

**CRC Report AV-03-04**

**Diesel Lubricity Additive Effect on  
Jet Fuel Thermal Oxidative Stability**  
with  
**Supplementary Information on Fatty Acid Methyl Ester  
and Jet Engine Nozzle Performance**



**August 2011**

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# **Diesel Lubricity Additive Effect on Jet Fuel Thermal Oxidative Stability**

with

## **Supplementary Information on Fatty Acid Methyl Ester and Jet Engine Nozzle Performance**

**SwRI<sup>®</sup> Project No. 08-12185**

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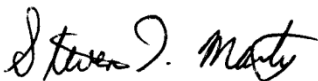
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## Executive Summary

The Coordinating Research Council (CRC) funded a preliminary study of the effect of diesel lubricity additives (DLAs) on thermal oxidative stability of jet fuel as evaluated by breakpoint in accordance with ASTM D3241<sup>[1]</sup>, commonly referred to as the JFTOT\*. The scope of this study was to test readily available jet fuel samples and perform a simple evaluation on the effect of the three primary classes of DLAs: amides (AM), esters (ES) and monoacids (MA). Also included in this report are results from related studies on fatty acid methyl ester contamination and on bench test of jet engine nozzle performance.

**CRC DLA Program.** The objective was to determine if DLA could be present in jet fuel at levels up to 200 mg/kg with no apparent harm to thermal stability. The two test fuels selected were similar to those used in a previous FAA-sponsored program on red dye<sup>[2]</sup>. The fuels represented a Marginal fuel with a breakpoint at or near the standard specification limit of 260°C and a Nominal fuel with a breakpoint in the 280–300°C range that encompasses most jet fuel. DLAs were selected to represent AM, ES and MA. Samples matched additives evaluated in previous studies, and new additives were also evaluated.

The first step was to screen DLAs to choose the three candidates that represented the best performer (the one generating the least deposits with no other adverse effect) from each category. The resulting deposits were evaluated by ellipsometry<sup>[3]</sup> and the normalized results were combined into a ranking. The next step was to evaluate the effects of the best candidates on thermal stability breakpoint of the two test fuels in a series of increasing DLA levels. Another step was added to evaluate the potential interaction of DLA with a standard turbine fuel lubricity additive<sup>[4]</sup>. **Conclusion:** It is possible to have DLA levels up to 200 mg/kg in jet fuel containing approved turbine lubricity additives without a significant effect on breakpoint.

**DLA-Energy Sponsored FAME Analysis.** The Defense Logistics Agency–Energy funded a separate small program<sup>[5]</sup> to provide a preliminary look at the effect of low levels of fatty acid methyl ester (FAME, also known as biodiesel) on jet fuel thermal oxidative stability. The limited scope included five standard D3241 tests with varying levels of five candidate FAMEs, using the same Marginal fuel as used in the CRC DLA program. **Conclusion:** While some differentiation between the FAME samples was possible, the data from the FAME study indicated no fundamental breakpoint issue at the trace levels tested.

**FAA Red Dye Program Sponsored Nozzle Testing.** The FAA Red Dye program advisory committee sponsored an evaluation of two DLAs and two FAMEs from the above efforts with the same bench test nozzles used in the Red Dye program. Actual jet engine nozzles were subjected to typical worst-case conditions such as simulating idle descent and evaluating the rate of fouling over a series of temperatures. **Conclusion:** While the testing was not sufficient to be definitive, the nozzle tests detected no fundamental issue with either DLA or FAME at the trace levels ( $\leq 100$  mg/kg) tested.

**Summary Conclusions.** These programs, in combination, have shown that it is possible to have DLA or FAME in an aviation turbine fuel with no adverse effect on thermal oxidative stability. However, there is not enough evidence yet to give blanket approval to either DLA or FAME. A reasonably cautious plan should allow the industry to function in the presence of low levels of contamination, in the range of 5 to 100 mg/kg. With increased chances of fuel being contaminated with materials having potential negative thermal oxidative stability, a case can be made that more formal requirements are needed. In practice, any DLAs destined for use in common carrier pipelines should be subjected to an approval program that tests their impact on breakpoint in a broad selection of fuels.

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\*Jet Fuel Thermal Oxidation Tester. JFTOT is the registered trademark of Petroleum Analyzers Company, Houston, Texas.

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## Table of Contents

<i>Section</i>	<i>Page</i>
EXECUTIVE SUMMARY .....	iii
CRC DLA PROGRAM.....	1
Background .....	1
Program Synopsis .....	2
Selection of Test Fuels .....	2
Selection of Additives .....	2
Laboratory Thermal Stability Testing .....	3
Basic Additive Effect Test Program .....	3
Progressive Additive Effect Test Program .....	6
CI/LI Compatibility Test .....	7
DLA Testing – Conclusion .....	9
SUPPLEMENTAL INFORMATION PART 1: DLA-ENERGY SPONSORED FAME ANALYSIS .....	10
Program Synopsis .....	10
FAME Analysis – Conclusion .....	14
SUPPLEMENTAL INFORMATION PART 2: FAA RED DYE PROGRAM SPONSORED NOZZLE TESTING .....	15
Program Synopsis .....	15
Nozzle Testing – Conclusion .....	18
SUMMARY CONCLUSIONS .....	20
REFERENCES .....	21

