

Total reflectance properties of certain black coatings  
(From 0.2 to 20.0 micrometers)

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Abstract

The total reflectance of certain black coatings which might be used as optical blacks has been measured at near normal incidence in integrating sphere spectrophotometers from 0.2 to 20.0 micrometers. Scanning Electron Microscope (SEM) pictures of some of the surfaces have been made. Some of the surfaces exhibit relatively constant spectral reflectance, but others show extensive spectral selectivity. Surface topography shows wide variations in structure and appears to correlate with reflectance properties. Renewed interest in the emissivity and absorptance of surfaces for thermal radiative transfer in cryogenics, space, solar applications, etc., has brought to bear technologies for measurement which were not practical in the early days of the space program. Two such technologies are SEM and integrating sphere spectrophotometers in the 2.5 to 20.0 micrometer range.

Introduction

With the increased sensitivity to optical radiation of electro-optical (E/O) guidance systems used by the military, the requirement arose for low reflectance surface treatments to control the problem of stray light or other forms of unwanted energy. Classical mechanical baffling is not possible in many cases, due to the size and weight limitations of these systems. The unwanted energy either must be absorbed at the surface of the various support structures or interfaces to prevent it from being reflected into the system. The unwanted energy can degrade system performance through 1) reduced signal-to-noise ratios, 2) loss of image contrast, and, in extreme cases, 3) complete masking of the primary optical signal.

Historically, paints, flocking velveteen, and some metal blackening processes, such as black anodize on modern camera parts, have been used, but no one single surface treatment has been developed that can satisfy all of the optical, thermal, electrical, and mechanical requirements typical of most E/O guidance systems. Consequently, many types of treatment are in use and more are under development.

This paper will report on the contributions that some of the more promising new treatments can make toward controlling unwanted optical energy in military guidance systems. Two basic surface treatments will be discussed. These are 1) treatments that are "painted on" and do not alter the substrate surface and 2) treatments that "alter" the substrate surface such as an acid etch or caustic anodize process. The thrust of this paper is to describe the utilization of several modified analytical techniques that are being used at Martin Marietta and to present the resultant data. Because of the complex nature of the surface analysis process, the equipment involved, and the limited number of samples available, no attempt will be made to interpret data presented. The samples on which data were taken are:

Bostic paint  
3M paint  
Denver paint  
Denver black anodize  
IBM tungsten

These were chosen as representative of the light absorbing surface treatments commonly used in industry, except for the IBM tungsten which is under development at Martin Marietta.

Equipment and analysis description

The equipment used to perform the surface analyses were a scanning electron microscope (SEM) and two types of spectrophotometers. By utilizing the magnifying power of the SEM to allow observation of the surface topography and spectral plots generated by the integrating sphere spectrophotometers, interesting comparisons and correlations can be made.

### SEM analysis and equipment

SEM analysis of the surface of the samples revealed information about some particular features: size, shape, and spatial density.

The photographs of the surfaces were taken with an ISI Alpha 9 microscope. This equipment provided SEM photographs of the sample surfaces at magnifications up to 5000X. Samples photographed at 1000X and at a 20 degree tilt angle appeared to provide the most clarity for obtaining topographical information.

The use of the SEM in this application requires some cautions. Normal SEM procedures cause considerable electrical charging of the sample's surface with a resulting loss of image contrast and resolution. Therefore, special techniques were required to prevent charging of the surface of some of the samples. Surface charging was reduced by operating the microscope at very low beam currents using a special pointed filament as supplied by the manufacturer, EBTECL<sup>2</sup>. Charging can be further reduced by using lower accelerating voltages on microscopes that offer this adjustment. The Alpha 9 has a fixed voltage of 15 KV. The painted surfaces (Bostic, 3M, and Denver Black) were sputter coated with 100 to 200 angstroms of gold-palladium. A coating of this thickness is undetectable by normal SEM techniques and does an excellent job of preventing surface charging. The anodized coating made by Martin Marietta Denver Aerospace was not sputter coated in order to prevent altering the sample. Special SEM techniques were not required on the IBM samples as their metallic surface did not exhibit any noticeable charging.

