Metal Deactivator Additive (MDA) Impacts on Thermal Stability

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Metal Deactivator Additive (MDA) Impacts on Thermal Stability

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Prepared for
Coordinating Research Council, Inc.
3650 Mansell Road, Suite 140
Alpharetta, GA 30022

Prepared by
George R. Wilson, III, Sr. Research Scientist
Nigil Jeyashekar, PhD., P.E., Research Engineer
Fuels and Lubricants Technology Department
Southwest Research Institute (SwRI®)
6220 Culebra Road
San Antonio, TX 78238

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Approved by:

Steven D. Marty, P.E., Director
Fuels & Lubricants Technology Department
EXECUTIVE SUMMARY

For over fifty years thermal oxidative stability has been a primary issue in the production, distribution, and use of jet fuel. During this time there has been only one generally approved additive solution to problems in this area – metal deactivator, MDA (N, N-disalicylidene-1, 2-propane diamine). This additive is primarily intended to complex catalytic metals, primarily copper, and prevents the catalysis driven generation of fuel deposits. Over the same time there has been some evidence that MDA has antifoulant properties in addition to its metal complexing capability. The purpose of this program was to evaluate this capability in actual hardware.

The original plan was to select two test fuels with D3241 Breakpoints between 245-260°C that had no readily measurable copper content. Once these fuels were selected they were to be evaluated for MDA performance in the laboratory and then in actual fuel nozzles. In practice, finding such fuels proved to be essentially impossible. Surveys of ASTM D3241 Breakpoint performance, such as the FAA Red Dye Program and the CRC World Fuel Survey, showed that sub 260°C fuels are rare. Those surveys were conducted before the de facto change to a minimum release value of 275°C by the common carrier pipelines in the United States.

The solution came when the MDA Working Group agreed to broaden the fuel scope. One member proposed providing a metal free, jet fuel quality (except for a Breakpoint of 230°C) feedstock. Another proposed, doping a metal free fuel with a typical contaminate to reduce its thermal stability into the range the program needed. These proposals were adopted and the program proceeded there from.

The nozzles to be tested were selected with the advice of the OEM community. The poor Breakpoint feedstock material was matched with the GE CFM 56 nozzle, a pressure atomizing unit. The doped material was matched with the PW 2040 nozzle, an air blast atomizing unit. If possible, the nozzles were to be used units, and that was achieved for most of the CFM 56 testing.

In the testing, the MDA proved to have clear benefits for thermal oxidative stability. As might be expected, based on the historical studies of this issue, the MDA performed better with the new nozzles than with the used nozzles. Still, it did provide a significant improvement even in a well used nozzle. Based on the results of the testing it appears there is a reasonable assurance that MDA provides a thermal stability benefit even in the absence of significant copper contamination.
PROGRAM SYNOPSIS

In November of 2006 the CRC distributed a RFP for “CRC MDA Program” (CRC Project No. AV-06-06). The program was intended to take two essentially copper free fuels with mild thermal stability failures and then test them in two kinds of turbine fuel nozzles in an engine condition simulator. Based on these results the CRC MDA Panel would make a recommendation for potential specification action.

The original plan was to get a series of fuels that were modest failures, having Breakpoints from 245-255°C, and then choose two that responded to MDA in D3241. When the group had no success at that level the range was increased to include up to 270°C Breakpoint fuels, recognizing the effect of the domestic (U.S.) pipelines raising their acceptance requirement to passing D3241 at 275°C. While there was a little more response at this level, no fuels were found that had modest thermal stability problems and would pass the copper screening test. Finally, the MDA panel agreed to a proposal to use a refinery process stream that met all jet fuel criteria except thermal stability and very good jet fuel that would be doped with a typical contaminate.

In the process of preparing for the testing the panel realized there was a unique opportunity to evaluate the recovery potential (that is how close it can return the fuel to uncontaminated problem) of MDA in non-copper contamination scenarios. The program was expanded to include testing the good jet fuel in the nozzle before adding the contaminate material. This would give additional information on how much benefit could be expected from MDA addition to contaminated fuel.

Three possible outcomes were described in the request for proposal for CRC.

