Do Conductive Residues on Electrical Wires and Contacts in Aircraft Fuel Tanks Pose a Combustion Hazard? Part I. Formation Mechanism

Robert E. Kauffman, UDRI, Dayton, OH
Michael McKubre, SRI International, Palo Alto, CA

ABSTRACT

Conductive deposits that form on the wiring and electrical contacts of fuel quantity indicating sensors (FQIS) have been identified as potential contributors to fuel/air combustion hazards as well as FQIS indication errors and malfunctions. Initial analyses of the conductive residues removed from aircraft parts determined that the residues were heterogeneous mixtures containing distinct layers of silver/silver oxide particles and copper sulfides bound to the surface by organic fuel gums. The conductive deposits only occurred in the presence of Ag plated nuts. The research focused on identifying the effects of exposed metal surfaces, fuel chemistry, and electrical fields on the formation of conductive deposits on electrical connections. It was determined that simple laboratory experiments simulating fuel tank electrical power applied to silver surfaces (wires/plated nuts), water and low sulfur (below 150 ppm sulfur) fuels could be used to produce conductive deposits with chemical and electrical properties similar to the residues removed from fuel tank components. Even for dc power conditions below 1watt, the conductive residues were capable of producing flashes of light, smoke and glowing hot spots with the potential of igniting fuel vapors. The probability of laboratory prepared conductive residues initiating fuel/air combustion was further studied in Part II of this research.

INTRODUCTION

Experience with black residues or deposits in fuel tanks extends back several decades and encompasses many technologies in addition to aircraft [1-6]. These deposits are known to contain sulfur and have often been referred to as “sulfides”. Until 1996 the focus of attention on aircraft fuel tank sulfide deposits was directed to the reliability of in-tank fuel monitoring equipment known as Fuel Quantity Indication Systems or FQIS. This problem has been recognized and studied, particularly by the Air Force, since it can result in under-fueling or misestimates of range capability. The problem is thought to derive from partial or intermittent conductive bridging of contacts electrically in parallel with FQIS capacitive sensing elements. If partial but stable, the problem can be corrected for, at least temporarily, by adjustment of resistive elements incorporated in the sensing system. If intermittent or transient, the problem is less easily addressed. Association of FQIS electrical reading errors with the presence of sulfide deposits indicates that such deposits are capable of conducting either electrically or ionically.

More urgent attention was directed to the presence and properties of sulfide deposits when these were found on and in association with FQIS components retrieved from the TWA800 incident site in 1996. Although the cause of this accident is still undetermined, what is known with reasonable certainty is that the loss of the Boeing 747-100 started with an explosion in the center wing fuel tank, and that the explosion probably resulted from the ignition of fuel vapors.

Aircraft designers have always assumed that the fuel-vapor/air mixture in the fuel tank ullage can be explosive, and have sought to assure safety by eliminating ignition sources in their electrical systems. Ignition sources are eliminated by preventing short circuits between high-voltage current-carrying wiring and by using electrical safeguards at the tank boundary that limit energy input under partial short-circuit conditions.

It is natural to inquire whether the proximity of electrically conductive sulfide deposits to FQIS elements or wiring may facilitate ignition or circumvent preventative electrical safeguards. As a result of the TWA800 inquiry, the NTSB became concerned that sulfide deposits or residues may play a role in precipitating a hazardous condition within the fuel tank of aircraft. On April 7, 1998, the NTSB recommended the FAA "*Require research into copper-sulfide deposits on fuel quantity indication system parts in fuel tanks to determine the levels of deposits that may be hazardous, how to inspect and clean the deposits and when to replace the components*"; (A-98-37).

In its response, the FAA directed research on 8 objectives or tasks as follows:

1. Investigate the characteristics of copper and silver sulfide deposits on probes and wiring, with emphasis on the chemical composition and electrical properties of these deposits.
2. Investigate the mechanism that creates the copper and silver sulfide deposits on probes and wiring in fuel tanks. Emphasis should be placed on factors, which contribute to the mechanism, estimated normal "growth" rates, factors affecting the "growth" rate, etc.
3. Attempt to "grow" the deposits under laboratory conditions.
4. Determine if there are any potential ignition threats from the copper and silver sulfide deposits during FQIS electrical system failures (including shorts to the FQIS wiring).
5. Investigate methods to mitigate the formation of the deposits on FQIS components.
6. Investigate the potential for interaction between Jet A fuel and nickel plated FQIS wiring and the formation of similar type deposits on such wiring.
7. Analyze FAA provided Jet A fuel samples for sulfur, natural antioxidant, and trace metal concentrations and attempt to determine what effect these concentrations have on the formation of the sulfides.
8. Examine the effects of the conductivity of the deposits on the accuracy of the fuel quantity indication.

The research discussed herein focused on the first 7 listed research objectives.

RESULTS AND DISCUSSION

Introduction

The research reported herein was performed in the following sequence:

1. Analysis of deposits on FQIS, terminal blocks and associated hardware from aircraft fuel tanks.
2. Analysis and stressing of Jet A fuels to identify possible contaminants.
3. Literature search to identify mechanisms capable of producing conductive deposits containing Ag, Cu and S.
4. Develop laboratory procedures involving terminal block materials and Jet A fuel capable of producing conductive deposits containing Ag, Cu and S.
5. Perform initial tests to evaluate combustion hazard of laboratory produced conductive deposits.

Analysis of Deposits from Aircraft Fuel Tanks

Although deposits containing Ag, Cu and S have been found on a wide range of components (FQIS, terminal blocks, bundled wires, pump wires and fuses) in aircraft fuel tanks [2-4], the focus of this paper is on the conductive deposits present on FQIS, terminal block and associated hardware. The conductive deposits on FQIS, terminal blocks and associated hardware reduce the accuracy of the FQIS fuel quantity determination. For this work, the deposits present on 10 FQIS and 10 terminal blocks with/without associated hardware were analyzed with SEM/EDS, XPS, AES and FTIR analytical techniques (Appendix).

Four basic types of deposits were observed on the FQIS and terminal block assemblies. The first type of deposit was yellow, non-conductive (greater than 10 M? at 1 mm) and wiped off easily with a paper towel. The yellow deposit was identified as CdS most likely produced by the interaction of Cd plated nuts with the sulfur compounds present in Jet A fuels.

The second type of deposit was black, non-conductive and wiped off easily with a paper towel. The black deposit was identified as Ag_2S most likely produced by the interaction of Ag plated wires with sulfur compounds in Jet A fuels. The black deposits were found primarily on wire insulation abrasions and near wire terminations at connectors (Figure 1) and other wire clamps. The majority of the deposits present on the FQIS and terminal block surfaces were non-conductive and analyzed as CdS or Ag_2S.

The third type of deposit was found on the end surfaces of two terminal block surfaces and was brown, gum-like material, non-conductive, and dissolved in solvents (could not be wiped off with a paper towel). The FTIR spectra of the brown gum matched the FTIR spectra of fuel oxidation gums [1] and fuel tank deposits in the TWA800 accident reports [3,4]. The brown gum contained minimal concentrations (less than 1%) of Cu and Ag but contained significant levels of C, O and S.