### Photometric analysis and equipment

A Willey 318S Fourier Transform Spectrophotometer<sup>3</sup> was used to measure the total reflectance of the surfaces from 2.0 to 20.0 micrometers. The samples were illuminated at near normal incidence and the reflected flux in all directions was registered by a HgCdTe detector in the wall of an integrating sphere. The photometric accuracy of the true double beam instrument is on the order of 1 percent over most of the spectrum. The peak instrument response is at about 10.0 micrometers and decreases with wavelength toward each end of the 2.0 to 20.0 micrometer region.

A Beckman 5270 spectrophotometer with an integrating sphere attachment was used to measure the total reflectance of the surfaces for the wavelength range of 0.2 to 2.0 micrometers. Over this spectral range, the measurements were taken in two segments - 0.2 to 0.8 micrometers using a photomultiplier detector and 0.8 to 2.0 micrometers using a PbS detector. The Beckman 5270 is a dual beam, double monochromator instrument with a photometric accuracy of less than 1 percent.

The data for each sample consisted of three separate spectral plots - two from the Beckman spectrophotometer and one from the Willey 318S spectrophotometer. These plots were digitized and the data fed into a computer for plotting. The computer's plotting routine does some data smoothing, but no loss of significant data was experienced.

### SEM photographic procedures

Experience at Martin Marietta in obtaining SEM photographs of these type surfaces is minimal and consequently no frame of reference was available to assist in choosing the best magnification and tilt angle to gain the most information. Therefore, a wide range of magnifications were tried as well as an equal number of tilt angles. Visual examination of many SEM photographs and comparisons to a variety of tilt angles indicated that a 400X picture at normal incidence and a 1000X picture tilted at 20 degrees with reference to the viewing axis appeared to reveal the most visual information about the surface topography.

### "Paint on " type surface treatments

The five paint samples, shown in Figures 1-5, were all sprayed by conventional methods onto aluminum substrates. One of the Bostic samples and the Denver black were the only samples sprayed over a chromated surface. These treatments do not alter the substrate surface.

### "Surface alteration" type surface treatments

In this type of treatment, the substrate is physically and/or chemically altered. Physical surface alteration is accomplished by sand blast, shot peen or, vapor hone. Chemical alteration may be by caustic or acid etching, and/or molecularly bonding of material, which is - the case of the IBM vapor deposition process where dendrites of pure metal are grown onto the surface after proper cleaning and etching preparations. Figures 6-8 depict representative surfaces of these types.

## Denver Black anodize 4,5

In this process the substrate (6061-T6 aluminum) is cleaned, vapor honed, sand blasted, cleaned, run through a standard commercial anodize process, and then sealed in a proprietary dye solution. It is then dried by proprietary methods to bring out the deep velvet black surface. This surface has some advantages over paint in that it will withstand higher temperatures, does not outgas, is chemically inert, and is more resistive than paint to certain environmental attacks. However, it is very easily damaged by touching or abrasion.

## IBM vapor deposition of Tungsten 6,7,8

The substrate in this process can be almost any material that can tolerate 400 degrees C. It can be deposited on all metals except aluminum and coats ceramics with ease. In a typical process, the substrate is cleaned, placed in a quartz retort, and then heated to 400 degrees C by an induction coil wrapped around the quartz retort. Hydrogen gas carrying minute traces of tungsten hexafluoride is then passed over the part. The pure tungsten plates out in 45 to 60 minutes. Dendrite size can be controlled to an extent. One may assume then that this process is capable of being fine tuned to meet the requirements of special spectral bandwidths. This phenomena has not been fully demonstrated but IBM has done some work, not reported, that appears to substantiate this assumption. The tungsten surface is unique among the other surfaces cited in that it is not an absorber, but uses the principle of multiple reflections to control the light. The metallic dendrites, under magnification, are multi-sized obelisks, much like a clump of Washington monuments. The light strikes a surface, is reflected down toward the base of the dendrite clump, where it strikes another dendrite and so on until it reaches the fine microstructure surrounding the taller dendrites and is finally totally physically trapped.

This surface holds great potential: it does not outgas, is chemically inert, and is the only surface tested to date that is fairly rugged to the touch. All the other surfaces tend to be damaged or reduced significantly in efficiency after being touched. Figure 8 is data of the dendrites "as grown". These seem to work best in the infrared (IR) wavelength regime. Figure 7 shows dendrites that have been grown and then given an IBM proprietary anodize treatment. This seems to make the surface work better in the visible wavelengths and may decrease its effectiveness at the IR wavelengths. IBM provided the two samples, therefore, no definitive statements can be made due to the limited amount of data. However, Martin Marietta expects to have a vapor deposition system ready by mid 1983, at which time work will be undertaken to fully characterize this interesting surface treatment.