1. Both fuel/nozzle pairs show a significant benefit from addition of MDA. In this case it should be possible to assign an average benefit. For example, if a fuel does not contain detectable dissolved metals, passes JFTOT at some minimum temperature (say, 245-250°C), and passes at 260°C with 2 mg/L MDA, then it could be considered to meet jet fuel specification requirements and the panel could recommend suitable action to revise jet fuel specifications.

2. One fuel/nozzle pair could show a significant benefit from MDA, and the other none. In that case, a further tie-breaking test may be wanted to determine which test was the exception, or the results could be considered a failure to demonstrate general benefits, or preferably, the average of the two tests could be used to calculate a benefit. There should be some agreement on the interpretation of this outcome before undertaking the program. A benefit in either case 1) or 2) that is not at least 5°C is not significant.

3. Both fuel/nozzle pairs could fail to show a benefit, or one or both have an increased fouling rate when MDA is added to the fuel. In this case the aviation fuel industry would have a basis to agree that MDA should be used only when dissolved metals are shown to be present, or in cases where downstream copper exposure is anticipated and the fuel passes JFTOT requirements without MDA.
The program found that the first outcome was the case and the conclusions are based on that finding.

SELECTING THE TEST FUELS

As simple as the task seemed, it proved almost impossible. Even when the panel raised the upper limit to 270°C to accommodate the de facto release limit of 275°C (promulgated by the U.S. pipelines) there were very few candidates offered for review. Those that did appear had easily measured copper.

As time went by and it started to look like no suitable fuel would be found, the panel considered an alternate approach. ExxonMobil (EM) Research had been working on a chemical dopant approach for developing a standard to evaluate D3241 breakpoint testing. The material in question, m-toluidine (MTOL), was something routinely found in the refining process and was associated with in-plant quality issues. With an initial approval to study this approach from the program group, SwRI inventoried the existing fuel supplies for a suitable candidate. There was a fuel available with no easily measured copper and a Breakpoint of 300°C.

SwRI provided EM a five gallon sample of this fuel and they conducted a series of tests to evaluate the use of MTOL. Their studies showed that 5000 ppm of MTOL would reduce the Breakpoint to 255°C. A sample was sent to SwRI and subsequent testing showed 5000 ppm dropped the Breakpoint below 200°C. The difference in effect was reviewed and the surmise made that the MTOL, as a technical grade material, had become more reactive in storage and transit. Based on that, the plan became to halve that dosage and add more if needed to get a similar result as EM.

While there was an agreement to use the EM approach, there were intellectual property clearances to be obtained before the program could proceed. The program committee could not approve testing with an unidentified dopant and EM had to get internal clearance to state the identity of the chemical, now known. During that timeframe the program actually managed to acquire a second sample due to the efforts of the program committee.

Working with their refinery contacts, one panel member isolated a jet kerosine stream with a Breakpoint of 230°C. SwRI tested an initial 5 gallon sample of this material and found the identical Breakpoint. The Breakpoint with MDA was 295°C, and the copper content was < 10 µg/kg. Based on these positive results ten drums of the sample were requested for the program. Because this fuel was available and perceived as more ‘real world’ than the doped fuel, the group decided to test this first. This material (AF-6990) thus becomes CRC MDA Fuel #1.

When the clearance was gained to identify the MTOL, the good jet fuel (AF-6861) became CRC MDA Fuel #2. In discussions about using it, the program group noted the unique opportunity to evaluate the recovery potential of MDA. At that point it was agreed to start the process by testing the neat fuel in the nozzle before the addition of the MTOL.
Finally a third fuel was chosen as a reference with which to compare the effect of MDA on Fuel #2. This fuel was chosen based on its Breakpoint value, 280°C, and the history of using fuel from the same source in nozzle testing. The need for the Reference fuel arose when the nozzle testing with Fuel #2 consumed fuel faster than the program anticipated. The idea was to compare the recovered Breakpoint quality of Fuel #2 with a fuel that had the same Breakpoint without additives.

