agent/gal water @ \$5/gal

Spray Pressure (psi)	Water Used per Surface Area (gal/ft^2)	Sheet Agent per Surface Area (gal/ft^2)	Total Sheeting Agent Used (gal)	Unit Cost (¢/ft^2)
1000	0.019	0.000007	2.812	0.0035
800	0.016	0.000006	2.368	0.0030
600	0.014	0.000005	2.072	0.0026
400	0.011	0.000004	1.628	0.0020
300	0.010	0.000004	1.480	0.0019

Total volume of solvent required for one 400,000 ft^2 field (using 300 psi spray): 4052 gal.

Number of truck reloads per field: $\frac{4052 \text{ gal}}{3600 \text{ gal reservoir}} = 1.13$

Number of hours for reloads: (0.5 hr/reload)(1.13 reloads) = 0.57 hrs

Number of hours required per field = (25 cleaning hrs) + (0.57 reload hrs)
= 25.57 hrs

Cost of fuel: (25.57 hrs) x (12 gal/hr)(56¢/gal)/400,000 ft^2 = 0.043¢/ft^2

Maintenance of equipment: The maintenance cost is assumed to be 10% of the total usage time required of the vehicle.

(1 vehicle)(25.57 hrs)(0.10)(\$15/hr)/400,000 ft^2 = 0.010¢/ft^2

Labor Costs: (25.57 hrs/field)(\$15/hr)/400,000 ft^2 = 0.096¢/ft^2

B. Capital Costs

The cost of one specially designed vehicle is assumed to be \$50,000. Assuming 12 cleanings per year and a capital recovery factor of 0.051019 for 30 years at 3% interest, the annual cost is \$2551, or:

(\$2551/12 washings)/400,000 ft^2 = 0.053¢/ft^2

Table 6 (continued)

C. Summary of Unit Costs

Item	Unit Cost per Cleaning (¢/ft²)	Percent of Cost
Materials		
Water (at 300 psi)	0.005	2.4
Sheeting Agent (at 300 psi)	0.003	1.4
Fuel	0.043	20.5
Labor	0.096	45.7
Equipment		
Maintenance	0.010	4.8
Capital Expenditure	0.053	25.2
Total	0.210	100.0

Table 7

UNIT COST SUMMARY USING DETERGENT WASH WITH SUBSEQUENT RINSE CLEANING PROCEDURE

Parameters

1. Total surface area to be cleaned is 400,000 square feet.
2. A wash cycle of 0.5 min, a rinse cycle of 0.5 min, and a 0.5 min transit time for each reflector is used.
3. The cleaning solution is 3% Lime-Brite in softened water, and the rinse cycle employs softened water.
4. Fuel consumption for the truck and spray apparatus is 12 gal/hr diesel at 56¢/gal.
5. 0.5 hr per truck reload is assumed.
6. The equipment depreciates to zero value over 30 years.
7. A labor cost of $15/hr is assumed.
8. One operator is required.

Calculations

$$\frac{1000 \text{ reflectors} \times 1.5 \text{ min/reflector}}{60 \text{ min}} = 25 \text{ hrs/field}$$

A. Direct Cleaning Costs

Water

Spray Pressure (psi)	Flow Rate (gal/min)	Time Required to Clean 400,000 ft² (hrs)	Water Used per Surface Area (gal/ft²)	Total Water Used (gal)	Unit Cost (¢/ft²)
1000	5.1	25	0.019	7650	0.019
800	4.3		0.016	6450	0.016
600	3.8		0.014	5700	0.014
400	3.0		0.011	4500	0.011
300	2.7		0.010	4050	0.010

Table 7 (continued)

Detergent at 3% concentration. The cost of the detergent is \$6.25/gal.

Spray Pressure (psi)	Flow Rate (gal/min)	Time Required to Clean 400,000 ft^2 (hrs)	Water Used During Wash Cycle (gal/ft^2)	Detergent Used per Surface Area (gal/ft^2)	Unit Cost (¢/ft^2)
1000	5.1	25	0.0095	0.00030	0.178
800	4.3		0.0080	0.00024	0.150
600	3.8		0.0070	0.00021	0.131
400	3.0		0.0055	0.00017	0.103
300	2.7		0.0050	0.00015	0.094

Total volume of solvent required for one 400,000 ft^2 field (using 300 psi spray) = 4172 gal.

$$\text{Number of truck reloads per field} = \frac{4172 \text{ gal}}{3600 \text{ gal reservoir}} = 1.16$$

Number of hours for reloads = (0.5 hr/reload)(1.16 reloads) = 0.58 hrs.

Number of hours required per field = (25 cleaning hrs) + (0.58 reload hours)
= 25.58 hrs.

Cost of fuel = (25.58 hrs)(12 gal/hr)(56¢/gal)/400,000 ft^2 = 0.043¢/ft^2

Maintenance of equipment: The maintenance cost is assumed to be 10% of the total usage time required of the vehicle.

(1 vehicle)(25.58 hrs)(0.10)(\$15/hr)/400,000 ft^2 = 0.010¢/ft^2

Labor Costs: (25.58 hrs/field)(\$15/hr)/400,000 ft^2 = 0.096¢/ft^2

B. Capital Costs

The cost of one specially designed vehicle is assumed to be \$50,000.

Assuming 12 cleanings/year and a capital recovery factor of 0.051019 for 30 years at 3% interest, the annual cost is \$2551 or:

(\$2551/12 washings)/400,000 ft^2 = 0.053¢/ft^2

Table 7 (continued)

C. Summary of Unit Costs

Item	Unit Cost per Cleaning (¢/ft^2)	Percent of Cost
Materials		
Water (at 300 psi)	0.010	3.3
Detergent	0.094	30.7
Fuel	0.043	14.1
Labor	0.096	31.3
Equipment		
Maintenance	0.010	3.3
Capital Expenditure	0.053	17.3
Total	0.306	100.0

The cost summaries prepared for the two cleaning methods yielded 0.21¢/sq. ft. for the high pressure spray method and 0.31¢/sq. ft. for the detergent wash plus rinse method. The high pressure spray method is obviously the least costly, but may not be applicable to areas where resident water supplies are heavily mineralized. However, the use of tap water with a sheeting agent instead of softened water with detergent resulted in an estimated 32% unit cost saving, in addition to being slightly more acceptable environmentally.

The major cost in both cost summaries is the labor cost, 31.3% of the total cost for the detergent wash plus rinse method and 45.7% of the total cost for the high pressure spray method. The detergent wash plus rinse method also had as a major cost the detergent, which constitutes 30.7% of the total cost. The labor costs can be reduced by utilizing a fully automated cleaning system. Although the system design would be costly, the capital expenditure can be amortized over the lifetime of the solar field and the total unit cost would quite probably be less than the contribution of continuing labor costs. Also, with a fully automated system, recycling of the solvents with appropriate filters and cleaning systems would become feasible, and the material cost savings would be significant.

Section 6
CONCLUSIONS

The following conclusions may be drawn from the data reported here:

- All three surfaces studied adsorb some soil in a nonreversible manner, in addition to soil which can be easily rinsed off.

- Nonreversible adsorption reduced the specular reflectance of glass mirrors by about 2%. Acrylic mirrors were reduced by 5-8%. Silicone surfaces were not measured, but visually they seem to adsorb much more soil and were harder to clean than glass or acrylic.

- In addition to the nonreversibly adsorbed soil, there was an accumulation of dirt which was rinsed off the mirrors, even after being on the surface for some months.

- Removal of the rinsable soil was accomplished either by a mild detergent rinse followed by a soft water spray, or by application of 300 to 1000 psi spray of ordinary tap water containing a sheeting agent.

- Each rinsing activity restored the reflector to the same specularity, 98% of the original for glass and 92-95% for acrylic. Further soiling and rinsing exercises always regenerate the same 2% specularity loss. No progressive degradation could be observed after 30 soilings and washings.

- The attachment of the soil to the surface was not the result of chemical interaction between soil and substrate, but was simply the result of the intimate molecular contact between the two materials.

- The glass reflector could be restored to 100% of its original reflectance at any time, either by scrubbing with detergent, or by a spray and rinse with CB 120. Acrylic reflectors could also be cleaned to 100% of their original specularity with CB 120, but scrubbing is not recommended because of the low abrasion resistance of this material.

Section 7
REFERENCES

1. J. J. Bikerman. The Science of Adhesive Joints. Academic Press, 1961; p. 135.

2. J. B. Blackmon. Dust Buildup Tests of Heliostats and Mirror Specimens. McDonnell Douglas Astronautics Company report MDC G7543, Sept. 1978.

3. D. L. King. Sandia Laboratories, Albuquerque, NM; private communication.

4. J. B. Blackmon. Interim Report Non-Inverting Heliostat Study - Effects of Dust Buildup. McDonnell Douglas Astronautics Company report MDC G7849, Mar. 1979.

Appendix A

Final Report of Cleaning Solution Formulation Studies Submitted by McGean Chemical Company, Cee Bee Division.

McGean Cee Bee

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FINAL REPORT

STUDY OF CHEMICALS FOR SOLAR MIRROR CLEANING

by J. L. Muller

for-

McDONNELL DOUGLAS ASTRONAUTICS COMPANY
Huntington Beach, CA 92647

Subcontract Number 78622335H

TER-OFFICE CORRESPONDENCE

McGEAN CHEMICALS

TO: W. R. SMITH
DATE April 16, 1979
COPIES:
ROM: J. L. MULLER
ECT: FINAL REPORT
SOLAR MIRROR CLEANING PROJECT

DOWNEY, CALIF.
/bg

INTRODUCTION

This is the final report on our experiments to find materials and methods to clean tenacious deposits from solar mirrors, with strong emphasis on glass mirrors. This work was performed under contract for McDonnell Douglas Astronautics Company, Huntington Beach.