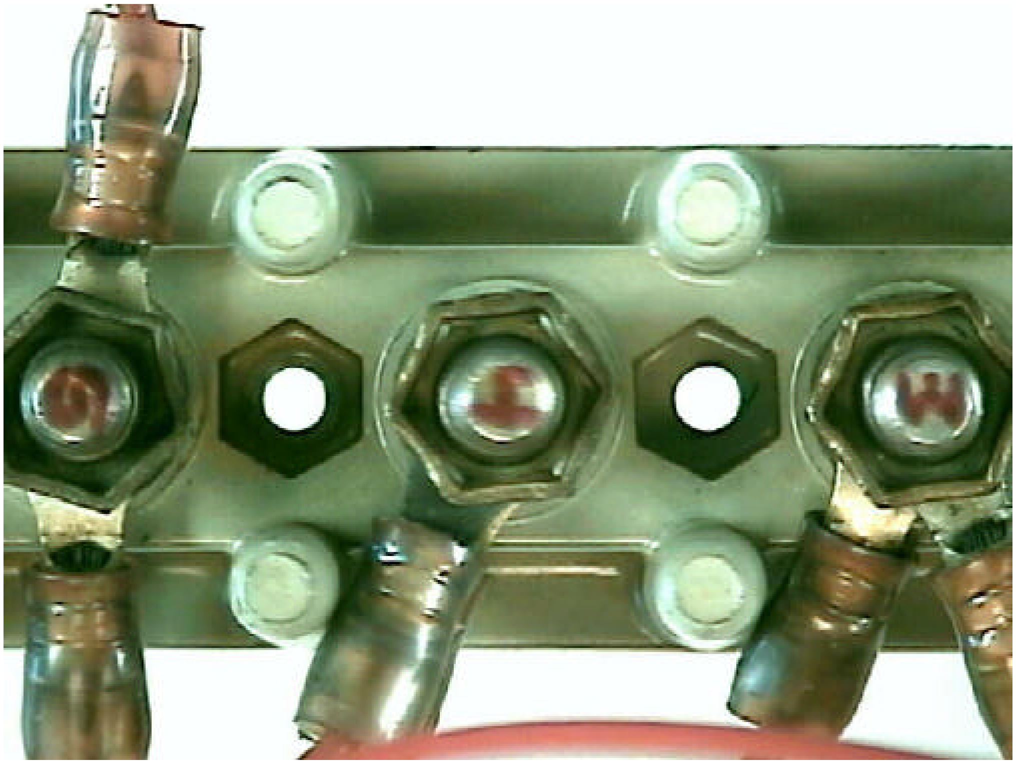

Figure 1. Terminal block with associated hardware. Light green surfaces are polymeric; hexagonal nuts, numbered studs and connectors metallic; Teflon heat shrink on junction of red wire bundles and connectors. Some deposits visible, middle connector and lower ledge.

The fourth type of deposit was found on three terminal blocks: nuts (interior and exterior surfaces), connectors, polymeric surfaces between the nuts and polymeric posts where the connectors rest (Figure 1). The fourth type of deposit was shiny, brown or black, conductive (below 10 K? at 5 mm) and could not be removed by wiping with a paper towel. Solvents were able to extract a gum-like material similar to the third type of deposit from the shiny, conductive deposits. Portions of the deposits were scraped off for analysis. The FTIR spectra of the conductive deposits were similar to the FTIR spectra of gum-like deposits (third type of deposits) and the fuel tank deposits in the TWA800 accident reports [3,4].

The surface analysis (XPS, SEM/EDS) results of the conductive deposits indicated that the deposits contained primarily C and O (cannot detect H) with varying amounts of Ag, Cu and S depending on the sampling location of the terminal block. The deposits on the nuts (Ag plated steel) had high (greater than 10%) levels of Ag and S while the deposits on the connectors (Sn plated Cu) had high levels of Ag, Cu and S. The deposits on the polymer surfaces contained low (~5%) levels of Ag, Cu and S. These surface analyses by location are in agreement with analyses previously reported [2] for a terminal block with conductive deposits that had been removed from a commercial airline experiencing refueling problems.

Although the XPS and SEM/EDS detected similar elements in the conductive deposits, the relative amounts of the detected elements differed greatly. The SEM/EDS analyses (1micron analysis depth) detected high levels of Ag and S on the polymeric surfaces of the terminal blocks while the XPS analyses (0.003 micron analysis depth) detected low levels of Ag and S. These differences indicated that the conductive deposits were heterogeneous with regard to deposit thickness. Therefore, AES analyses with elemental depth profiling were performed and determined that the conductive layers were basically three separate layers. The outer layer (farthest from polymeric surface) was primarily C, O, S (fuel gums) with minimal Ag or Cu content. The middle layer contained C, O and S at significant levels but contained a high concentration (20-40%) of Ag and minimal Cu (below 5%). The results also indicated the Ag was most likely present as Ag metal or Ag_2O particles instead of Ag_2S. The inner most layer also contained significant levels of C, O and S but contained a high level of Cu (10-20%) and minimal Ag (below 5%). The results indicated that Cu was present as CuS.

Consequently, the analytical results indicate that only the deposits containing fuel gums and distinct Ag/Ag_2O and CuS layers were conductive. The Ag/Ag_2O layer was postulated to be responsible for the conductivity of the deposit. Another observation was that the conductive deposits only occurred on terminal blocks with Ag plated nuts (Ag plated nuts also present with conductive residues in Reference 2) further indicating that the Ag/Ag_2O layer was responsible for the deposit's conductivity. The fact that the Ag containing deposits were present on the polymeric surfaces and metal connectors of the terminal block (Figure 1) indicated that the Ag particles were created at the Ag plated nuts then transported to the adjacent surfaces and coated with fuel gums providing adherence to the surfaces.

World –Wide Survey of Jet A Fuels

Since fuel gums appeared to be involved in the formation of the conductive deposits, 69 Jet A fuels obtained from aircraft and fuel reserves located in U.S., Europe and Asia were analyzed. The fuels were analyzed for natural antioxidants, total sulfur content, Ag reactivity, thermal-oxidation and gum content. The total sulfur concentrations of the Jet A fuels ranged from 0.003 to 0.15% (determined by FAA and commercial laboratories) with the lowest sulfur fuels obtained from European and Asian aircraft fuel tanks. The fuels with the lowest sulfur contents also had the lowest natural antioxidant concentrations (phenol and amine containing compounds, analysis described in Appendix and Reference 1). When soaked overnight in the different Jet A fuels to evaluate their Ag reactivities, only 2 fuels (U.S. fuels) created Ag_2S films on the surfaces of the Ag wires.

The Jet A fuels were then heated at 290°F in air for four hours (Appendix) to test their thermal-oxidative stabilities, 7 fuels oxidized rapidly producing hydroperoxides, carboxylic acids and gums. The 7 fuels that oxidized rapidly are referred to as "low sulfur" fuels since the sulfur compounds present in the fuels are low in concentration or low in capability to inhibit fuel oxidation [7]. The FTIR spectra of the gums isolated from the oxidized "low sulfur" fuels (solvent soluble) were similar to the FTIR spectra of the gums that were solvent extracted from the terminal blocks with conductive deposits [1].

Finally, the Jet A fuels were analyzed for gum contents to see if the gums found on the terminal blocks with conductive deposits were formed by evaporation of fuels with existing gum contents. All of the fuels had minimal (below 0.2%) residues by TGA (Appendix) decreasing with sulfur content. The produced residues were primarily inorganic in content and did not produce a well-defined FTIR spectrum [1].

To test the capabilities of the Jet A fuels to produce gums in the vapor phase (terminal block in vapor phase of fuel tank), Ag plated Cu wires were heated in the different fuels (Appendix) at 350°F in air. Only the "low sulfur" fuels produced gums and deposits on the wires in the vapor phase. The "low sulfur" fuels also produced gums in the heated liquid fuel.

The analyses of the deposits on the Ag plated wires detected C, O, S and Cu but did not detect Ag. Also, the produced gums and deposits had resistances (~1 M?) much higher than the conductive residues (~10 K?) but lower than the original fuel (>100 M?) [1].

Literature Search

Since the Jet A fuel oxidation studies were able to produce gums but not conductive, Ag containing deposits, a literature search focused on the formation of conductive deposits containing organic, Cu and Ag compounds was performed. Although numerous references on the sulfur corrosion of Ag and Cu surface were identified [1], several references on electrochemically produced deposits containing Ag organic compounds were also identified [1].

The most pertinent reference to this work was a NASA report [5] which identified a reaction between Ag plated Cu wire carrying 28V dc and ethylene glycol coolant solutions that produced a conductive Ag residue. In the presence of oxygen, the reaction also caused smoke and flashes of light. The reaction was proposed to be the cause of the fire that occurred during the Apollo AS-204 incident in 1967 [5]. The researchers showed that the formation of the conductive Ag residue could be inhibited by adding a specific chemical to the ethylene glycol coolant or could be eliminated by replacing the Ag coated Cu wires with Ni coated wires.