LABORATORY THERMAL STABILITY TESTING

The laboratory testing for evaluating the fuel thermal stability was conducted as described in Appendix X2 ‘Determination of Breakpoint’ of ASTM D3241, Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels. The Breakpoint has been the standard method for evaluating the relative thermal oxidative stability of turbine fuel since the inception of this type of testing with the CFR Coker, ASTM D1660 (1959). Numerous programs have shown the Breakpoint to be a reasonably objective measure of how neat fuels will perform in most nozzles, relative to other fuels. (Nozzle design has an effect on the absolute severity.) Over the past five decades of use, the most singular question has been regarding its reliability when fuel is treated with an aggressive metal complexing material like MDA.

For various reasons there are no metal specifications for jet fuel. Most metals cannot make it through the refining process to the fuel, but post processing exposure to copper, Cu, and zinc, Zn, is a problem often exhibited in fuel with poor thermal stability. The D3241 test is sensitive to these metals, especially Cu. Copper has been shown to be a potential issue with thermal stability as low as the common detection limit, about 10-15 µg/kg. Measuring Cu to this level is hard for routine testing, so D3241 results are considered sufficient protection. Once it is proved that metal is the problem, and MDA is added, a passing test is considered sufficient proof of effectivity. What about the situation where the test fails but little or no Cu (or Zn) is found?

Testing on this issue in the 1980’s extended the time of the D3241 test from 2.5 hours to 5 hours. In this testing some fuels treated with MDA to pass at the standard time would subsequently fail. The question was then asked if the MDA was simply passivating the surface and fooling the test. The counter argument was that if all fuels were tested for 5 hours a lot more would fail. Therefore this program has a sub-purpose beyond determining if MDA has antifouling properties. That additional purpose is to validate that the D3241 test is effective at confirming MDA effect on fuels of marginal stability.

NOZZLE TESTING

The purpose of these tests is to determine the fouling rate characteristics of fuel spray nozzles due to the presence of metal deactivator additive (MDA) in jet fuel. The scope of the work was to evaluate the fouling rate characteristics due to the presence of metal deactivator additive (MDA) in jet fuel on two different types of fuel spray nozzles, namely a pressure atomizer and an air-blast atomizer. All of this was done in an apparatus that simulates actual engine
conditions, the Nozzle Test Rig (discussed below). The test objectives for each fuel nozzle are outlined below.

i. *Pressure Atomizer*
   a. Establish fouling rate curve with CRC MDA Fuel #1 (AF 6990).
   b. Establish fouling rate curve with MDA additive in jet fuel at 2 mg/L.
   c. Verify the linearity of flow number profile for 50 hours for 2 mg/L additive to ensure long term effect.
   d. Compare fouling rates at 2 mg/L and 5.7 mg/L of MDA in jet fuel.

ii. *Air-Blast Atomizer*
   a. Establish fouling rate curve with CRC MDA Fuel #2 (AF 6861).
   b. Establish fouling rate curve for jet fuel with 2500 ppm m-toluidene.
   c. Establish fouling rate curve for the fuel in b, with 2 mg/L MDA.
   d. Establish fouling rate curve for reference fuel to compare against fouling rate curves in a, b, and c.

**NOZZLES, INSTRUMENTATION, TEST PARAMETERS AND TEST RIG**

The two fuel spray nozzles used for the test were:

- GE CFM56 pressure atomizer fuel nozzle.
- PW 2040 air-blast atomizer fuel nozzle.

The fuel spray nozzles were equipped with a fuel collection cup to capture and discard the spent fuel. The air-blast nozzle had air supply through the central air swirler. Thermocouples were used to measure the skin temperature of the nozzle at two locations and the inlet air temperature was measured just before the hot air entered the fuel spray nozzle. Fuel inlet and outlet temperatures were monitored to ensure consistent operation. The pressure drop across the nozzle was monitored using a differential pressure transducer. The fuel and air mass flow rates were also recorded.

The operating temperatures and flows for the nozzles were determined by consultation with the appropriate OEM during previous programs and reflect the severe operating conditions, typically idle descent, where there is maximum heat soak and minimum flow rate. The primary values for evaluating the fouling rate were the fuel inlet temperature, the mass flow rate, and the differential pressure. Unless there was a specific time requirement, the nozzle tests are only run at a specific fuel inlet temperature long enough to establish the fouling rate. The operating parameters for the two nozzle tests are listed in Table 1 and a schematic of the test rig is shown in Figure 1.
### Table 1: Test Parameters for Nozzle Test