Both direct cleaning of the mirrors and indirect cleaning through a removable barrier layer have been investigated and are presented here.

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

No alkaline nor acidic cleaning solution compounded in this laboratory were able to remove the soiling mineral coating directly from glass or acrylic mirrors, except Cee-Bee C-120, a proprietary formulation.

Barrier coatings that can be removed along with the dirt deposited on them, also show promise.

Recommended for limited field trial are Cee-Bee C-120 and two silicone containing stearic acid coating materials (page 6).

METHODS OF EVALUATING THE CLEANING PROCESS

It became apparent, after some initial attempts to clean soiled mirrors, that it was necessary to study the nature of the soil more closely and to observe, under strong magnification, actual soil removal from the mirror surface.

A microscope with a "Differential Interference Contrast by Incident Light" attachment proved very effective in viewing the ridges and films of mineral deposits and made it possible to observe whether they were actually affected during cleaning.

Reflectivity measurements, also useful for cleanliness evaluation, give a general idea of effectiveness of dirt-film removal but do not reveal much of the surface activity involved in cleaning.

NATURE OF SOILS

Observation through the DIC mircroscope made it apparent that at least two kinds of soil were present; particulate matter, moved onto the mirror surface from the surrounding environment, and non-particulate films.

To our observation, the particulate soil consists of large particles (0.05-0.1 mm) that adhere loosely to the surface, and very fine particles (few microns), which adhere much more tenaciously. The non-particulate layers and ridges appear to have been formed in situ and apparently consist of silicious mineral. Part of the particulate soil is cemented to the mirror surface by this deposit.

pH EFFECT

A scale of buffers from pH 2 to 11 in 1.0 pH steps did not remove the non-particulate film and ridges. Zero-point-of-charge of silicious materials often falls within the 2 to 4 range and it was thought that, if the attractive forces were solely electrostatic, pH should have an effect.

Buffer composition: citric acid, phosphate

SURFACTANTS

Several surfactants belonging to the general groups of nonionics, anionics, cationics and amphoterics were tried by themselves and in combination with an alkaline and an acidic builder base. All were ineffective in removal of the non-particulate deposit.

<u>Surfactants @ 1%</u>

Triton X-100 (Rohm & Haas)
Ethomeen S-25 (Armak)
Velvatex BC (Textilana)
Dodecylbenzene sulfonic acid
Igepon T-33 (GAF)
Miranol C2M-SF (Miranol)
Armeen 12D (Armak)

Builder bases

1) trisodium phosphate (3%), water and phosphoric acid to pH 11.
2) phosphoric acid (3.8%) and water to pH 2.1.

Another set of surfactants was tried in a different acidic builder base. The surfactants belonged to the general groups of blocked ethoxylates and fluorocarbons of the anionic, nonionic, cationic and amphoteric types. The non-particulate film and ridge deposits were not removed.

Surfactants

Triton CF-10 (Rohm & Haas) @ 2%
Triton CF-87 (Rohm & Haas) @ 2%
Triton DF-12 (Rohm & Haas) @ 2%
Zonyl FSC (DuPont) @ 0.1%
Zonyl FSB (DuPont) @ 0.1%
FC-98 (Monsanto) @ 0.1%
FC-170 (Monsanto) @ 0.1%

Builder base

Gluconic acid @ 10% in water

All above compositions used at full strength and at 10%.

CHELATING AGENTS

Chelating agents were added to all of the combinations of surfactants and builder bases mentioned above. There was no effect on the removal of the mineral deposits.

Chelators

Citric acid @ 2%
Gluconic acid @ 5%
Nitrilotriacetic acid @ 2%
Gluconic acid @ 10%

ACIDS

Several strong acids were added to an acidic builder formula. They had no effect on the removal of the non-particulate deposits.

Cee-Bee C-120, a McGean proprietary acidic cleaner, effectively removes the mineral deposits when used at a 5% dilution with water. At use concentration of 5% it is somewhat corrosive to glass.

Acids

phosphoric acid @ 5%
nitric acid @ 5%
formic acid @ 5%
hydrochloric acid @ 5%
sulfuric acid @ 5%
hydroxyacetic acid @ 5%

Builder base

Gluconic acid (10%), dodecylbenzene sulfonic acid (4%), water

ORE FLOTATION CHEMICALS

Ore flotation chemicals, such as dithiophosphonates and dithiocarbonates (Xanthates) had no influence on the mineral deposits. Some differential coating of particles and mirror might have been expected if all the soil was particulate and only bound electrostatically to the mirror surface.

Ore Flotation Chemicals in water solution

1) Sodium diethyl dithiophosphonate (Sodium Aerofloat Promoter by Cyanamid) @ 1%
2) Sodium ethyl xanthate (Dow) @ 1%

BARRIER LAYER

It had become apparent that no ordinary cleaning solution, except Cee-Bee C-120, would touch the tough mineral deposits. A different approach was needed. The concept of a removable barrier layer was tried. This layer, when removed, takes the soil deposits with it.

Two general types of coatings were studied, single layer coatings and double layer coatings.

In the double layer coatings the bond between the base coat and the topcoat is of the amine-carboxylic acid ester type. A strongly alkaline cleaner is expected to remove the topcoat.

The single layer coatings incorporate acidic materials, such as stearic acid, and can thus be removed by an alkaline cleaner. Also a substantive amine was investigated and removal here would probably be best performed by an acidic cleaner.

To simulate desert conditions, dusting, dew formation and drying cycles were performed. The following parameters were investigated.

- a) Interference with specular properties. This was done visually, observing presence or absence of a haze layer.
- b) Ease of application.
- c) Dust adhesion to the dry surface.
- d) Soil removal from the barrier layer by a plain water rinse leaving the barrier layer intact.
- e) Removal ease of the barrier layer and with it the adhering soil.

Double layer barrier coatings

The following base coats were investigated:

A-1100 Silane by Union Carbide (gamma-Aminopropyltriethoxysilane), a reactive coupling agent. The amino group would be free to react with a waxy acid.

Barium hydroxide. Assuming substantivity of Ba^{++}ions to the acidic mirror surface.

Experiments:

A-1100 Silane base coats @ 0.05 to 1.0% in IPA were evaluated. Only the ones with 0.1 and 0.05% gave clear coatings without "greasy" droplets.

Topcoats evaluated:

1) stearic acid (0.05 to 0.5%) + KOH in IPA + water for stability to pH of 8
2) hydroxyacetic acid (0.5%) in IPA
3) propionic acid (0.25%) in IPA
4) acrylic copolymer (ASE-95%)(1%) in IPA
5) oxalic acid (0.05 to 0.2%) in IPA
6) citric acid (0.05 to 0.2%) in IPA
7) acrylic acid (0.1%) in IPA

Only the lowest percentages gave clear coatings and only oxalic acid over a 0.05% coating of A-1100 Silane showed some promise. The coating was clear and did not attract dust excessively. However, the whole process was rather cumbersome and when A-1100 Silane was left without an overcoat, much dust was attracted. This type of double coating was not further pursued.

Overcoating barium hydroxide with stearic acid (0.5%) produced a hazy layer which washed off with water.

Single layer barrier coatings

All of the following were dissolved in IPA and applied by flooding:

1) A-1100 Silane (0.05 to 1%) + water (1%)
2) A-1100 (0.05 to 1%)
3) Hyamine 10X (0.1%), a cationic
4) Stearic acid (0.01 to 0.05%) + L-31 (0.01% to 0.05%), a reactive silicone fluid by Union Carbide
5) Stearic acid (0.01%) + L-7001 (0.01%), a silicone fluid by Union Carbide
6) Monazoline S (0.01%), a substantive imidazoline derived waxy material (Mona Industries)
7) Cee-Bee A-6 Barrier Coating (McGean Chemical Co., Inc.)

Only No. 4 and No. 5 showed promise. They were hydrophobic and did not attract dust excessively (temperatures above ambient might soften them enough to reverse this). Repeated formation of dew and drying did not change their hydrophobic character and they washed off clean with an alkaline cleaning solution.

The other single layer coatings attracted excessive dust. Cee-Bee A-6 was rather difficult to remove in a single cleaning process.

CONCLUSIONS

Nature of Soils

It appears that the non-particulate layers and ridges were formed in situ and consist of silicic mineral. Fine dust particles and some of the larger ones were found cemented by this material to the mirror surface.

Microscope with a Differential Interference Contrast by Incident Light Attachment

An efficient tool to study mineral deposit removal.

pH

Not effective as such.

Apply by flooding well cleaned mirrors. Remove with an alkaline cleaner, such as McGean's Cee-Bee A-69M Super @ 10% dilution with water by spray-on or flooding.

b) Barrier #4 is readily removed by an alkaline cleaner and is easily reapplied.

Formulation: IPA, 99.98%, + Stearic acid, 0.01%, + L-31, a reactive silicone fluid by Union Carbide, 0.01%.

Apply by flooding well cleaned mirrors. Remove with an alkaline cleaner, such as McGean's Cee-Bee A-69M Super @ 10% dilution with water by spray-on or flooding.

I recommend that the following experiments and observations be made in the field:

1) Observe dust attraction to the dry surface.

2) Observe dust attraction versus temperatures of the mirror. The barrier coatings will soften at higher temperatures.

3) Rinse with demineralized water; early in the morning when the mirrors are wet with dew, is probably the best time. My observation here is that dust can be easily rinsed from the coatings without coating removal.

APPENDIX

If the barrier coatings perform reasonably well in the field it is possible that the hardness of the films could be improved. Also, incorporation of antistatic agents could conceivably be effective in reducing dust attraction.

Detergents
No direct influence on mineral deposit removal.

Builder bases
No special influence

Chelating agents
No direct influence

Strong acids
Not effective except for Cee-Bee C-120, an acidic cleaner, which removed the mineral deposits.

