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PROGRESS REPORT

ON

CONDUCTIVE PAINTS

February 28, 1994- June 13, 1994

Submitted by

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This report covers the work performed from February 28, 1994 through June 13, 1994 under a subcontract from Sayles Enterprises entitled "A Study of Conductive Paints".

I. Exposure to Elevated Temperature - Electrical Resistivity

This test is intended to determine the stability of the resistivity of the paints upon exposure to elevated temperatures. The results obtained here reflect the paints ability to perform in environments operating above room temperature, such as enclosed electronic systems.

Samples of each paint were prepared and baked at temperatures of 100, 200, and 300 C. These samples, along with air dried samples, were placed in an oven at elevated temperatures and their electrical resistance was periodically measured over the course of three weeks. The resistance was determined by the van der Pauw method. It should be mentioned that the maximum baking and exposure temperature was limited to 300 C, since it has been shown that the paints soften due to binder degradation at temperatures in excess of 300 C. The results are seen in the following figures.

A. Air Dried Paints

Relative Resistivity vs Exposure at 200C, air-dried paints

Relative Resistivity vs Exposure at 300C, air-dried paints

The air dried paints all exhibit a drop in resistivity upon initial exposure to elevated temperature. However, after this initial decrease they remain stable. Furthermore, the decrease in resistivity is approximately to the same level as that which occurs when the paints are simply baked at the exposure temperature first. This implies that the air dried paints remain electrically stable, until they are baked, and once baked they remain stable up to their baking temperature.

In view of these results, the paints can be applied to a circuit board, for example, air dried, and placed into service at an elevated temperature where their electrical resistivity will only improve as a result of the elevated operating temperature.

B. Paints Baked at 100 C

Relative Resistivity vs Exposure at 100C, paints baked at 100C

Relative Resistivity vs Exposure at 200C, paints baked at 100C

Relative Resistivity vs Exposure at 300C, paints baked at 100C

The paints baked at 100 C are stable upon exposure to 100 C temperatures. They exhibit a slight drop at elevated temperatures, but then remain stable. Again, the stable resistivity is approximately that observed when the paints are initially baked at the exposure temperature, indicating stability up to the baking temperature. These results reinforce those obtained from the air dried paints.

C. Paints Baked at 200 C

Data for paints exposed at 100 C are seen in the Appendix.

Relative Resistivity vs Exposure at 200C, paints baked at 200C

Relative Resistivity vs Exposure at 300C, paints baked at 200C

The paints baked at 200 C are stable at exposure temperatures equal to or less than 200 C, and show only a slight drop at 300 C. Again, the stable resistivity is approximately that observed when the paints are initially baked at the exposure temperature, indicating stability up to the baking temperature. These results are identical to those obtained from the air dried and 100 C baked paints.

D. Paints Baked at 300 C

Data for paints exposed to 100 C and 200 C are contained in the Appendix

Relative Resistivity vs Exposure at 300C, paints baked at 300C

The paints baked at 300 C are stable regardless of exposure temperature, up to 300 C.

E. Summary

The electrical resistivity of all the paints is extremely stable upon long term exposure to elevated temperatures. The overall trend is that the paints are stable up to exposure at their baking temperature. Upon exposure to temperatures in excess of the baking temperature, the resistivity decreases and then remains stable. This is excellent performance and clearly indicates that, electrically, all paints can withstand long exposure to elevated temperatures. Therefore, another criterion must be used to select the "best paint".

II. Exposure to Elevated Temperature - Hardness

In some applications, such as decorative coatings or shielding where the paint may be subject to abrasion or wear, the hardness of the paint may be important. In view of this, samples of each paint were prepared and baked at temperatures of 100, 200, and 300 C. These samples, along with air dried samples, were placed in an oven at elevated temperatures and their hardness was periodically measured over the course of three weeks. The hardness was determined by the ASTM method outlined in the previous report. These samples were exposed simultaneously with those used in the electrical measurements in the previous section. The results are seen in the following figures.

A. Air Dried Paints

Hardness vs Exposure at 200C, air-dried paints

Hardness vs Exposure at 300C, air-dried paints

The air dried paints either remained stable or hardened upon exposure to elevated temperatures. Again, this is an excellent result, showing that paint properties improve upon exposure to a temperature beyond the baking temperature.