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>GE CFM 56 (Pressure Atomizer)</th>
<th>PW 2040 (Air-Blast Atomizer)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fps units</td>
<td>SI units</td>
</tr>
<tr>
<td>Fuel flow</td>
<td>15.0 lbm/hr</td>
<td>6.8 kg/hr</td>
</tr>
<tr>
<td>Air flow</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Skin temperature</td>
<td>530.0 °F</td>
<td>276.7 °C</td>
</tr>
<tr>
<td></td>
<td>549.8 °K</td>
<td></td>
</tr>
<tr>
<td>Air temperature</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Figure 1: Schematic of the Nozzle Test Rig**

- **Fuel Tank**
  - Mass flow meters
  - \( m_f \) – Fuel mass flow meter
  - \( m_A \) – Air mass flow meter

- **Thermocouples**
  - \( T_{in} \) – Fuel nozzle inlet temperature
  - \( T_{out} \) – Fuel nozzle outlet temperature
  - \( T_A \) – Air temperature (PW nozzle only)
  - \( T_S \) – Skin temperature
  - \( T_{SA} \) – Sand bath temperature

- **Test Rig**
  - **Air Compressor**
  - Drain taps

- **Air Exhaust**
  - Fluidized bed

- **Back-pressure regulator**
  - \( P_E \)
  - Test Exchanger

- **Pressure transducers**
  - \( P_B \) – Back-pressure valve
  - \( \Delta P \) – Differential pressure transducer across the nozzle
  - \( P_R \) – Pressure switch
TEST RESULTS

**CRC MDA Fuel #1**

**Laboratory Results:** Before running the laboratory stability tests on Fuel #1 all ten drums were put in a freshly cleaned tank to composite the sample. This would provide at least reasonable assurance that the testing, lab, and nozzle, would be done on a uniform sample.

The Breakpoint of the composite sample was 235°C, slightly higher than the original 5 gallon test sample but well within the normal variation of the test. Adding 2 mg/l of MDA increased the Breakpoint of the sample to 295°C, the same as the original sample. The results are shown in Figure 2 below:

![Figure 2: Thermal Oxidative Stability Results for Fuel #1](image)

While the Breakpoints are determined by the specified visual means, the data is plotted on an ellipsometer graph, with the VTR Code for each test noted adjacent, for additional clarity. While the minimum failing deposit, VTR Code 3, is typically 80-100 nm in depth, it is not unheard of to reach such levels at lower deposit depths as seen with the MDA treated Fuel #1.
**Nozzle Results:** Fouling rate curves were established for GE CFM56 pressure atomizer nozzle with tests conducted using Fuel #1 (AF 6990) neat and with MDA at 2 mg/L concentration. A comparison of the fouling rate curves is shown in Figure 3. The fouling rate values for the neat fuel versus fuel with the MDA additive have been summarized in Table 2. The nozzle fouling test for fuel with the MDA additive was conducted at higher temperatures and the results were extrapolated to the conditions of the neat fuel test. The extrapolated results have been included in Table 2.

![Figure 3: Comparison of Fouling Rate Curves for GE CFM56 Pressure Atomizer](image)

