

THE INTERACTION OF A METAL DEACTIVATOR WITH METAL SURFACES

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INTRODUCTION

In modern aircraft fuel systems, the fuel is used as a heat transfer medium to dissipate heat from the avionics and hydraulic systems. Under these conditions, the fuel can undergo autoxidation. Autoxidation of jet fuel can result in the formation of insoluble gum and sediment which can impair operation of the jet engine. In addition, hydroperoxides which form during autoxidation have been known to attack certain elastomeric fuel system components. Thus, the thermal oxidation stability of the fuel becomes an important consideration. Trace quantities of certain transition metals will catalyze fuel autoxidation. Dissolved copper has been shown to be the most reactive (Pederson, 1949; Smith, 1967). Copper contamination of fuels can and does occur, particularly in shipboard fuel handling systems from contact with copper lines, brass fittings, admiralty metal, and other copper-bearing alloys.

Metal deactivator additives (MDA) were developed to counteract the catalytic activity of dissolved metals. These additives (N,N'-disalicylidene-1,2-propanediamine and N,N'-disalicylidene-1,2-cyclohexanediamine) can act as polydentate ligands for copper (Pederson, 1949). Chelate complexes derived from similar hydroxyaromatic Schiff bases are known to be thermally stable (Marvel, et al., 1956). The military specification, MIL-T-5624, allows for the addition of up to 5.8 mg MDA per liter in JP-4 and JP-5, while the ASTM specification for aviation turbine fuels, D1655-85a, (Annual Book of ASTM Standards, 1987) allows up to 5.7 mg per liter.

Laboratory scale tests, such as the Jet Fuel Thermal Oxidation Tester (JFTOT), have been relied upon to evaluate the thermal oxidation stability of aviation fuels. In the ASTM Method for assessing thermal oxidation stability of aviation fuels (Annual Book of ASTM Standards, 1988), the fuel is passed once over the outside of a resistively heated aluminum tube (the heater tube) at a flow rate of approximately three ml/min. In previous work (Morris, et al., 1988; Morris and Turner, in press), we have observed that the addition of a metal deactivator resulted in significant reductions in deposits on 304 stainless steel JFTOT heater tubes from 280 to 310°C.

In tests conducted with an injector feed-arm simulator, metal deactivator reduced deposit formation in two fuels by two and fourteen fold respectively onto clean steel surfaces (Kendall and Earls, 1985). However, after an induction period,

rapid deposition ensued at a rate similar to that observed in the absence of MDA. From this it was concluded that MDA passivated the clean steel surface towards thermal deposits, but was ineffective once the surface became coated with an organic deposit (Kendall, et al., 1987). The effectiveness of MDA in JFTOT testing of metal-free hydrotreated fuels was also attributed to passivation of the clean metal surface of the JFTOT heater tube (Clark, 1988).

The strong influence exerted by MDA in JFTOT testing has raised questions about the applicability of the method for ranking fuels with respect to thermal oxidation stability in the presence of metal deactivators. If MDA produces a disproportionately strong inhibition of deposition in the JFTOT, then fuels ranked stable may form insolubles during use. We have thus directed our efforts at ascertaining the various mechanisms by which MDA can act, particularly in accelerated stability testing. One objective of this study was to determine to what extent interactions with metal surfaces of the test apparatus govern the effectiveness of metal deactivators. This paper describes an examination of metal surfaces exposed to MDA solutions to determine under what, if any, conditions metal passivation can occur.

EXPERIMENTAL

X-ray photoelectron spectroscopy (XPS) was used to determine the presence of a continuous layer of MDA on metal surfaces. Analyses were performed using a Surface Science Instruments SSX-100-03 X-ray Photoelectron Spectrometer. Quantitative estimates of the surface composition were obtained using the analysis program supplied with the spectrometer. The base pressure was at least 2×10^{-8} torr for all samples analyzed. Fourier transform infrared spectroscopy (FTIR) was performed with a Digilab FTS-15/90 Fourier transform infrared spectrometer. Secondary ion mass spectroscopy (SIMS) was performed in a static mode with a time of flight instrument constructed at the Naval Research Laboratory (Hues, et al., 1988). A pulsed alkali ion gun with a thermionic emitting source was used which produced 2-5 ns pulses of 13.0 keV cesium ions, resulting in an impact energy of 8.0 keV for positive ions.

