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MOISTURE INTERACTION AND STABILITY OF ZOT THERMAL CONTROL SPACECRAFT COATING*

Gordon R. Mon, Charles C. Gonzalez, Ronald G. Ross, Jr.,
Liang C. Wen, and Timothy O'Donnell
Jet Propulsion Laboratory

ABSTRACT

Two of many performance requirements of the zinc orthotitanate (ZOT) ceramic thermal control paint covering parts of the Jupiter-bound Galileo spacecraft are that it be sufficiently electrically conductive so as to prevent electrostatic discharge (ESD) damage to onboard electronics and that it adhere to and protect the substrate from corrosion in terrestrial environments. The bulk electrical resistivity of ZOT on an aluminum substrate was measured over the ranges 22°C - 90°C and 0%RH - 100%RH and also in soft (10^{-2} Torr) and hard (10^{-7} Torr) vacuums. No significant temperature dependence was evident, but measured resistivity values ranged over 9 orders of magnitude: 10^5 ohm-cm @ 100%RH; 10^{10} ohm-cm @ 0%RH; $> 10^{12}$ ohm-cm in a hard vacuum. This latter value violates the ESD criterion for a typical 0.019 cm. thick coating. The corrosion study involved exposing typical ZOT/substrate combinations to two moisture environments--30°C/85%RH and 85°C/85%RH--for 2000 hours, during which time the samples were periodically removed for front-to-back electrical resistance and scratch/peel test measurements. It was determined that ZOT/AL and ZOT/MG systems are stable (no ZOT delamination) although some corrosion (oxide formation) and resistivity increases observed among the ZOT/MG samples warrant that exposure of such parts to humid environments be minimized.

INTRODUCTION

Two important in-flight performance functions of spacecraft paints and coatings are (1) to passively control spacecraft temperatures (requiring low and stable solar absorptance to emittance ratios) and (2) to maintain external surfaces at ± 10 volts equipotential in order to (a) prevent electronics-disrupting static discharge events and (b) minimize the effects of spacecraft surfaces on the charged particle environment. The Galileo Project ESD criterion is as follows:

$$p_V * t < 2\times10^{10} \text{ ohm-cm}^2 \qquad (1)$$

where p_V is the paint bulk resistivity and t is the paint thickness.

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Because of launch delays following the Challenger tragedy, another property of the paint has recently received considerable attention--namely, the effects on it of long-term exposure to terrestrial storage environments: will the paint protect the substrate from corrosion without itself delaminating and will the paint maintain its desirous electrical conduction properties until launch and, indeed, for the duration of the mission? To answer these questions and to test the ESD criterion for ZOT paint, we first measured the bulk electrical resistivity of ZOT paint on an aluminum substrate and then determined the effects on the ZOT paint of long-term exposure to a moist environment.

MATERIAL DESCRIPTION

In the 1970's IITRI reported on the development of an inorganic thermal control coating, formulation designation YB-71, which uses a zinc orthotitanate pigment with a potassium silicate binder (designated PS7 by Sylvania Electric Products Corporation) (refs. 1, 2). This coating is herein referred to as ZOT paint, or ZOT. Further details on ZOT processing and material characteristics can be found in a paper by Harada and Mell (ref. 3). ZOT resistivity has been reported (refs. 2-4) as being nominally 10^8 ohm-cm. However, test details and test environments are generally lacking. Lockerby, et al. (ref. 4), measured nominal resistivity values of 10^{12} ohm-cm for ZOT on aluminum but discounted the validity of this measurement in favor of a measured 10^7 ohm-cm value for ZOT on fiberglass.

ZOT RESISTIVITY MEASUREMENTS

In this section we report measured bulk resistivity values of ZOT paint in humid air and in vacuum. We also establish that lateral ionic conduction through ZOT paint can be explained in terms of bulk conduction--i.e., using measured bulk conductivity values to calculate lateral conductance yields lateral conductance values of the same order of magnitude as was observed by direct measurement.

All JPL ZOT samples were prepared in accordance with an internal Fabrication Specification FS511315.

Bulk Resistivity

Bulk electrical resistivity of ZOT paint was measured for eight samples consisting of 0.019 cm of ZOT paint applied to 5 cm x 10 cm x 0.16 cm aluminum (6061-T6) substrates. Resistivity measurements were sequentially made in the following nominal environments:

(1) 30°C/50%RH;
(2) 30°C/85%RH;
(3) 85°C/50%RH;
(4) 85°C/85%RH;
(5) 20°C and 60°C "soft" vacuum (3×10^{-2} Torr); and
20°C - 50°C "hard" vacuum (10^{-7} Torr).

Chamber equilibrium was achieved within two hours of initiation of the environment. Achievement of sample equilibrium with the environment may require considerably more time. Accordingly, samples were measured in the same environment over a period of at least 26 hours and, in some cases, longer. Every 30 minutes data were acquired over two minute intervals.

