

THE ROLE OF SURFACE COMPOSITION IN FUEL DEPOSITION

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Abstract: Experiments were performed in a Hot Liquid Process Simulator (HLPS) configured and operated such that it performed under conditions similar to Jet Fuel Thermal Oxidation Tester (JFTOT) ASTM D 3241 requirements. The JFTOT heater tubes used were 316 stainless steel (SS), 304 SS, and 304 SS tubes coated with aluminum, magnesium, gold, and copper. A low sulfur Jet A fuel with a breakpoint temperature of 254°C was used to create deposits on the heater tubes at temperatures of 300°, 340°, and 380°C. Deposit thickness was measured by dielectric breakdown voltage and Auger ion milling. Auger ion milling of the deposits showed the order of deposition to be copper > magnesium = 316 SS > gold > aluminum. The dielectric strength method indicated that 316 SS > 304 SS > gold > magnesium = aluminum = copper. The pronounced differences between the deposit thickness measuring techniques suggest that the dielectric strength of the deposit is strongly affected by metal ions that become included in the bulk of the deposit. The results show that the surface temperature and composition play an important role in deposition.

Introduction: The effect of fuel system metallurgy on fuel stability is an important concern in the development of high efficiency/advanced engine technology such as adiabatic, low heat rejection engines and hypergolic injection systems. Several studies have shown that trace metals adversely affect the thermal stability of hydrocarbon fuels.(1,2) Metal concentrations as low as 15 ppb of copper, 25 ppb of iron, 100 ppb of zinc, and about 200 ppb of lead have been found to cause significant change in the thermal stability of jet fuels. These studies suggest that the slightest metallic contamination could cause a significant change in the thermal oxidative stability of hydrocarbon fuels. In fact, the theory has been advanced that all hydrocarbon autoxidations are trace metal catalyzed.(3)

Recent work (4), in which only limited data are available, suggests that aluminum tubes with magnesium-enriched surfaces tend to have lower deposit buildups than the standard aluminum tubes. If such minor changes in surface metallurgy cause significant changes in the rate of deposit formation, major changes in surface composition could dramatically effect processes such as deposit adherence and oxidation catalysis.(5) Experiments with metal deactivator in dodecane using JFTOT equipment suggest that the effect on deposit reduction may be a consequence of interactions in the liquid-phase rather than a reduced adherence to the hot metal surface.(6)

One measure of the thermal stability of aviation fuels is the quantity of deposits formed on heated metal surfaces.(7) In accelerated stability tests conducted in accordance with the JFTOT procedure (ASTM D 3241) (8), the rating methods currently employed involve either visual comparisons or measurements of reflected light by the tube deposit rater (TDR), both of which are sensitive to deposit color and surface texture. In the research reported in reference 7, deposits formed on stainless-steel JFTOT heater tubes were examined by the TDR, a gravimetric carbon combustion method, and two new nondestructive techniques for determining deposit volumes based on measurements of dielectric strength and optical interference. Measurements of total carbon content by combustion were used as a reference. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the total TDR often yielded misleading results. The purpose of the present study was to investigate the role of JFTOT metal surface composition in deposit formation.

Experimental: Experiments were performed in an Alcor model HLPS300 Hot Liquid Process Simulator (HLPS), which is a modular version of the JFTOT apparatus used for the ASTM D 3241 method. The HLPS was operated to give conditions equivalent to D 3241 requirements except that Triton-treated fuel prefilers were not used. In the development of the experimental technique, there was a desire to achieve a more isothermal temperature profile over the length of the tube so that greater accuracy could be achieved in the measurement of rate parameters such

as activation energies for deposit formation. In the first attempt to broaden the hot zone over the tube, a "heated line transformer with line clips" was used to preheat the fuel. Figure 1 shows the result of fuel preheating on the longitudinal temperature profile of the JFTOT heater tube. In Figure 1, station 0 in the fuel inlet and station 60 is where the fuel leaves the JFTOT heater tube jacket. Preheating the fuel to 150°F (66°C) and 200°F (93°C) at heater tube temperatures of 300° and 340°C did not demonstrate any significant hot zone broadening advantages over fuel at room temperature. Figure 2 shows the results of a second approach to broadening the temperature profile using a reverse fuel flow by the JFTOT heater tube. The reverse flow approach did, in fact, achieve a much higher degree of isothermal tube temperature behavior, but because it was less standard and could possibly hinder comparisons with other studies, it was not used in the experiments reported here.

