

ELECTROSTATIC HAZARD CONSIDERATIONS FOR ODC SOLVENT REPLACEMENT SELECTION TESTING

by

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ABSTRACT

ODC solvents are used to clean many critical substrates during solid rocket motor production operations. Electrostatic charge generation incidental to these cleaning operations can pose a major safety issue. Therefore, while determining the acceptability of various ODC replacement cleaners, one aspect of the selection criteria included determining the extent of electric charge generation during a typical solvent cleaning operation. A total of six candidate replacement cleaners, sixteen critical substrates, and two types of cleaning swatch materials were studied in simulated cleaning operations. Charge generation and accumulation effects were investigated by measuring the peak voltage and brush discharging effects associated with each cleaning process combination. In some cases, charge generation was found to be very severe. Using the conductivity information for each cleaner, the peak voltage data could in some cases, be qualitatively predicted. Test results indicated that severe charging effects could result in brush discharges that could potentially result in flash fire hazards when occurring in close proximity to flammable vapor/air mixtures. Process controls to effectively mitigate these hazards are discussed.

INTRODUCTION

At the outset of the ODC program, a series of tests were devised to identify any electrostatic discharge (ESD) hazards that might result in solid rocket manufacturing operations coincidental to the introduction of different cleaners. Specifically, tests were performed to determine the electrostatic response of various solvents when used to clean a sundry variety of RSRM motor production "critical" substrates. These tests included cleaner conductivity, peak voltage, and brush discharge testing.

RESULTS AND DISCUSSION

Solvent Conductivity Testing

When measured, a solvent's conductivity value provides a qualitative indication of the solvent's polarity and the amount of charge that is likely to be generated during a cleaning operation using this solvent. When a cleaning operation using a solvent-soaked cleaning cloth is performed, the amount of charge generated is a function of 1) the relative speed of contact and separation action involved in the circular wiping motions, 2) the speed at which the cleaning cloth is ultimately removed from the surface being cleaned, and 3) the relative affinity/aversion for electrons exhibited by each of the intimately contacting media. A solvent's conductivity can dramatically affect the amount of charge accumulation on the materials by controlling whether charge—decoupled during the cleaning process—can migrate back and equalize with its counterpart before the separation process is ultimately complete.

The conductivity was measured for each of the following solvents:

- ◆ Reveille
- ◆ PF Degreaser
- ◆ Isopropyl Alcohol (IPA)
- ◆ Prime
- ◆ Ionox BC
- ◆ TCA

To effectively measure each solvent's conductivity, two conductivity meters were utilized. The first meter was a calibrated Emcee Electronics Model 1152 liquid conductivity meter. It was used to measure the conductivity of those solvents believed to non-polar because its range capability ranges from 0 to 2000 picosiemens per meter. This meter was used to measure the conductivity of both Reveille and PF Degreaser. The second meter employed was an Orion Model 140 conductivity meter. The Orion meter was used to measure the conductivity of those solvents believed to exhibit varying degrees of polarity. This included the remaining solvents IPA, Prime, Ionox BC, and TCA. The Orion meter was calibrated just prior to testing using the potassium chloride reference solutions delineated in the 1995 revision of ASTM D1125 entitled, "Standard Test Methods for Electrical Conductivity and Resistivity of Water." A calibration curve was then produced for the Orion meter by which the measured solvent conductivity values could be adjusted to their correct and true values.

After performing the conductivity tests described above, the following results were compiled:

<u>Solvent Name</u>	<u>Conductivity (microsiemens/cm)</u>	<u>Temperature</u>
Reveille	0.00000002	71.6° F
PF Degreaser	0.00000001	71.2° F
Isopropyl Alcohol (IPA)	0.24	71.2° F
Prime	5,810	71.6° F
Ionox BC	0.63	72.0° F
TCA	0.14	71.0° F

From these conductivity results, each of the tested solvents was essentially grouped into one of two categories: non-polar and polar. Specifically, Reveille and PF Degreaser are very non-polar while the rest of the solvents are relatively polar. What is implied by this categorization is that the non-polar solvents will be strongly inclined toward electrostatic charging and build up. This charge generation/build up inclination is primarily the result of the time constant for these two solvents is greater than the contact-break time involved in the cleaning operation itself. In contrast, the polar solvents will permit charge relaxation to occur and thereby resist charge accumulations on the substrate and swatch involved in the cleaning operation. Indeed, some of these trends can be seen in the test data obtained in the peak voltage/brush discharge testing test results.