The bulk resistivity of ZOT paint was determined by establishing a uniform electrical field across the ZOT paint in the direction of its thickness. This was achieved by applying voltage to the sample aluminum substrate, serving as the positive electrode, and collecting the measurement current at the ZOT surface by means of a cylinder-and-guard-ring electrode system consisting of a conductive elastomeric rubber mounted at the end of a moveable core of a pneumatic solenoid that can be forced into intimate contact with the ZOT surface when it is desired to make a measurement. The applied voltage and the voltage drop across a known precision resistor in series with the sample are measured and the sample resistance and its bulk resistivity are determined from the following formulas:

$$R_{ZOT} = R_k * (V_P - V)/V \qquad (2)$$

$$pV = R_{ZOT} * (PI * r^2/t) \qquad (3)$$

where

t = paint thickness, 0.019 cm
r = electrode radius, 0.333 cm
R_k = precision resistance, ohm
V_P = applied voltage, volts
V = voltage across R_k, volts
R_{ZOT} = bulk resistance of ZOT, ohm
p_V = bulk resistivity of ZOT, ohm-cm

A schematic of the measurement set-up is depicted in figure 1.

Lateral Resistance

In order to measure lateral resistance through ZOT paint, samples were fabricated consisting of a concentric metal electrode system (0.03 um Ti/0.30 um Al) vacuum evaporated onto a borosilicate glass (Pyrex 7740) surface to which 0.019 cm of ZOT paint was then applied. Glass-only samples (no ZOT) were first measured to quantify contributions from the glass (ref. 5); then the ZOT/glass samples were measured. A schematic of the measurement set-up is depicted in figure 2.

Measurements were made at essentially the same nominal environments following essentially the same measurement procedures as for the bulk measurements but with the exception that voltage was continuously applied to these samples. Positive polarity voltage was applied to the large central interfacial electrode; current was collected at the concentric ring electrode. The lateral resistance is determined from the measured applied voltage and the measured voltage drop across the precision resistor using

$$R_T = R_k * (V_p - V)/V \qquad (4)$$

where R_T is the lateral interelectrode resistance; it is composed of several terms including:

(1) ZOT/glass lateral interface resistance; (2) ZOT lateral bulk resistance; (3) interface-to-surface ZOT bulk resistance; and (4) ZOT surface resistance terms. Determining surface and interface resistance from lateral and bulk resistance measurement data requires complex analytical models. Rather, we shall compare the measured lateral interelectrode resistance R_T with the lateral resistance calculated using bulk resistivity values obtained from the "bulk measurement" data, using

$$R_c = p_V * \ln(r_2/r_1)/2*PI*t \qquad (5)$$

where

r_1 = electrode radius, 3.651 cm
r_2 = guard ring radius, 3.810 cm
R_c = calculated lateral resistance, ohms.

See figure 2 for measurement details.

Test Results

ZOT paint bulk resistivity data, obtained from the measurements on four samples at several oven temperature/humidity setpoints, are presented in figure 3, together with the best linear regression line through the data. Note that ZOT bulk resistivity varies by five orders of magnitude over the full range of relative humidity; little or no temperature sensitivity was observed. In other words, the bulk resistivity of ZOT paint exhibits almost no sensitivity to temperature variation in the range of the measurements (20°C to 85°C) but exhibits enormous sensitivity to moisture in the ambient air.

ZOT bulk resistivity data obtained in vacuum are also presented in figure 3. As a result of a 100hr/100°C bakeout the ZOT bulk resistivity in a 10^{-2} Torr vacuum increased from 3.5×10^{10} ohm-cm at 22°C and 1.6×10^{11} ohm-cm at 60°C to about 3×10^{12} ohm-cm. ZOT bulk resistivity data gathered in a 10^{-7} Torr vacuum are also presented in figure 3; values as high as 10^{14} ohm-cm were measured.

The ESD acceptability criterion, equation (1), is violated for 0.019 cm thick ZOT if $p_V > 1 \times 10^{12}$ ohm-cm. The hard vacuum measurements flag possible concerns that ZOT paint may not be sufficiently conductive to provide its intended ESD function in the hard vacuum of space; the plasma (ionizing radiation) environment of Jupiter, however, is expected to provide compensation.

Lateral ("surface") resistivity of the ZOT/glass samples, determined from measurement data on three samples, is presented in figure 4 together with the lateral resistivity calculated using bulk resistivity values determined from the "bulk measurement" data. The values determined from the bulk data agree quite well with the directly measured values. We infer from this that lateral conduction in ZOT paint is bulk-dominated, i.e., surface and interface resistances are of the same or larger order of magnitude than the lateral bulk resistance.

As a point of information, the bulk resistance data was obtained 3 - 10 minutes after the application of sample voltage; this interval between the application of the voltage and acquisition of the data may not have been sufficiently long in some cases to allow current transients to dissipate. Two typical cases are presented in figure 5, showing that at 22°C/40%RH the 10-minute reading may differ from the equilibrium value by more than a factor of 5; whereas at 85°C/5%RH the variation between the 10- and 1000-minute readings is less than a factor of 2. This effect is less pronounced at lower sample moisture content levels and is typically less than the measurement scatter noted in figure 3.

AGING STUDIES ON ZOT PAINT

In this section we present the results of investigating the effects on coating/substrate combinations of long term exposure to moist environments. ZOT/AL, ZOT/MG, and ZOT/SIKKENS/GOLD-PLATE/MG (ZSGM - "SIKKENS" is a black thermal control paint) samples were aged, i.e., exposed for long periods of time to constant temperature/humidity environments--30°C/85%RH and 85°C/85%RH--as indicated in table 1. The samples were periodically removed from the exposure environments for scratch/peel testing, visual observations of degradation, and total front-to-back electrical resistivity (effective bulk resistivity of the ZOT coating) measurements.