Procedure for Coating Heater Tubes. Aluminum, gold, carbon, magnesium, and copper were deposited on sets of three each 304 SS heater tubes. Basically, the objective was to make coatings on the heater tubes thick enough to cover the surface completely yet thin enough to minimize possible effects of both electrical and thermal conductivity. The coatings were accomplished with a Denton model DV-502 vacuum deposition apparatus that was set up to produce a thin layer of the test element onto standard 304 SS JFTOT heater tubes. In developing the procedure for coating the tubes, it was found that the success of the method depended greatly on the cleanliness of the heater tube surface. Quality adherence of the coatings was achieved when the heater tubes were cleaned with trichloroethane in a sonic bath for about two minutes and dried in a laboratory specimen dryer.

Deposit Measurement Device. The deposit thickness measurement device (DMD) determines the thickness of a deposit on a conductive surface by applying a voltage across the deposit while measuring the dielectric breakdown of the layer at various points.(9) The DMD used in this work was first reported in reference.(10) The DMD voltage measurements were shown to relate thickness of deposits with 350 volts equal to 1 micrometer.(10) Methods for calculating deposit volume on JFTOT heater tubes were also discussed in reference.(10) This procedure was used to develop DMD data correlations to carbon burn-off values reported in reference 7.

Auger Milling Technique. The raw data from Auger ion milling are given in units of time. To determine thickness repeatably, it is necessary to make the appropriate calibration. For the deposit thickness measurements, a piece of tantalum foil with a layer of tantalum oxide of known thickness was ion-milled at a given rate until the oxide was removed. For a given milling rate, it was then possible to measure thickness in terms of time. JFTOT deposit thicknesses were determined assuming that the rates of material removal from the deposit and the tantalum oxide standard were equivalent. However, it was expected that the deposit would mill at a somewhat faster rate since it is primarily carbon and hydrogen, i.e., lighter elements than the oxygen and tantalum. Since the mass removal rate for the deposit could be faster than that of the standard, the actual deposit thicknesses may have been somewhat larger than those reported in this paper.

Test Fuel. The objective in choosing a test fuel was to find one that could provide assessable deposits on 304 SS heater tubes at test temperatures of 300°, 340° and 380°C. After evaluating several fuels, a West Coast Jet A fuel was found to give measurable levels of deposit on 304 SS heater tubes at all three of the chosen test temperatures. This fuel met ASTM D 1655 specification at the time of manufacture; it had a code 3 breakpoint temperature of 254°C when the work was started.

Test Procedure. Stainless steel (304) tubes were evaluated using the West Coast Jet A fuel and test durations of 0.5, 1.0, 1.5 and 2.5 hours at maximum heater tube temperatures of 300°, 340°, and 380°C. These data are summarized in Table 1. The 1.5-hour test period was selected for use in the metal surface evaluations because it produced a deposit that was relatively nascent, yet assessable by the DMD and Auger measuring techniques.

Results and Discussion: The results in Figure 3 show the longitudinal temperature profile of the heater tubes at controlled maximum temperatures of 300°, 340°, and 380°C. These data were used as a reference to determine the temperature at a particular heater tube station. Figures 4 through 9 summarize the deposit thickness by DMD for the West Coast Jet A using the 316 SS heater tube, the 304 SS heater tube, and the 304 SS heater tubes coated with aluminum, magnesium, gold, and copper. Auger milling measurements of deposit thickness were made at

several of the heater tube stations for the various surfaces as shown in Figures 4 through 9. Note that Auger results were not available for the 304 stainless steel.

