Contents



# 8. Investigation of Conductive Thermal Control Coatings by a Contactless Method in Vacuo


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## Abstract


A technique for determining the conductance per unit area of thermal control coatings for "electrostatically clean" spacecraft is described. In order to simulate orbital conditione more closely, current-density-voltage (j-V) curves ore obtained by a contactless method in which the paint on an aluminum substrate is the anode of a vacuum diode configuration with a tungsten filament Cathode. Conductances per unit area which satisfy the International Sun Earth Explorer (ISEE) requirement of $j/V \geq 10^{-9}$ A/V $cm^2$ have been observed on black painte containing carbon and in "white" and green painte filled with zinc oxide which has been "fired" in order to induce defect conductivity. Because of surface effecte and the non-homogenedue nature of paints, large discrepancies are found between meaeurementb with the contactless method and measurements employing metallic contacte, particularly at low current densities. Therefore, measurements with metallic contacts are considered to be of questionable value in deciding the suitability of coatings for electrostatic charge control.


## 1. INTRODUCTION

In order to minimize interferenee of spacecraft charging with low energy plasma and electric field measurements on the ISEE missions, potential differences between dark and illuminated sections of the spacecraft surface are to be kept to lees thah 1 volt. Under net hdrrent densities (j) of &bout $10^{-9}$ A $cm^{-2}$ resulting from photoelectrons and plasma electrons id ISEE orbits, conductance per unit area of $\Sigma/A = j/V \geq 10^{-9}$ A $cm^{-2} V^{-1}$ are therefare required of thermal control coatings over metal surfaces. In terms of material parameters. this requirement can be expressed as

$$\frac{V}{J} = R \cdot A = \rho \cdot d \leq 10^{9} \Omega cm^{2} \quad (1)$$

where $\rho$ is the specific resistivity in $\Omega$ cm and d the thickness of the coating in cm. For their product the term "area resistance" seems to be appropriate, Bince it is aleo the product of a resistance, R. and the area, A, over which it is measured.

Thermal control paints are typically $5 \cdot 10^{-3}$ to $10^{-2}$ cm thick. and resistivities of $< 10^{11}$ $\Omega$ cm are therefore required. Inorganic paints, particularly thoee based on zinc oxide and alkali silicates, were considered as promising candidates with "semiconducting" zinc oxide a i pigment. Their preparation, optical properties. and environmental stability are described in a previous paper. [1]

By expressing the resistivity requirement in the form of Eq. (1), one tacitly assumes that—at Constant temperature—$\rho$ is a true niaterial parameter, independent of voltage, that is, the conductibn mechanism is ohmic in nature. In wide gap semiconductors and insulators, however. ohmic conduction is the exception, rather than the rule, because it occurs only if the concentration of (thermally generated) free, or conduction, electrons far exceeds that of injected (space charge) electrons. Since the concentration of thermal electrons in insulators is m a l l afid injected and trapped charge densities are strongly field dependent, conduction in thin films of insulators or semiconductors is strongly Voltage dependent with the ohmic (linear) portion of the j-V curve occurring at low voltages, where it is easily obscured by contact effects, that is, by interface potentials at the semiconductor-contact interface. Recognizing that Conductivity is bbth voltage and electrode! dependent, we prefer to express the "conductivity specification" as a condudtanhe-per-Wit-area requirement in the form

$$\frac{j}{V} > 10^{-9} \text{ A cm}^{-2} V^{-1} \text{ for } V \leq 1 \text{ Volt} \quad (2)$$

with the added stipulation that such conductance be measured under conditions closely simulating thole of the actual application, that 18, with e "free"—or eontactless—surface in an electrofl plasma. Such a contactless te.hnique has beed described by Bentlage et al,[2] and applied to determine the changes in conductance resulting from durface contamination of conductive coatings. We have adapted this method to the measurement of thermal control paints and other spacecraft coatings. in the course of developing conductive paints for the ISEE program.