Scratch/Peel Test Results

The scratch/peel tests were conducted in conformance with ASTM test standards (ref. 6):

> "An X-cut is made in the film to the substrate, pressure-sensitive tape is applied over the cut and then removed, and adhesion is assessed qualitatively on the 0 to 5 scale...
>
> 5A No peeling or removal
> 4A Trace peeling or removal along incisions
> 3A Jagged removal along incisions up to 1/16 in. on either side
> 2A Jagged removal along most of incisions up to 1/8 in. on either side
> 1A Removal from most of the area of the X under the tape
> 0A Removal beyond the area of the X"

Observed post-exposure degradation and pre- and post-exposure scratch/peel test results are listed in the last two columns of table 1.

Visual Observations

The ZOT/AL samples exhibited only minor visible degradation and no loss of adhesion of the ZOT to the aluminum. The same is essentially true for the ZOT/MG samples, although for these samples some limited edge delamination of

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the ZOT coating and the formation of an interface oxide layer was observed. The ZSGM samples faired poorly--samples exposed to the 30°C/85%RH environment exhibited localized spots of ZOT delamination, while those samples in the 85°C/85%RH environment degraded so much that they were removed from the aging chamber after only 95.5 hours of exposure. The ZOT surfaces on these samples were extensively pock-marked with what appeared to be oxide bits of the magnesium substrate that had upwelled through the coating at many locations, a phenomenon known as "magnesium flowering", figure 6. In addition, delamination of the coating at the Sikkens/gold interface was common.

Electrical Resistance Measurements: Substrate Corrosion

Electrical resistance data were acquired at room ambient conditions. The resistance measured was that between the exposed ZOT surface and the underside of the substrate. The measured resistance values include contributions from the ZOT paint layer and interfacial oxide (corrosion product) layers, if any; we refer to the measured value as the effective coating resistance. Effective coating resistivity (calculated using the thickness of the ZOT paint) is plotted against time-of-exposure for ZOT/AL, ZOT/MG, and ZSGM, respectively, in figure 7.

The ZSGM system is comparatively the most resistive. The rate of corrosion of ZSGM in an 85°C/85%RH environment is significantly greater than in a 30°C/85%RH environment. The ZOT/AL and ZOT/MG systems are initially equally resistive, but upon exposure to steady temperature/humidity environments, the ZOT/AL systems become somewhat less resistive, while the ZOT/MG systems become somewhat more resistive. When account is taken of the large variation of ZOT resistivity with moisture content (five orders of magnitude: figure 3), the spread of the 2000-hr data and the relatively small changes in resistivity with aging (about one order of magnitude or less: figure 7), it is not unreasonable to conclude that the ZOT/AL systems exhibit essentially no resistivity change after 2000 exposure hours, but that the ZOT/MG systems do exhibit an increase in effective resistivity. The actually observed small decrease in resistivity of the ZOT/AL systems is attributed to excess moisture in the ZOT paint: the time between removal of the samples from the environments and measurement of their resistances--about 24 hours--was perhaps insufficient to allow the samples to achieve moisture equilibrium with the room ambient. On the other hand, the increase in resistance of the ZOT/MG samples has been confirmed as due to the formation of high resistance magnesium oxides at the ZOT/MG interface.

Aluminum forms a thin protective oxide layer which we believe retards the formation and build-up of reaction product. The magnesium substrate, on the other hand, is chemically less stable when in contact with moisture (sorbed in the ZOT)--the build-up of resistive reaction product dominates the resistance properties of the ZOT/MG system.

Additional post-exposure resistance measurements were made on selected samples to determine which layers were dominating the overall front-to-back resistance measurement. This was done by scraping away the ZOT and exposing the substrate at a corner of the samples. Thus resistance measurements between the ZOT surface and the corroded and freshly exposed substrate could be made. For the ZOT/AL samples, the measured resistances were those of the bulk ZOT. It was verified that the increasing resistance of the ZOT/MG systems is attributable to the formation and growth of a magnesium oxide layer between the ZOT and the magnesium substrate. The curious fact that the effective resistivity of the ZSGM systems was almost two orders of magnitude higher than that of the other systems was also verified by this means.

The ZOT in the ZSGM systems actually measured higher for resistivity than did the ZOT in the other systems--irrespective of substrate materials. This may suggest a different coating morphology for ZOT on Sikkens/Au-plate/Mg than for ZOT on aluminum or even on magnesium by itself.

MOISTURE DESORPTION

The moisture desorption behavior of ZOT paint in a soft vacuum ($3x10^{-2}$ Torr) at room temperature has been measured using a Cahn Electrobalance. The procedure followed was to first determine the desorption behavior of ZOT/GLASS samples and then of GLASS samples alone. By subtraction, the desorption behavior of ZOT paint was deduced. The data indicate that ZOT paint will lose most of its physically sorbed moisture within an hour after injection into space.