Peak Voltage/Brush Discharge Testing

The other series of tests performed included peak voltage and brush discharge testing. The peak voltage measurements indicate, worst case, how much electrical charge is generated by the cleaning action and ultimately accumulates on the cleaning cloth and critical substrate. A solvent's conductivity affects the amount of charge migration during the cleaning process—as noted above—and in this way, solvent conductivity does influence the peak voltage data resulting from a cleaning operation.

The peak voltage testing was conducted by performing the following steps:

1. Neutralize the electric charge on all candidate cleaning cloth and substrate surfaces
2. Soak the cleaning cloth swatch with the candidate solvent—not to dripping wet
3. Zero adjust the electrostatic voltmeter and measuring the zero volt level on the solvent-soaked cloth, dry-wipe cloth, and critical substrate surface

4. Performing the simulated wet-wipe and dry-wipe cleaning operations measuring the potentials resulting on each cleaning cloth and substrate surfaces versus time
5. If a surface potential exceeds 5,000 volts, then attempt to produce a brush discharge

The peak voltage tests essentially consist of measuring the results of a simulated critical substrate cleaning contact-electrification process. This cleaning process involves a number of parameters that can give rise to wide variability in the measured surface voltage variable. For this reason, the measured voltages resulting from the simulated cleaning operation were confirmed by performing each operation twice using both Rymple cloth and Poly Wipes for each solvent candidate and critical substrate combination.

All surface voltage measurements—including zero volt levels—were digitized and stored. Further, following each test, the zero volt levels were used to determine the peak voltage points for each simulated cleaning operation and these peak voltage data points were then recorded in data tables.

During the peak voltage testing, if the peak surface potentials were sufficiently high, it was considered possible to produce a brush discharge from the highly charged, non-conductive surface. (Electric charge is generated on conductive substrates but since these substrates are typically grounded in use, the charge build up and resulting spark discharge potentials were not considered in this study.) Therefore, the second part of this test involved checking for the advent of a brush discharge following the solvent cleaning process, if the surface voltage exceeded 5,000 volts. The actual brush discharge testing consists of approaching the charged substrate with a grounded, 1/2" diameter metal probe with a 1/4" radius on the end while monitoring for electromagnetic radiation using a heterodyne receiver. If as the probe approaches the charged surface, a sudden discharge of the surface electric charge occurs, the receiver will detect a time-varying magnetic field and convert it into an audio signal that is recognized by the test technician.

If the critical substrate being tested was non-conductive, it was positioned atop a non-conductive table top that was physically located at least 18" away from the nearest earth ground. If the substrate was conductive, it was placed atop a conductive and grounded stainless steel panel.

All peak voltage measurements were performed with a calibrated Monroe Model 175 electrostatic voltmeter using an 1017 HV high voltage probe positioned on a non-conductive mechanical arm. (This mechanical arm was fastened to the top of the non-conductive table top noted above.) This meter has a rated precision of +/- .1 percent of full scale which equates to +/-20 volts for a calibrated surface potential measurement. This meter achieves this precision by making the surface potential measurement using a field-nulling principle. This simple means that at the controlled 1-cm standoff, the

probe is driven to the voltage of the surface under measurement and therefore, does not reduce the surface potential via capacitive loading. Since when performing the testing, the length of the mechanical arm resulted in minute probe-to-surface standoff changes, the author felt the surface voltage could realistically be resolved to the nearest +/- 100 volts. Therefore, the peak voltage data recorded in the noted data tables is reported with a tolerance of +/- 100 volts.