Producing Conductive Fuel Deposits: Ag Plated Cu Wires on Glass Slides Tests

In an attempt to duplicate the NASA test [5], two Ag plated Cu wires were placed parallel (1 mm apart) on a glass slide (Appendix). The Ag/Cu wires were connected to a 9V dc battery and a drop of water was pipetted between the parallel wires. Immediately a black deposit formed at the positively charged wire and bubbles (H_2 gas) formed at the negatively charged wire. The resistance between the wires decreased from above 10 M? to below 10 K? in less than a minute as the black deposit grew across the gap to the negatively charged wire. Analysis of the black deposit indicated it was CuO particles with minimum Ag present.

Once the black deposit filled the gap between the wires, a drop of fuel was pipetted next to the water drop between the wires. If a fresh Jet A fuel or oxidized “typical “ fuel was used, the deposit continued to grow without observation of other effects. However, if oxidized “low sulfur” fuel was used, flashes of light and smoke were observed at the water:fuel interface. Regardless of the fuel used, the resistance of the black deposit decreased to below 50 ? and the analyses of the black deposits detected much higher levels of Ag than when the deposits were formed with just water.

Producing Conductive Fuel Deposits: Metal Wires in Ceramic Rod Tests

Introduction - Although the parallel wires on the glass slide tests were able to produce conductive deposits and flashes of light/smoke in agreement with the NASA research [5], the water and fuel drops flowed away from the wires and off of the slide. To better control the positioning of the water and fuel drops, ceramic rods with two metal wires pushed through two bores (1mm diameter, 1mm apart) were used to produce conductive residues (Figure 2) as described in the Appendix.

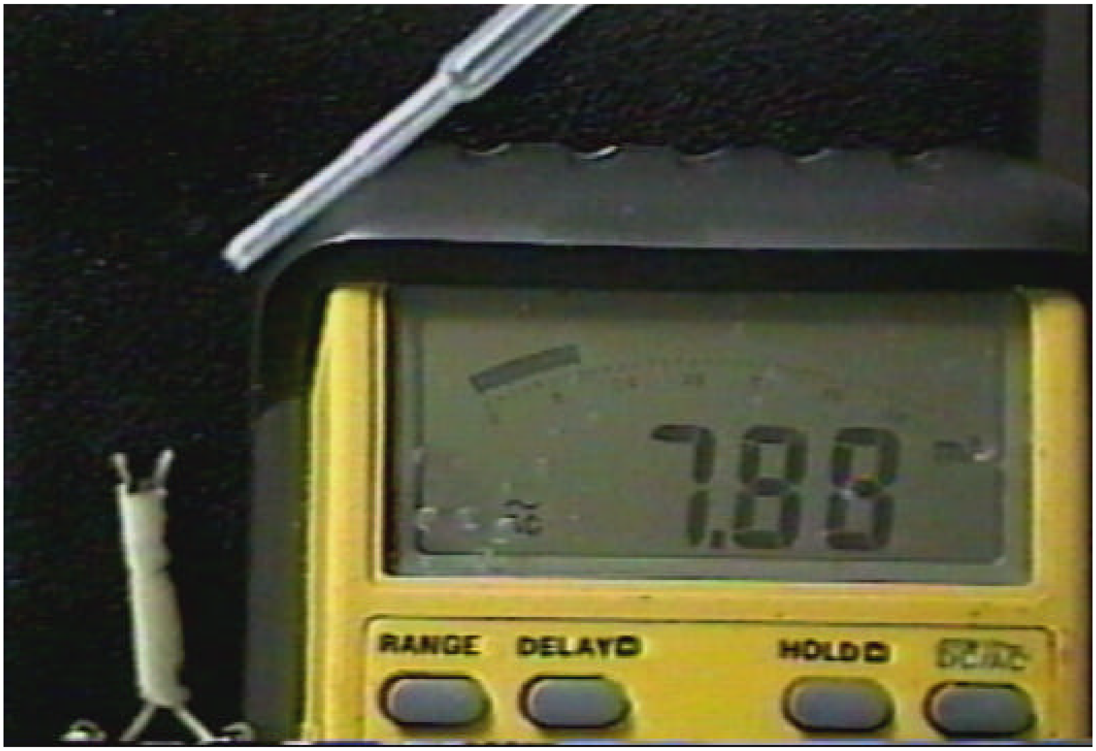

Figure 2. White ceramic rod with two metal wires extending out of top and two wires and alligator clips (only tips seen) on bottom. Plastic pipette used to dispense water/fuel drops on top of ceramic rod and multimeter used to measure current. Black deposit forms between top wires.

Ag Wire-Water-Electricity Reactions - The first ceramic tests were performed with Ag wires positioned in the ceramic rod. A drop of water was pipetted onto the ceramic rod and formed a bead engulfing the exposed ends of the Ag wires. The characteristics of the produced conductive Ag deposits were dependent on the type of electricity applied to produce the deposits. If dc voltage (Appendix) was applied, the water drop became black with particles and the resulting deposit was composed of small (less than 1 micron) Ag/Ag_2O spheres (Figure 3). The deposit covered the entire ceramic surface and was highly conductive (50 ? -10 K?). When the dc voltage was a 9V dc battery (no current limitation), radio frequencies (RF) were detected as the water drop reacted. No bubbling was observed at the negatively charged Ag wire as observed with the glass slide tests.

If the 50V ac, 30 mA, 60 Hz power supply (Appendix) was used, the water drop became black with particles but the resulting deposit was amorphous. Although, the deposit covered the entire ceramic surface, the deposit was poorly conductive (greater than 50 K?). No RF was detected. However, if the modified function generator (Appendix) was used (28V ac, 20 mA limitation, cycle rates of 400, 2000 and 7400 Hz to simulate FQIS power), the water drop remained clear as the particles formed a straight line on the surface of the ceramic rod directly between the Ag wires. The deposit was highly conductive (1? -1 K? even though 1mm width) and was composed of large (>10 micron) hexagonal crystals and dendrites (fern-like structures) of Ag/Ag_2O (Figure 3). It appears that arcing may have occurred between the crystals due to the damaged regions of the crystals.

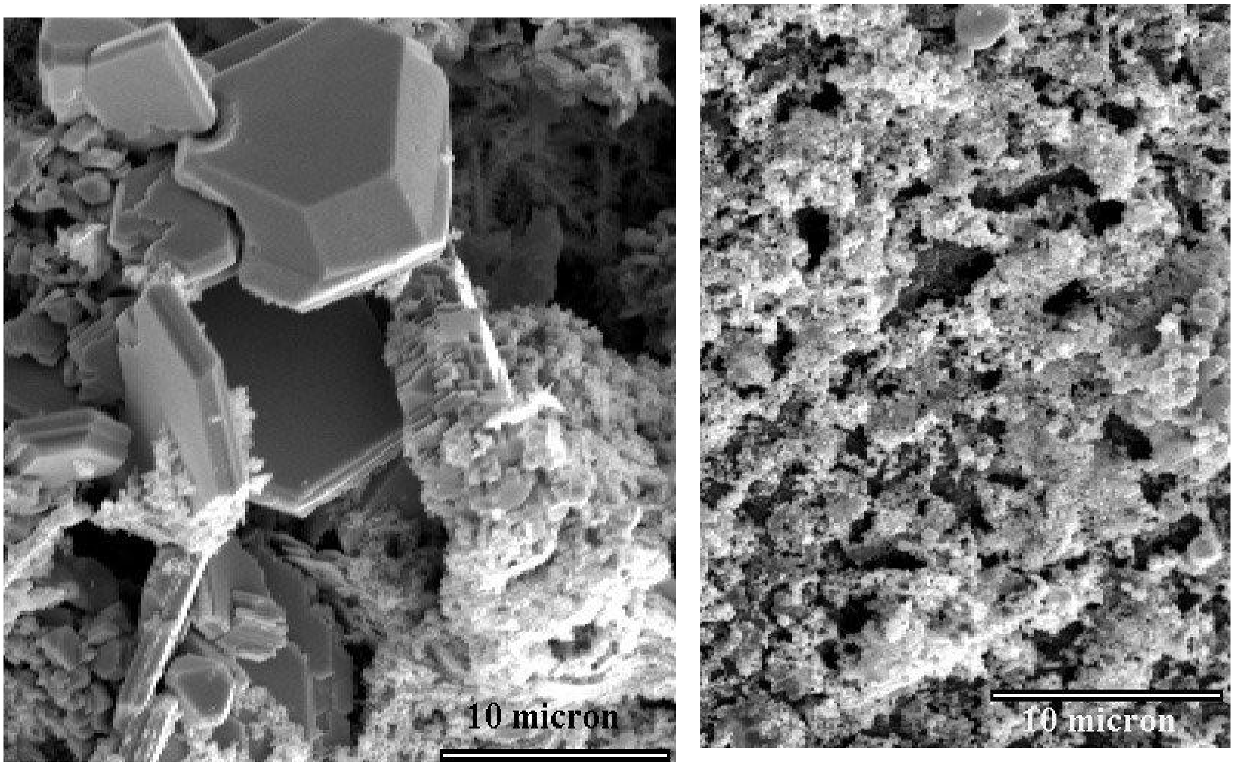

Figure 3. Large hexagonal crystals (left picture) and small spheres (right picture) produced by Ag wire/water reactions with ac (7400Hz) and dc voltage experiments, respectively.