### Data analysis

Figures 1-8 are a composite of information on each sample - a graph of the total reflectivity from 0.2 - 20.0 micrometers and two photomicrographs at 400 X and 1000X.

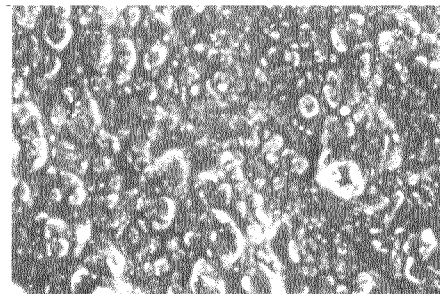
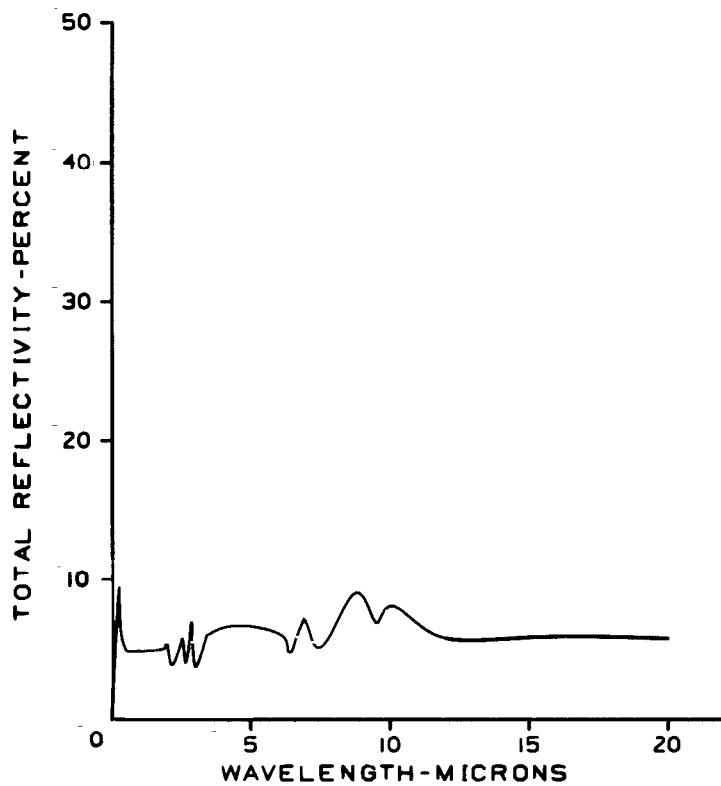
Figures 1 and 2 are both samples of Bostic 463-3-8 paint, however, Figure 1 is on bare aluminum and Figure 2 is on aluminum coated with ZnCr primer. Note the porosity and sharp roughness of the primed sample. The cause of this is not known at this time. Both curves are similar, showing a slight increase around 0.2 micrometers and 10.0 micrometers and excellent absorption at near normal incidence throughout the spectral range.

Figures 3 and 4 are samples of the discontinued 3M Nextel Black Velvet paint, so familiar in the optics industry, and the new 3M SCS-2200 paint that has been introduced by 3M as the replacement for the Nextel. The Nextel, like the Bostics, shows a slight increase in reflectivity around 10.0 micrometers, but otherwise has excellent absorption throughout the spectral range. The contrast in Figure 4 is dramatic. The reflectance region around 5.0 micrometers approaches a mirror-like quality, and additionally the rest of the spectral range is not as good an absorber as the other paints. The surface of the Nextel has the appearance of a variety of sizes of micro-balloons, whereas the SCS-2200 has the appearance of a highly crystalline surface with many flat faces.

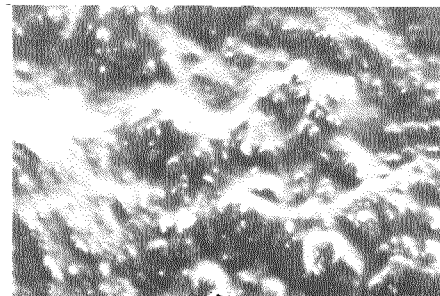
Figure 5 is the Denver Z306 paint that shows an excellent absorption throughout the spectral region. Its structure has the appearance of random "globs" of micro-balloons, but not as wide a variety of sizes as the Nextel sample.