In order to minimize the risk of surface contamination from trace impurities in a fuel, a model fuel consisting of n-dodecane (Philips 66, Pure grade, 99 mol% min.) was used. XPS analyses were conducted on flat metal coupons exposed to the model fuel and the model fuel containing MDA. N,N'-Disalicylidene-1,2-propylene-diamine (MDA) was obtained from Pfalz and Bauer and dissolved into the dodecane to obtain a final concentration of 5.8 mg/l. MDA-copper complex was prepared by combining equimolar quantities of MDA and copper(II) ethylacetoacetate in dodecane.

Coupons measuring 2.5cm x 1.2cm consisting of copper, 6061 aluminum and 304 stainless steel were used as substrates. All surfaces were ground to 4000 grit using silicon carbide paper with triply distilled water as the lubricant. Coupon samples used for (FTIR) were further polished with 0.05 micron alumina. The stainless steel samples examined by SIMS were 1cm x 1cm and were prepared as described above. After polishing, the coupons were rinsed with triply distilled water and allowed to air dry in acid cleaned glassware. Samples were immersed in either pure dodecane or dodecane containing MDA at room temperature for two and one half hours. Afterwards the samples were withdrawn from this solution and rinsed with HPLC grade n-heptane, covered with aluminum foil and analyzed

within an hour. Samples that were analyzed by SIMS and FTIR were also rinsed with low residue toluene (Baker).

Stainless steel and aluminum JFTOT heater tubes were also examined by XPS. JFTOT stressing was carried out with dodecane and solutions of MDA at 5.8 mg/l in dodecane at 260°C and 310°C for one hour. The tubes were washed with hexane immediately after a JFTOT experiment.

RESULTS AND DISCUSSION

XPS signal intensity ratios for carbon, nitrogen and oxygen cannot be utilized as a quantitative measure of the amounts of MDA on the surface and can only be used as a qualitative indication of the presence of MDA. Almost any surface that has been exposed to air will have adsorbed oxygen and carbon. It was thus necessary to rely on the intensity of the nitrogen signal alone as the most reliable indication of the presence of MDA on the surface since it is unique to that compound and is not present in the pure dodecane.

An XPS survey scan of the copper-MDA complex demonstrated that the surface binding energies were similar to those reported for a copper-Schiff base analog of MDA (Dillard, et al., 1974). It is clear from analysis of the observed peaks that all the expected elements are present. The nitrogen peak was quite intense relative to both the carbon and oxygen peaks. Although nothing definitive can be said from the spectrum about the relative atomic concentrations, the relative intensities of the carbon, nitrogen and oxygen peaks should give a reasonable indication of the expected intensity ratios for this chelate if it were present as a very thick film. Analysis of signal intensities from high resolution scans of these peaks allowed an estimation of the atomic concentration of the elements present. The calculated copper concentration was a factor of two higher than expected, while the atomic ratios of the other elements were what were expected. Although the exact reason for this discrepancy is not understood, the relative intensities of the peaks should provide a reasonable indication of the amount of MDA present on an uncontaminated surface.

Copper coupons: While it is not practical to attempt to remove all copper-bearing components from shipboard fuel delivery systems, MDA may play a role in inhibiting the dissolution of copper into the fuel. For this reason it was felt that MDA adsorption onto copper surfaces should be studied to provide an insight into the role it may play, if any, in passivating the exposed copper parts. Prepared copper coupons were exposed to dodecane and dodecane containing MDA at room temperature for 2.5 hours. The strips were then removed and rinsed with heptane (HPLC grade), mounted onto the XPS carousel and introduced into the vacuum system within two hours using a quick insertion system that is part of the apparatus. The XPS survey scan from the freshly cleaned copper surface, which was mounted as soon as it was air dried, had weak carbon and oxygen peaks and strong copper peaks, indicating that the sample preparation procedure used produced an acceptably clean surface. Exposure to the MDA solution had clearly increased the amount of carbon on the surface but no nitrogen was observed in the broad scan. This indicated that at most there could only be a very thin film of the MDA on this surface. Otherwise, the nitrogen intensity would be comparable with that found in the complex above. High resolution scans of the peaks for each element were obtained and the composition of the surface was estimated. The results of this are shown in Table I for the freshly polished