All the DMD deposit profiles were consistent in that they each exhibited a shift toward the fuel inlet (station 0) as the maximum heater tube temperature was raised. General comparison of Auger milling values to DMD thickness values suggest:

- * Auger milling gives much greater thicknesses for deposits formed on copper coated tubes. The two methods give similar deposit profiles and locations of maximum thickness.
- Magnesium coated tube deposit values by Auger were increasingly higher than DMD values at higher heater tube temperatures.
- 316 SS tube deposit values by Auger were increasingly higher than DMD values at higher heater tube temperatures.
- Aluminum coated tube deposit thickness by Auger was approximately one-half of that by DMD.
- * Gold coated tube deposit thickness by Auger milling was essentially equal to DMD measured values.

Auger ion milling of the deposits showed the order of deposition to be copper > magnesium = 316 SS > gold > aluminum. The dielectric strength method indicated that 316 SS > 304 SS > gold > magnesium = aluminum = copper.

The pronounced differences between the deposit thickness measuring techniques suggest that the dielectric strength of the deposit is strongly affected by metal ions that become included in the bulk of the deposit. The results show that the surface temperature as well as composition plays an important role in deposition. Other than for variation in the thickness of deposits formed during 1.5-hour tests using various metal surfaces, the most dramatic effect observed was that the bulk of deposits moved to lower tube temperature as the maximum tube temperature was increased from 300° to 380°C. These data suggest that this fuel is unique in that it deposits over a relatively narrow temperature range; compared to the other surface materials, copper tends to shift this temperature to somewhat lower limits (See Table 2).

Basically, there are two theories on the role of metals in fuel stability. When fuels are exposed to hot metal surfaces, it is believed that naphthenic acids react with surface oxides and produce fuel-soluble metal naphthenates. In solution, the trace metals may either initiate autoxidation reactions or enhance reaction rates by decomposing hydroperoxides and producing more reactive free radicals. The other theory is that gums formed in the autoxidation process have different affinities for surface materials and thus adhere to some surfaces more than others. If it is simply the adherence of gums to the surface that matters, the effect would be expected to be important only in the formation of nascent deposits, and the composition of the deposit would not be changed by the metal. If the mechanism is based solely on the dissolution of metals by acidic constituents in the fuel, one would not anticipate a change in the rate of deposition as the deposit builds up. Also, metal ions would probably become incorporated homogeneously in the deposit since metals tend to form chelates with the relatively polar gum molecules in the fuel.

In ASTM D 3241-88a, note 8 states: "Heater tubes should not be reused. Tests indicate that magnesium migrates to the heater tube surface under normal test conditions. The enriched magnesium surface may reduce adhesion of deposits to re-used heater tubes." The topography of the deposit formed on the magnesium surface was found to be somewhat different than that of the other metal surfaces. A cursory examination of photographs taken with the scanning electron microscope (SEM) at magnifications of 1000X and 2000X showed hemispherical deposits on the magnesium surface and flat platelet-type deposits on the other metal surfaces. Before the tests, the magnesium coatings showed no apparent abnormalities; all of the metal coatings were made with essentially the same thickness. After the test, the deposit thickness profiles appeared to be similar to those formed on the other metal surfaces. The results indicate either adhesion of agglomerated insolubles or the formation of deposits from soluble gums at particular sites on the magnesium surface. The adhesion of agglomerated insolubles seems to be a more likely candidate because the Auger deposit thickness measurements were higher than those with the DMD and the difference tended to increase with rising temperature. The results indicate that greater amounts of

magnesium become incorporated into the structure of the deposit as the temperature is raised. This suggests, as mentioned above, that magnesium dissolution is an important process as the fuel is prestressed on its journey to the hot section of the heater tube. Perhaps the dissolved magnesium initiates nucleation of soluble gums and causes agglomerates to form which then deposit (adhere) on the surface.