**Table 2: Summary of Nozzle Fouling Test Results for GE CFM56 Pressure Atomizer**

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Temperature</th>
<th>1000/T (K^-1)</th>
<th>Fouling Rate [lbm/(hr².(psi)⁰•⁵)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Fuel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>315.0°F (157.2°C)</td>
<td>430.4 (K)</td>
<td>2.324</td>
<td>0.003124</td>
</tr>
<tr>
<td>340.0°F (171.1°C)</td>
<td>444.3 (K)</td>
<td>2.251</td>
<td>0.008917</td>
</tr>
<tr>
<td>365.0°F (185.0°C)</td>
<td>458.2 (K)</td>
<td>2.183</td>
<td>0.018410</td>
</tr>
<tr>
<td>MDA (2 mg/L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>365.0°F (185.0°C)</td>
<td>458.2 (K)</td>
<td>2.183</td>
<td>0.007400</td>
</tr>
<tr>
<td>390.0°F (198.9°C)</td>
<td>472.0 (K)</td>
<td>2.119</td>
<td>0.01841</td>
</tr>
<tr>
<td>415.0°F (212.8°C)</td>
<td>485.9 (K)</td>
<td>2.058</td>
<td>0.04819</td>
</tr>
<tr>
<td>MDA (2 mg/L)</td>
<td>(extrapolated)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>365.0°F (185.0°C)</td>
<td>458.2 (K)</td>
<td>2.183</td>
<td>0.007400</td>
</tr>
<tr>
<td>MDA – 2 mg/L</td>
<td>365.0°F (185.0°C)</td>
<td>458.2 (K)</td>
<td>2.183</td>
</tr>
<tr>
<td>10 hour test</td>
<td>MDA-2 mg/L</td>
<td>365.0°F (185.0°C)</td>
<td>458.2 (K)</td>
</tr>
<tr>
<td>MDA-5.7 mg/L</td>
<td>365.0°F (185.0°C)</td>
<td>458.2 (K)</td>
<td>2.183</td>
</tr>
</tbody>
</table>
It can be observed from Table 2 that the nozzle fouling rate was reduced by 59%, at 365°F, due to the presence of MDA at neat fuel-inlet test temperatures. The next test was to check the stability of MDA treatment with time. This testing is included because earlier work with D3241 testing suggested the non-complexing affect of MDA might be short lived. The stability check was performed by conducting 50 hour test with fuel containing MDA additive at 365 F fuel inlet temperature.

This 50 hours flow number profile was compared against the flow number profile obtained for neat fuel (Figure 4). The flow number profile is considered to be linear and invariant for the neat fuel and 50 hours of testing with MDA treated fuel at 365 F fuel inlet temperature. The fouling rate reduces by a factor of two during the 50 hours of testing the fuel with MDA compared to the neat fuel. It can be concluded based on the above result that the effect of MDA to reduce nozzle fouling rate remains consistent and that the additive has a stable performance over a long period of time.
All of the testing, through the 50 hour stability test was conducted with a single, previously used, fuel nozzle. Unfortunately, the GE CFM56 test nozzle was plugged beyond acceptable limits after the 50 hours of testing. The effect of MDA concentration on nozzle fouling was evaluated on a new GE CFM56 nozzle by conducting fouling tests at 365 F for 10 hours with 2 mg/L and 5.7 mg/L. The result (Figure 5) indicates that there is no change in flow number for both concentrations of MDA. The testing showed that an increase in the concentration of MDA from 2 mg/L to 5.7 mg/L in the neat fuel has no adverse effect on nozzle fouling.

**CRC MDA Fuel #2**

*Laboratory Results:* When running Fuel #2 the approach was a little more involved. The neat, poisoned and then additized fuel were all done in series from the same blending tank. The Breakpoint of the neat fuel was 300°C. When the nozzle testing was completed on the neat fuel, the tank was poisoned with 2500 ppm of MTOL. A test was performed to ensure the Breakpoint was less than 260°C and, once proven, the Breakpoint was determined to be 230°C while the nozzle test was in process. Following that series the tank was additized with 2 mg/l of MDA and the Breakpoint of the resulting mixture was found to be 280°C. Interestingly, the Breakpoint was determined by an increase in differential pressure in the D3241 test.

As will be discussed in the nozzle section, the fuel use rate in the nozzle was much higher than projected. When it became apparent that there would be insufficient fuel to run the 50 hour stability test, or even a shorter version, an alternative benchmark plan was developed. Besides the issue of the validity of the additive performance in the absence of significant copper, there is the question of how it works in comparison to neat fuel with a similar Breakpoint. Fortunately, the fuel for the program that was to follow this one was just such a fuel. It was a JP-5 type and is from the same source as used for the FAA Red Dye testing. The Breakpoint was a little lower than previous batches, at 280°C, but perfect as a reference fuel for this program. The data from these four Breakpoint series is seen in Figure 6, below.

![Figure 6: Thermal Oxidative Stability Results for Fuel #2 and the Reference Fuel](image-url)
It is interesting to note that in this graph, Fuel #2 appears better than the 300°C Breakpoint would suggest. The tests above 300°C failed because the deposits were rated as Abnormal, which is they had an unusual color. The depth values at the higher temperature are only slightly higher than what would be associated with FT-SPK, a synthetic blending component per D7566 that has a required D3241 specification value of 325°C. The MDA recovered Fuel #2 and the reference fuel has the same Breakpoint but the ellipsometry data suggests that the former might be slightly better.