## 2. MEASUREMENT SETUP AND PROCEDURE

The test setup as schematically shown in **Figure 1** is a vacuum diode configuration consisting of a tungsten filament cathode and 2 symmetrically arranged anodes. Both anodes are 2.5 cm diameter aluminum dis s, one of which is covered on one side with the coating to be measured and the oth... serves as reference diode. They are mounted in e copper block, which can be heated and cooled by means of copper coils through which liquid $N_2$ or hot air is passed. Electrical insulation of the anodes against the copper block is provided by a Teflon mount and an effective anode surface of 1 cm2 area is defined by an aperture In the form of a copper ring preceding the anode. This aperture is directly attached to the copper block, which is at ground (cathode) potential.

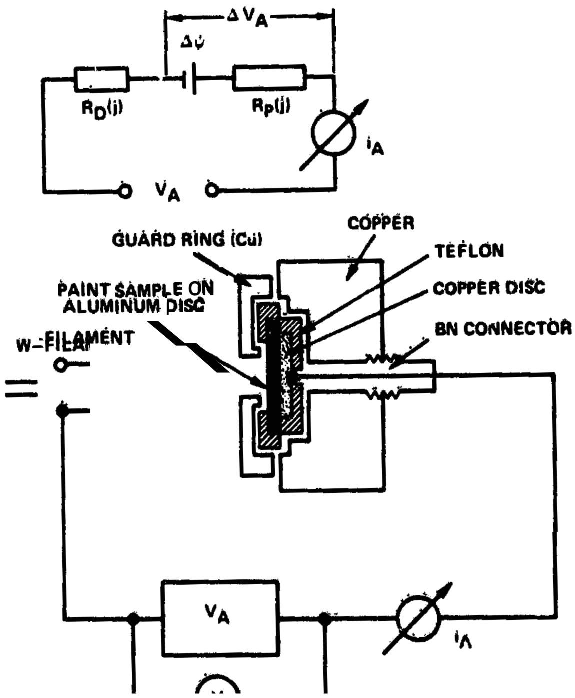


Figure 1 Schematic of Teet Setup for the Contactless Measurement of Paint Resistances (Lower Part), end its E juivalent Electrical Circuit (Upper Part,. The reference anode, arranged symmetrically tb the filament, is not shown

Filament power is supplied by a current regulated dc power supply[a] and anode voltage by either a bipolar[b] or positive regulated power supply.[c] Anode vbltage and current are measured by means of a high impedance (> $2 \cdot 10^{10}$ Ω) digital voltmeter[d] and digital picoamp-meter,[e] respectively. All electrical connections are made by means of shielded cables, permitting current measurements above a noise current of approximately $2 \cdot 10^{-11}$ amperes.

The equivalent circuit of the meaeurement setup can be represented by a resistance, $R_p$, in series with the internal resistance of the diode and an EMF, , equal to the work function difference between the paint and its substrate (aluminum). Accordingly, the codductance per uhit area of the paint is determined from the difference id slope of the j-V curves of the reference diode, and of the (painted) me&&-urement diode of equal area, A, a5 illustrated in **Figure %**For a given current density, j, the anode voltage $V_A$, across the measurement diade is higher by $\Delta V_A = jR_p \cdot A + \Delta\psi$ than that across the reference diode. For $j \rightarrow 0$, this difference becomes equal to $\Delta\psi$ and the conductance per unit area of the paint can be determined as

$$\left(\frac{\Sigma}{A}\right)_{paint} = \frac{j}{\Delta V_A - \psi} \quad (A\ cm^{-2} V^{-1}) \tag{3}$$

The Cbnductarice of the reference dibde at current densities of $10^{-9}$ A $cm^{-2}$ $< j < 10^{-7}$ is of the order of $5 \cdot 10^{-6}$ A $cm^{-2}$ $V^{-1}$, which determines the upper limit of conductance valued that can be reliably measured as approximately $10^{-7}$ A $cm^{-2} V^{-1}$. The lower limit is set by the noise current and a maximum anode voltage of ~ 200 V as ~ $10^{-13}$ A $cm^{-2} V^{-1}$.