Conclusion: Under JFTOT D 3241 test conditions thickness profiles of deposits formed on a variety of surfaces, 316 SS, 304 SS, Al, Mg, Cu and Au, were compared using the DMD (dielectric breakdown voltage) and Auger milling. Except for gold and aluminum, the deposit thicknesses measured by DMD were substantially lower than those measured by Auger milling, and the disparity in the two methods seemed to grow with increased deposit thickness. Some deposits, especially those on the copper coated tubes, gave particularly low DMD thickness values compared to Auger milling values. Metal dissolution and subsequent inclusion into the deposit is thought to be responsible for the increased conductivity of the deposit, an effect which becomes more pronounced at higher tube temperatures. Aside from variations in the thickness of deposits due to metallurgy, the most dramatic effect observed was that the bulk of deposits moved to tube locations of lower temperature as the maximum temperature of the tube was increased from 300° to 380°C. These results suggest that the fuel used in this study forms its deposit over a relatively narrow temperature range; compared to the other surfaces this effect was observed at lower temperatures on the copper coated tubes. A cursory examination of photographs taken with the scanning electron microscope (SEM) showed hemispherical deposits on the magnesium surface and flat platelet type deposits on the other metal surfaces. Deposit morphology will be further studied and new experiments are planned using heater tube surfaces under more isothermal conditions with fuel flow across the tube (as opposed to longitudinal flow).

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TABLE 1. Summary of Deposit Measuring Device (DMD) Evaluation of JFTOT Tubes Along With Standard ASTM D 3241 Ratings

Test No.	Tube Metal	Total Test Time, hr	Prefilter	Temp, °C	Pressure Drop, mm of Hg at Time	TDR Spun Rating at Station, mm	Visual Rating	DMD, Max. Thickness, cm x 10 ⁷ at Station, mm	DMD, Vol. of Deposit, cm ³ x 10 ⁷
253-H	304 SS	2.5	No	300	125 at 46.5 min	50+ at 44-58	>4 Peacock	2394 at 54	3785
254-H	304 SS	2.5	No	340	125 at 38.1 min	50+ at 32-50	>4 Peacock	2277 at 40	2999
255-H	304 SS	2.5	No	380	125 at 52.1 min	50+ at 26-58	>4 Peacock	2005 at 32	3226
157-T	Al	2.5	Yes	260	2 at 148.7 min	12 at 38-45	<4	42 at 54	54
256-H	304 SS	1.5	No	340	125 at 36.0 min	50+ at 34-58	>4 Peacock	1862 at 40	2282
257-H	304 SS	1.5	No	300	125 at 31.2 min	50+ at 45-58	>4 Peacock	1968 at 50	2255
258-H	304 SS	3.5	No	300	125 at 63.3 min	50+ at 40-58	>4 Peacock	2742 at 54	2742
259-H	304 SS	0.5	No	300	5.3 at 30.0 min	47 at 50-52	4	345 at 54	439
260-H	304 SS	1.0	No	300	125 at 56.1 min	50+ at 45-58	>4	1811 at 54	1835
261-H	304 SS	0.5	No	340	19.5 at 30.0 min	50 at 38-42	>4	591 at 42	651
262-H	304 SS	1.0	No	340	125 at 48.0 min	50+ at 36-49	>4	1845 at 42	2091
257-H	304 SS	1.5	No	300	125 at 31.2 min	50+ at 45-58	>4 Peacock	1968 at 50	2255
263-H	Al/304 SS	1.5	No	300	125 at 56.0 min	36 at 54	4 Peacock	1168 at 52	1256
264-H	Au/304 SS	1.5	No	300	125 at 66.3 min	50+ at 50-56	>4 Peacock	1411 at 52	1294
266-H	Mg/304 SS	1.5	No	300	125 at 52.1 min	Too Dark to Rate	4	1082 at 54	1558
267-H	Cu/304 SS	1.5	No	300	125 at 18.5 min	50+ at 38-58	4 Peacock	862 at 46	1164
279-H	316 SS	1.5	No	300	125 at 58.2 min	50+ at 28-58	>4 Peacock	2211 at 54	2669
256-H	304 SS	1.5	No	340	125 at 36.0 min	50+ at 34-58	>4 Peacock	1862 at 40	2282
268-H	Al/304 SS	1.5	No	340	125 at 33.5 min	50+ at 40-45	>4 Peacock	1200 at 42	1649
269-H	Au/304 SS	1.5	No	340	125 at 31.5 min	50+ at 40-45	>4 Peacock	1917 at 42	2048
270-H	Mg/304 SS	1.5	No	340	125 at 40.5 min	Too Dark to Rate	>4	1297 at 42	1944
271-H	Cu/304 SS	1.5	No	340	125 at 30.0 min	50+ at 29-58	>4 Peacock	751 at 36	682
278-H	316 SS	1.5	No	340	125 at 40.9 min	50+ at 24-56	>4 Peacock	2668 at 40	2440
272-H	304 SS	1.5	No	380	125 at 52.4 min	50+ at 30-40, 49-54	>4 Peacock	2137 at 34	2191
273-H	Al/304 SS	1.5	No	380	125 at 48.1 min	50+ at 32-36	>4 Peacock	1805 at 34	1633
274-H	Au/304 SS	1.5	No	380	125 at 56.9 min	50+ at 32-36	>4 Peacock	2248 at 34	1824
275-H	Mg/304 SS	1.5	No	380	125 at 58.3 min	Too Dark to Rate	>4	1237 at 36	1782
276-H	Cu/304 SS	1.5	No	380	125 at 31.2 min	50+ at 24-58	>4	1148 at 30	812
277-H	316 SS	1.5	No	380	125 at 35.5 min	50+ at 18-58	>4 Peacock	2477 at 34	1757