<u>Ag Deposit-Fuel-Electricity Reaction</u> - Once the water drop was converted to the conductive Ag deposit, a drop of fuel was then added. In the case of the dc battery tests (9-45V:Appendix), flashes of light and smoke (Figure 4) were produced when the fuel drop was added and the current increased (residue resistance decreased). After 20-40 drops of fuel with the dc battery tests, the flashes of light were replaced by a constant glow and the liquid fuel on the ceramic rod and adjacent clamp ignited (Figure 4). The ignitions occurred with 27-45V dc and ~2A (approximate since maximum of current spikes unmeasured) and with 45V dc and 0.2A (current limited).

In addition to the battery tests, a 40V, 74 mA limited dc power supply (Appendix) was used with the ceramic rod tests. For residues with 10 K? resistance (4 mA current), the addition of fresh or oxidized “typical fuels” caused the resistance of the residue to increase (current fell below 0.5 mA) without the occurrence of flashes of light or smoke. However, if fresh or oxidized “low sulfur” fuels were added to the conductive residue (10 K?), the resistance dropped to 2-5 K? (current increased to 8-20 mA) and flashes of light and smoke were observed, especially for the highly oxidized “low sulfur” fuels with gum contents. Numerous fuel drop tests with the 40V dc power supply were not performed to produce the constant glow and determine the potential of fuel ignition.

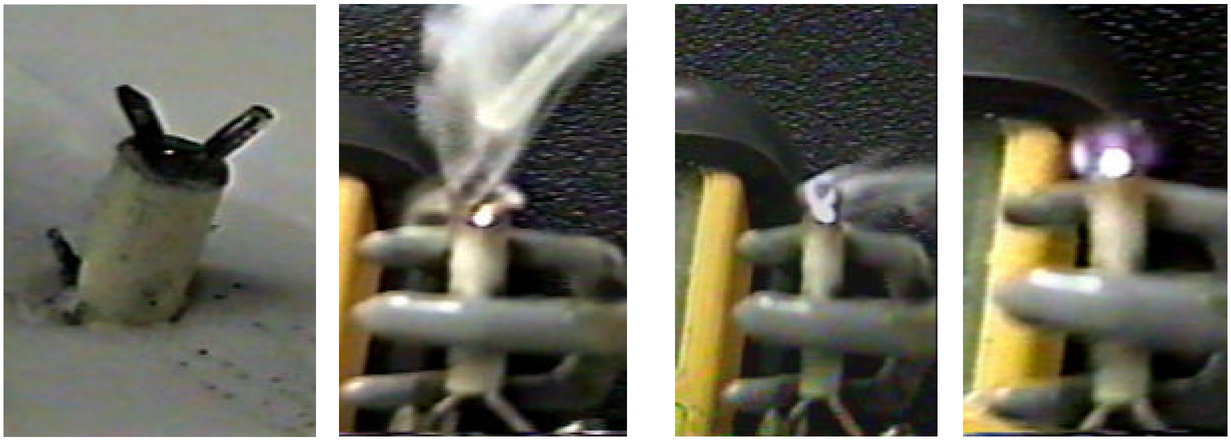

Figure 4. From left to right : small flash, constant glow with smoke, vapor ignition and blue flame produced by reaction of fuel with dc voltage and 50Vac on ceramic rod with Ag wires.

In contrast to the dc tests, the ac tests with the modified function generator (28V ac, 20 mA limitation) at cycle rates of 60, 400, 2000 and 7400 Hz only produced small amounts of smoke when fuel drops were added to the conductive residue. The smoke was seen at all four cycle rates (60, 400, 200 and 7400 Hz) and with different types of fresh or oxidized “low sulfur” fuels.

Since the 28V ac modified function generator was limited to 20 mA, the conductive Ag residues produced by the generator were also tested with the 50V ac, 300 mA, 60 Hz power supply (simulate a short between FQIS and power lines). When a fuel drop was added to the previously generated conductive Ag residues and the 50V ac power was applied to the leads of the ceramic rods, flashes of light and smoke were observed (Figure 4). After several drops of fuel, the flashes of light were replaced by a constant glow. Eventually, the fuel on the ceramic rod and clamp ignited (Figure 4) with continued applications of the fuel drops and 50V ac, 300 mA limited, 60 Hz power.

<u>Metal Wire-Water/Fuel–9V dc Battery Tests</u> - To determine if other metals present in aircraft fuel tanks were capable of producing conductive residues as well as flashes of light/smoke/fuel ignition with water/fuel drops, a wide range of metal wires were tested with a 9V dc battery and the ceramic rod setup. The metal wires tested included Ag, Al, Au, Cd, Cu, Ni, Sn, Steel (316) and Ti. Combinations of the metal wires were also tested.

For each metal, a drop of water was pipetted onto the ceramic rod surface and a fresh 9V dc battery was connected to the electrical leads of the rod. Of the metals tested, only Ag, Cd and Cu produced RF during the water reaction and produced conductive residues (resistances below 20 K?) in the presence of water. Ni and Al produced large amounts of non-conductive (resistances above 2.6 M?) residues. Au, Sn, 316 Steel and Ti produced small amounts of non-conductive residues.

However, when the fuel drop was added to the wet conductive deposits produced by Cd, Cu and Ag, only the Ag residue became more conductive and produced flashes of light and smoke. Upon the addition of fuel, the Cd and Cu residues became non-conductive (resistances above 2.6 M?).

Combinations of metal wires produced conductive residues with water/fuel and produced flashes of light and smoke only when Ag was the positively charged wire.

Current Spikes During Flashes of Light - Although the multimeter (rapid value changes) and strip chart (pen deflection) responded to the flashes of light/ignition, the maximum current value during the spike could not be determined. Since knowledge of the actual current flows during the flashes of light/ignition is important in designing a transient suppression unit for fuel tanks, the current spikes during the flashes of light were documented with a recording oscilloscope (Appendix). The 10^8 samples per second acquisition rate of the recording oscilloscope was triggered each time a 5 mA change in the current flow occurred. The tests were performed with a 40V dc, 30 mA power supply and "low sulfur" fuel to study the low current flashes that occurred in the 4-10 mA range with the ceramic rod setup. Each time a flash of light was observed, the oscilloscope triggered and recorded the current flow. A current (mA) versus time (microseconds) plot representative of the 35 observed flashes is shown in Figure 5.