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[a]Kepco Model Ck8 - 5 MHS

[b]Kepco Model BOP 72, $-70\ V < V_A < +70\ V$

[c]Kepco Model HB 4 AM, far $0 < V_A < 300\ V$

[d]Multimeter H. P. 34'

[e]Keithly Model 44b

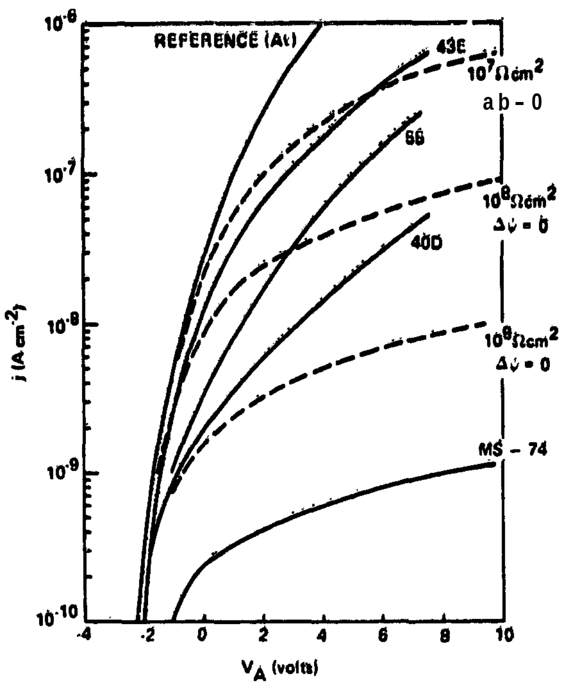


Figure 2, Typical Current-density vs Voltage Curves for the Reference Anode (Aluminum) add Anodes Painted With Various Zinc Oxide-Silicate Paints (Solid Curves). Calculated curves for "ohmic" coatings having area resistances of $10^7 \Omega cm^2$, $10^8 \Omega cm^2$ and $10^9 \Omega cm^2$ and the same work function as the reference anode (Al) are shown for comparison. Real paints are characterized by a change in wark function ($\Delta\psi$) and a voltage-dependent conductance per uhit area

## 3. COATINGS

The inorganic coatings investigated here are modifications of a previouely %eveloped stable, white paint. designated as MS-74. This flight-proven coating is formulated with calcined zinc oxide pigment of the type SP-500 (NewJersey Zinc) and potassium silicate as vehicle. By substituting "conductive" zinc oxide for SP-500, electrically conductive coatings can be prepared. Commercially available conductive oxides as well as "fired" SP-500 have been investigated with potassium silicate, sodium silicate, and a mixture of lithium and potassium silicate as binders. The "firing" process consists cf heating the SP-500 to 1150°C for 15 min in air. The process employed for the commercial oxides HC 616 and HC 238 are proprietary to the manufacturer. The lattice defects introduced by these processes result in donor, abcdptor, and trapping centers that not only govern the charge transport but also act as Color centers and therefore affect the optical properties a8 well. Considerable effort was, therefore, expanded to arrive at coatings which meet both the conductance requirement of $j/V > 10^{-9}$ A $cm^{-2} V^{-1}$ and aolar absorptance requirement of $\alpha_S \lesssim 0.3$ of the "White" areas of the ISEE spacecraft. For the main body of the satellite, fhermel design celled for a green paint of $\alpha_S \sim 0.8$, which has been achieved by adding ~ 2 percent of cobalt oxide tb the einc oxide before firing. For black surfaces, a commercial, carbon filled polyurethane paint (Chemglaze H322) with $\alpha_S$ e 0.98 and $\epsilon_n$ = 0.86 was recommended. We include measurements of this paint because it exhibits the most marked difference between contactless conductance values and conductance measured with metallic?(Ag-paint) contacts.