Figure 6 is the Martin Marietta Denver Black, which is an alteration of the surface of the substrate instead of painted on surface. It is an anodize process, for aluminum only that is proprietary to Martin Marietta. At about 3.0 micrometers and again at around 5.0 micrometers, this surface has a significant reflection band. The surface has the appearance of an arid desert or dry lake bottom.

Figures 7 and 8 are of dendritic tungsten hexafluoride. This surface treatment is effective on all known metals except aluminum. Both curves have the same general shape, showing a significant absorption band at 10.0 micrometers, however, the interesting point is

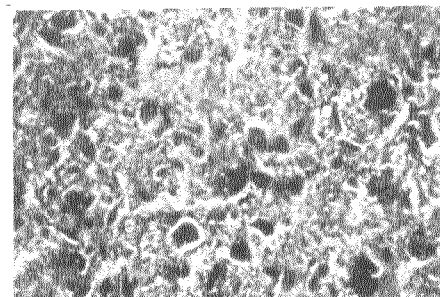
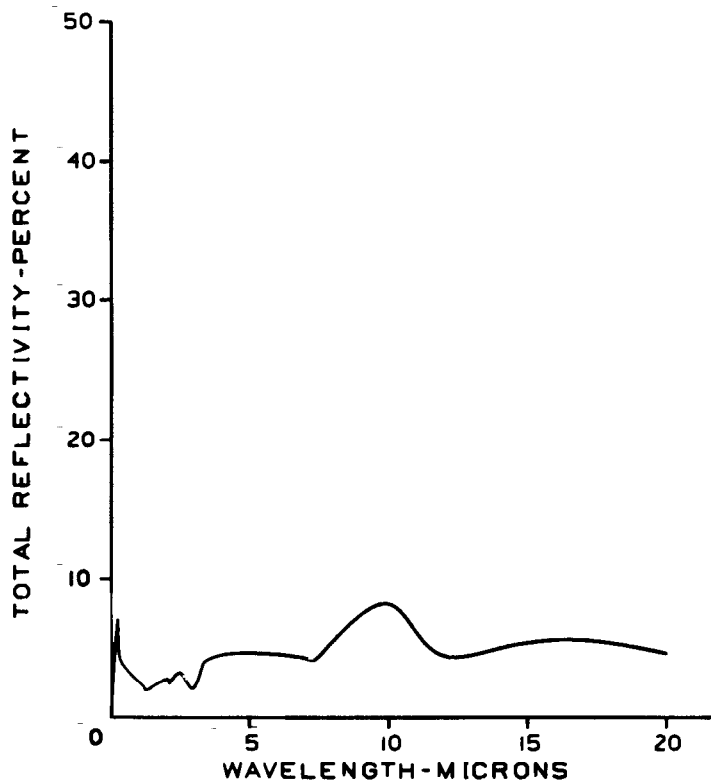


400X

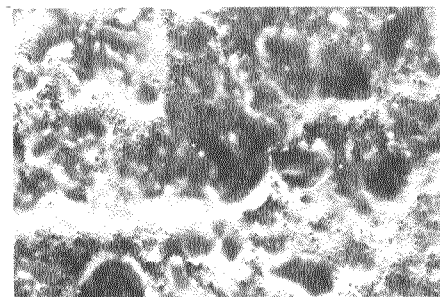


1000X

Figure 1. Paint-Bostic 463-3-8 on bare A.