Figure 8 exhibits typical weight-time response to forepump vacuum application. There is an initial jump in weight due to buoyancy--a mass weighs more in vacuum than it does in air--followed by an approximately exponential loss of weight due to desorption of volatiles, assumed to be moisture. Also plotted in figure 8 is the pressure vs. time profile as measured in the Cahn Balance chamber during a typical data acquisition run. Most of the air is lost almost immediately, but the sample weight loss is a more gradual exponentially decreasing function of time. Figure 8, therefore, approximates the sample weight response to a step change in ambient pressure.

The buoyancy, B_e, is obtained from experimentally measured data using the equation $B_e = W_1 - W_o$, where W_1 is the initial weight after forepump vacuum is achieved, and Wo is the initial weight in air.

Desorption

The large loss of sample weight upon initial vacuum application (approximately the first minute) is due to desorption of loosely (physically) bonded surface moisture. The remainder is due in small part to some desorption of chem-adsorbed moisture and in larger part to the diffusion to the surface and desorption of loosely sorbed moisture.

The total weight of desorbed moisture, W_m, is given by the equation $W_m = W_1 - W_2$, where W_2 is the equilibrium vacuum weight. The sample dry weight, W_d, is determined from the equation $W_d = W_2 - B$. The desorption D, as reported in table 2 is given, in mg/gm, by $D = W_m/W_d$.

Data and Results

Sorption data and results for ZOT paint are presented in table 2. Each gram of ZOT loses at least 13 mg of moisture in the vacuum of space; or in terms of area, each cm^2 of ZOT surface loses at least 0.4 mg of moisture (for a 0.019 cm coating thickness).

As can be seen from figure 8, most of the moisture desorbed from the ZOT is freed within a few minutes after vacuum application. Very little desorption occurs after just a few hours. Therefore, we conclude that ZOT paint will lose most of its physically sorbed moisture content shortly after being injected into the space environment, and will experience a corresponding increase in resistivity.

As a final note, it was observed that the moisture sorption process was reversible--i.e., after testing, the test samples fully recovered the moisture that had been desorbed.

SUMMARY AND CONCLUSIONS

The important bulk resistivity measurement data are summarized as follows: the bulk resistivity of ZOT paint exponentially increases by five orders-of-magnitude as the ambient relative humidity decreases from 100%RH to 0%RH; in vacuum, the bulk resistivity of ZOT paint continues to rapidly increase as its moisture content decreases, from 10^{10} - 10^{11} ohm-cm @ $3x10^{-2}$ Torr up to 10^{12} - 10^{14} ohm-cm @ 10^{-7} Torr. ZOT paint is hygroscopic and its low resistivity in ambient conditions is due to moisture-induced ionic conductivity (not unlike the behavior of classical humidity sensors).

ZOT/AL was observed to be a chemically stable system--the ZOT appears to be tenaciously attached to the aluminum substrate. In ZOT/MG systems, the substrate magnesium exhibits a greater tendency to corrode than does the substrate aluminum in ZOT/AL systems, but ZOT/MG is substantially more durable than the ZSGM systems tested. The ZSGM system is questionable on two accounts: (1) in humid terrestrial environments, the substrate corrodes and disrupts the ZOT surface layer (the galvanic Au-Mg couple may contribute substantially to the corrosion of this system); and (2) in a space vacuum environment, its resistivity, like that of ZOT on aluminum, may be too high to satisfy the Galileo mission ESD constraint.

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Table 1
Aging Data, ZOT Paint

SAMPLE	Time @ $30^oC/85\%RH$ (hr)	Time @ $85^oC/85\%RH$ (hr)	Observed Degradation	Scratch Test Results (1)	(2)
ZOT/AL	1969		None.	4A	3A
ZOT/AL		1969	Some discoloration, yellowish blotches.	4A	3A
ZOT/MG	1994		A few yellowish spots.	3A	3A
ZOT/MG		2012	Yellowing. ZOT delam along edges. Blackened Mg.	4A	3A
ZSGM	1994		Yellowing. Localized delams.	4A	3A
ZSGM		95.5	Extensive yellowing. Mg "flowers" protruding thru coating.	4A	0A

(1) pre-exposure
(2) post-exposure

Table 2

Desorption Data, ZOT Paint

SAMPLE	W_0 (gm)	W_1 (gm)	W_2 (gm)	B_e (mg)	W_m (mg)	W_d (gm)	D (mg/gm)
ZOT/GLASS	4.5308	4.5341	4.5306	3.3	3.5	4.5273	.77
GLASS	5.7496	5.7522	5.7508	2.6	1.4	5.7482	.24
ZOT							13.0