(L.A.M.F.)

Table 2. Tube Locations of Maximum Deposit For Three Control Temperatures

Tube control temp. = <u>Metal Surface</u>	Deposit Peak Locations, mm		
	<u>300°C</u>	<u>340°C</u>	<u>380°C</u>
316 SS	52	40	32
Mg/304 SS	52	40	34
Cu/304 SS	46 (301°C)*	36 (325°C)*	30 (340°C)*
Au/304 SS	52	40	32
Al/304 SS	52	44	34
304 SS	50 (298°C)*	40 (335°C)*	34 (345°C)*

* Approximate Tube Temperature, °C, at location, estimated from Figure 3.

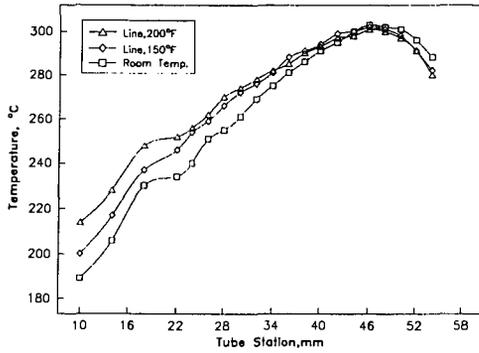


Figure 1. HLPS temperature profiles at 300°C

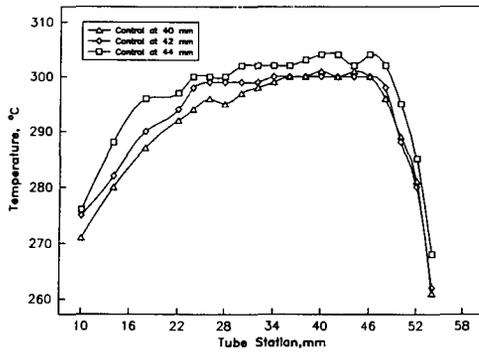


Figure 2. HLPS temperature profile with fuel flow through top of the 304 stainless steel heater tube at 300°C