The list of critical substrates—with their physical dimensions—that were run through the peak voltage/brush discharge testing in combination with the previously mentioned solvents includes the following:

- ◆ Aluminum Witness Panel: 12" X 8" X ½" thick
- ◆ D6AC Steel Witness Panel: 12" X 8" X ½" thick
- ◆ Dexter Crown 6656 Primer/6611 Topcoat-Painted Aluminum: (see above)
- ◆ Rustoleum 5690 Primer/5691 Topcoat-Painted Steel: (see above)
- ◆ Cured EA 913NA Adhesive: 10" X 13" X ¼" thick
- ◆ Cork : 12" X 12" X ¼" thick
- ◆ Cured PR1122 B2 PolySulfide: 10" X 13" X ¼" thick
- ◆ Cured RTV (DC 90-006): 10" X 12" X ¼"
- ◆ Cured EA 946 Adhesive: 10" X 13" X ¼"
- ◆ Cured Carbon-Filled EPDM Rubber: 8" X 12" X ½" thick
- ◆ Cured ASNBR Rubber: 8" X 12" X ½" thick
- ◆ Dupont Primer/Topcoat Teflon[®]-Coated Steel: 8" X 12" X ½" thick
- ◆ Cured DC 732 RTV: 10.5" X 13" X 125 mils thick
- ◆ Glass-Cloth Phenolic: 12" X 8" X 640 mils thick
- ◆ Carbon-Cloth Phenolic: 12" X 8" X 640 mils thick
- ◆ Cured RSRM Main Grain Propellant: 12" X 8" X ½" thick

The conductivity values for each of the critical substrates tested was either known previously or was discovered indirectly via the peak voltage test results. Specifically, if the conductive/nonconductive nature of a specific substrate was not known, the surface voltage produced through contact-electrification was monitored. If the voltage was non-zero and additionally exhibited no decay, the substrate was considered to be non-conductive. Using this newly gained information and that known from prior testing, the substrates were appropriately grouped into the following conductive/dissipative/non-conductive categories:

Conductive: Aluminum Witness Panel

D6AC Steel Witness Panel

Cured Carbon-Filled EPDM Rubber

Carbon-Cloth Phenolic

Dissipative: Cured ASNBR Rubber

Cured RSRM Main Grain Propellant

Non-Conductive: Cured EA 913NA Adhesive

Cork

Cured PR 1122 B2 PolySulfide

Cured RTV (DC 90-006)

Cured EA 946 Adhesive

Cured DC 732 RTV

Glass-Cloth Phenolic

According to these groupings, the substrates identified as conductive and dissipative were grounded during testing while the non-conductive substrates were not grounded. Those substrates that essentially consisted of a thin non-conductive film or coating applied to a conductive material were considered conductive because the underlying material was grounded during testing. These included Dexter Crown 6656 primer/6611 topcoat, Rustoleum 5690 primer/5691 topcoat, and Dupont primer/topcoat Teflon®.

Examples of some of the voltage versus time traces recorded during the peak voltage testing are included in Figures 1, 2, and 3 below.