Flotation chemicals
Not effective

Double layer barrier coatings
With A-1100 Silane underlayment, proved too soft and collected dust.

Single layer barrier coatings
Two formulas were effective and possible candidates.

RECOMMENDATIONS FOR LIMITED FIELD TRIALS

1. CEE-BEE C-120 (McGean Chemical Co.)
   This product effectively removes the mineral deposits from glass and acrylic mirrors. Since it is slightly corrosive to glass, field trials should be made to determine uniformity of glass removal and possible specular changes with frequency of use. Use concentration is 5% by dilution with water. Application is by spray-on or flooding. pH of use solution is 3.5 to 4.0.

2. BARRIER COATINGS
   Prevention of formation of a mineral layer directly on the mirror surface through application of a barrier coating.

   a) Barrier #5 is readily removed by an alkaline cleaner and is easily reapplied.

      Formulation: IPA, 99.98%, + stearic acid, 0.01%, + L-7001 (a silicone fluid by Union Carbide), 0.01%.

Appendix B

Final Report of Soil Classification and Adhesion Studies Submitted by California State University, Fullerton, Earth Sciences Dept.

INVESTIGATION OF SOILING OF CANDIDATE MIRRORS FOR SOLAR POWER INSTALLATIONS

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Work performed under subcontract #672
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SUMMARY

The objectives of this study were to determine the nature of the soil found on solar mirrors, the manner(s) in which the soil is bonded, and how the soil may be removed. The study was approached through the use of SEM/EDAX, optical, and X-ray techniques. It was found that the initial soil was composed of dry-deposited wind-blown particulates with diameters mostly in the 1 to 5 μ range. Most were common silicate and non-silicate minerals and all were typical of desert environments. Adherence of these particles was by electrostatic and/or van der Waals forces. Repeated wetting/drying cycles by natural rain and dew formed grain "drops" which resulted in gradual, local buildups of chemical precipitates. The resulting cement chemically bonded the grains to the mirror. The majority of grains remaining after washing had planar faces. It appears that wash solutions find it difficult to penetrate between the planar grain face and the mirror to attack the cement, hence the surface remains soiled.

Several methods for removal of the soil are recommended. The most critical aspect is to remove the grains before cementation and chemical bonding can begin. The best solution appears to be to clean the mirrors with an air jet or by use of ultrasonic vibrations before a wetting/drying cycle occurs. Reduction of surface reactivity would help as would the incorporation of operational strategies designed to minimize exposure of the mirrors to wetting in the first place.

A number of problems still need to be resolved. These are discussed in the last section of this report.

STATEMENT OF PROBLEM

Utilization of solar energy in an economically competitive manner for large scale generation of electricity depends in part upon efficient reflection of the solar energy from mirrors. Freshly installed mirrors exhibit a high spectral reflectance in the visible, but it has been found that exposure to field conditions in arid regions (quite possibly in any region) can cause up to a 10% decrease in reflectance in as little as 21 days. This decrease, which becomes progressively more pronounced with time, is considered to be unacceptable and must be eliminated.

The reflectance decrease has been ascribed to the accumulation of dust on the mirror surfaces. Studies by the McDonnell Douglas Astronautics Company (MDAC) and subcontractors indicate that it is not possible to remove the soil to a sufficient degree using moderate pressure spray systems and a wide range of commercial cleaning agents.

The objectives of the study reported here have been to

1. identify the composition and physical characteristics of the soil
2. determine the mechanism(s) responsible for the soil and the apparently strong adherence to the mirror
3. suggest methods to either prevent soiling or to remove the soil once formed.

APPROACH

Soiled mirrors measuring 5"x5" were supplied by MDAC for study. The mirrors were either second surface glass mirrors or second surface glass mirrors with a protective acrylic first surface. Natural soiling of the mirrors was accomplished by leaving the mirrors in test racks on the sites for approximately six weeks or two years. To provide specimens early in the project, mirrors were artificially soiled by driving a truck upwind of a rack containing premoistened mirrors. Most natural and artificial mirrors were studied as received from the field, although some were cleaned with a deionized water rinse from a laboratory squeeze bottle or with commercial cleaners of undisclosed composition. Descriptions of the samples are given in Table I.

Initially, it was planned to study the soil using optical, scanning electron microscope (SEM) with EDAX, electron microprobe, X-ray diffraction, and atomic absorption techniques. However, early in the program it was found that the most effective combination of techniques was SEM/EDAX, optical microscopy and X-ray diffraction (XRD) spectrometry. Accordingly, project resources were concentrated on these techniques.

TABLE I

TEST MIRRORS

Sample Number	Mirror Type	Location of site	Type of Soil	Exposure Length (days)	Treatment
FG-1	Glass	Daggett, CA	Artificial	<1	None
FA-2	Acrylic	Daggett, CA	Artificial	<1	"
DG-1	Glass	Daggett, CA	Artificial	<1	"
DA-23	Acrylic	Daggett, CA	Artificial	<1	"
DG-37	Glass	Daggett, CA	Artificial	<1	"
DA-80	Acrylic	Daggett, CA	Artificial	<1	"
DA-25	Acrylic	Daggett, CA	Artificial	<1	"
AG-08	Glass	Albuquerque, NM	Artificial	<1	"
AA-18	Acrylic	Albuquerque, NM	Artificial	<1	"
DG-20	Glass	Daggett, CA	Natural	≈45	None
DG-21	Glass	Daggett, CA	Natural	≈45	"
DNG-1A	Glass	Daggett, CA	Natural	≈45	Deionized H_2O rinse
DAN-1	Acrylic	Daggett, CA	Natural	≈45	
AAN-1	Acrylic	Albuquerque, NM	Natural	≈45	"
AGN-1	Glass	Albuquerque, NM	Natural	≈45	"
ADO	Glass	Daggett, CA	Natural	≈45	None
RDF-1	Glass	Daggett, CA	Natural	≈45	Finally on surfac
DG-31	Glass	Daggett, CA	Natural	≈45)	Washed with unknown cleaning agents
DG-32	Glass	Daggett, CA	Natural	≈45)	
DG-33	Glass	Daggett, CA	Natural	≈45)	
63-24	Acrylic	Ft. Irwin, CA	Natural	≈700	None
50-3	Glass	Ft. Irwin, CA	Natural	≈700	"

A. SEM/EDAX Investigations

Test mirrors were cut into small fragments with a glass cutter, mounted on the standard holder and carbon coated. Physical characteristics of the soil were determined by visual observation of the display photographs. Approximate chemical compositions were determined by analysis of electron-generated X-rays with an energy dispersive multi-channel solid state detector and recording system (EDAX). The mineral identification of a particular soil particle was made by comparing the relative peak intensities of different elements for the soil particle to relative peak intensities of known minerals. An approximate match of intensities was interpreted to mean a similar mineralogy. In several instances visual observation of the particles being analyzed helped significantly in confirmation of mineral identity. The EDAX technique is only semi-quantitative because the slope of the grain surface affects the response of elements differently. Also, low atomic weight elements (e.g. C, N, O) cannot be excited by this method, and for the smaller grains the beam penetrated into the substrate so that the substrate contributed to the observed signal.

Both artificially soiled and naturally soiled mirrors were examined. Some of the naturally soiled mirrors were unwashed, others were washed. Samples analyzed were from Albuquerque, Daggett, and Fort Irwin. Magnifications up to 10,000X were used.

B. Optical Investigations

These consisted of two aspects: optical characterization; and grain adhesion experiments.

1. Optical characterization

The artificially soiled mirrors were examined under a binocular microscope at 3X, 30X, and 60X magnification for gross mineralogy and textural clues. The water drop residues (significance to be disucssed shortly) on the borders of the soiled acrylic mirrors were examined in transmitted light at 460X for shape, textural relations, index of refraction and birefringence of the grains. The water drop residues on the opaque mirrors were studied in reflected light using the metallographic attachment at 100X. By using index oils without coverslip, the mean index of refraction could be determined. The index of refraction of the individual rays could not be determined because the mirrors were too big to rotate on the stage and the polarizing accessory was not adjustable for this kind of work. The highest magnification could not be used with the reflecting attachment when the oil was uncovered. A naturally soiled mirror that had been cleaned with the standard wash was examined in transmitted light at 460X after removing the acrylic and metal backing from a fragment of the mirror.

2. Grain-adhesion experiments

Two minerals found in abundance on the mirrors, feldspar and montmorillonite clay, and common in desert areas were crushed and separated into 50, 10, 5, 1, and 1/2 micron sizes by settling through liquid in a burette. A 100 micron fraction was separated by sieving. Suspensions of each grain size were dropped on glass slides to simulate drops on solar mirrors. A polar (distilled water) and a non-polar (benzene) liquid were used for settling the grains to determine whether water is necessary for adhesion or whether small grain size alone causes adhesion. Half the slides were air dried at laboratory temperature; the other half were oven dried at $50^{\circ}C$ to simulate summer-desert temperatures. To test the nature of bonding, the slides were rinsed with a polar solvent (water and an ion-exchanger (1 molar NaCl), and an acid (3N HCl). The drops were examined microscopically before and after washing.

The above procedure was then applied to

- Dolomite - $CaMg(CO_3)_2$, a carbonate less soluble than calcite (or caliche) which might precipitate from CO_2-bearing dew or rainwater.
- Gypsum - $CaSO_4 \cdot 2H_2O$, a common mineral in arid regions and a likely constituent of atmospheric-borne deposits, considering the composition of the desert atmosphere (see Table II).