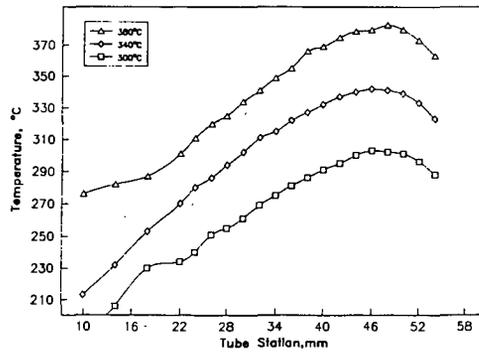


Figure 3. HLPS temperature profile of three temperatures using 304 stainless steel heater tubes

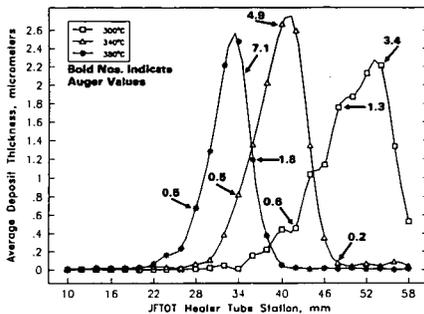


Figure 4. Deposit thickness on 316 stainless steel heater tube run at 300°C, 340°C, and 380°C

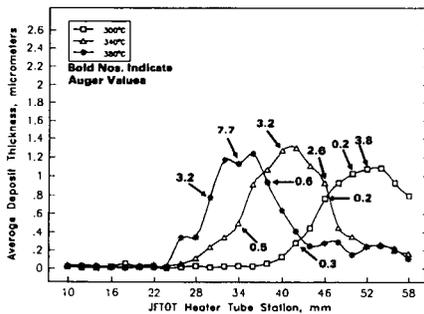


Figure 5. Deposit thickness on magnesium plated heater tube run at 300°C, 340°C, and 380°C

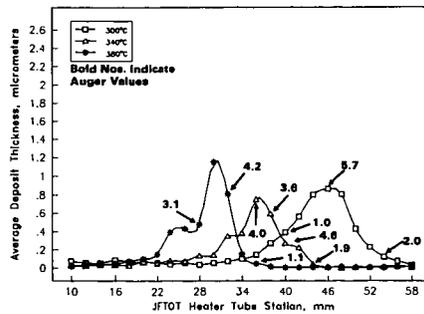


Figure 6. Deposit thickness on copper plated heater tube run at 300°C, 340°C, and 380°C

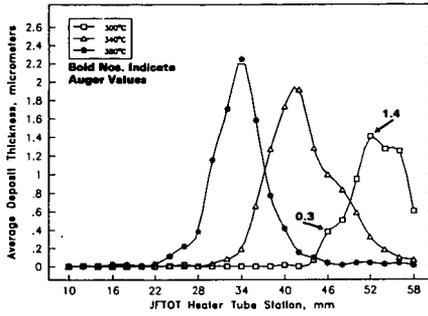


Figure 7. Deposit thickness on gold plated heater tube run at 300°C, 340°C, and 380°C

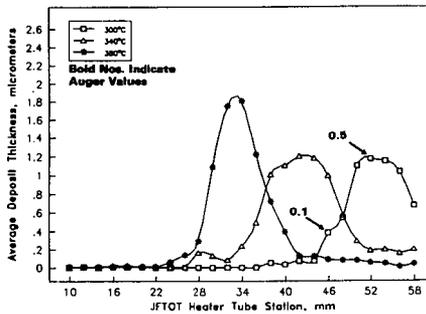


Figure 8. Deposit thickness on aluminum plated heater tube run at 300°C, 340°C, and 380°C

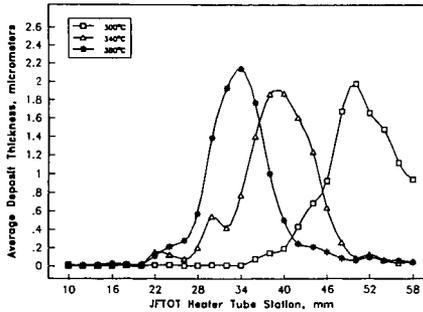


Figure 9. Deposit thickness on 304 stainless steel heater tube run at 300°C, 340°C, and 380°C