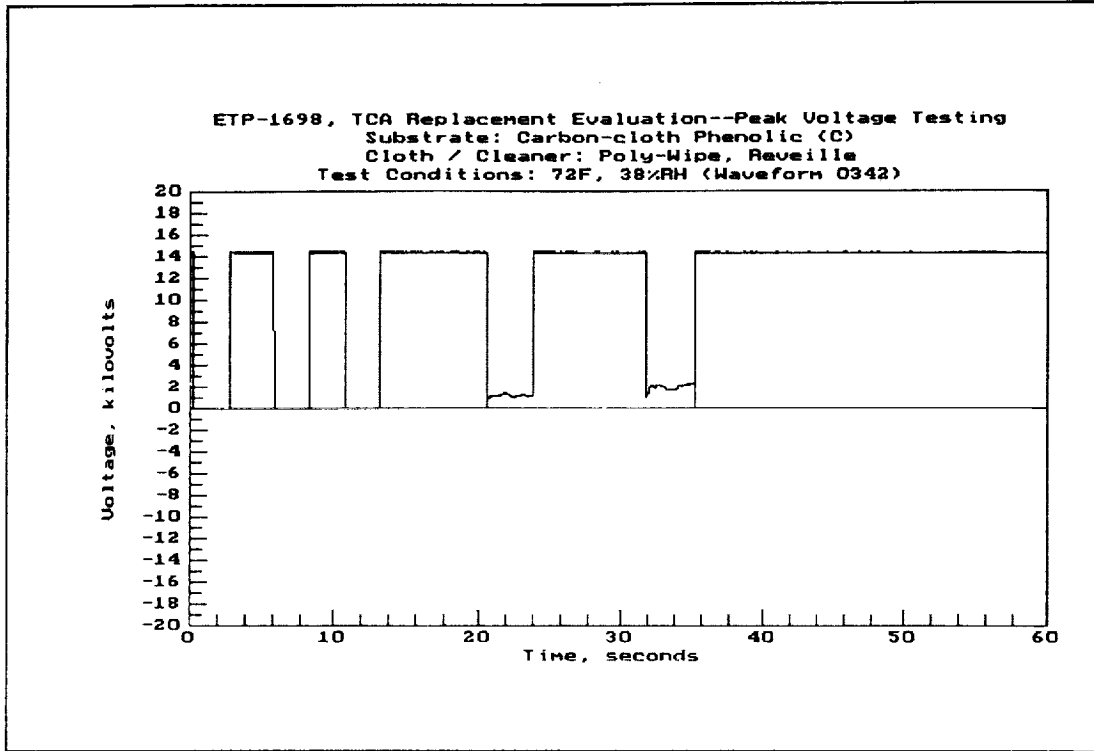


Figure 1. Carbon-Cloth Phenolic & Poly Wipe Surface Voltages: Reveille Cleaning Solvent