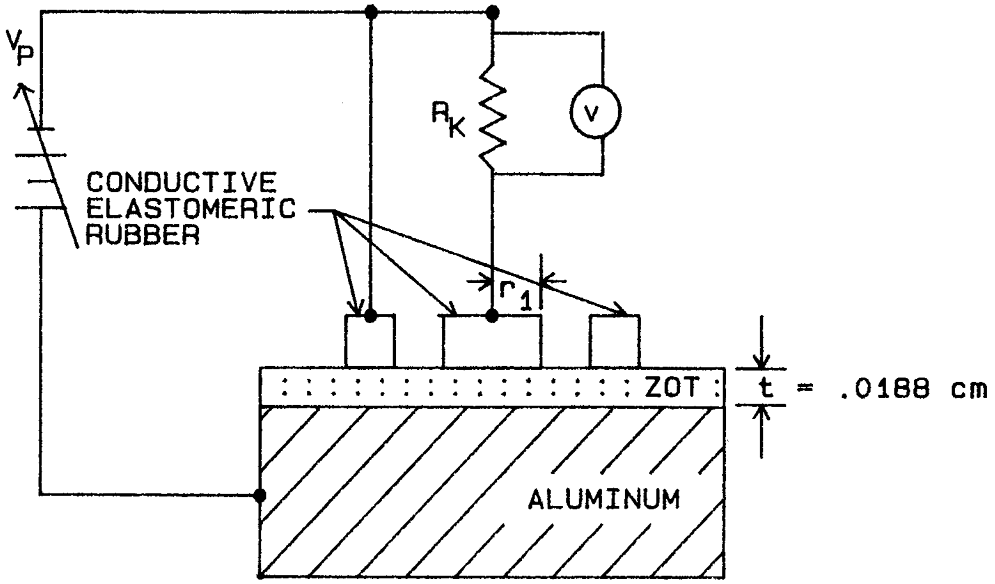

Figure 1. Bulk Resistivity Measurement Schematic

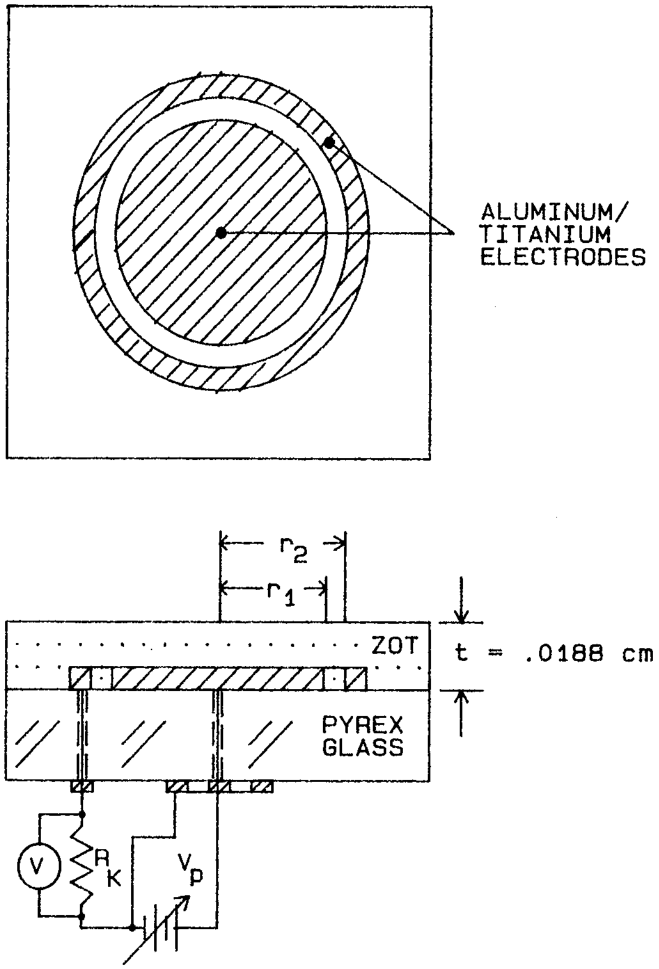

Figure 2. Lateral Resistance Measurement Schematic

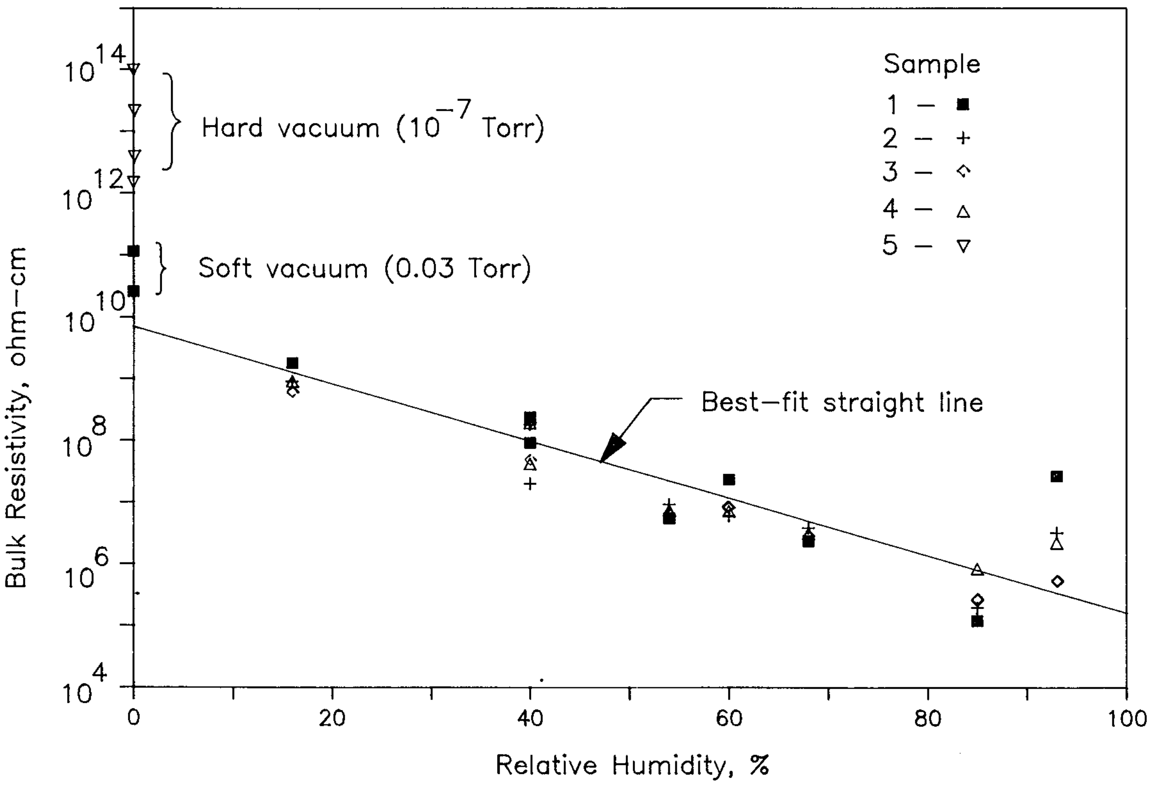