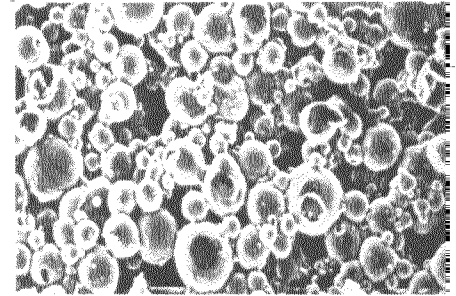
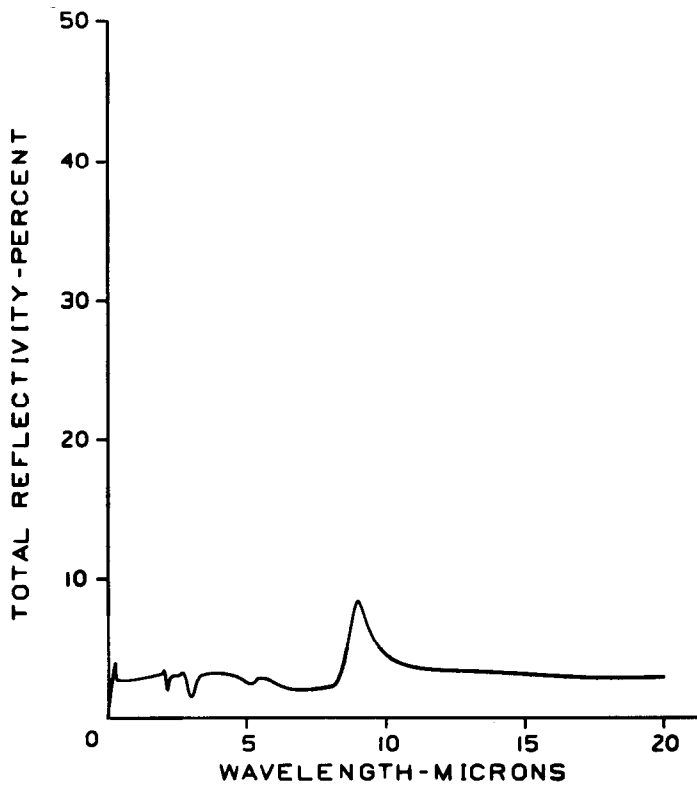


400X



1000X

Figure 2. Paint-Bostic 463-3-8 over ZnCr primer

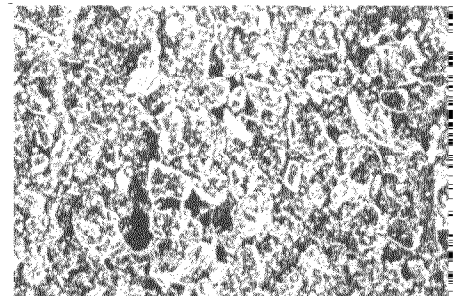
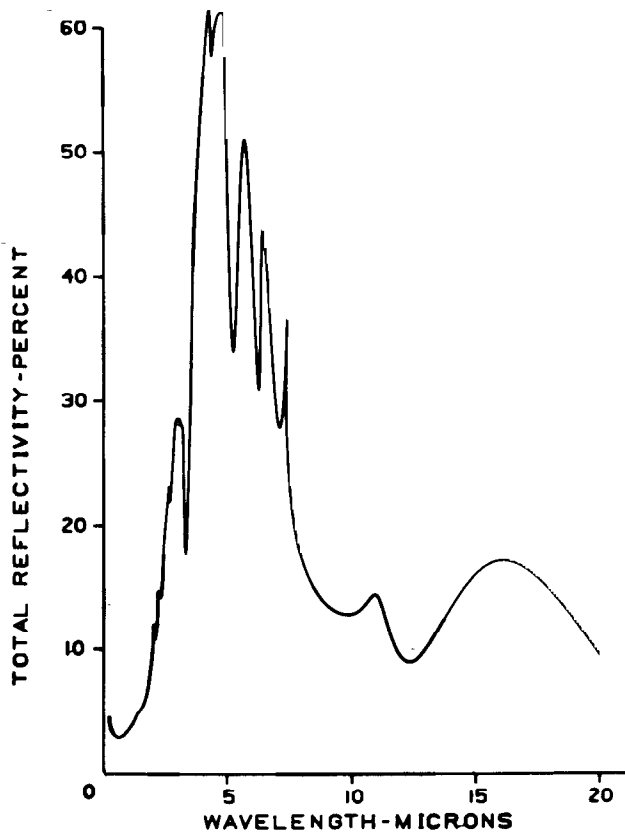