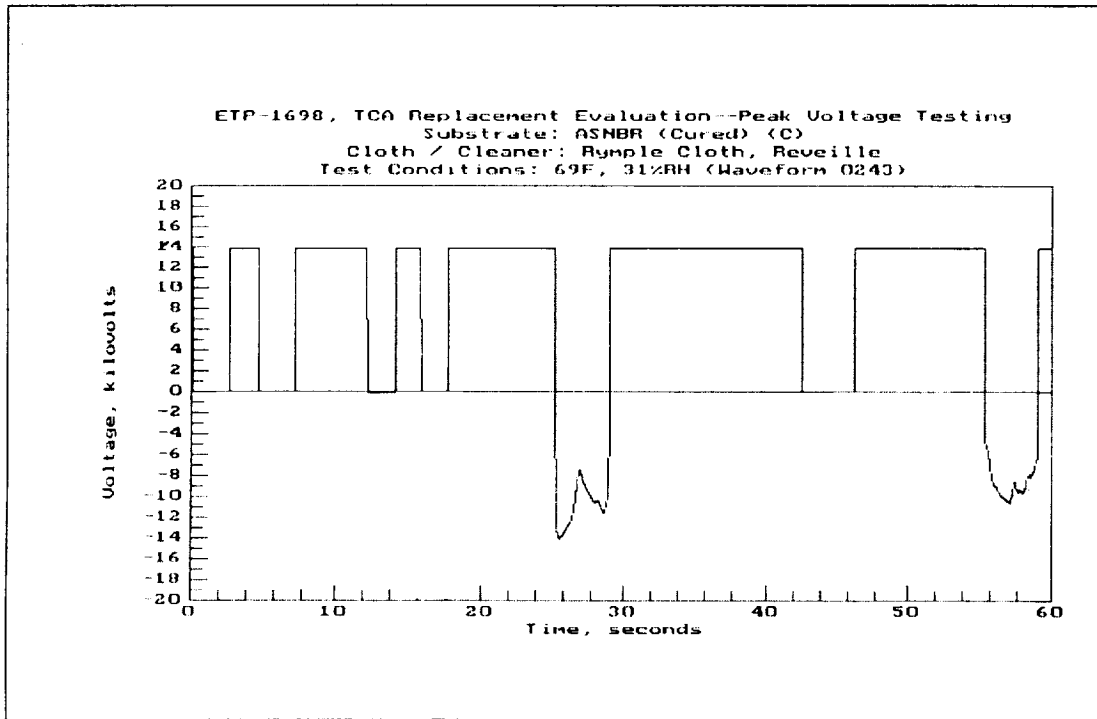


Figure 2. Cured ASNBR & Rymple Cloth Surface Voltages: Reveille Cleaning Solvent

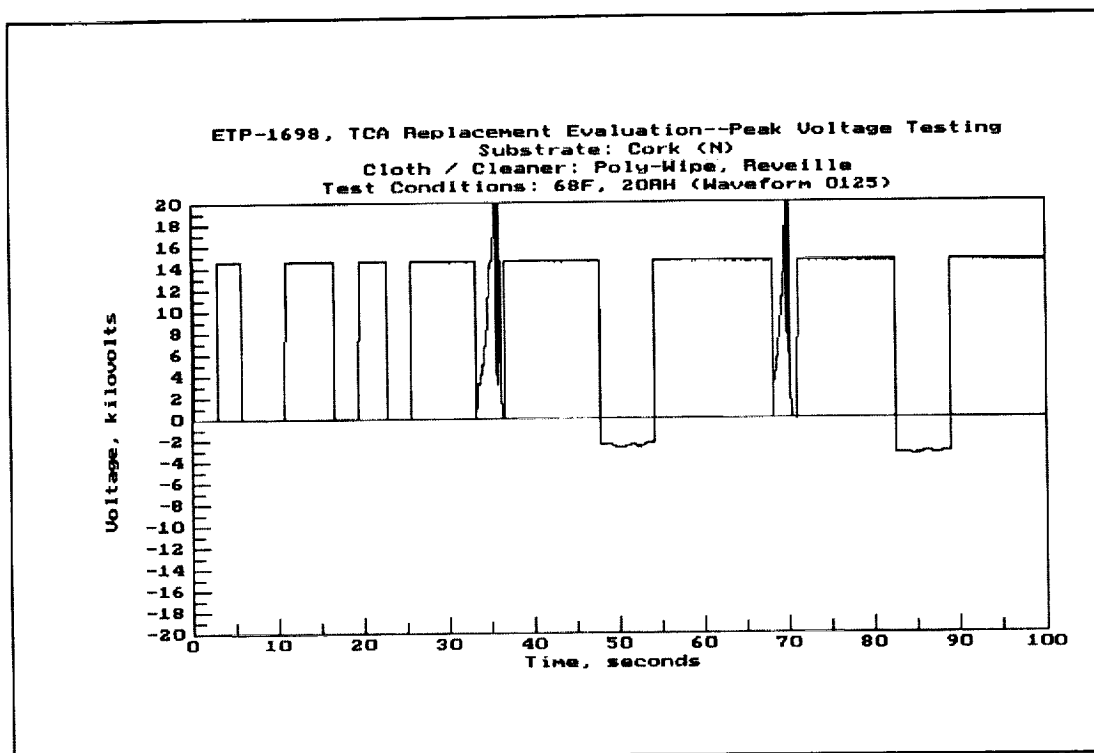


Figure 3. Cork & Poly Wipe Surface Voltages: Reville Cleaning Solvent

All of the surface voltage test results were resolved into figure plots similar to those shown above. In fact, a total of 386 such figure plots were generated to support this testing campaign.

The peak voltage data for all of the cleaning solvent and critical substrate combinations using both rymple cloth and poly wipes in wet- and dry-wipe cleaning processes were compiled into a number of data tables. These peak voltage data tables are provided in the attached Tables I through XXXII.