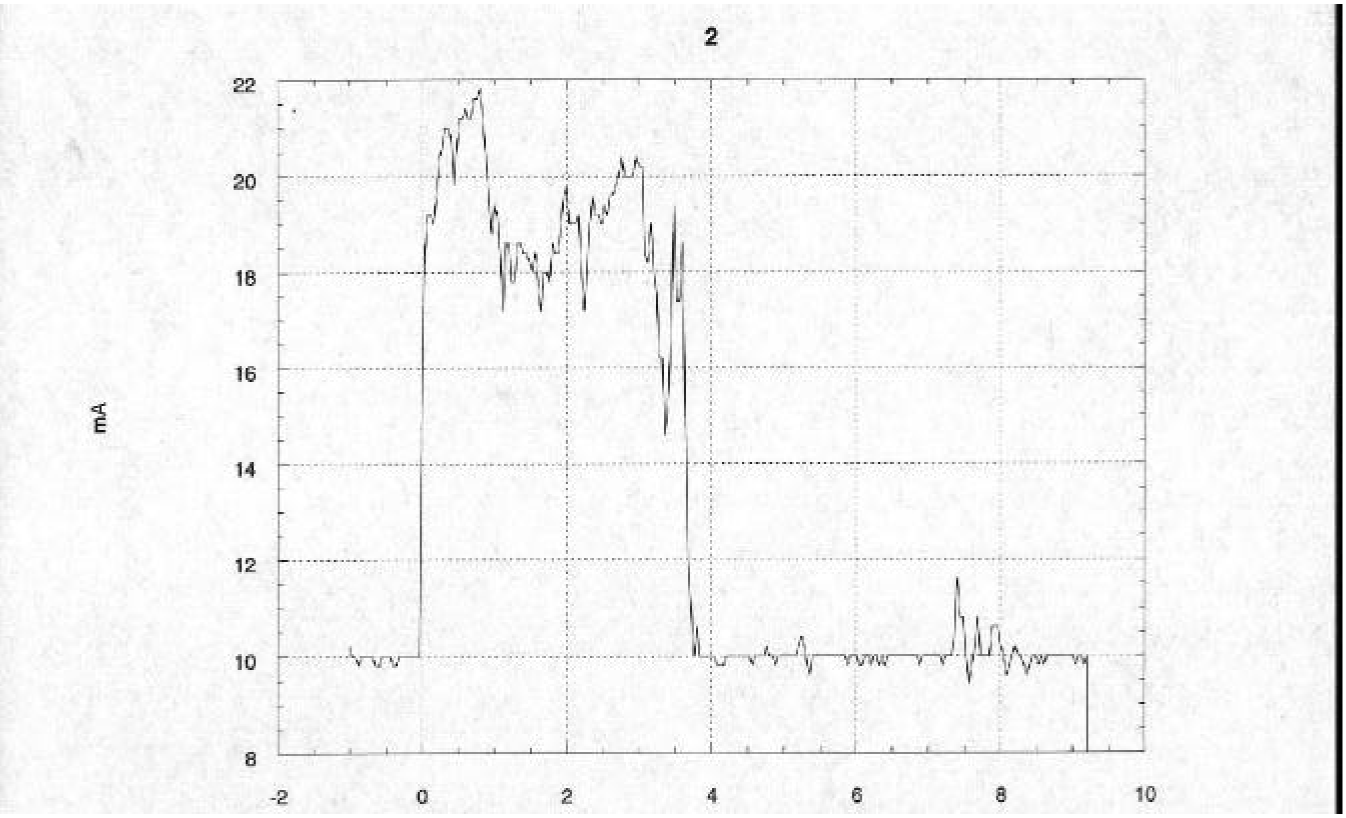

Figure 5. Representative current (y-axis: milliamps) vs time (x-axis: microseconds) plot recorded during one of the flashes of light on the ceramic rod with 40Vdc, 30mA power.

The current vs time plot in Figure 5 shows that prior to the flash of light, the current was 10 mA in agreement with the multimeter connected in series with the oscilloscope. During the flash of light the current increased to 20-22 mA for 4 microseconds prior to returning to the previously measured 10 mA. The flashes of light recorded during the test with the 40V dc, 30 mA power supply had maximum current levels of 16-30 mA (current limit) for 1-5 microseconds. The short duration of the flashes of light, limits the energy and time available to transfer heat to the fuel [6] explaining the lack of fuel ignition when the flashes of light occur in the ceramic rod tests. Ignitions were only observed during the ceramic rod tests with the 27-45V dc battery and 50V ac, 300 mA, 60 Hz power supplies when a constant glow (current fluctuations minimal) was present and the current was above 200 mA.

Producing Conductive Fuel Deposits: Ag Wires/Ag Plated Nuts on Terminal Block Tests

Introduction - In an attempt to simulate the terminal block conditions in the aircraft fuel tank, tests were performed on unused terminal blocks with Ag wires and Ag plated nuts spaced 10-15 mm apart (gap between nuts on terminal blocks in Figure 1). To further simulate the fuel tank, the fuel drops were added on top of the water prior to applying power (Figure 6) instead of allowing the deposit to form and dry prior to fuel addition (ceramic rod tests). The tests were performed on the back of the terminal blocks to simplify the water/fuel drop additions, i.e., steel studs, hexagonal holes, polymeric posts, etc. hinder pipetting of water/fuel drops (Appendix).

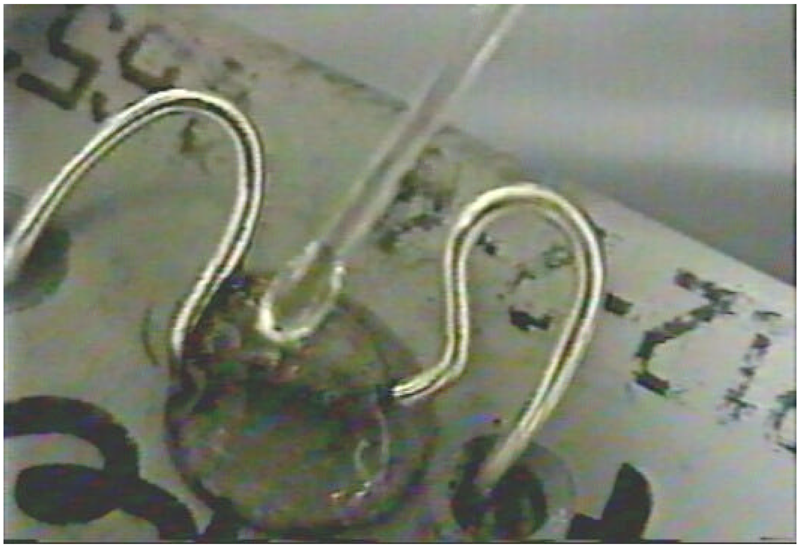

Figure 6. Pipetting fuel drop (5 microliters) onto water drop between two Ag wires on back of terminal block.

Ag-Water/Fuel-dc Electricity Reactions - When the "low sulfur" fuel/water drops were pipetted onto the terminal block with the Ag wires (Figure 6) and the 40V dc power applied, bubbling (H_2 gas) occurred at the negatively charged wire and a shiny, silver film accumulated between the water and fuel layers (fuel on top due to lower density). After several minutes, when the shiny silver layer reached the negatively charged wire (Figure 7), the bubbling ceased and the current reached the maximum of the power supply (30-74 mA). As detailed in the Appendix, the voltage at the residue dropped to below 3V at the deposit when the current reached the maximum for the power supply minimizing the Ag/water reaction. When the maximum current was reached, the water/fuel drops were allowed to dry without further liquid addition to produce a conductive, shiny Ag residue (crystals and spheres similar to Figure 3).

Figure 7. From left to right: silver layer forming at positively charged Ag wire (right wire), constant glow/smoke created by initial fuel drop and fuel vapor ignition by constant glow for terminal block experiments with “low sulfur” fuels and 40Vdc, 30 – 74 mA power supplies.

Ag Residue-Fuel-dc Electricity Reactions - As opposed to the ceramic rod tests, which required over 20 fuel drops to produce a constant glow, the silver deposit produced constant glows with the 40V dc power supplies (30-74 mA) upon the addition of the first drop (Figure 7) of “low sulfur” fuel. The constant glows had durations of up to 12 seconds and appeared to ignite the fuel vapor above them (Figure 7). Craters over 5 mm in diameter and 1 mm in depth were created in the polymer surface by the constant glows. The size and brightness of the constant glows decreased as the current limitations of the 40V dc power supplies decreased from 74 to 30 mA. The maximum power attainable by the 40V dc supplies ranged from 0.75 to 0.32 watts for the 74 to 30 mA supplies, respectively. The maximum power was attained when the resistance of the residue matched the internal resistance of the 40V dc power supply.

When the Ag wires were replaced with Ag plated nuts for the 40V dc tests, the results for the nuts were similar to those of the wires (conductive, shiny Ag residue and constant glows produced).