TABLE II

COMPOSITION OF PRECIPITATION AND AEROSOLS,
SOUTHWESTERN DESERT AREA

	Constituent	Concentration	Remarks
1. Precipitation (pH ≈6)			
	Cl^-	0.2-0.3 mg l^{-1}	Mojave, Arizona, New Mexico Junge (1963, p. 319)
	F^-	≈0.02	Valach (1967), indicating $Cl^-/F^- \approx 11$
	Br^-	0.003	Duce et al. (1965) Normalized to Cl^-
	I^-	0.001	"
	NO_3^-	1.3	Junge (1963)
	NH_4^+	0.1	"
	$SO_4^=$	2.0	"
	Na^+	0.8	"
	K^+	0.2	"
	Ca^{++}	1.5	"
	H_2CO_3, HCO_3^-, $CO_3^=$	≈1.0	" (mostly as H_2CO_3 and HCO_3^-)
2. Aerosols (Death Valley, Gillette and Blifford, 1971)			
	Cl	0.42 μg m^{-3} air	
	S	0.31	
	K	0.24	
	Na	0.21	
	Si	0.41	
	Ca	0.44	
	Ti	0.08	

References:

Duce, R. A., J. W. Winchester, and T. W. Van Nahl, Iodine, bromine and chlorine in the Hawaiian marine atmosphere, J. Geophys. Res., 70, 1775-1799, 1965.

Gillette, D. A., and J. H. Blifford, Composition of tropospheric aerosols as a function of altitude, J. Atmos. Sci., 28, 1199-1210, 1971.

Junge, C. E., Air Chemistry and Radioactivity, International Geophysics Series, vol. 4, Academic Press, New York, 1963.

Valach, R., The origin of the gaseous form of natural atmospheric chlorine, Tellus, 19, 509-516, 1967.

- Kaolinite - $Al_4Si_4O_{10} \cdot (OH)_8$, an inert clay that is reported to be 5 to 20% of southwestern desert clay-sized material. Montmorillonite ranges from 35 to 70% and illite ranges from 35 to 70% (Droste, J. B., Clay minerals in the playa sediments of the Mojave Desert, California, Calif. Div. Mines, Spec. Rpt. 69, 1961)
- Labradorite - $6CaAl_2Si_2O_8 \cdot 4NaAl_3Si_3O_8$, a calcium-rich feldspar less common in desert sands than microcline feldspar (KAl_3SiO_3). Comparison of labradorite with microcline might reveal differences between large univalent ions and smaller divalent ions in adhesion effects.

These additional tests were run to ascertain whether or not: carbonate is removed in an acid wash; gypsum can be removed by washing; inert clay responds differently than an expansive clay to wash solutions; and, a monovalent feldspar adheres differently than a divalent feldspar.

C. X-Ray Investigations

For the XRD studies, the entire soil coating on the mirror was utilized by scraping it from the mirror surface with a clean, sharp razor blade. Particular caution was taken to avoid removing any of the acrylic coating. After scraping, the mirrors appeared to be very clean. The soil scraped from the mirror was loaded into 0.3mm diameter glass capillary tubes and mounted into 57 or 114 mm diameter X-ray diffraction film cameras. The samples were irradiated with Cu radiation (40kv, 15ma) for 3 or 15 hours depending on camera diameter, and the film was developed by conventional techniques. The relative peak intensities and peak spacings were measured on a Nonius microdensitometer. Identification of minerals in the mirror soil was made by comparing the peak spacings and intensities of the mirror soil film patterns to those of known mineral samples and published standard patterns. In most instances, two or more of the most intense peaks were required to be present before a mineral presence was recorded; a single peak was generally not considered to indicate presence of a mineral. A crude estimate of relative mineral abundance was made by comparing the microdensitometer readings for the most intense peak of each mineral; the strongest, most intense line was assumed to represent the most abundant mineral. The detection level for a mineral in the bulk mirror soil is assumed to be approximately 5%.

RESULTS

The loss of spectral reflectance is largely due to two classes of soil on the mirror surface: abundant discrete grains of common minerals and plant debris and less abundant intergranular cement. Artificially soiled mirrors have only discrete mineral grains on the surface and the adhesion of grains is primarily size dependent, increasing with decreasing grain size. This was demonstrated quite clearly in the grain adhesion experiments where grains of various sizes were fluid-deposited on glass substrates. Difficulty in grain removal increased with decreasing grain size, a result which is not at all surprising. Naturally soiled mirrors have both discrete mineral grains and cement with the relative abundance of cement increasing with the length of exposure time to the environment.

The mineral grains on the mirrors are very small with most in the micron to ten's of microns range. Investigations of naturally and artificially soiled mirrors indicates that the grain size differs greatly between the two types of soiling. Natural soil particulates typically range from 1 to 25 μ in diameter with most grains in the 1 to 5 μ size range. Artificial soil, however, typically ranges from 10 to 90 μ with many grains in the 30 to 40 μ range. The much larger grains on artificially soiled mirrors, especially in light of grain size dependent adhesion studies reported below, indicates that the artificially soiled mirrors are not sufficiently similar to naturally soiled mirrors to warrant use. Artificially soiled mirrors were studied only in enough detail to substantiate that the soil was roughly similar in mineral composition and distribution on the mirror surface to natural soil.

The grains on the mirror surface are of widely varying composition with more than 13 different minerals being recognized (Table III, IV and V). Quartz, feldspars (k-feldspar and plagioclase) and micas (muscovite, biotite, chlorite) are by far the most abundant minerals; however, clay minerals are identified in a few samples and their presence is suspected in many more, particularly among the fines. These fines are tabular and stacked at the edge of drops (see below) or stuck to the faces of large grains (Figure 1). Montmorillonite appears to be the most common clay, but the presence of illite and kaolinite is suggested. Other minerals such as sphene, apatite, rutile, alunite, zircon, and barite are far less abundant than any of the above minerals.

The major evidence that the clay minerals may constitute a very significant portion of the fines (<10 μ diameter) comes from the optical studies. The fines do not dissolve in the index oil. The fines are both equant and capsule shaped. The shapes are identical in the Daggett and Albuquerque samples, in wetted beach sand, and in a sample of wetted montmorillonite clay. The fines on

TABLE III

MINERALOGY OF SOIL ON MIRRORS BY SEM/EDAX COMPOSITION DETERMINATIONS*

(Figures indicate the number of grains of the specific mineral or mineral class identified and analyzed)

*Grains like carbonate or sulfate observed but not analyzed.

Mirror Number	Quartz	K Feldspar	Plagioclase	Muscovite Biotite Chlorite	Hornblende	Clays	Fe-Ti Oxides	Trace & Unknown	Cement			Total	Glass
									Calcite	Sulfate (Gypsum)	Halide (Sylvite & Halite)		
NATURAL SOIL													
Ft. Irwin, CA													
Unknown		1										1	
63-24 (acrylic)		3	1	1		1	2	1	3	2	1	15	
50-3	5	1		1	3	1		1 Sphene	3	3		18	11
Daggett, CA													
DNG-1A	1			1	2			1 Apatite 2		1		8	
DAN-1	1			2	2			1 Barite				6	1
ADO-1	4	5	12		1	5		1 Apatite 1	1	1		31	6
RDF-1	6	3	3	3		5		1	11	5	5	42	4
Albuquerque, NM													
AGN-1			1		1			1 Barite	*	*	3	6	5
AAN-1	1		2			6		1 Rutile	*	2	5	17	1
ARTIFICIAL SOIL													
Ft. Irwin, CA													
FG-1	1	1				1		4				7	
FA-2	3			1	1		1		1			7	
Daggett, CA													
DA-80	1	2	2	1			1	1 Apatite	1			9	7
DA-25	4	5	13	1		5			1			29	
Albuquerque, NM													
AG-08	1	5	2					1				9	6
AA-18	1	2	1			1						5	

TABLE IV

MINERALOGY OF MIRROR SOIL BY X-RAY DIFFRACTION METHODS

	Minerals in Decreasing Abundance*					
Mirror #	1	2	3	4	5	Unknowns?
Artificially Soiled						
DA-23	Quartz	Feldspar				Yes
DG-1	Quartz	Feldspar				No
DG-37	Quartz	Feldspar	Micas**			Yes
Naturally Soiled (45 days)						
DG-20	Quartz	Calcite	Feldspar	Micas		Yes
DG-21	Quartz	Calcite	Feldspar	Micas	Gypsum	Yes
Naturally Soiled (≈700 days)						
50-3	Calcite	Quartz	Feldspar	Micas		No
Naturally Soiled (45 days) and Washed						
DG-31	Quartz	Feldspar	Calcite	Micas	Kaolinite	Yes
DG-32	Quartz	Feldspar	Micas	Calcite		Yes
DG-33	Quartz	Feldspar	Calcite	Micas		Yes

*Blanks indicate no other mineral identified. X-ray diffraction peaks from unknown minerals are very weak and mineral abundance is considered to be very low.

**Micas are probably much more abundant than shown in this table, high abundance havin been observed optically. It may be that the orientations of the mica flakes made it difficult to observe their X-ray patterns.