## 4. RESULTS AND ANALYSIS

### 4.1 Contactless Measurements.

Typical conductance vs Voltage curves are shown in Figure 3. At low voltages current density increases linearly with voltage (Ohm's Law) Which cad be expressed as

$$j = n_o e\mu_o \frac{V}{d} \qquad (4)$$

where $n_o$ is the equilibrium carrier density, e the electronic Charge, $\mu_o$ the mobility and d the thickness of the eemple. With paint thicknesses of approximately $10^{-2}$ cm., conductivities, $\sigma = n_o e\mu_o$, range from $\sim 10^{-12}$ $(\Omega cm)^{-1}$ for calcined SP-500 in K-silicate to $\sim 10^{-9}$ $(\Omega cm)^{-1}$ for fired SP-500 in the Na-silicate; HC-018 yields conductivities comparable to thoee of fired SP-500, whereas HC 238 is only marginally higher than (unfired) SP-500. The vehicle-or binder-also affects the conductance per uhit area: Na-silicate based coatings are more conductive than K-silicate coatings and mixed Li-K-silicate paints give intermediate Values.

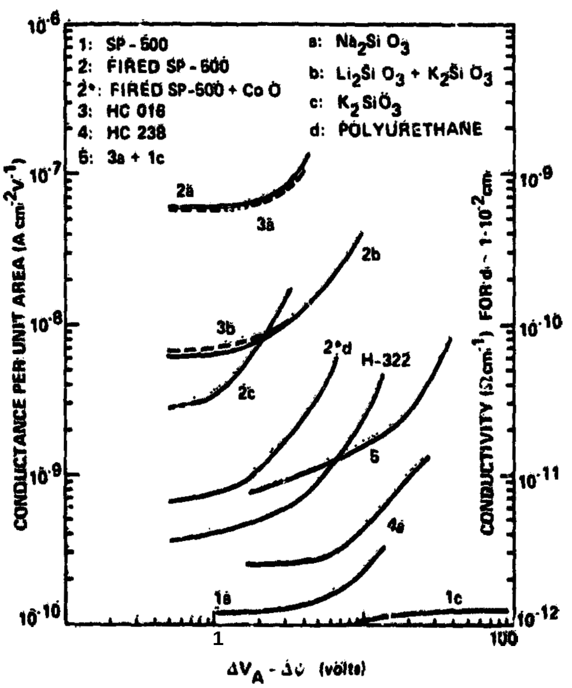


Figure 3. Conductance Per Unit Area as a Function of Voltage for Various Zinc-Oxide/Silicate Combinations and for Carbon (Chemglaze H-322) and Conductive-Zinc Oxide in Polyurethane

When the voltage is increased, current density increases quadratically with voltage (Child's Law), or the conductance increases linearly with voltage. This characteristic is typical of Space Charge Limited Conductance (SCLC), that is, of charge transport governed by the interaction of injected (space) charge with trapping centers of the material, whose energy levels lie between the steady state Fermi level and the conduction band. According to the theory of SCLC, summarized in Figure 4, the relationship between current density, j, and voltage, V, is given by

$$j = \frac{9\mu\theta\epsilon\epsilon_o}{8d^3} \cdot V^2 \qquad (5)$$

Where $\mu\theta$ is an effective mobility, $\epsilon$ the dielectric constant and d the thickness of the material. The trapping factor, $\theta$, is the ratio of free space charge, $\rho_f$, (in the conduction band) and the trapped space charge $\rho_t$, under equilibrium conditions and is given by

$$\theta = \frac{\rho_f}{\rho_t} = \frac{N_C}{N_t} \exp - \frac{E_C - E_T}{kT} \qquad (6)$$

where $N_C$ is the density of states in the conduction band and $N_T$ the density of electron traps at an energy $E_T$ below the conduction band, situated at energy $E_C$.