Ag-Water/Fuel ac Electricity Reactions - When the 40V dc power supplies were replaced by the 40V ac function generator (limited to 20 mA) for the Ag wire/terminal block tests, a shiny Ag layer formed at the water/”low sulfur” fuel interface without bubbling occurring at either Ag wire. In contrast to the 40V dc tests, the shiny Ag layer followed the fuel/water interface instead of connecting the Ag wires. The water/fuel drop dried to produce conductive, shiny Ag surfaces (similar to crystals and dendrites in Figure 3) regardless of the cycle rate: 60, 400, 200 or 7400 Hz.

Ag Residue-Fuel-ac Electricity Reactions - In contrast to the 40V dc tests which produced constant glows, addition of “low sulfur” fuel to the shiny Ag surface produced only flashes of light and smoke for the 40V ac function generator regardless of the cycle rate and number of fuel drops. The maximum power of the 40V ac function generator was 0.45W and occurred when the resistance of the residue equaled the internal resistance of the function generator.

Effects of Fuel and Water Types on Reactions - Regardless of whether 40V ac or 40V dc power supplies were used, when “typical” fuel drops were used with the water drops on the terminal block only flashes of light and smoke were observed, i.e., no constant glows produced by “typical” fuels. In general, the measured currents were lower during the formation of the shiny Ag layer and the number of flashes of light/smoke was lower with the “typical” fuels in comparison to the “low sulfur” fuels. In contrast to the fuels, the type of water (deionized, distilled, condensed by humidifier) had no discernible effects on the reactivities of produced Ag residues.

CONCLUSIONS

This paper indicates that the conductive “Ag/Cu sulfide” deposits present on electrical components in aircraft fuel tanks are actually fuel gums containing distinct Ag/Ag_2O and CuS layers. The conductive deposits on terminal blocks in fuel tanks only occur in the presence of Ag plated nuts and the Ag/Ag_2O layer is most likely responsible for the conductivity of the deposit. The Ag/Ag_2O layer of the conductive residue is created by the electrochemical reaction of water with the Ag plated nuts on the terminal block and forms under normal operating conditions (28V ac, 10 mA) and inerted conditions (occurs under water/fuel drop). Other metals present in the fuel tank do not react with water and electricity to produce conductive residues.

The results also indicate the “low sulfur” fuels (oxidize rapidly to produce hydroperoxides, acids, gums) support conductive deposit formation. The addition of “low sulfur” fuel to a layer of Ag/Ag_2O particles decreases the resistance of the layer (increases current). Since fuel is non-conductive, the fuel most likely reduces the Ag_2O particles/surfaces to more conductive Ag particles/surfaces increasing the overall conductivity of the layer. Also the “low sulfur” fuels are oxidized (Ag_2O reduced) to produce hydroperoxides, carboxylic acids and gums capable of enhancing electrical connections between adjacent Ag particles. The gums bind the Ag particles together and to the terminal block surface helping to maintain the conductivity of the layer of Ag particles. The “typical” fuels do not oxidize to form gums and the sulfur present in the fuels may react with Ag surfaces to produce Ag_2S increasing the resistance of the Ag layer. The conductive deposits on the terminal block posts had a shiny Ag appearance adhered to the polymeric surface and appeared continuous under magnification in agreement with the terminal block tests using “low sulfur” fuels.

For highly conductive Ag resides (current above 200 mA) on the ceramic rods, smoke and flashes of light were produced with ac or dc voltage (above 30V) using all types of fuels. Fuel ignitions occurred with both ac and dc voltages only after the flashes of light had been replaced by a constant glow (required 20-40 drops of fuel), which lasted for several seconds.

Less conductive (current below 20 mA) Ag deposits on the ceramic rod and terminal block produced flashes of light and smoke for both ac or dc power if the voltage was above 30V and “low sulfur” fuel was added. For the Ag residues formed on the terminal blocks with 40V dc and “low sulfur” fuels, areas of constant glow (required only 1 drop of fuel) were produced at currents below 30 mA, which were capable of fuel vapor ignition (power below 0.7W).

Therefore, the results of this paper indicate that conductive Ag residues formed under normal operating conditions on FQIS and terminal blocks do pose a combustion hazard. The combustion hazard increases dramatically if equivalent dc voltage or higher current (> 220 mA) ac voltage are applied to the FQIS wiring through abraded wire bundles or other electrical isolation failures. The probability of fuel vapor ignition by the flashes of light and constant glow produced by conductive Ag residues is presented in the following paper.

RECOMMENDATIONS

FQIS Reliability

Since the conductive Ag residues form under normal or inerted conditions in the presence of Ag plated nuts, replacement of the Ag plated nuts is the only short-term solution to inhibiting conductive residue formation and improving FQIS reliability. Redesigns of the terminal blocks or capping the nuts to inhibit water drops from electrically bridging adjacent nuts would also stop the formation of conductive deposits. A long-term solution would be to identify a chemical compound (similar to NASA [5]) capable of passivating the Ag plated nuts and other exposed Ag surfaces to inhibit the initial Ag water reactions that produce the conductive Ag particles.

Combustion Hazard

Although the effect of conductive residues on FQIS reliability is well known, the combustion hazard of the conductive residues is less certain. To minimize the combustion hazard, the 28V ac FQIS wires should not be bundled with 28V dc wires such as those powering the automatic fuel shutoff valve. Also power limitation devices to filter out all dc power and any ac power above normal operating conditions (30V ac, 10 mA) from entering the fuel tank should be utilized to eliminate the possibility of areas of constant glow (increased probability of fuel ignition) in previously formed conductive Ag residues.

ACKNOWLEDGEMENTS

This research was supported by the FAA Aircraft Catastrophic Failure Prevention Group, Atlantic City International Airport, NJ with William Emmerling serving as technical monitor. The authors would also like to thank Robert Swaim of the NTSB, Washington D.C. and George Slenski of AFRL, Wright-Patterson Air Force Base, Ohio for providing the terminal blocks with the conductive residues.

REFERENCES

1. Kauffman, R. E., UDRI Interim Reports to SRI International in support of FAA Contract No. DTFA03-98-D-00008 dated October 1999 and November 2001.

2. Minutes of NTSB Systems Sub-group meeting regarding residues, Washington DC, April 29, 1998.

3. Report No. WL/MLS 97-102. “747 Fuel Probe Evaluation – A/C N93119 TWA Flight 800”.

4. Figures from NTSB public meeting on TWA800 accident. http://www.ntsb.gov/Events.twa800

5. NASA Technical Note NASA TN D-4327, “Chemically Induced Ignition in Aircraft and Spacecraft Electrical Circuitry by Glycol/Water Solutions,” W.R. Down, Manned Spacecraft Center, Houston, Texas, April 1968, NTIS No. N68-22213.

6. Colwell, J. D. and Peck, R. E., “Hot Surface Ignition of Jet A Fuel by Conductive Deposits,” Arizona State University Interim Report to SRI International in support of FAA Contract No. DTFA03-98-D-00008 dated July 2001.

7. Kauffman, R. E., “The Effects of Different Sulfur Compounds on Jet Fuel Oxidation and Deposition,” ASME J. of Eng. for Gas Turbines and Power, 119, 322-327 (1997).

APPENDIX

EXPERIMENTAL

Supplies

Terminal Blocks - The ten used terminal blocks and ten used FQIS with associated wiring, connectors and nuts (Figure 1) analyzed during this research were supplied by the NTSB (Robert Swaim) and the Air Force Research Laboratory (AFRL) (George Slenski). The terminal blocks were removed from either retired B-747 aircraft or from B-747 aircraft experiencing FQIS malfunctions.

Jet A Fuels - The Jet A fuels analyzed during this research were supplied by the FAA, an aerospace company and the AFRL. The 64 fuels supplied by the FAA were obtained at US and European airports from the center fuel tanks of commercial airliners after landing.

Three of the four fuels supplied by the aerospace company were obtained from fuel line components of commercial airliners operating in Asia and experiencing clogged fuel lines/fuel oil coolers. The fourth fuel supplied by the aerospace company was obtained from a fuel farm located in Arizona. The two fuels supplied by the AFRL were obtained from the fuel reserves of local airports.

Metal Wires and Nuts - The metal wires (1 mm diameter) used in this study to produce residues were obtained from Aldrich Chemical Company and had purity levels of greater than 99.99%. The following metals were studied as wires: Ag (Silver), Al (Aluminum), Au (Gold), Cd (Cadmium), Cu (Copper), Ni (Nickel) and Ti (titanium). 316 Stainless Steel wire was also used.