The testing procedure utilized to resolve all of the peak voltage data onto a single figure plot will now be discussed while referring to Figure 3 above.

The time base of the above figure plot is 100 seconds. To effectively complete this particular test, a number of voltage measurements had to be taken using a method by which one test could be discerned from the next. To accomplish this task, the analog output of the electrostatic voltmeter was connected to the digital storage oscilloscope (DSO) via a relay. When a voltage measurement was not being taken, the voltmeter was disconnected from the DSO and a 7.25 volt signal was inserted in its place. The result is that in between each measurement, a +14,500 volt marker was recorded. Using

this scheme, a total of eight separate/distinct and consecutive voltage measurements were recorded in Figure 3. In order, they were:

Prior to Testing (zero-voltage confirmations)

1. Ground plate (baseline reference)
2. Critical Substrate
3. Wet-wipe solvent swatch
4. Dry-wipe swatch

Following Wet-Wipe Test

1. Solvent swatch
2. Critical Substrate

Following Dry-Wipe Test

1. Swatch
2. Critical Substrate

In this particular case, the substrate was non-conductive. However, when the substrate is conductive as shown in Figure 1 above, only five voltage measurements were recorded. This is because with a grounded conductive substrate, the substrate's voltage was known to be zero and therefore three of the eight measurements were not necessary.

When comparing the results of these tests to those obtained previously, it was noted that there was a significant magnitude increase in the data obtained in this present testing effort. To ensure that these differences were real, the test methods used in both cases were closely reviewed.

The first data obtained was non-ETP data performed simply as a screening test. For this testing, a hand-held Monroe model 255 electric field meter was utilized. In contrast, the test results presented in this study were obtained using a carefully configured laboratory setup using a Monroe model 175 electrostatic voltmeter. As stated earlier, this model 175 meter was used for reasons of precision and repeatability. However, the model 175 meter would automatically provide higher voltage values than the model 255 meter simply because of the way it functions. Specifically, the model 255 meter is a ground-referenced electric field meter and would therefore, capacitively load and thereby diminish the surface voltage being measured. The model 175 meter does not do this and would provide results that are more representative of what actual voltage conditions are.

Knowing this fact, why was the model 255 meter used then? Because it is a small, hand-held meter that is used for live process static voltage monitoring and our tests were simply screening tests that were intended to be related back to measurements made during an actual process. In comparison, the model 175 meter is a large laboratory type instrument that weighs about 40 pounds. However, because the results of this study were performed in an ETP setting, the author felt that the model 175 meter was the better choice—given the testing requirements and desired accuracy.

When the results of the peak voltage testing were discussed, a question was asked regarding whether increased humidity might be expected to reduce the measured peak voltage values. The answer to this question is as follows. Since water is not miscible with the non-polar solvents, a wet-wipe using a non-polar solvent would not be expected to benefit by increased humidity and thereby exhibit a corresponding voltage reduction. In fact, moisture with a non-polar solvent may actually aggravate electric charge generation due to the presence of a two-phase system. In contrast, if the cleaning swatch and/or the substrate being cleaned is hygroscopic, some voltage diminution could result provided the operation was using a polar solvent or simply utilized a dry-wipe.

The peak voltage testing was performed over many days and the relative humidity varied from one day to the next. In fact, the relative humidity conditions at the time of testing ranged from 12 to 42 percent—as can be seen in the attached data tables. According to the description given above, this varying humidity most certainly affects the measured test data and thereby added some confounding to test results. However, since Thiokol does not have a humidity controlled room wherein this testing could be performed, the testing was performed and the humidity conditions at the time of testing were recorded.

How do these peak voltage data and brush discharge occurrence information relate to ESD hazards in rocket manufacturing processes? The answer to this question is multifaceted.