400X

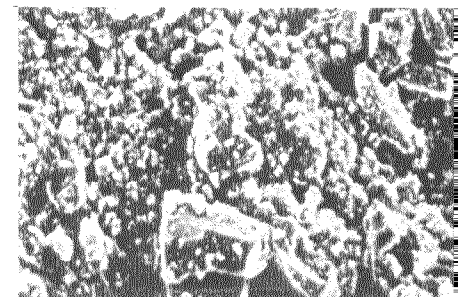


1000X

Figure 3. Paint-3M Nexte black velvet

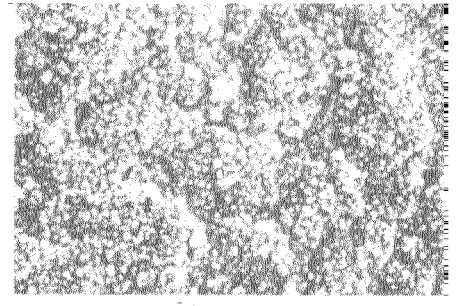
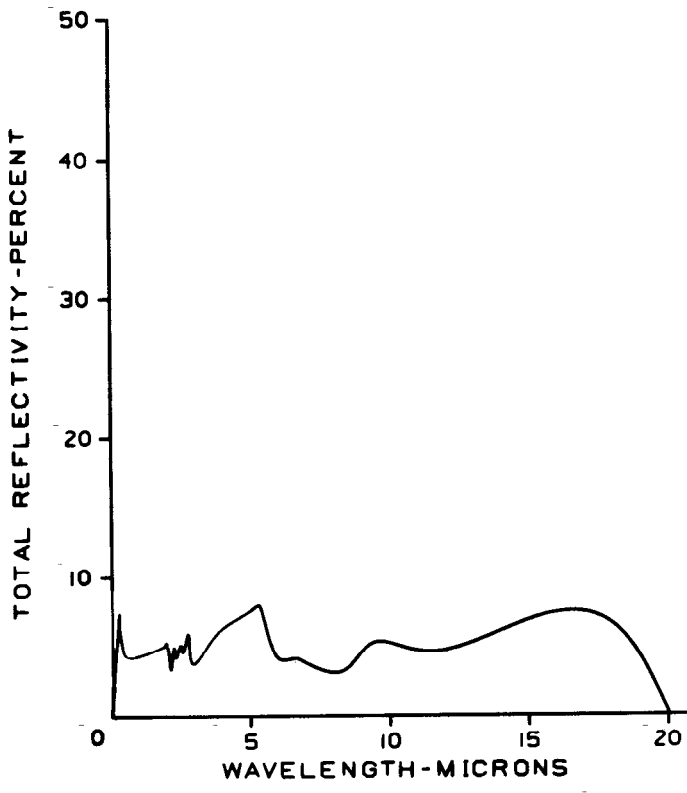


400X

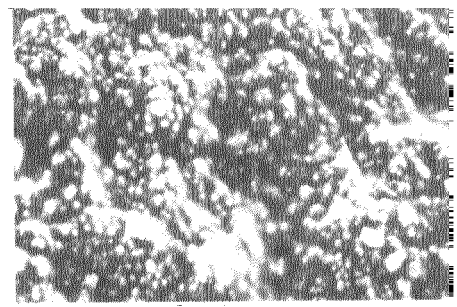


1000X

Figure 4. Paint-3M SCS-2200

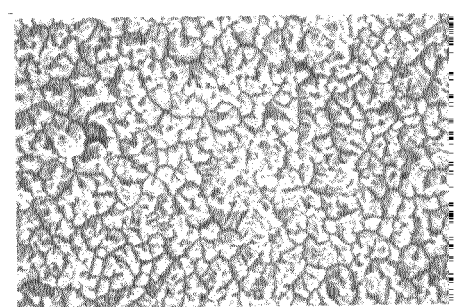
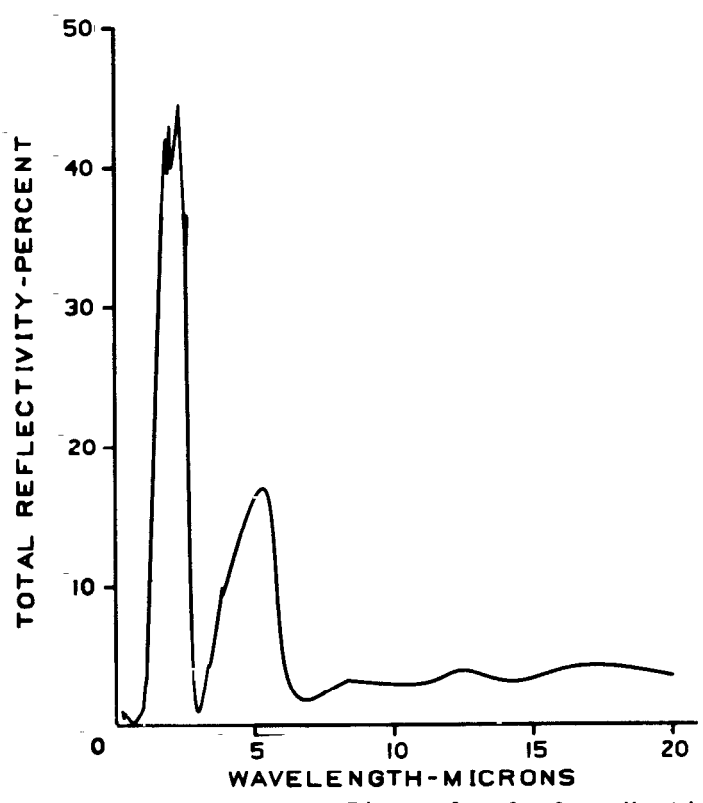