In addition to the metal wires, Ag and Cd plated nuts, new and used, supplied by the FAA and NTSB, respectively, were also used in this study to produce residues.

Water - Three types of water were used in this study: deionized, distilled and condensed water removed from the plastic pan of a room dehumidifier. In every case, drops (1 cm in diameter) of the different waters had measured resistances of greater than 2.3 mega ohms (M?) using the needle tip probes of a digital multimeter.

Ceramic Rods - The ceramic rods used in this research were 3 mm in diameter and contained two bores running the length of the rod. The bores were 1 mm in diameter and were spaced 1 mm apart. The ceramic rods were alumina in composition with a porcelain coating.

Analytical Techniques

The following analytical tests were used to analyze the “as received” (fuel tanks, fuel line components, fuel reserves) and stressed Jet A fuels and to characterize the deposits present on the terminal blocks and associated wires, nuts and connectors.

Voltammetric Instruments - The RULER? instrument was used to determine the concentrations of the phenol compounds (naturally occurring and produced by stressing) present in the “as received” and stressed fuels. The PERFECT? instrument was used to determine the hydroperoxide concentrations in the “as received” and stressed fuels using ASTM Method D6447-99. The voltammetric procedures of the RULER? and PERFECT? instruments have been previously described in detail [1,7].

Thermogravimetric Analysis (TGA) – TGA was used to determine the gum contents of “as received” and stressed fuels. 10 ?L of fuel was weighed in a platinum pan and heated from room temperature to 400°C in a nitrogen atmosphere. The % remaining weight versus temperature was plotted. The weight remaining at 300°C was considered the gum content of the tested fuel.

X-Ray Photoelectron Spectroscopy (XPS) - XPS was used to determine the elemental [Ag, C, Cu, N, O and S (H not detected)] composition of the residues and particles and to differentiate between the oxidation states of Ag, Cu and S present in particles and residues. The XPS was performed in an evacuated chamber with a magnesium X-ray source and analyzed the top (outer) 3 nanometers of the residue or particle.

Auger Electron Spectroscopy (AES) - AES was used to perform elemental [Ag, C, Cu, N, O and S (H not detected)] depth profiles of the deposits present on terminal block and associated hardware surfaces. An argon ion beam was used to sputter the deposits at a rate of 2 nm min^{-1} to perform the AES elemental depth profiles in an evacuated chamber.

Scanning Electron Microscopy/Energy Dispersive Spectrometer (SEM/EDS) - SEM was used to obtain magnified (4nm resolution) photographs of the particles and residues. The EDS analyses were used to perform elemental [Ag, Cu, O and S (H not detected, C and N poor detection)] analyses of the deposits on the terminal block and associated hardware surfaces. The SEM/EDS analyses were performed in an evacuated chamber.

Fourier Transform Infrared Spectrophotometry (FTIR) - FTIR was used to determine bulk bonding differences (C-H, C=O, C-OH, C=C) among “as received” fuel, stressed fuel and residues. The FTIR analyses were performed at atmospheric pressure in the forms of solid flakes, liquid drops, liquid film between two potassium bromide (KBR) plates or plates formed by compressing a mixture of KBR powder and residue particles.

Experimental Procedures

<u>Fuel Oxidation/Vapor Deposition</u> - To evaluate the oxidative stabilities of the fuels and the tendencies of heated fuels to produce deposits in the vapor phase (terminal block in vapors above fuel), 10 mL of each fuel was dispensed into a 25 mL glass Erlenmeyer flask. Cu wires (0.2 mm diameter) with a Ag coating (similar to fuel tank wiring) were also placed into each flask. The wires were positioned so that one end of the wire was submerged in fuel and the other end extended out of the open mouth of the flask. The glass flasks containing the fuels were heated at 350°F for 1 hour (with the wire) and at 290°F for 4 hours (without the wires) on top of a hot plate. After 1 hour at 350°F and 4 hours at 290°F, the remaining liquid fuel was analyzed for oxidation (increased levels of hydroperoxides and phenol compounds) and for particles or dissolved gums. The Ag coated Cu wires heated at 350°F were visually examined for deposits and analyzed by FTIR to characterize the deposits.

<u>Conductive Deposit Formation</u> - *Glass Slide with Parallel Ag Coated Cu Wires* - Two Ag coated Cu wires (0.2 mm diameter, 4 cm length) were placed parallel on a glass microscope slide and the ends of the wires were glued to the glass slide. The wires were spaced 1 mm apart. Electrical connections were made to one end of each Ag plated Cu wire and a 9V dc battery was used to supply power to the system. When a drop [100 microliters (?L)] of water was dispensed between the wires so that the water made contact with each wire, a black deposit initiated at the positive wire and spread across the water to the negative wire. Simultaneous with the black deposit formation, bubbling was observed at the negative wire. A digital multimeter and an analog strip chart were placed in series with the parallel wires to monitor the current flow through the water drop/deposit. Drops (100 ?L) of various fuels were added between the parallel wires so that the fuel was in contact with the wires and water drop. The black deposits with and without fuel present were isolated and analyzed using SEM/EDS.

<u>Conductive Residue Formation</u> - *Ceramic Rod with Parallel Metal Wires* - A metal wire (1 mm diameter, 3 cm length) was pushed through each bore in the ceramic rod (2 cm length) so that 0.5 cm of wire extended from each end of the rod (Figure 2). A drop of glue (RTV, super glue, etc) was placed on one end of the ceramic rod to seal the metal wires extending from the bores. Once the glue had hardened, electrical leads were connected (alligator clips) to the metal wires extending from the sealed bores. The electrical leads were then placed in a polymer coated adjustable clamp and situated so that the ceramic rod was held vertical when the clamp was tightened. The ceramic rod was positioned so that the end of the ceramic rod with the glue/electrical connections was on the bottom as shown in Figure 2. The digital multimeter (Figure 2) was placed in series with the electrical connections of the ceramic rod to measure the current flowing in the circuit.

For each experiment, the power supply (described in later section) was selected and connected to the electrical leads of the ceramic rod. A drop of water (50 ?L) was dispensed using a plastic pipette onto the upper surface of the ceramic rod between the two metal wires extending above the surface (Figure 2). Due to its surface tension, the water drop formed a bead engulfing the metal wires and ceramic surface. The selected power supply was then turned ON causing the water drop to undergo electrolysis (black deposit forms). A radio tuned to a local AM radio station was positioned 3 feet from the ceramic rod. If radio frequencies (RF) were produced during the electrolysis of the water drop, the AM radio station program would be replaced by static.

Once the water drop was no longer visible (1-60 minutes depending on power supplied) and a deposit was visible on the ceramic surface (Figure 2), the resistance of the residue was measured with a digital multimeter. If the resistance of the residue was above 10 Kilo-ohms (K?), another drop of water was dispensed onto the surface of the ceramic rod between the metal wires and the power reapplied. The process of adding water drops and applying power was repeated until the resistance of the resulting residue was below 10 Kilo ohms (K?). If the resulting residue had a resistance below 50 ? , the residue was washed away with a stream of water or wiped away with a paper towel. The process of adding water drops and applying power was then repeated with the cleaned ceramic rod until a residue with a resistance below 10 K? was produced.

Once a residue with a resistance between 50 ? and 10 K? was produced (only occurred with Ag wires), a drop of fuel (50 ?L) was dispensed onto the Ag deposit with a plastic pipette (Figure 2). Due to its lower surface tension, the fuel drop wetted the Ag residue and formed a thin layer of liquid on the surface of the ceramic rod. The selected power supply was then turned ON causing smoke with flashes of light. Once the Ag residue appeared dry (fuel evaporated), another drop of fuel was added to the residue causing additional smoke and flashes of light.