B. Paints Baked at 100 C

Hardness vs Exposure at 100C, paints baked at 100C

Hardness vs Exposure at 200C, paints baked at 100C

Hardness vs Exposure at 300C, paints baked at 100C

Paints baked at 100 C are stable at exposure to 100 C while they harden upon exposure to 200 and 300 C temperatures.

C. Paints Baked at 200 C

The data for paints exposed to 100 C is in the Appendix.

Hardness vs Exposure at 200C, paints baked at 200C

The paints baked at 200 C are stable for 100 and 200 C exposures, while they harden upon exposure to 300 C.

D. Paints Baked at 300 C

The data for paints exposed to 100 C and 200 C are in the Appendix.

These paints are stable upon exposure to an elevated temperature up to 300 C.

E. Summary

All paints exhibit excellent hardness stability upon exposure to elevated temperature. Furthermore, they harden when exposed to temperatures above their baking temperatures and then remain stable. Again this indicates that the paints can be processed

at any time after application, they have characteristics associated with their highest process temperature, and they maintain those characteristics for prolonged exposure.

III. Exposure to Elevated Temperature - Adhesion Strength

In virtually every application, the paints must adhere well to the substrate. Therefore we have measured the adhesion strength of the paints as a function of baking temperature and long term exposure to elevated temperatures. Samples of each paint were prepared and baked at temperatures of 100, 200, and 300 C. These samples, along with air dried samples, were placed in an oven at elevated temperatures and their adhesion strength was determined by the Sebastian IV Thin Film Adhesion Strength Tester. It should be mentioned that the maximum baking and exposure temperature was limited to 300 C, since it has been shown that the paints soften due to binder degradation at temperatures in excess of 300 C.

Based on the previous results which indicate that the paints do not change upon exposure to temperatures at or below their baking temperature, data on adhesion strength was only taken at exposure at or above the baking temperature. The results are seen in the following figures.

A. Air Dried Paints

Adhesion Strength on Glass vs Exposure at 200C, air dried paints

Adhesion Strength on Glass vs Exposure at 300C, air dried paints

The adhesion strength increased initially upon exposure and then remained stable for all paints. Furthermore, the stable adhesion strength corresponds to that achieved when the paints are baked at the exposure temperature.

B. Paints Baked at 100 C

Adhesion Strength on Glass vs Exposure at 100C, paints baked at 100 C

Adhesion Strength on Glass vs Exposure at 200C, paints baked at 100 C

Adhesion Strength on Glass vs Exposure at 300C, paints baked at 100 C

The adhesion strength did change upon initial exposure. At 200 C some of the paints did show a decrease and then stabilize. This is the same behavior the paints exhibit as a function of baking temperature. That is, the adhesion strength decreased as the baking temperature is increased from 100 C to 200 C. Furthermore, the stable adhesion strength corresponds to that achieved when the paints are baked at the exposure temperature.

C. Paints Baked at 200 C

The adhesion strength remained stable for all paints upon exposure to 200 C, and increased upon exposure to 300 C. This is the same behavior the paints exhibit as a function of baking temperature. That is, the adhesion strength increases as the baking temperature is increased from 200 to 300 C. Furthermore, the stable adhesion strength corresponds to that achieved when the paints are baked at the exposure temperature.

E. Paints Baked at 300 C

The paints baked at 300 C are stable upon exposure to 300 C.

E. Summary

All paints exhibit excellent adhesion strength stability upon exposure to elevated temperature. The adhesion strength does change when exposed to a temperature above the baking temperature. However, it attains a value equal to that at the given process temperature. Again this indicates that the paints can be processed at any time after application, they have characteristics associated with their highest process temperature, and they maintain those characteristics for prolonged exposure.

III. Summary-Elevated Temperature Exposure

All the paints are extremely stable at elevated temperatures. Any changes in their properties occur during the initial stages of exposure and then the properties remain stable. The key point is that the paints do not appear to change until they are processed at an elevated temperature and then maintain their properties until exposed to a higher temperature. Therefore, in order to insure stability, the paints need to be baked at a temperature higher than the maximum operating temperature. However, if this is not possible, the paint properties will simply attain the values associated with them at the maximum exposure temperature.