Figure 3. Bulk Resistivity of ZOT Paint

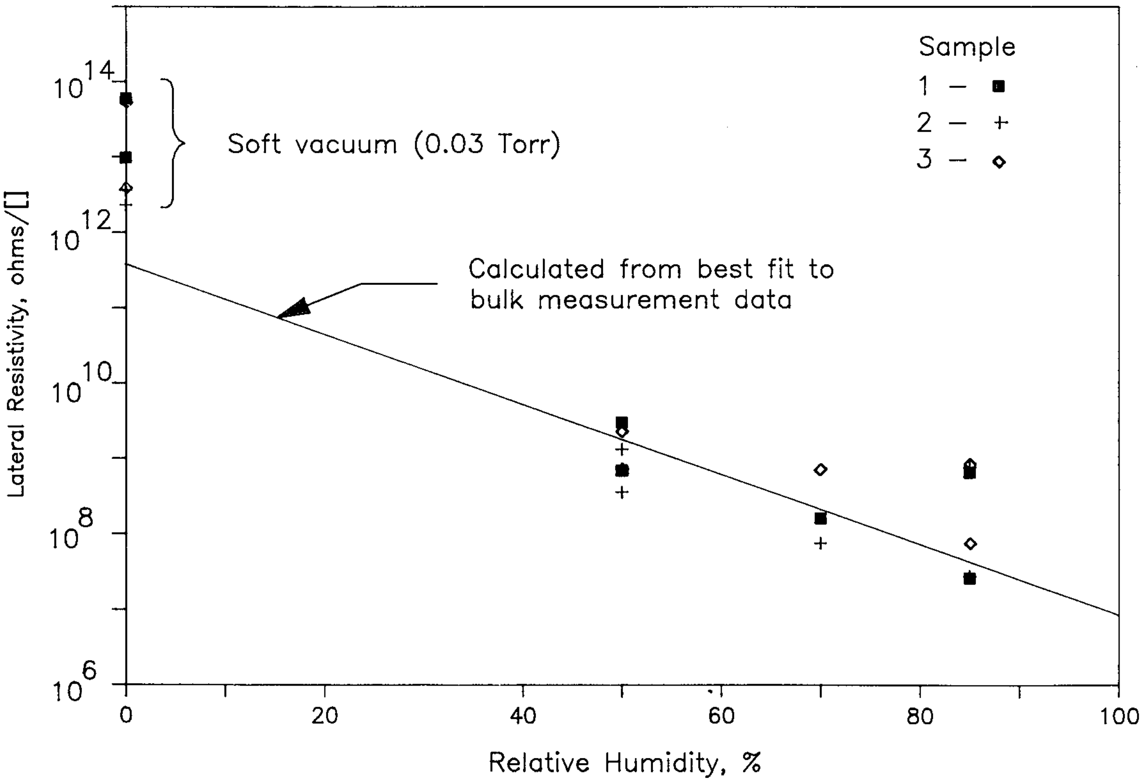

Figure 4. ZOT Lateral Resistivity - Measured, and Calculated from Bulk Data

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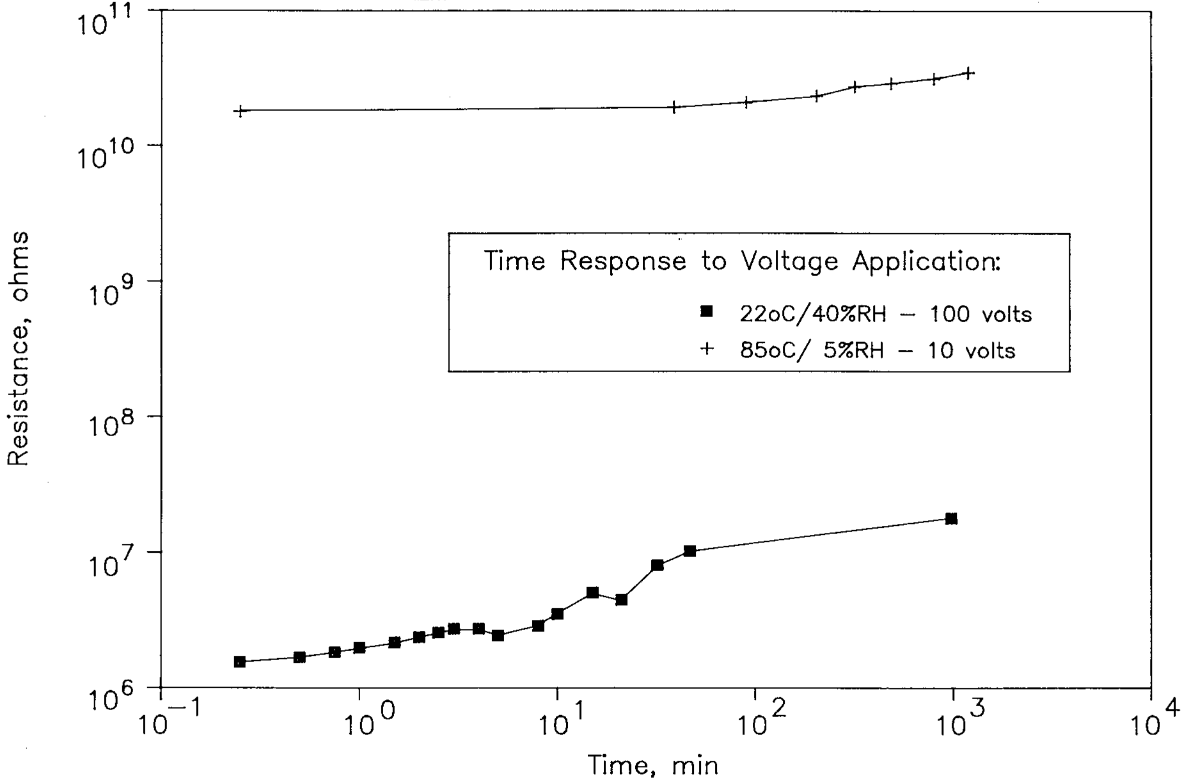