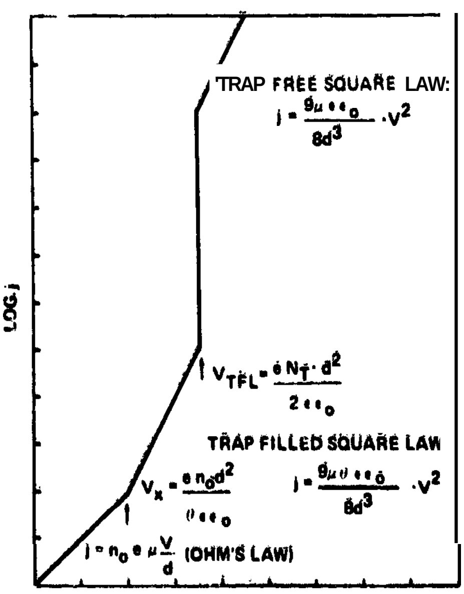


Figure 4. Space Charge Limited j-V Characteristic for an Insulator Containing Shallow Traps

### 4.2 Temperature Dependence

It is apparent from Eqs. (5) and (6) that the temperature dependence of the effective mobility, or of the conductivity, will give the position of the trap level in the band gap. For our standard paint MS-74 (SP-500 in K-silicate), the temperature dependence is plotted in Figure 5,* from which the energy of the trap level is obtained as $(E_C - E_T) \doteq 0.75 \pm 0.05$ eV in good agreement with published values for high-resistivity, Li-doped ZnO.[3] It is important to note here that conductivity variations from sample to sample of the same batch ere of the order of a factor 3 to 5, and to point out that measurements on a different batch showed the same temperature dependence and variation within the batch, but conductivity was about 16 times higher overall. We attribute these variations to the heet treatment inherent in the measurement procedure, in which the samples are heated to ~ 200°C for various lengths of time and measured while cooling. Room temperature conductivities of MS-74 which has never been heated are about $10^6$ times higher than those shown in Figure 5. After heating to 300°C for 30 min, a decrease in conductivity by a factor of 10 to 20 was noted. Preliminary experiments on fired SP-500 in Na-silicate did not reveal any dependence on heat treatment, but further work is required to establish the mechanism responsible for this effect.

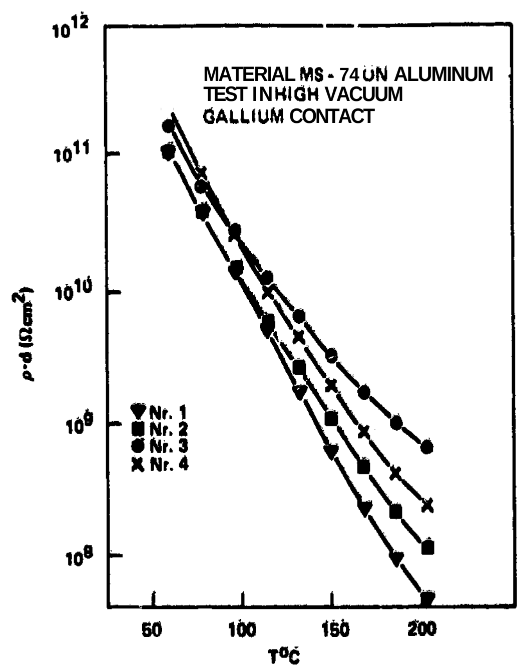


Figure 5. Temperature Dependence of the Area Resistance of MS-74 Paint. (SP-500 in Potassium-Silicate)

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*These data in Figure 5 were obtained at DFVLR, Braunschweig, Germany, with liquid gallium contacts.

## 4.3 Trade-off Between Solar Absorptance and Conductance

As was alluded to earlier, the "firing" process which results in increased electrical conductivity of zinc oxide, also induces color centers. In the case of SP-500, the oxide turns yellow and eolar absorptance increases from 0.2 to 0.4. The conductive commercial oxide HC 016 rlso has an $\alpha_S$ of ~ 6.4. In attempts to produce whiter paints while staying within the ISEE conductance specification, we investigated mixtures of the highly conductive formulation (3, a = HC 016 in Na-silicate) and our standard white paint MS-74 (1, c = SP-566 in K-silicate). The results Ire summarized in Figure 6 from which it is apparent that paints having conductance-per-unit-area of $\geq 10^{-9}$ A $cm^{-2}$ $V^{-1}$ and eolar absorptances of $<0.3$ cannot be obtained by thie approach. whether a better trade-off can be achieved by variations of the temperature, time. and atmosphere of the zinc oxide firing process remains to be investigated.