surface and after exposure to MDA. The carbon and oxygen levels, although still quite high, are small compared with those found from any other cleaning procedures that were tried. As expected, the calculated carbon contents on surfaces that were exposed to the organic solutions were higher than on the freshly cleaned surfaces. In addition, the quantities of carbon were about the same for the surfaces of both the sample exposed to pure dodecane and to MDA. Nitrogen levels were at or below the detection limit of 1-2 atomic percent. The lack of any nitrogen signal suggests that the formation of an MDA coating on the copper surface was not occurring, since XPS can easily resolve monolayer thicknesses.

Examination of the copper surface by FTIR revealed the presence of an organic acid on all samples exposed to the dodecane. The magnitudes of the C-H and C=O stretches that characterized the surface adsorbed acids were influenced by the MDA concentration. This may indicate some interactive effects between acids adsorbed on metal surfaces and the MDA.

Stainless steel coupons: The results from the XPS examination of 304 stainless steel coupons exposed to dodecane and dodecane containing 5.8 mg MDA/l for 2.5 hours at room temperature are shown in Table I. Higher levels of oxygen were found on the freshly cleaned stainless steel surface than on the copper surface, presumably because of the presence of metal oxides. Nitrogen content was at or below the limit of detection. FTIR analysis of stainless steel strips exposed to dodecane again revealed the presence of a carboxylic acid on the surface, from strong C-H and C=O absorptions. No changes in surface acid concentration were evident, nor was MDA detected on surfaces exposed to dodecane containing 5.8 mg MDA/l. Treatment of the dodecane with silica gel before use was sufficient to eliminate the presence of adsorbed carboxylic acids on the metal surfaces. The presence of a few parts per million of dodecanoic acid was confirmed by HPLC analysis of the base-extractable component of the dodecane. Thus, the acid adsorbed on the metal surface was most likely dodecanoic acid, derived from autoxidation of the dodecane.

In an effort to gain a more sensitive measure of the presence of MDA on the surface, SIMS analysis was performed on a stainless steel surface which had been exposed to neat dodecane and a dodecane solution of 5.8 mg MDA/l for 2 hours at room temperature. The positive secondary ions thus formed showed that indeed some MDA was present on the surface, while none was detected on the neat dodecane exposed blank. Since the surface had been rinsed with toluene, it is assumed that the MDA present was tightly bound to the surface. However, a more intense signal was obtained at 52 Daltons higher than the MDA peaks, suggesting that most of the MDA was bound to chromium. These findings demonstrate that after exposure of 304 stainless steel to a solution of MDA at room temperature, some MDA will be bound to the surface, predominantly at chromium sites. However, the coating is far from complete and would not significantly alter the surface reactivity towards deposition.

Stainless steel JFTOT heater tubes: While 6061 aluminum is the material most commonly used in the construction of JFTOT heater tubes, 304 stainless steel is often employed in research efforts involving the JFTOT apparatus. Furthermore, many fuel system components are constructed from stainless steel. XPS analyses were performed on selected areas of stainless steel JFTOT heater tubes used to stress samples of dodecane with and without 5.8 mg MDA/l in the JFTOT apparatus for one hour. Nitrogen on heater tubes heated at 260°C was near the detection

limit. The metal contents (i.e., Fe, Cr, Mn, etc.) on the tube surfaces were very low (Table II). Chromium levels were at or below the detection limit of 1 atomic percent, compared to a nominal level of 18% in the base metal. This indicates multilayer deposit formation was taking place regardless of whether MDA was present or not. At 310°C in the presence of MDA, similar results were obtained except that the carbon levels were higher. These findings demonstrate that within one hour of JFTOT testing, it is possible to produce multilayer coatings of carbonaceous thermal oxidation products on the stainless steel JFTOT heater tube surface from a relatively unreactive "fuel", i.e., dodecane.