400X

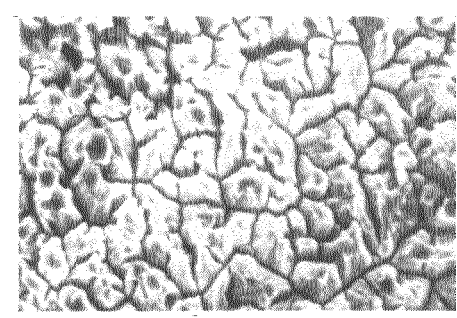


1000X

Figure 5. Paint-Denver Z306

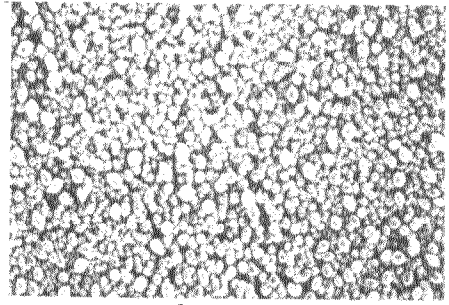
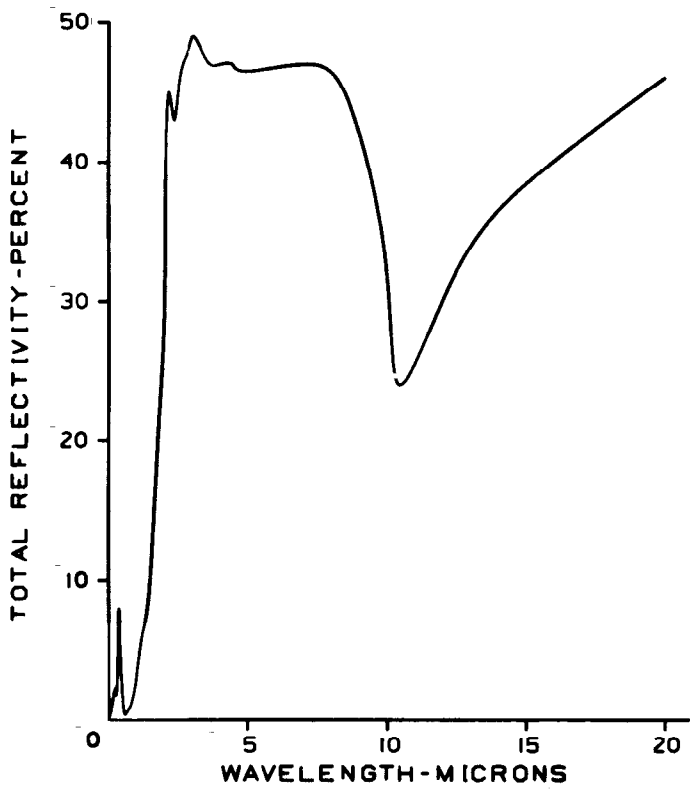


400X

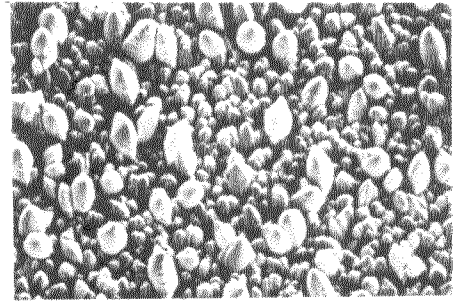


1000X

Figure 6. Surface-Martin Denver (black)