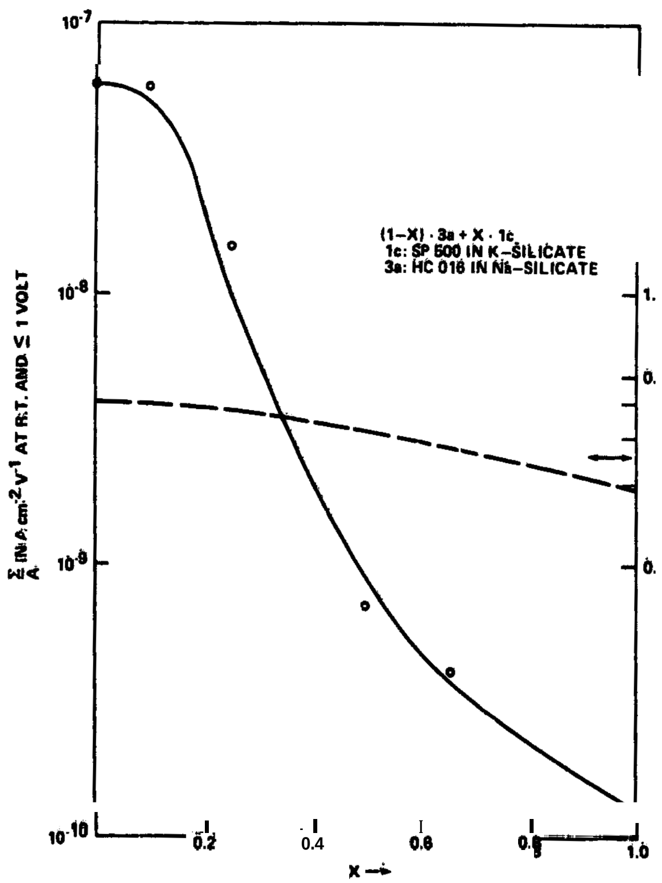


Figure 6. Solar Absorptance ($\alpha_S$) and Conductance Per Unit Area ae a Function of the Mixing Ratio Par Mixtures of a Conductive Paint (3, a = HC 016 ZnO in Na-Silicate), and a White, Non-Conductive Paint MS-74 (1, c = SP-500 ZnO in K-Silicate)

#### 4.4 Comparison of Contact and Contactless Measurements

In general, conductance obtained with silver paint contacts show the same strong voltage dependance, but ate higher by up to Several decades than those obtained by the contactless method and they are higher in air than in vacurlm. The differences between the two methods in vacuum is most pronounced for paint formulations in @hickthe conductivities of pigment and binder &re orders of magnitude apart, as illustrated in Figure 7 for catbon and conductive zinc oxide in polyurethane. The commercial black paint Chemglaze H-322 (5 weight % carbon) appearl about $10^5$ times more conductive with metal electrodes than with the