IV. Vacuum Applications of Paints

The paints were tested for ultra-high vacuum (UHV) compatibility. The method of testing was to place the paints into a UHV system and monitor their outgassing properties with a residual gas analyzer (RGA) as the paints were heated. The initial test

was run on the sample holder with no paint sample attached. The purpose of this test was to determine the outgassing properties of the holder so that there would be no question about the origin of the emitted gasses. Tests were run on all types of Sayles' paints which had been dried at room temperature and processed at 300 C. The results of the best (paint that outgassed the least) and one of the worst are presented in this report along with the results from the sample holder itself. However, it must be noted that there is very little difference between the best and the worst, so there is no way to state that one paint processed in one manner would be better than any other.

As a consequence of a tiny leak in the vacuum system, the base pressure was 5×10^{-9} Torr. However, this was more than an adequate vacuum for the testing of outgassing properties of these paints. Figure 1 is the background pressure of the system, i.e. the sample holder without a paint sample. Note on these curves, the horizontal axis does not align with the proper mass. For some reason which we have not yet been able to cure, the calibration between the RGA and the parameter analyzer which generates the curves and stores the data is not exact. For example, the actual mass 29 aligns with 30 on the graph. Be assured that the number assigned to each peak is the correct mass number. At 27 C nothing unusual appears on the mass scan. That is, the major peaks are hydrogen (mass 2, this is present because we sputter Si in an atmosphere of Ar and H₂ in this system), water vapor (mass 18, one of the hardest gasses to remove from UHV systems), nitrogen (mass 28, the predominant gas in the air), and many smaller peaks which result from residue from the cleaning process or from sputtering. All these smaller peaks have a total pressure contribution of less than 10^{-10} Torr.

As the holder was heated, the total pressure in the system did not change substantially. For example, at 150 C, the actual total pressure went down and all major peaks either remained about the same or also went down. Figure 2 is a picture of the results at 300 C and you can see very little change, that is the total pressure is about the same and the major gasses are still H₂, H₂O, and N₂. However, the hydrogen and water vapor peaks went way down. It does not look that way on the curve, but note that there was an automatic change of scale and the vertical axis is 13.1/division in Fig. 2 while it was 31.64/division in Fig. 1.

The "best" sample we studied was our sample number 150, paint 3003 baked at 300 C on a glass substrate. Figure 3 shows the RGA curves with the sample at 30 C and a background pressure of 5.3×10^{-9} Torr. You can see that the dominant gasses are again hydrogen, water vapor and nitrogen. The major change that occurs at 100 C is that the total pressure has risen to 1.4×10^{-8} Torr. However, at 200 C things began to change rapidly. Figure 4 is the RGA output at a temperature of 201 C. Note that the total pressure, 2.6×10^{-8} has less than doubled from what it was at 100 C, but the paints are not giving off a large variety of undesirable gasses. Major peaks are occurring at masses 15, 39, 41 and 44 with minor peaks at higher masses than seen before. Also note that the hydrogen peak has increased substantially, this is typical of these paints. All these new peaks are products of the breakdown of the hydrocarbons in the binder. The most likely culprit is the breakdown of the methyl methacrylate which is present, as described in patent No. 4,980,225. Figure 5 is the RGA output of this sample at 297 C, and it can be seen that the pressure has risen to an intolerable level of 3.3×10^{-7} Torr. Note that at this temperature the dominant peak has become that of mass 41, a breakdown

product of methyl methacrylate. All the high mass peaks have also increased considerably also as has the H_2 peak.

One of the worst samples was our sample number 142, paint 1001, also processed at 300 C and on glass. Figure 6 at 36 C is very similar to what we have seen at room temperature for all the samples. Again, not much happens until a temperature of 200 C is reached. The pressure rose to 5.2×10^{-8} Torr and the new dominant peaks occur at masses 15, 39, 41, and 44. Figure 7 shows the results of this test at 299 C. The total pressure is 2.1×10^{-6} Torr and the major peaks are at mass 2, 28 and 41. The interesting part of this analysis is that the best and worst samples were both processed at 300 C. However, not a lot of significance can be placed on this since the samples were all very similar.