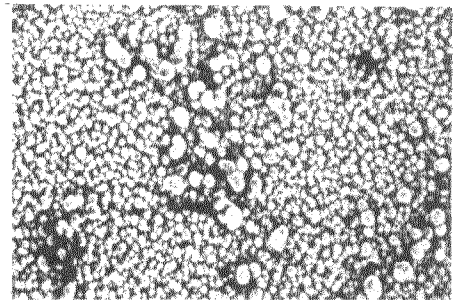
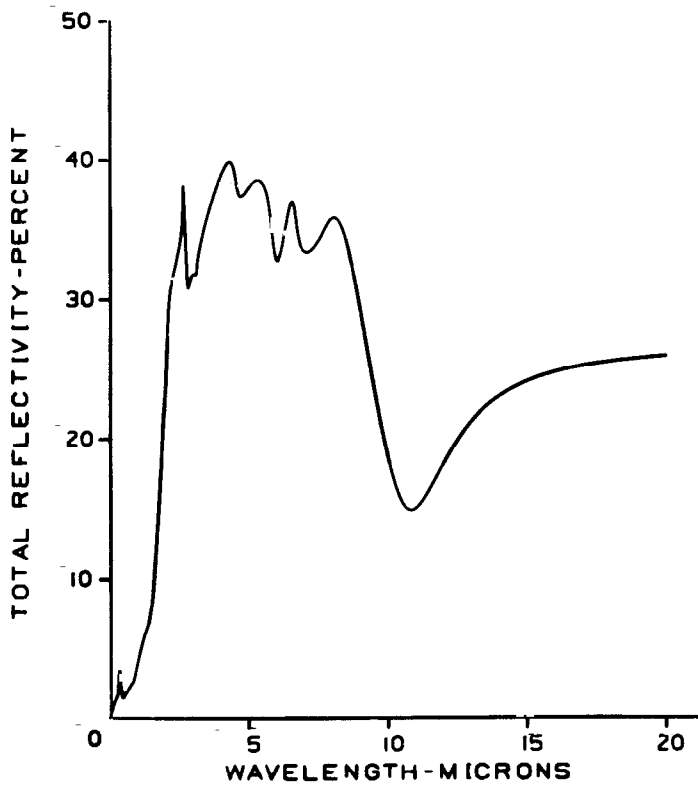


400X

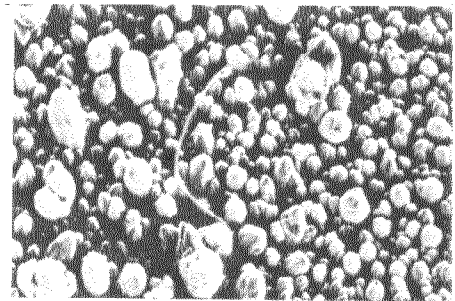


1000X

Figure 7. Surface-Tungsten Hexafluoride (anodized)



400X



1000X

Figure 8. Surface-Tungsten Hexafluoride (black)

the apparent better absorption of the "as grown" surface (Figure 8) at the longer wave - lengths than the anodized surface (Figure 7). Figure 7 does show a slight reflectance spike at 0.365 micrometers that is reduced in Figure 8. The surface appearance of both samples is of a crystalline nature with a variety of crystal sizes, but the crystals are not as "mirror-like" as the 3M SCS-2200 paint.

#### Summation

The problems of understanding and quantifying the reflectance/absorptance properties of coatings designed to produce this effect are many and, unfortunately, the equipment and technology for its use is only now starting to catch up to the problem. Because of this, these and other surfaces have been developed largely by empirical methods. Heretofore, the analysis has been mostly photometric in nature. The requirement to assess the surfaces in the near to far IR regime has brought on a host of new problems, some of which are being handled by devices like the Beckman 5270 and the Willey 318S spectrophotometers utilizing integrating sphere attachments. However, considerable additional data must be taken by goniometric type devices, which look at the near grazing incidence angle absorption efficiency of these surfaces. Normal-to-the-surface measurements are satisfactory for applications like solar collectors, but in E/O military systems the critical angles are seldom more than 10 degrees from the surface or 80 degrees from the surface normal. Devices and techniques to do this type of assessment are few in number and seem to contain many variables, device to device. Getting good, repeatable, standardized data, therefore, has been a problem. It was the opinion of the authors that considerable insight into the method of control of primary energy by these surfaces could be gained if SEM photographs were placed beside photometric curves. The evidence presented in this paper seems to substantiate our belief, and we plan to use this approach on all future surface development work designed to control light energy in any way.

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