Figure 5. Resistance Measurement Time Response of ZOT Paint

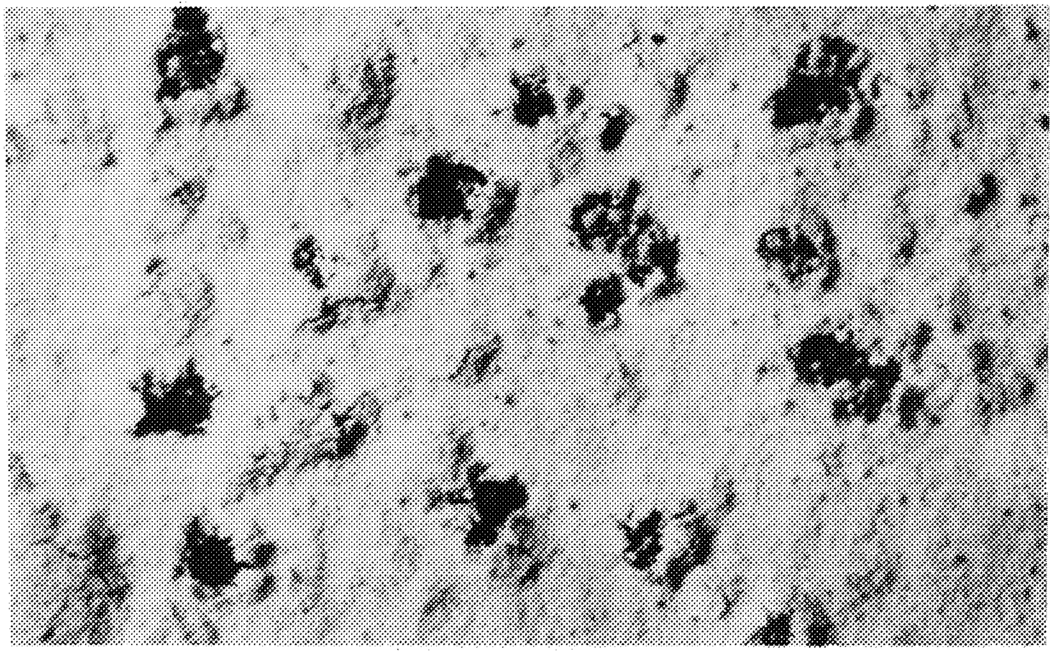

Figure 6. Magnesium "Flowers" Forming at Substrate and Upwelling through the ZOT Paint