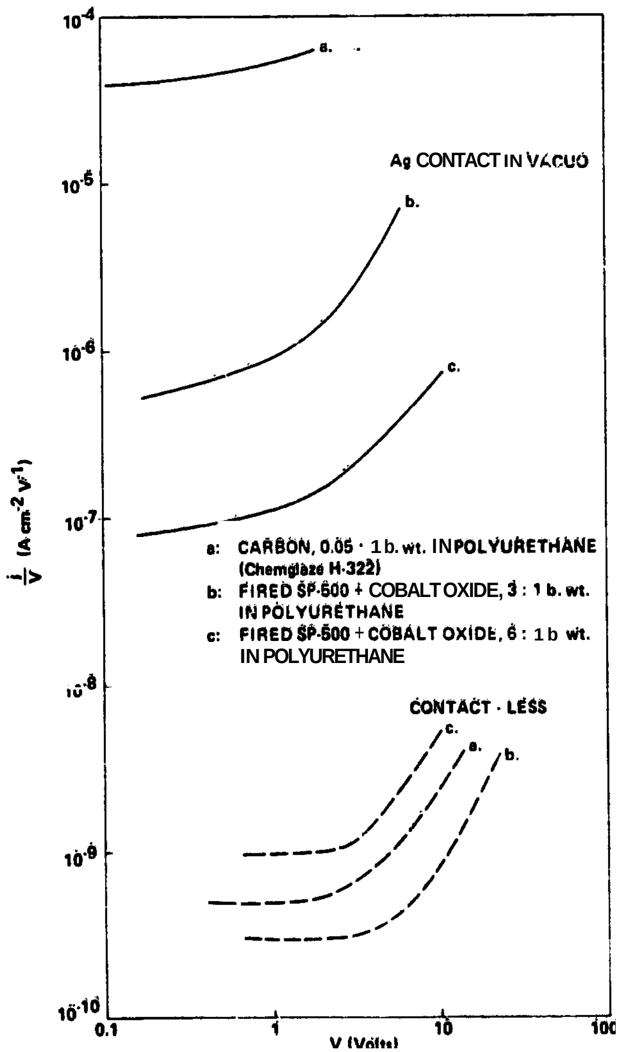


Figure 7. Comparison of Conductance Values of Carbon/Polyurethane arid kine-Oxide/Polyurethane Paints Obtained by Measurements with Ag-Paint Contacts (Solid Lines) and by Contactless Measurements (Broken Linea)

electron plasma as surface contact. In the case of the more heavily loaded zinc oxide/polyurethane paint, the difference is about a factor of $10^3$ which, at least in part, is due to the lower conductivity of zinc oxide as compared to carbon. The different results obtained by the two contacting techniques can perhaps be qualitatively understood as being due to the heterogeneous nature Of paints OR 4 microscopic scale. As a dispersion of a "conductive" phase (the pigment) in a "non-conductive" dielectric (the binder), the paint Burface, consisting of conductive islands in a non-conductive matrix chargee to a highly non-uniform surface potential, with insulating areas essentially at cathode potential arid conductive areae at anode potential, respectively. The effective potential, which governs the anode current, is a complex function of absolute and relative island geometry, that is, of particle size and concentration of the pigment. With a metallic contact, on the other hand, the surface becomes an equipotential surface. The resistive areas are "shorted out" and the measured conductance is the sum of the conductance8 of all conductive paths through the Bample, and therefore mainly a characteristic of the conductive component alone, rather than of the paint as a whole.

## 5. CONCLUSIONS

Thermal control paints which meet the ISEE conductances specification of $j/V \geq 10^{-9}$ A $cm^{-2}$ $V^{-1}$ at V = 1 valt and T ~ 300 K have beerl formulated with semiconducting zinc oxide pigment and alkali silicate binders. As in semiconductors, their charge transport properties are strong functions of voltage end temperature and depend on both pigment and binder. Because of surface effects add the heterogeneous nature of paints, order-of-magnitude discrepancies are found between conductance values measured with metallic contacts and thbee bbtained with a contactless method employing a thermal electron plasma in vacuum. In the evaluation of surface coatings for electrostatic charge control oh spacecraft, careful definition of measurement parameters and bf appropriate measurement techniques are therefore essential.

## Acknowledgments

The authors thank Mr. Walter Wilkens and co-workers of DFVLR-Braunschweig/Germany for the data presented in Figure 5 end for valuable personal communications and discussions.

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3. Seitz, M.A., and Whitmore, D.H. (1968) Electronic drift mobilities and space charge limited current in lithium doped einc oxide, J. Phys. Chem. Solids 29:1033-1049.