TABLE V

MINERALOGY OF MIRROR SOIL BY OPTICAL STUDIES

Minerals	Albuquerque (AA-19)	Daggett (DA-20)	Daggett (DG-36)
Quartz	76%	64%	34%
Feldspar	17	13	24
Mica, Chlorite, Hornblende, etc.	4	17	40
Tourmaline, Apatite, Zircon, etc.	2	3	tr.
Fibers	1	3	2
Opaques	0	0	0
	100%	100%	100%

AA-19 - Artificially soiled, acrylic mirror, not washed

DA-20 - Artificially soiled, acrylic mirror, not washed

DG-36 - Naturally soiled, glass mirror, standard wash the unwashed Daggett mirrors were of two types: 1) larger specks, about 5 microns, with a mean index of refraction of 1.57 and a birefringence of about .02-.04; and 2) more numerous smaller fines, about 2 microns, with a mean index of refraction of 1.54 and a birefringence between .02 and .05. The fines on the Albuquerque mirrors were of the same two types: 1) larger fines, 5 to 10 microns, with a mean index of refraction of 1.57 and a birefringence between .02 and .05; and 2) more numerous smaller fines, 2 to 5 microns, with a mean index of refraction of 1.54 and a birefringence between .02 and .05. The fines on the naturally soiled mirror of Fort Irwin were of three types: 1) larger crystals, about 10 microns, with a mean index of refraction of 1.52; 2) fines, about 2 microns, with a mean index of refraction of 1.47; and 3) exceedingly tiny fines that were too small to determine. The fines on the washed mirror at Daggett were of four types: 1) brown flakes, about 10 microns, with an index of refraction slightly greater than 1.585; 2) rounded grains, about 10 microns, with an index of refraction slightly less than 1.555; 3) angular chips, about 5 microns, with an index of refraction between 1.575 and 1.555, with moderate birefringence (this is the chief constituent, about 75%); and 4) tiniest fines, about 1 or 2 microns, attached as a plaque on other grains, with white interference colors that indicate extremely high birefringence, and lowest index of refraction less than 1.495 (these fines are less than 10% of the total). Of the 1200 or more minerals and inorganic salts listed in the U.S.G.S. Bulletin 848 and the Handbook of Chemistry and Physics, only about 30 have all these: 1) an index of refraction between 1.53 and 1.55, 2) a birefringence between 0.015 and 0.06, and 3) a composition of common elements. Of these the most likely candidates by far are the clays, particularly those of the montmorillonite group and illite series, which are known to be relatively abundant in desert regions.

Examples of various grain species observed with the SEM are shown in Figures 2 through 5. Examples of EDAX analyses are given in Figures 6 through 8.

The relative abundances of all minerals are in approximately the same proportions as would be found in the ground surface materials. Hence, it is believed that the largest proportion of mirror soil is simply wind-carried mineral grains from the ground surface of soil or bedrock.

The mineral grains are not regularly distributed on the mirror surfaces. Typically the mirror surfaces have ovoid to irregular concentrations (referred to as "drops") of grains with approximately 30% fewer grains between the "drops" (Figure 9). These "drops" are generally less than 0.5 cm in diameter and more poorly formed on acrylic surfaced mirrors than the 0.5 cm or larger "drops" on glass surfaced mirrors. The "drops" often show faint internal structure with the smallest grains concentrated near the edge and larger grains toward the inside border of the "drop".

Experiments with finely ground feldspar, montmorillonite and other minerals indicate that the "drop" of grains results from the beading up of water on the mirror surface. Surface tension of the water drop tends to draw the smaller grains toward the drop edge whereas larger grains are stranded nearer the center. Once the water evaporates, the grains define the shape of the water drop, hence the "drop" of grains. Acrylic surfaced mirrors tend to have smaller and less well defined "drops" because the water does not form large beads on the mirror surface.

The formation of water drops with suspended mineral grains is a critical stage in mirror soiling, because after evaporation of the water, the grains adhere tightly to the mirror surface. Further confirmation of this is provided by the grain adhesion experiments where droplets containing mineral grains, when deposited on a glass substrate and the fluid allowed to evaporate, left a residue of small particles concentrated at the boundary of the original droplet. These particles were extremely difficult to remove and upon removal almost invariably left a residual soil.

The adhesion of small mineral grains to the mirror surface as "drops" or isolated grains after wetting and drying gives the mirror a "memory". When water is applied a second time, it draws up into beads that conform to the "drops" of mineral grains formed previously, or draws up around isolated mineral grains. Evaporation of the water from the second, and subsequent, wettings does not modify the grain distribution except probably in cases of prolonged precipitation or water freezing.

Evaporation of the water from the mirror surface causes precipitation of dissolved chemical species in the rain or dew. Although the amount of dissolved species is not great in natural precipitation (Table II), the repeated formation of water beads around the grain "drops" or isolated grains means that soiling materials accumulate primarily in these areas, not all over the mirror surface. Therefore if precipitates do form they should be concentrated near grains and should have chemical compositions of the materials dissolved in precipitation.

Naturally soiled mirrors with as little as six weeks exposure to precipitation and evaporation show moderate build-up of precipitates. Around the edges of grain "drops" (Figure 10), precipitates cement the grains together and form an arcuate pattern that forms psuedomorphs of the grain "drop". The concentration of precipitates near the water bead edges is what is expected if the precipitate formed during evaporation of the rain or dew. Isolated grains also have small spherules of precipitate covering the exposed surfaces. When these grains are turned over, the small spherules are found on the grain surface next to the mirror and on the mirror surface as well. Although the small size of these spherules prevents accurate chemical composition or optical microscope identication, they appear to be identical to the precipitate formed at the edges of "drops".

The precipitates are composed of chemical species abundant in rain and dew, i.e. cations of calcium, sodium and potassium and anions of sulfate, carbonate and halides. Unstable species such as NH_4^+ and NO_3^- were not found or expected because of their easy chemical breakdown or dissolution. The exact mineralogical identification of some precipitates is not possible in most cases because they are not abundant enough to be detected by X-ray diffraction methods. Only calcite was routinely identified by X-ray studies; gypsum was identified in only one instance. However, tentative mineralogical identification of other precipitates can be made by noting which chemical species are characteristically associated. For instance, when sulfur was present, calcium also was present; therefore the mineral is assumed to be gypsum ($CaSO_4 \cdot 2H_2O$), a common mineral in arid environments. Similarly the association of sodium and potassium with chlorine suggests the presence of halite (NaCl) and sylvite (KCl).

The mineralogical composition and abundance of precipitates apparently varies with length of exposure. Artificially soiled mirrors with less than one day exposure do not have any observable precipitate, and calcite possibly of wind-blown dust origin is of very minor amount (Table III). Naturally soiled mirrors with approximately six weeks exposure have readily observed precipitates (Figure 10) that are identified as calcite, gypsum, sylvite and halite in approximate order of decreasing abundance (Table III and IV). Calcite has become so abundant on these naturally soiled mirrors that it is apparently more abundant than all wind-borne grains with the exception of quartz. Gypsum is occasionally so abundant that it can be detected by X-ray methods (Table IV). Differences in precipitate composition between sites in California and New Mexico are apparent with halides being more abundant in New Mexico sites and calcite in California sites. However, the sampling size is not sufficient to determine whether or not this difference is statistically significant.

Prolonged exposure for up to two years results in the loss of much of the highly water soluble cements (Mirrors 63-24 and 50-3). Halite and sylvite are of major abundance, gypsum is relatively abundant (as indicated by the SEM/EDAX results), whereas calcite is the most abundant cement and is apparently more abundant than all other wind-blown grains (Tables III and IV). The predominance of calcite on these mirrors is to be expected because it is the least soluble of the cements. The loss of the more water soluble cements during the two year exposure may be due to longer-lived rain events during the two year period than during the six week period; however, no substantive data could be assembled to support this speculation.

Prolonged exposure may also induce other changes in the nature of soil materials or possibly the mirror surface itself. High magnification of two year old mirror surfaces from Fort Irwin has revealed the presence of minute spherules and rhombohedral shaped crystals across the entire mirror surface. This is shown in Figures 11 through 13. These show progressively greater magnification. The tiny grains are too small to be analyzed, but the suggestion from visual observation is that they may be calcite. The presence of these grains is potentially important since they affect reflectivity and may represent a long-range problem not previously recognized.

GRAIN ADHESION MECHANISMS AND MIRROR CLEANING

Several mirrors (DG-31 through DG-33) that had been washed with commercial cleaners were examined by X-ray, SEM and optical techniques to determine what remained on the mirror surface. Washing removed essentially all of the largest particles, particularly minerals like quartz which do not have planar surfaces. However, isolated small grains were still present and the edges of the grain "drops remained clearly observable. Optical microscope observations of the cleaned surfaces revealed that the remaining particulates were predominantly planar or tabular grains of biotite and other micas, with the remainder of the grains consisting of quartz and feldspar. The continued presence of clays was suggested. The X-ray studies also showed an increase in micaceous minerals, but not as strongly as the optical methods, probably because of the reason given in Table IV.

The cement or precipitate remaining on the mirrors is much less than on the unwashed mirrors. X-ray and optical analysis of the washed mirrors suggests that sulfates and halides were completely removed. Calcite is largely removed and becomes such a minor phase that it is barely detectable in some instances (DG-32). But the presence of minor calcite cement is considered to be very significant in causing spectral reflectance losses which are not recovered by the washing. A number of mineral grains were carefully removed from the washed mirror surfaces. Their removal revealed the presence of minute white specks on the bottom of the grains and on the underlying mirror surface. These specks have the optical characteristics of calcite and it appears that the calcite acted to cement the grains (predominantly planar and mostly mica, also possibly clay to some extent) to the surface. This cement was protected from the wash solutions by the grains. Planar grains of the micas (also clays) are preferentially resistant to removal by wash solutions because the wash solutions cannot effectively penetrate the narrow planar gap between the grain and the mirror surface to dissolve the cement. This can be generalized to say that any mineral grain with perfect cleavage, of which the micas are a classic example, and/or of sheet structure (which includes the clays) will be difficult to remove from a polished surface, especially when cemented to the surface. The residual edges of grain "drops" on washed mirrors thus appear to be due to the progressive concentration of grains and cement in these locations through exposure to repeated rain and dew events.

The following scenario thus evolves. When the mirrors are initially exposed to the environment, dry deposition of wind-borne grains occurs. These grains are loosely held to the mirror surface, probably because of electrostatic forces and in the case of planar grains by van der Waals forces also. The grains should be easily removable at this point.

The critical step toward the formation of strong adhesion comes when the surface first becomes wet from rain or dew. Grain adhesion studies, after water evaporation, show that the adhesion is grain size dependent. Grains 10 μ diameter or smaller adhere rather strongly. However, the bonding after initial wetting and drying is generally not strong, being mostly of the electrostatic and/or van der Waals variety. Some chemical bonding of clays to the surface could occur between the OH of the glass or acrylic surface and cations of the clay. It does not appear that cement derived from dissolved chemical species in rain or dew or from solution of grains is a significant factor at this stage because cements are not generally observed nor is there any indication of etching or partial dissolution in the controlled laboratory studies.