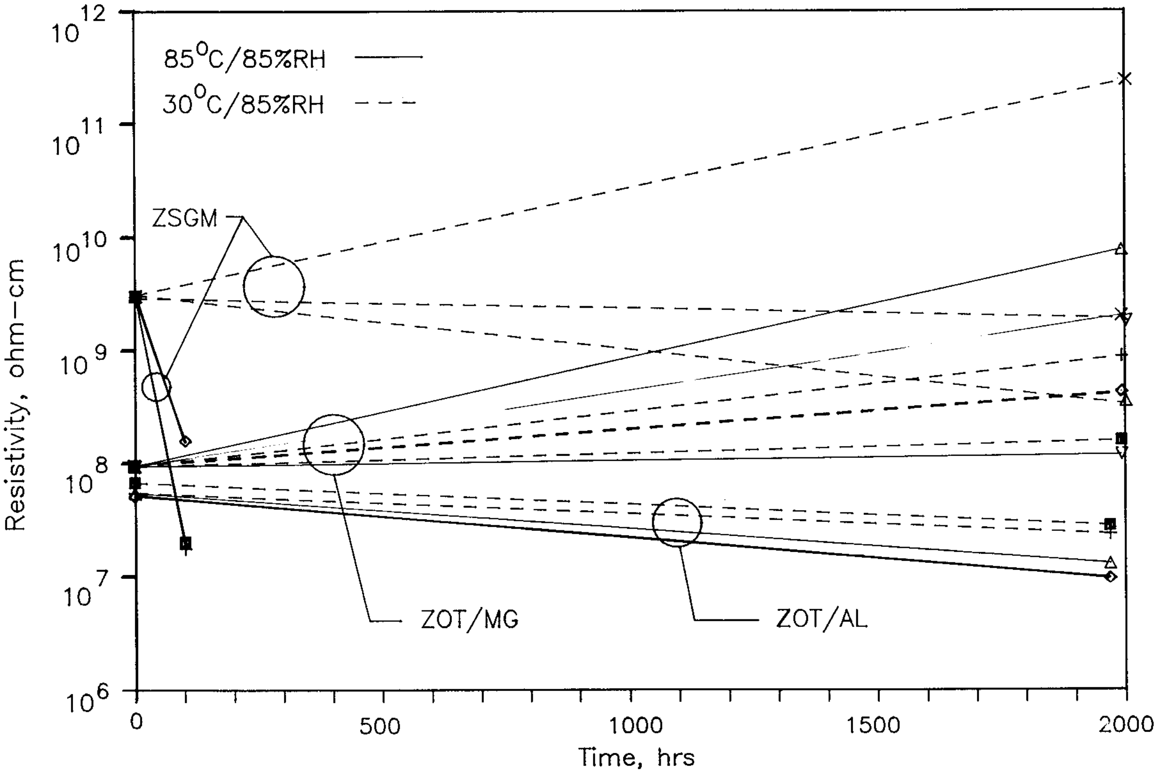

Figure 7. Effective Coating Resistivity vs. Exposure Time

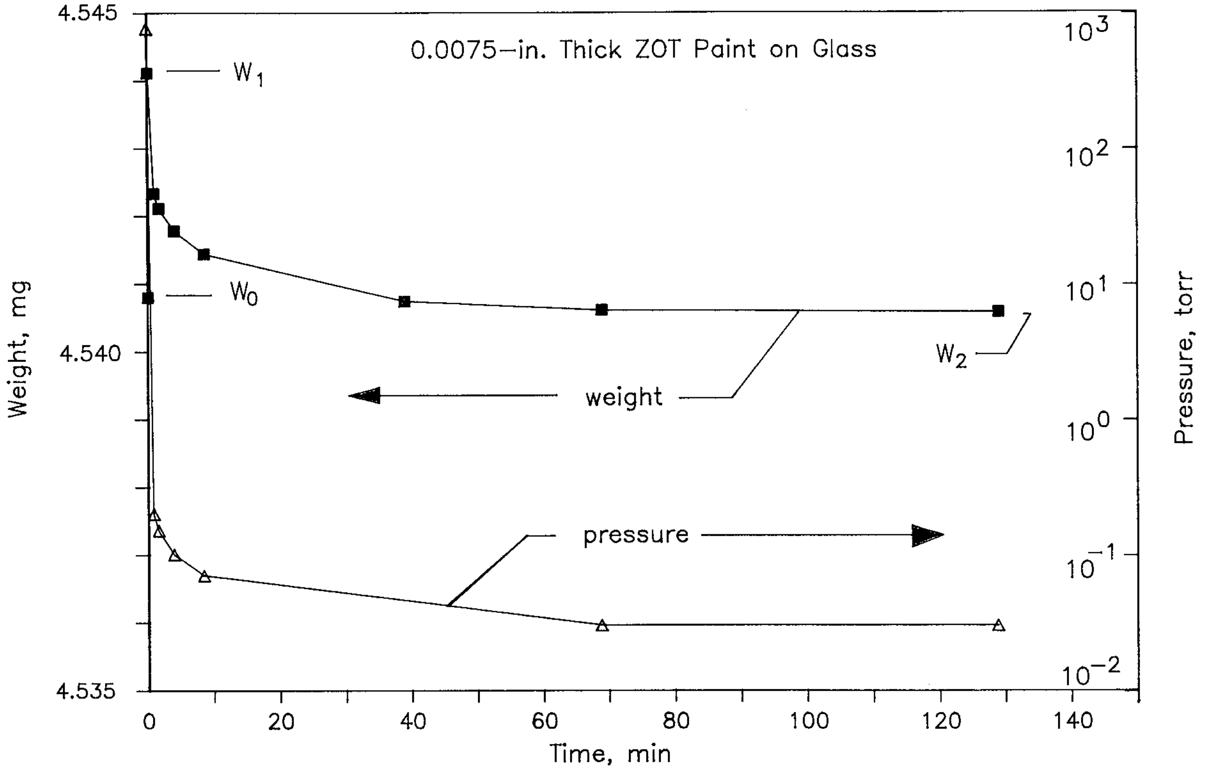

Figure 8. Weight Response to Vacuum Application