The process of adding drops of fuel to the Ag residue was repeated until the flashes of light caused the resistance of the residue to increase to above 10 K? . Once the resistance increased above 10 K? , the process of adding water drops and applying power was repeated until the resistance of the produced residue was between 50 ? and 10 K? . The process of adding fuel drops and applying power to produce flashes of light was then repeated with the lower resistance residue. In some cases, inverted glass vials were used to capture the smoke produced by the flashes of light and to affect the air:fuel (smoke = fuel vapor) ratio above the flashes of light. After 20-40 drops of fuel, the flashes of light were replaced by a constant glow upon the addition of a fuel drop to the residue. The residence times of the fuel drops decreased from minutes to seconds in the presence of the constant glow. Once the Ag residue exhibited the constant glow in place of the flashes, each additional drop of fuel produced the glow and did not further affect the characteristics of the Ag residue. In some cases the addition of successive fuel drops (spaced approximately 2 seconds apart) resulted in ignition of the fuel residing on the ceramic rod and clamp.

<u>Conductive Residue Formation</u> - *Terminal Block with Ag Wires or Ag Plated Nuts* - As illustrated in Figure 6, the back of the terminal block in Figure 1 is flat with equally spaced holes (15 mm apart). For experiments with Ag wires, the ends of the Ag wires were secured to two adjacent steel studs on the front of the terminal block with steel nuts. The unattached ends of the Ag wires were then guided through adjacent holes in the terminal block and arched so that the end of each Ag wire pressed against the surface of the terminal block (Figure 6). The ends of the Ag wires were spaced 10-15 mm apart (spacing of nuts in Figure 1). Electrical connections were then made to the steel posts to supply power to the moveable Ag wires.

In the case of the Ag plated nuts, steel wood screws were guided through two nuts and into two adjacent holes to secure the nuts to the surface of the terminal block. Alligator clips were then used to make electrical connections to the Ag plated nuts.

The terminal block was then placed in a polymer coated, adjustable clamp with the backside of the terminal block on top and the electrical connections and steel studs on the bottom. Once the clamp was tightened to hold the block horizontal, a large water drop (250 ?L) was dispensed with a plastic pipette onto the surface between the Ag wires or Ag plated nuts. The plastic tip of the pipette was then used to engulf the ends of the Ag wires in the water drop by touching the edges of the water drop with the tip and dragging the water to the outer side of each Ag wire. In the case of the Ag plated nuts, the tip of the pipette was used to drag the edges of the water drop against at least two edges of each nut. A glass tube pipette was then used to dispense small drops (2-5 ?L) of fuel onto the upper surface of the water drop (Figure 6). Although a portion of the dispensed fuel flowed off of the water drop onto the terminal block surface, the majority of the fuel remained suspended on top of the water drop due to its lower density.

Within minutes of turning ON the selected 40V power supply, a film with a shiny silver appearance formed between the fuel and water surface. If the 40V power supply was dc voltage based, bubbles (H_2) were observed at the negatively charged Ag wire as the shiny Ag layer formed at the positively charged Ag wire. If the selected 40V power supply was ac voltage based, no bubbles were observed at either Ag wire and the shiny Ag layer formed at the fuel:water interface regardless of its location with respect to the Ag wires. As the shiny Ag grew in size, the measured current increased until it reached the current limitation of the power supply. In most cases, the power was applied until the water drop was no longer observed leaving behind a shiny Ag coating on the terminal block surface. In some cases, the power supply was turned OFF when the measured current reached the current limitation of the power supply and the water drop was allowed to evaporate (several hours) leaving behind a shiny Ag coating. If the measured current (digital multimeter) of the residue was below 1 mA, the water:fuel drop process was repeated with applied power until a current above 1 mA was measured with the dried residue. A fuel drop was then dispensed onto the dry Ag residue and the selected 40V power supply turned ON. Flashes of light and smoke were produced regardless of the 40V power supply selected when the measured current (digital multimeter) was between 2 mA and 80% of the current limitation of the power supply. Above 80% of the current limitation of the power supply, the voltage measured at the Ag residue fell to below 10V and the flashes diminished. In the case of the 40V dc power supplies (described in later section), the flashes of light were replaced by constant glows (lasted up to 20 seconds) after only the first or second drop of fuel. Apparent ignitions of fuel vapor above the constant glows were observed for all of the 40V dc power supplies.

Inverted glass vials were used to affect the air:fuel (majority of smoke = fuel vapor) ratio above the flashes of light and constant glow. Small drops of water (50 ?L) were sometimes dispensed at the Ag wires and Ag plated nuts to improve the electrical contact (increase current) between the wires and nuts with the dry Ag residue.

Power Supplies

dc Power Supplies - Two types of dc power supplies were used in this work: 9V dc battery and 40V dc power supply. The 9V dc batteries were connected in series to obtain dc voltages of approximately 9, 18, 27, 36 and 45V dc. The measured voltages of the 9V dc batteries varied between 8.5 and 9.5V prior to use and decreased to below 7V during use. Consequently, each Ag residue was produced with a new battery supply, single or combined. When necessary, an adjustable resistor was placed in series with the battery and residue to limit the current to below 500 mA. Unrestricted, the batteries supplied up to 3A of current.

The 40V dc power supplies were produced by combining a constant output 40V dc power modular supply (115V ac power input) with an internal resistance of 540, 816, or 1333 ? to limit the supply's maximum current to 74, 49 or 30 mA, respectively. Although the power supplies were regulated at 40V dc, the measured voltage (in parallel with/across the residue) and current (in series with/through the residue) were totally dependent on the resistance of the Ag residue. As the resistance of the Ag residue decreased and the current in the circuit increased, the voltage measured at the residue decreased for the different 40V dc power supplies in a linear fashion. Consequently, the maximum power supplied by the 40V dc power supplies were well below the 1 to 3 watts (W) calculated from the supplies' current limitations of 30 to 74 mA, respectively. The actual power maximum of the 40V dc power supplies ranged from 0.3 to 0.8W and occurred when the resistance of the residue equaled the internal resistance of the 40V dc power supply.

ac Power Supplies - Two types of ac power supplies were also used in this work: 60 Hz ac power supply and modified function generator. The 60 Hz ac power supply was produced by combining a constant output 50V ac power module (115V ac power input) with an internal power resistor to limit the current to 300 mA. When the current exceeded 300 mA, the power supply automatically turned OFF. An adjustable resistor was placed in series with the produced residue and power supply to limit the current to below 250 mA to avoid the power supply from turning OFF.

The output (6V maximum) of a function generator was amplified using a voltage amplifier with a 1:10 (input:output) ratio. The output of the function generator was adjusted to 4V to obtain 40V from the voltage divider. The function generator was capable of producing an ac voltage with cycle rates of 1 hertz (Hz) up to 100 KHz (400, 2000, and 7400 Hz used by commercial FQIS) in three different waveforms: triangular, square and sine. Although the maximum current of the modified function generator was 30 mA (limited by internal resistance), the current was limited to 20 mA during actual practice due to effects of temperature (generated during use) on the electrical components used to amplify the voltage. As was the case with the 40V dc power supplies, the measured voltage (in parallel to residue) and current (in series with residue) of the 40V ac tests were totally dependent on the Ag residue. In contrast to the dc power supplies, the voltage decreased non-linearly as the resistance of the residue decreased and the current increased. The maximum power of the 40V ac function generator was 0.45W (not 0.8W = 40V x 20 mA) and occurred at a residue resistance of 1600? .

Electrical Measurements

The voltage and current measurements were made with digital multimeters, analog strip chart recorders, and a recording oscilloscope. The digital multimeters were placed in parallel with the residue to directly measure the voltage drop at the residue. The digital multimeter was placed in series with the residue to directly measure the current flow in the circuit and residue. To trend the current flow of the residue, a 1? resistor was placed in series with the residue and the inputs of a strip chart (100 mV full scale) were connected in parallel with the 1? resistor. Consequently, the voltage drop across the 1? resistor measured by the strip chart was equal to the current flow in the circuit and residue (V = IR = I when R = 1?).

Although the multimeter and strip chart measurements responded to each puff of smoke or flash of light, the maximum current could not be measured due to the short (less than 1 millisecond) duration of the events. Therefore, a recording oscilloscope with a 10^8 Hz sampling rate was used to obtain an accurate current measurement during each flash of light and puff of smoke. Due to the high acquisition rate of the oscilloscope and the sporadic nature of the flashes of light/smoke, the parameters of the oscilloscope were set so that the oscilloscope recorded the current whenever a 5 mA rise in the current was detected. With this setup, the oscilloscope recorded the current of each flash of light or puff of smoke observed during testing as shown in Figure 5.