After the first wetting the smaller grains are re-deposited mostly around the border of evaporated drops, producing higher concentrations in these areas. Repeated wetting and drying cycles result in the accumulation of chemical cement in the grain "drops" and around isolated grains. This is due to the tendency of drops to form at the same sites as the relict drops and hence the cement concentration increases from the repeated evaporation of dilute solutions. The formation of these cements means that the grains are now chemically bonded to the mirror surface. At this point the cleaning problem has become quite severe,

It may be possible to find a cleaning technique that will suffice and be cost effective even when the most severe stage of adhesion is reached. Certainly the use of an HF solution which attacks the mirror surface and silicates directly could solve the problem. But this does not appear particularly attractive because of environmental concerns and since removal of the planar flakes through destruction by HF attack will inevitably cause severe degradation of the mirror surface. Our grain adhesion experiments showed that small grains of calcite (and dolomite) can be dissolved with a prolonged HCl wash, calcite more quickly than dolomite. The experiments also showed that the halides are readily removed by distilled water and that gypsum, a moderately soluble sulfate, was easily removed by an NaCl wash. However, the major problem is chemical bonding of the planar grains to the surface. The amount of cement required to cause this problem does not appear to be great because as little as 45 days exposure of mirrors DG-31 through DG-33 resulted in soiling that could not be removed by any of the commercial cleaners.

Removal of soiling after the initial wetting/drying cycle looks more attractive. A critical aspect at this stage is to reduce the chemical reactivity of the glass surface. The partial chemical and electrostatic bonding most likely involves hydroxyl groups on the mirror surface. Deactivation of the reactive sites should help eliminate the adhesion. The role of reactive sites in glass is supported by the observations that acrylic-coated mirrors are generally somewhat cleaner than glass mirrors with the same exposure time. Additionally, a glass mirror (RDF) treated with "FINALLY", a commercial "soil preventer" of undisclosed composition, was considerably cleaner than untreated glass mirrors. With reduction of surface chemical reactivity, solutions such as HCl or NaCl, or simply distilled water, could well be effective at this stage of the adhesion process.

However, from the viewpoint of ease with which soil can be removed the first stage is most attractive, that is before any surface wetting has occurred. The grains at this stage should be easily removed by compresssed air, especially if the mirror surface has been treated to reduce surface electrical charges. An alternative approach would be to vibrate the mirror ultrasonically, sweeping in frequency to achieve resonances. The ultrasonic technique could well suffice after the first wetting/drying cycle. If air cleaning is used, this could be followed by a distilled water wash after the wetting/drying event. Techniques such as these require that cleaning cycles be dictated by weather conditions rather than scheduled on a regular calendar basis.

The critical problem is allowing the mirrors to become wet from rain or dew in the first place. It is not possible to prevent the mirrors from becoming soiled by dry deposition, but this deposit can be removed with relative ease, as described above. However, it is possible to prevent the mirrors from becoming wet, or at the very least to greatly reduce the amount of wetting. The only thing this involves is proper prediction and monitoring of weather conditions combined with suitable changes in mirror orientation, possibly with the addition of some nocturnal heating when dew is predicted.

CONCLUSIONS

The chief conclusions of this study are:

1. The "soil" on naturally soiled mirrors consists of wind-blown grains and chemically precipitated cement.
2. The wind-blown grains are 1 to 25 μ in diameter with most in the 1 to 5 μ range. Mineralogically there are at least 13 common and accessory silicate and non-silicate minerals present which are derived primarily from the local and regional area. The grains are initially held to the surface by electrostatic and/or van der Waals forces.
3. The sub-10 μ wind-blown grains adhere firmly to the mirror surface after the first wetting/drying cycle and form a "memory" for later wetting/drying cycles. Bonding is still electrostatic and/or van der Waals to an extent but some degree of chemical bonding is probable, particularly with respect to the clays.

4. Repeated wetting and drying cycles of natural rain and dew form grain "drops" which results in a gradual build-up of chemical precipitates from the rain and dew, and from soluble grains. The chemical precipitates are calcite, gypsum, halite and sylvite. The resulting "cement" chemically bonds the wind-blown grains to the mirror.
5. Removal of chemically cemented grains is difficult since the majority of these grains have planar faces which makes it very hard for cleaning solutuion to penetrate along the contact and dissolve the cement.

RECOMMENDATIONS FOR FUTURE STUDIES

Significant problems remain in the study of solar mirror soiling. Some of these are:

1. The number of wetting and drying cycles required for significant cement formation is unknown. Removal of grains before cement formation will probably be less costly economically and environmentally, however it would be uneconomic to remove the grains before every wetting/drying cycle. Therefore a series of tests should be run on mirrors at various sites with a complete recording meteorological station to determine how many wetting/drying cycles are allowed before cement formation causes a significant bonding of grains to the mirror surface. The meteorological data would also be necessary before any estimates of frequency of mirror cleaning can be made.
2. The effects of long term exposure of mirror surfaces are unknown. One mirror examined (50-3), exposed for 700 days, showed minute spherules and diamond or rhombohedral shaped crystals of unknown origin (Figures 11-13) which show that significant surface degradation has

occurred. Careful studies should be undertaken to determine whether these are forming from dissolution and precipitation of mirror materials or as epitaxial growth of chemical species dissolved in rain and dew.

Additional long-term studies should be undertaken to determine the effect of numerous washings on mirror surfaces and the relative effectiveness and effect on mirror surfaces of frequent washings with mild chemical solutions versus infrequent washings with very strong solutions.

3. Alternative methods of preventing mirror soiling should be investigated. One would be to test the removal of soil by compressed air or ultrasonic vibration before any wetting/drying cycles take place. Another, which could be done in conjunction with the first, would be to evaluate various methods of reactive site neutralization so as to lessen electrostatic or van der Waal's bonding of dry soil particles to the mirror surface. Neutralization of reactive sites should also be considered in conjunction with cleaning of natural soil after single and multiple wetting and drying cycles.

Figure 1. Plaque of minute grains of clay and/or salt deposits on a quartz grain. Daggett, naturally soiled glass mirror. 2900 X.

Figure 2. Cluster of gypsum crystals with typical parallelogram outline. These occur well inside a drop.

Daggett, naturally soiled glass mirror. 9000 X.

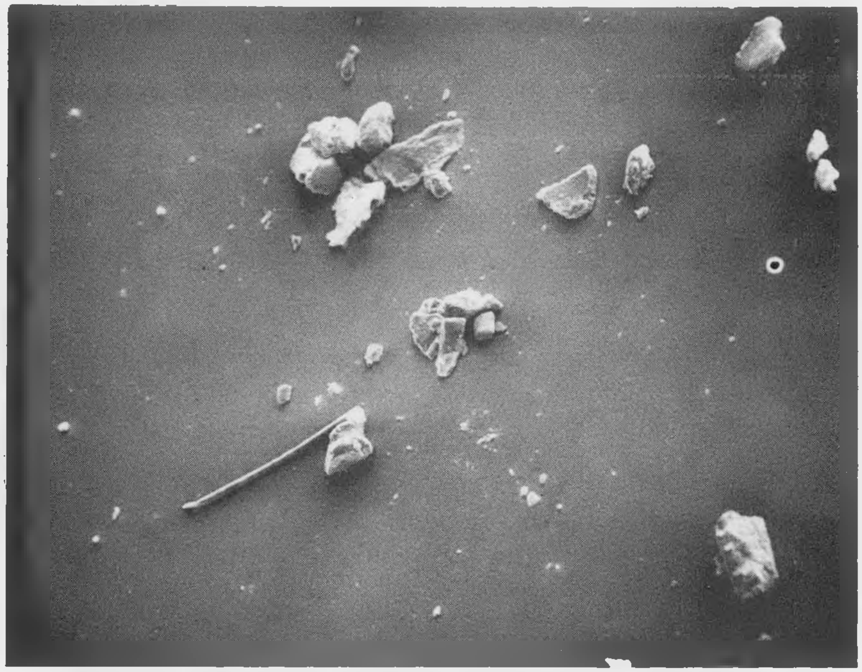

Figure 3. Wind-deposited grains. Note the preponderance of mica flakes. Daggett, naturally soiled glass mirror. 90 X.

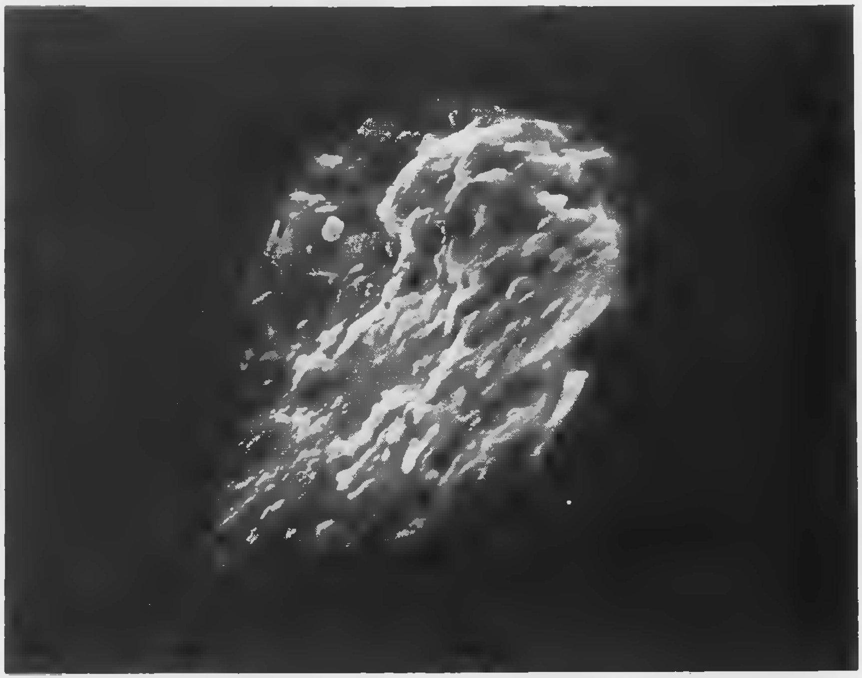

Figure 4. Tabular alumino-silicate grain with minute grains that adhere to its surface. Probably a mica, characterized by flaky habit. Albuquerque. 2800 X.