V. Conclusions-Vacuum Applications

The Sayles' paints can be used in high vacuum systems, systems with base pressures in the low 10^{-6} Torr range, with no problems. This can be stated because the highest outgassing that occurred at 300 C raised the total pressure to only 2.1×10^{-6} Torr. The major outgassing is due to breakdown of hydrocarbons and since high vacuum systems are normally pumped with oil diffusion pumps, a good source of hydrocarbons themselves. An excellent use of the paints would be as electrical contacts and adhesive for conducting and, especially nonconducting, samples to be tested in scanning electron microscopes.

The paints can also be used in UHV, but extreme care must be used. I recommend that the paints not be used if they will reach a temperature greater than 150 C. Above that temperature they will outgas hydrocarbons which will be deleterious to any UHV work of interest.

APPENDIX

I. Resistivity vs Exposure

Relative Resistivity vs Exposure at 100C, paints baked at 300C

Relative Resistivity vs Exposure at 200C, paints baked at 300C

Relative Resistivity vs Exposure at 100C, paints baked at 200C

II. Hardness vs Exposure

Hardness vs Exposure at 100C, paints baked at 200C

Hardness vs Exposure at 100C, paints baked at 300C

Hardness vs Exposure at 200C, paints baked at 300C

***** GRAPHICS PLOT *****

VM1
(mV)

sample # 1
Date 27, 1994
Temp 27°C
Pressure 5.4 x 10⁻⁴ Torr

Variable1:
VS1 -Vs1
Linear sweep
Start .0000V
Stop 10.000V
Step .0100V

Constants:

MASS (AU) = 10*VS1

Figure 1

***** GRAPHICS PLOT *****

VM1
(mV) $T = 306^{\circ}\text{C}$
 $P = 5.3 \times 10^{-4} \text{ Torr}$
May 27, 1969

Variable1:
VS1 -VS1
Linear sweep
Start .0000V
Stop 10.000V
Step .0100V

Constants:

MASS (AU) = 10*VS1

Figure 2

***** GRAPHICS PLOT *****

Sample #150 P = 5.3×10^{-4} Torr
 VM1 (mV) June 2, 1994 T = 30°C

Variable1:
 VS1 -VS1
 Linear sweep
 Start .0000V
 Stop 10.415V
 Step .0100V

Constant1:

MASS (AU) = 10*VS1

Figure 3

***** GRAPHICS PLOT *****

VM1
(mV) Sample #150 $\rho = 2.6 \times 10^{-8} \text{ Torr}$
June 2, 1990 $T = 201^\circ\text{C}$

Variable1:
VS1 -Vs1
Linear sweep
Start .0000V
Stop 10.415V
Step .0100V

Constants:

MASS (AU) = 10*VS1

Figure 4

***** GRAPHICS PLOT *****

Sample #150

$\rho = 3.3 \times 10^{-7} \text{ Torr}$

VM1
(V)

June 2, 1994

$T = 297^\circ \text{C}$

Variable1:

VS1 -V01

Linear sweep

Start .0000V

Stop 10.415V

Step .0100V

Constants:

MASS (AU) = 10*VS1

Figure 5

***** GRAPHICS PLOT *****

Sample #142
 VM1 (mV) June 2, 1994
 $P = 5.8 \times 10^{-4}$ Torr
 $T = 36^\circ\text{C}$

Variable1:
 VS1 -Vs1
 Linear sweep
 Start .0000V
 Stop 10.415V
 Step .0100V

Constants:

MASS (AU) = 10*VS1

Figure 6

***** GRAPHICS PLOT *****

VM1
(V) Sample 142 $P=2.1 \times 10^{-4} \text{ Torr}$
June 2, 1994 $T=299^\circ \text{C}$

Variable1:
VS1 -Vs1
Linear sweep
Start .0000V
Stop 10.415V
Step .0100V

Constants:

MASS (AU) = 10*VS1

Figure 7

**DATE
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7/21/94

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