**Nozzle Results:** Nozzle fouling tests were conducted with a single PW 2040 air-blast atomizer in four steps. The tests were started with a new nozzle as there were no suitable used nozzles; however, it was significantly used, by SwRI standards, by the time the MDA tests were conducted. All of the testing on Fuel #2, and the reference fuel, was completed on the first step involved obtaining the fouling rate curve for the neat Fuel #2 (AF 6861). In the second step, MTOL (2500 ppm) was added to the neat fuel to degrade the thermal stability and hence reduce the break-point temperature of the fuel. The third step was to study the effect of MDA (2 mg/L) on the thermally degraded fuel. This was accomplished by obtaining the nozzle fouling rate curve for the fuel with MDA and comparing it against the fouling curve from the neat and thermally degraded fuel.

The plan was to run stability tests similar to the test done on the first fuel but there was insufficient fuel due to the higher than anticipated fuel consumption for this nozzle. The alternative exercise agreed to was to compare a reference fuel with a neat Breakpoint similar to the MDA additized Fuel #2. That is the fourth curve measured in the process. All the fouling curves are shown in Figure 7.

![Figure 7: Comparison of Fouling Rate Curves for PW 2040 Air-Blast Atomizer](image)
When comparing the Breakpoint results (Figure 6, above) to the nozzle results (Figure 7, above, and Table 3, below), the similarity is notable. Neat Fuel #2 is very good. The MTOL destroys the oxidative stability in the lab and in the nozzle. The MDA recovers the fuel by a significant margin in the lab and in the nozzle. That recovery is similar in performance to the neat reference fuel of identical Breakpoint. The suggestion in the Breakpoint testing, that the recovered Fuel #2 might be slightly better than the reference fuel, is duplicated in the nozzle testing.

Table 3: Summary of Nozzle Fouling Test Results for PW 2040 Air-Blast Atomizer

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Temperature</th>
<th>1000/T (K^-1)</th>
<th>Fouling Rate [lbm/(hr^2.(psi)^0.5)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°F)</td>
<td>(°C)</td>
<td>(K)</td>
</tr>
<tr>
<td>Neat Fuel</td>
<td>365.0</td>
<td>185.0</td>
<td>458.2</td>
</tr>
<tr>
<td></td>
<td>380.0</td>
<td>193.3</td>
<td>466.5</td>
</tr>
<tr>
<td></td>
<td>395.0</td>
<td>201.7</td>
<td>474.8</td>
</tr>
<tr>
<td>m-toluidine (2500 ppm)</td>
<td>350.0</td>
<td>176.7</td>
<td>449.8</td>
</tr>
<tr>
<td></td>
<td>365.0</td>
<td>185.0</td>
<td>458.2</td>
</tr>
<tr>
<td></td>
<td>380.0</td>
<td>193.3</td>
<td>466.5</td>
</tr>
<tr>
<td>MDA (2 mg/L)</td>
<td>365.0</td>
<td>185.0</td>
<td>458.2</td>
</tr>
<tr>
<td></td>
<td>380.0</td>
<td>193.3</td>
<td>466.5</td>
</tr>
<tr>
<td></td>
<td>395.0</td>
<td>201.7</td>
<td>474.8</td>
</tr>
<tr>
<td>Reference Fuel</td>
<td>365.0</td>
<td>185.0</td>
<td>458.2</td>
</tr>
<tr>
<td></td>
<td>380.0</td>
<td>193.3</td>
<td>466.5</td>
</tr>
<tr>
<td></td>
<td>395.0</td>
<td>201.7</td>
<td>474.8</td>
</tr>
</tbody>
</table>

When the data is compared to the neat Fuel #2, it can be seen that the fouling rate increased, with the addition of MTOL, by a factor of 31.4 at 365°F and 73.9 at 380°F. Adding 2 mg/L of MDA reduced the relative fouling rates to 9.9 at 365° and 7.6 at 380°F. A comparison between fouling rate curves for a reference fuel which has the same Breakpoint temperature as the poisoned Fuel #2 treated with MDA yields similar characteristics, ratios of 12.0 at 365° and 11.8 at 380°F, compared to the neat Fuel #2. This data compares well to the Breakpoint deposition data which indicated that, with the same Breakpoint value, the reference fuel would produce slightly more fouling than the MDA recovered fuel.