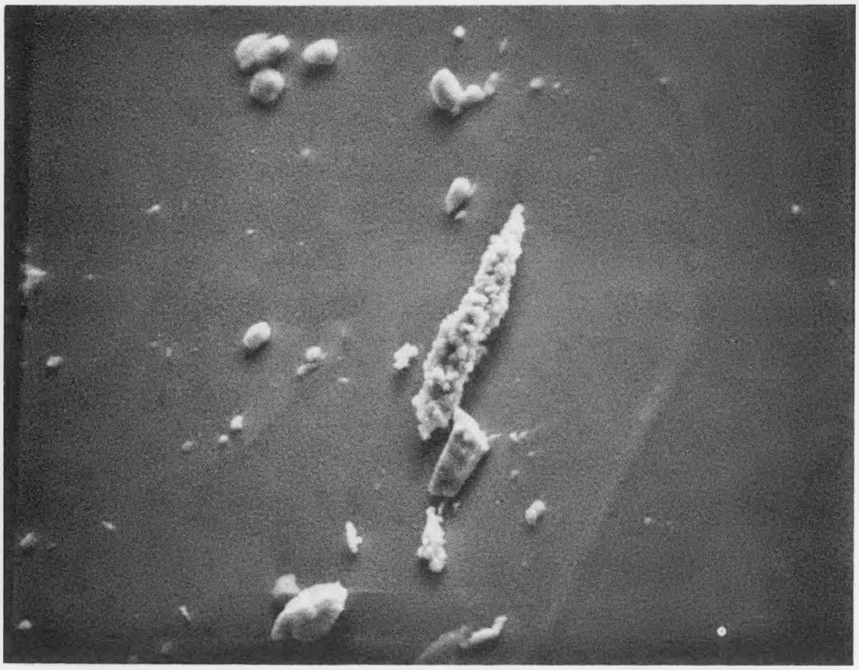

Figure 5. Two bladed crystals (center) are covered with a drusy crust of rhombohedral calcite but a tabular grain between them is not encrusted. Somewhat rounded-tetrahedral grains in the upper left are not encrusted.

Daggett glass mirror, naturally soiled, treated with anti-static, and washed. 2000 X.

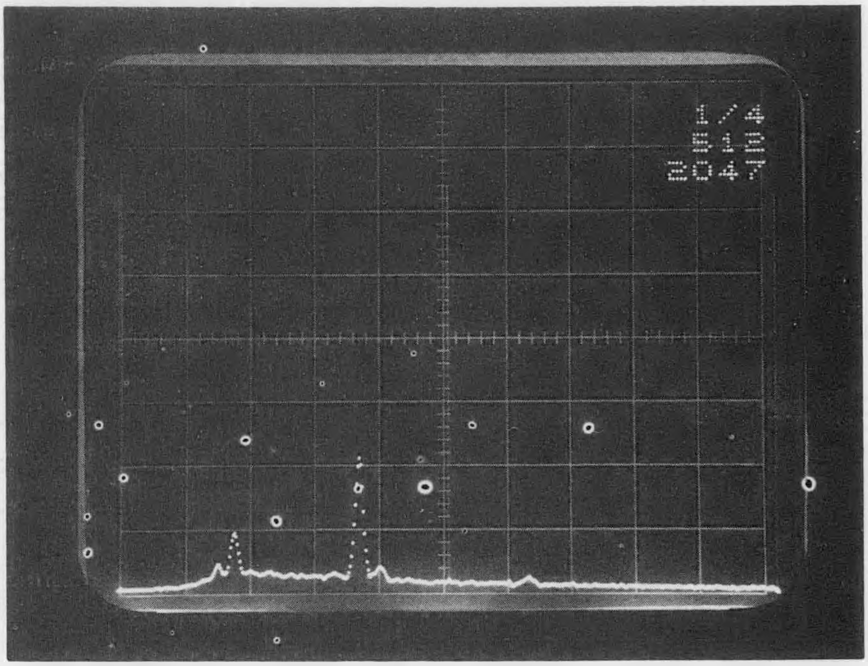

Figure 6. EDAX analysis of a calcite plaque on biotite showing the high Ca peak of 2.2 on a background of 0.3 Al, 1.0 Si, and 0.2 Fe.

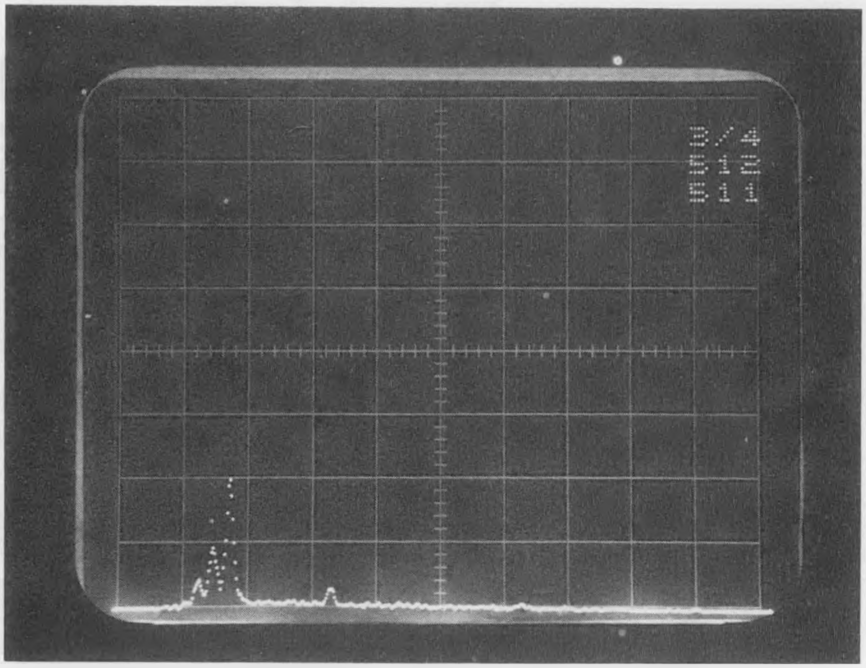

Figure 7. EDAX analysis of a typical alumino-silicate from Albuquerque. The composition: 0.3 Mg, 1.0 Al, 2.0 Si, 0.2 K, tr. Fe is typical of illite clay. Biotite is similar with more Fe.

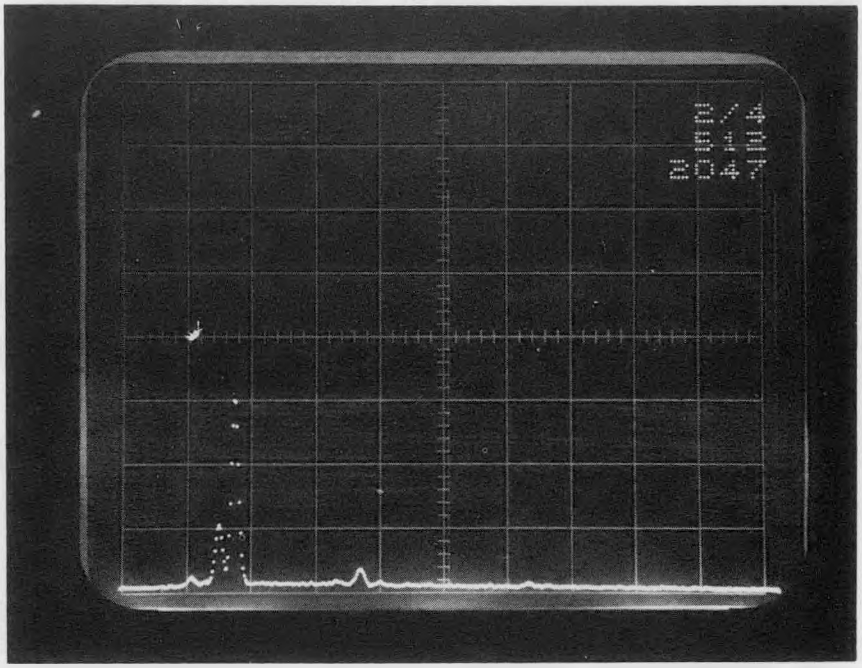

Figure 8. EDAX analysis of a blocky grain of plagioclase: 0.2 Na, 1.1 Al, 3.0 Si, 0.3 Ca.

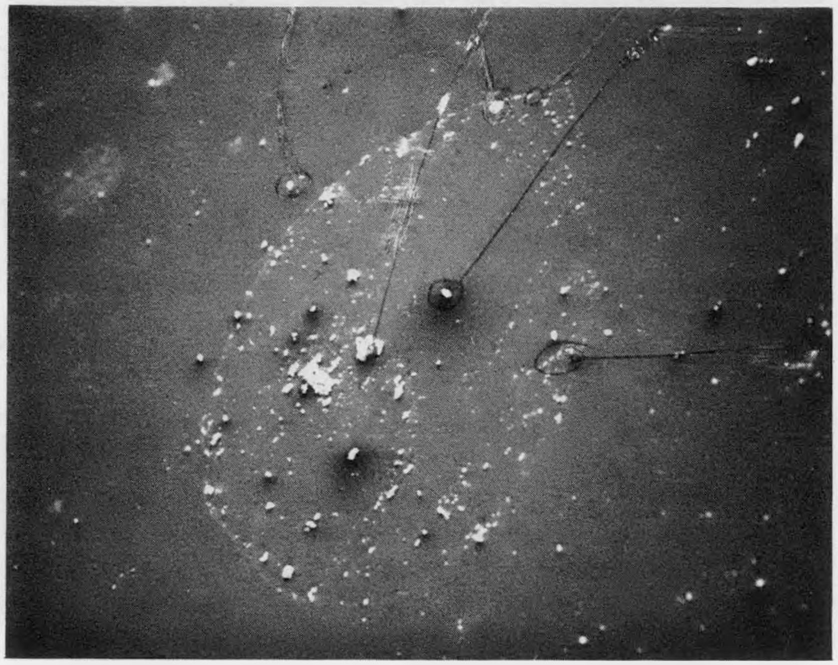

Figure 9. Drop outline showing the distribution of fine grains at the very edge of the drop.