Aluminum JFTOT heater tubes: XPS examinations of 6061 aluminum JFTOT heater tubes tested at 260°C for one hour in dodecane and dodecane with 5.8 mg MDA/l revealed that, in both cases, carbon levels were lower than on the stainless steel tube surfaces (Table III). There was no evidence of multilayer structure of thermally degraded dodecane over the full length of the tube. This substantiates earlier reports that while the liquid-phase chemistry is identical for both tube materials (Hazlett, et al., 1977), heavier deposits tend to form on stainless steel heater tubes (Faith, et al., 1971; Kendall, et al., 1987). Nitrogen was at or below the detection limit in both cases, however, slightly more nitrogen was evident on tubes heated in the MDA solution.

CONCLUSIONS

Surface analyses of copper, aluminum and stainless steel exposed to MDA in static solutions and in JFTOT testing, point towards a different mechanism than what would be expected if the surface were deactivated towards deposition by a contiguous layer of MDA. While these findings suggest that the surface contains some MDA, it is sparsely distributed. In addition, there may be some interactive effects between MDA and surface bound carboxylic acids. On stainless steel, it appears that the MDA is predominantly bound to chromium sites on the surface but this coating is also a fraction of a monolayer and thus would not significantly change the surface activity. There was no evidence that MDA was coating a pure copper surface.

In the JFTOT, there was more deposition onto the 304 stainless steel tubes than on the 6061 aluminum. If surface passivation was responsible for the strong response of the JFTOT to the presence of MDA, then one would expect to observe at least a monolayer of MDA on the tube surface over the entire test duration of two and one half hours. However, in this study, multilayer thermal oxidation deposits were produced on 304 stainless steel JFTOT tubes after only one hour of JFTOT testing at the specification test temperature, 260°C. Therefore, the time required for monolayer deposition of thermal oxidation products onto stainless steel heater tubes during JFTOT testing was well within the limits of the test.

While it does not seem likely that surface passivation is occurring in the JFTOT, there is still no doubt that MDA exerts a powerful inhibiting influence on thermal deposition and the question of validity of the JFTOT results in the presence of MDA remains to be answered. Measurements of oxidation of JFTOT effluent have shown inhibition by MDA in some cases and none in others. This suggests the possibility that the effects exerted by MDA in the JFTOT may be a consequence of interactions in the liquid-phase.

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Table I. Composition of Films Formed on Polished Flat Coupons Exposed to Dodecane and 5.8mg MDA/l Dodecane in Atomic Percent

Copper

Condition	C	O	Cu
Freshly Polished	39	27	35
Dodecane, 2.5 hrs	63	23	12
MDA/dodecane, 2.5 hrs	54	28	18

304 Stainless Steel

Condition	C	O	Fe
Freshly Polished	21	58	14
Dodecane, 2.5 hrs	46	37	8
MDA/Dodecane, 2.5 hrs	35	49	11

Table II. Composition of Films Formed on Stainless Steel JFTOT Tubes in Atomic Percent after Stressing for 1 Hour

Dodecane, 260°C			
Temp. (°C)	C	O	Fe
174-208	57	38	3
208-238	41	49	7
238-257	52	40	5
257-260	78	20	1

5.8 mg MDA/l in Dodecane, 260°C			
Temp. (°C)	C	O	Fe
174-208	56	38	2
208-238	43	46	4
238-257	48	42	4
257-260	82	18	0

5.8 mg MDA/l in Dodecane, 310°C			
Temp. (°C)	C	O	Fe
212-253	40	45	11
253-287	56	38	4
287-305	82	14	0
305-310	93	6	0

Table III. Composition of Films Formed on Aluminum JFTOT Tubes in Atomic Percent after Stressing for 1 Hour

Dodecane, 260°C			
Temp. (°C)	C	O	Al
141-193	31	47	20
193-232	29	47	21
232-256	32	46	18
256-260	28	48	19

5.8 mg MDA/l in Dodecane, 260°C			
Temp. (°C)	C	O	Al
141-193	31	45	19
193-232	33	43	18
232-256	34	43	19
256-260	44	36	17