**GENERAL SUMMARY**

Following are two graphs that relate D3241 Breakpoint testing and Nozzle Fouling directly. In the first (Figure 8), the relative fouling between the neat fuel and the MDA additized fuel are compared at the only temperature, 365°F Fuel Inlet, where both were run. Each column is also identified with the Breakpoint for that fuel.
The reduced fouling in the nozzle test corresponds to the increase in Breakpoint. The 60% (approx) reduction in fouling is a factor of 2.5 which, while directionally identical, is less than might be expected (from SwRI experience) for such a difference in Breakpoint.

The results for Fuel #2 allow a more extended comparison. There are two common temperatures, 365°F and 380°F fuel inlet, and two additional points, neat fuel and reference fuel, to measure. In the following graph the data is also expanded along the x-axis to emphasize the Breakpoint temperature differences.
Since Fuel #2 was of extremely high quality in its neat form there was an opportunity to benchmark the recovery potential of MDA. For Fuel #1, for example, MDA made it better but just how good the fuel could be and how close the addition recovered the fuel to that potential is unknown. For Fuel #2 the fouling at the common test temperatures was assigned the value of 1 and the other test compared to that level.

Poisoning Fuel #2 reduced the Breakpoint from 300°C to 230°C. This also affected nozzle performance, increasing the fouling by approximately 31 times at 365°F and by 74 times at 380°F. Adding the MDA made a dramatic improvement at both temperatures but did not recover the thermal stability all the way back to that of the original fuel by either Breakpoint or by nozzle testing. The Reference fuel, having the same Breakpoint as the MDA treated Fuel #2, had very similar fouling characteristics to the latter.

The fouling was reduced by approximately 70% at 365°F and 90% at 380°F with MDA addition to test Fuel #2. This compared to a reduction of approximately 60% at 365°F for Fuel #1. While both fuel/nozzle systems responded well to MDA addition the larger increase for Fuel #1 did not translate into a larger improvement in the nozzle tests. The D3241 test is a laminar flow system, compared to the turbulent nozzle system, and that is believed to amplify surface effects.

CONCLUSIONS

Three major points seem to emerge from this effort:

1. It was difficult to find a fuel that had marginal thermal stability with non-detectable copper content.
2. MDA has actual antifouling properties in addition to its metal complexing ability.
3. When 2 mg/L of MDA was added to fuels in the heated nozzle test rig, reduced fouling rates were observed, just as when MDA is added to fuels tested according to D3241.

It was difficult to find fuels that had marginal thermal stability for this study. Of those found, no fuels in the field with marginal thermal stability had a copper content less than 10 µg/kg. This suggests the overall stability quality of fuels in the marketplace is very good.

Historically there have been questions about MDA performance in the absence of metal to complex. Based on some extended (5 hour) D3241 tests where the fuel failed when it had passed the standard test, the proposition was offered that the MDA ‘fooled’ the test. The results of this testing, where D3241 and actual nozzles are compared, supports the opposite conclusion that MDA, in absence of significant metal amounts, has significant antifouling properties.
Conversely, this testing also validates the use of the D3241 thermal oxidative stability test to confirm the application of MDA. Of course this is not an exhaustive test but it was conducted on two very bad fuels. This should be sufficient for the modest allowance proposed in the following recommendations.

Another point to consider is the potential usefulness of MTOL as a hardware evaluation aide. As the FAA Red Dye Program, the CRC World Fuel Survey, and the difficulty in finding fuel for this program demonstrates that fuel with marginal thermal oxidative stability is rare. Still, OEMs are still subject to experience with fuel of marginal quality. Perhaps this would be a path to a protocol for generating a marginal jet fuel, Jet T, for component and engine evaluation.

**SUMMARY CONCLUSION**

The purpose of this program was to determine if MDA would provide improved performance for essentially copper free fuels with poor thermal stability. This has been demonstrated with two fuels on two nozzles. Based on these results the CRC MDA Task Group recommends a modest allowance of 15°C for the use of MDA where copper is not detected.

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