Artificially soiled acrylic mirror from Albuquerque. 90 X.

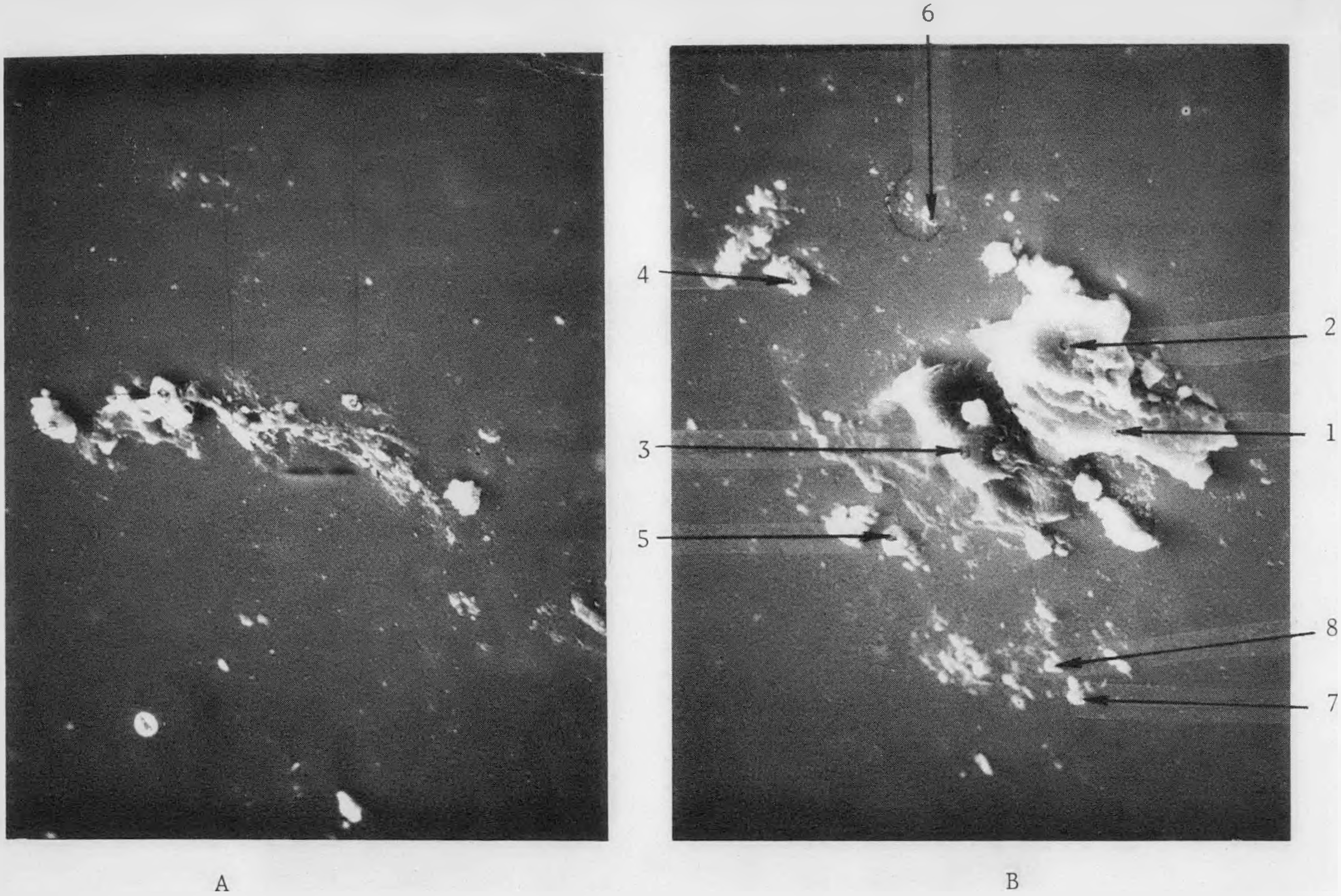

Figure 10.

A. Naturally soiled acrylic-surfaced mirror from Albuquerque (AAN-1) shows equant, angular mineral grains cemented to mirror surface with arcuate shaped mass of unknown precipitate (most likely to be calcite, gypsum or sylvite).

B. Naturally soiled glass mirror from Daggett shows mineral grains (#1, 2, 4 and 5) with solution etched crystals of gypsum (#3) acting as cement. Smaller grains such as #6 have compositions indistinguishable from glass whereas grains such as #7 and 8 may be clay minerals.

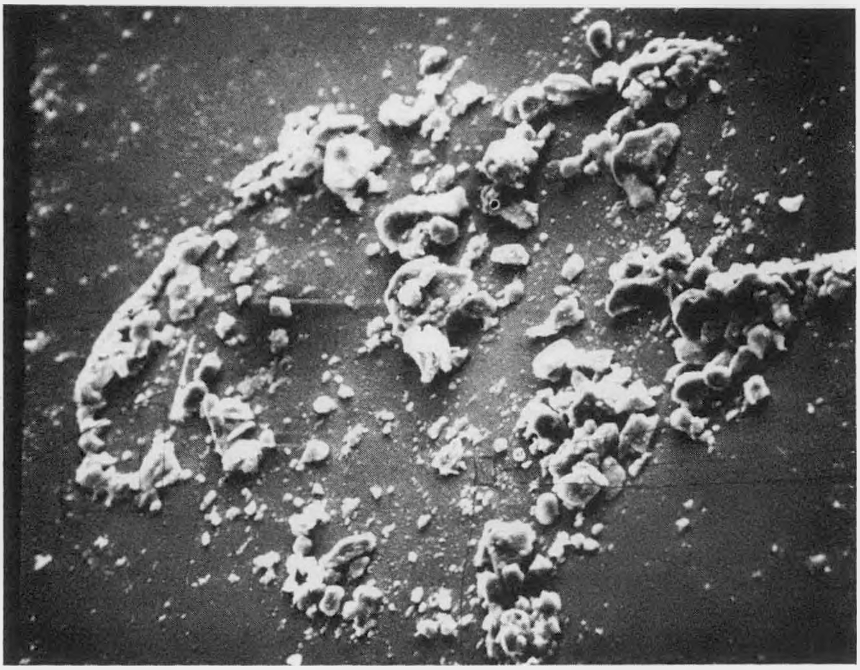

Figure 11. Aggregate of grains in drop-form on heavily soiled mirror. Note the merged grains on the left edge of the drop.
Fort Irwin glass mirror, naturally soiled and unwashed after two years. 360 X.

Figure 12. Close-up of the edge of the drop from the preceding photograph. Tabular crystals of gypsum are oriented normal to the drop border. The glass surface is covered with minute spherules. Fort Irwin glass mirror, naturally soiled and unwashed after two years. 2000 X.

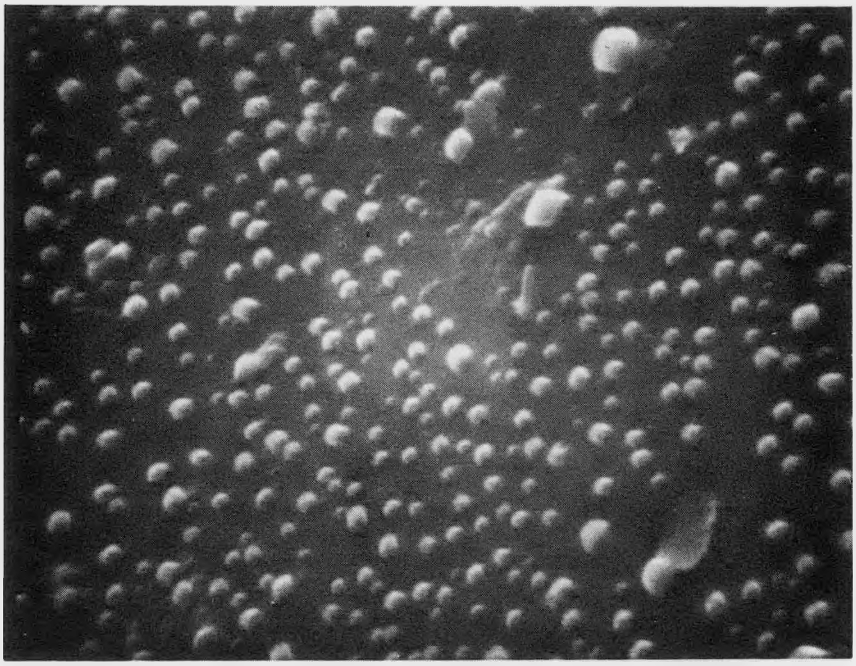

Figure 13. Close-up of the minute spherules from the preceding photograph. They are evenly spaced as if a precipitate or electrostatically controlled. Some grains (c.f. upper center) have a rhombohedral shape like calcite. An experiment has shown that solution growth of calcite preferentially forms a rhombohedral face.

Fort Irwin glass mirror, naturally soiled and unwashed after two years. 10,000 X.