Since it can be shown that in some worst case scenarios, there is sufficient energy in a brush-type discharge to ignite flammable solvent vapors, cleaning operations where brush discharges are expected to occur (e.g., non-polar solvent wet-wiping or dry-wiping), should not be performed around flammable solvents. When one looks at the number of factors that need to coexist in order to enable a brush discharge to successfully ignite a flammable vapor/air mixture, the probability of such an event occurring is very low. This statement is certainly corroborated by the fact that we have performed many dry-wiping operations without having experienced a flash fire mishap. However, the possibility does exist and therefore warrants prudence in how cleaning operations are performed.

It should be noted here that if the charge generated by either a wet-wipe using a non-polar solvent or simply a dry-wipe were to accumulate on an ungrounded conductor, a spark-type discharge could result. Further, the probability of this type of discharge successfully igniting a flammable vapor/air mixture is relatively high. For this reason, the cautionary measure of grounding of all conductive objects during these type of cleaning operations is critically important.

When reviewing the likelihood of igniting solid rocket propellants via a brush type of discharge event, the ESD ignition sensitivity data suggests that such a scenario is very unlikely—except perhaps with some severe cases involving ferrocene- or catocene-filled propellants. It should be understood that there are qualifiers to this statement. For example, equivalent energy amounts imparted to the propellant in a pressurized environment can easily result in the propellant transitioning to a sustained ignition event. Further, if the same amount of electric charge generated by the wiping operations physically resided on a solid nonconductive propellant, the electric field strength inside the propellant medium would be very close to the propellant's dielectric breakdown strength.

CONCLUSIONS

After reviewing all the solvent conductivity, peak voltage, and brush discharge test results collectively, the following conclusions/observations were made:

- ◆ Voltages on the substrate and opposing cleaning swatch, have opposite polarities (e.g., charge is conserved)
- ◆ Voltages on substrates are generally less than on the cleaning swatch. (This is most likely due to voltage suppression associated with the substrate)
- ◆ Comparatively, when used in a wet-wipe cleaning operation, the non-polar solvents generate much higher surface voltages than observed with the solvents that exhibit some degree of polarity. However, work function differences—relative affinity for electrons—can also dominate the amount of charging that can occur (see Prime data in Table XVI)
- ◆ Of all the combinations tested, the highest peak voltages were observed with cleaning operations involving the following critical substrates:
 - ◆ Rustoleum 5690 Primer/5691 Topcoat-Painted Steel

- ◆ Cured EA 913NA Adhesive
 - ◆ Cork (Stock #6566)
 - ◆ Cured RTV (DC 90-006)
 - ◆ Cured Carbon-Filled EPDM Rubber
 - ◆ Cured ASNBR Rubber
 - ◆ Dupont Primer/Topcoat Teflon[®]-Coated Steel
- ◆ Voltages on the cleaning swatch are not necessarily less when cleaning a conductive versus a non-conductive substrate
 - ◆ Generally speaking, Poly wipes do not in all cases, charge more aggressively than does rymple cloth nor visa versa
 - ◆ When using the polar solvents, the dry-wiping operation comparatively generates higher surface voltages than observed with a wet-wipe operation. This trend is especially aggravated with the higher vapor pressure solvents IPA and TCA
 - ◆ Discharging effects can be exhibited during cleaning operations where either non-polar solvents or dry-wiping is utilized. In other words, depending upon the specific substrate being cleaned, when performing either a wet-wipe with non-polar solvents or a dry-wipe with either rymple cloth or poly wipes, sufficiently high surface voltages can be produced to give rise to brush discharging effects
 - ◆ Depending upon the solvent, swatch type, and substrate involved in the cleaning process, brush discharges can be observed off both the cleaning swatch and the substrate itself

RECOMMENDATIONS

The following recommendations are made with regard to how the test results reported in this study potentially affect process safety:

1. Where possible, separate operations involving flammable vapors and cleaning operations that use either non-polar solvents or dry-wiping. Where these type of cleaning operations are still necessary, ensure that all component and personnel grounding practices are followed

2. The necessity and implementation of non-polar solvents or dry-wiping cleaning in rocket motor manufacturing operations should be carefully reviewed for potential ESD hazard effects

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