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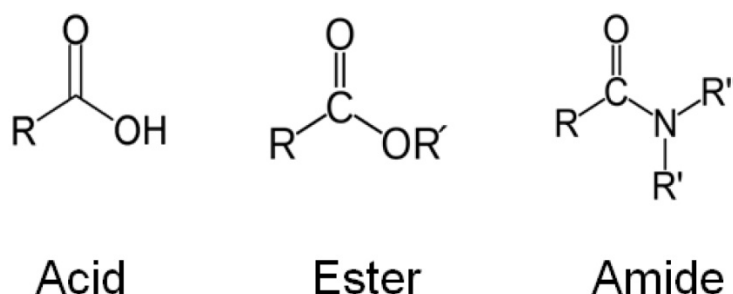


## CRC DLA Program

### Background

The advent of the demand for ultra-low sulfur diesel led to lubricity problems with diesel fuel. This was not unanticipated, based on military experience with very low sulfur jet fuel in the 1990s, which led to the use of lubricity additives in all military fuel from then on. Those additives, while working acceptably with low viscosity distillates, were found to be inadequate for standard diesel fuel operations. Based on the need to protect engines, the need for diesel lubricity additives (DLAs) became obvious. What also became obvious was the potential contamination of jet fuel from DLA trailback (the residual material left from the passing of a fuel through common use systems). The primary concern was thermal stability, as the additives are surface active materials and thermal stability is primarily a surface deposition issue.

Consider the three most common chemistries for lubricity additives (Figure 1).



**Figure 1: Basic Chemistry of Additives Tested**

The oxygen and nitrogen in these groups make the materials more surface active. That is good because it brings the long chain R group to the metal surface where the film increases lubricating qualities and, often, provides some amount of corrosion protection. For DLAs the R groups are primarily from long chain fatty acids, typically C<sub>14</sub> – C<sub>20</sub> monomers. (The exception is in aviation fuel, where the acids are typically in the dimer and trimer form from cross linking unsaturated fatty acids around the C<sub>18.1</sub>, linoleic, range.)

A typical reaction product of fatty acid is to combine it with an alcohol to form an ester. In an ester the R' group can be a variety of alkanes, the choice affecting the specific properties. A special case is where R' is a methyl group, from the esterification of fatty acid with methanol. This would be a fatty acid methyl ester (FAME), also known as biodiesel. Esters are considered more oxidatively stable than raw fatty acids but that is more of a bulk property than a heated, potentially catalytic surface issue.

Another reaction product path is to combine the acid with an amine to form an amide. The R' and R'' groups are varied to affect the physical properties of the product. The material is surface active and that is likely why it has lubricating properties. The historical use of amine and amide materials has been in corrosion protection in crude pipelines and process units. The nitrogen content is known to be good for protection against chloride salt corrosion.

## **Program Synopsis**

The basic plan was to obtain three samples of each main class of additive and then test the effects on two fuels: the fuel at or near the typical specification D3241 requirement of 260°C and a second near the median of measured relative thermal stability, 285°C<sup>[6]</sup>. The first step would be to see if there are significant differences in additive effect. If there are, the best-performing material (the one generating the least deposits with no other adverse effect) from each category would be subjected to additional evaluations with an eye to providing a path for guidance in selecting DLAs that would have a minimum impact on aviation turbine fuel.

### **Selection of Test Fuels**

Southwest Research Institute (SwRI) intended to select two fuels, Marginal and Nominal (in regard to thermal stability), from available inventory. It was considered a plus if the Nominal fuel came from a source of known quality from which additional fuel could be obtained for nozzle testing.

For this program, Marginal and Nominal fuels are:

Marginal – A fuel with a breakpoint between 260° and 270°C, based on the ASTM D1655<sup>[7]</sup> specification requirement that the fuel pass the D3241 test at a minimum of 260°C.

Nominal – A fuel with a breakpoint between 275° and 290°C, based on the data from the CRC World Fuel Sampling Program that shows nearly 60% of all fuel breakpoints fall in this range.

SwRI maintains significant inventories of aviation turbine fuel. Most of that fuel is acquired for large-scale component testing and is handled as most commercial fuel purchases are handled. The initial plan was to use the same fuels used in the FAA Red Dye program for the Base and Reference fuels. In that testing the Reference fuel had a consistent 260–265°C breakpoint. A new breakpoint test of this fuel confirmed it was still suitable (breakpoint = 260°C) to serve as the Marginal fuel. This fuel was a JP-8 from a major Houston area refiner that uses the Mercox<sup>®</sup> process, provided by the DLA Energy Group of the Defense Logistics Agency (DLA-Energy, formerly DESC).

It was hoped that the same fuel that was used in the Red Dye program could be acquired for the Nominal fuel. Throughout the Red Dye program this fuel performed consistently from refinery batch to refinery batch. Unfortunately, the batch received at the time this program commenced was contaminated and another source needed to be selected. The available jet fuels were surveyed and SwRI selected a Jet A from a local San Antonio area refiner that typically produces fuel, using hydroprocessing, with a characteristic breakpoint of 280–285°C. This fuel was tested and found to be suitable (breakpoint = 280°C) for the project to serve as the Nominal fuel.

### **Selection of Additives**

The program solicited the fuel and additive industry for current diesel lubricity additives. The goal was to acquire a minimum of three DLAs for each category – amide (AM), ester (ES) and monoacid (MA). That goal was achieved for the esters and monoacids but only one amide was received. SwRI had an additional amide DLA on hand from a government-funded program and it was made available for this

project. The additives were collected on the promise of anonymity. The suppliers wanted assurance that a negative result would not compromise their diesel fuel applications. Also, since this effort would represent only a small part of a comprehensive fit-for-purpose evaluation<sup>[8]</sup> of an additive it would be inappropriate to identify one or more additives as suitable for jet fuel.

### **Laboratory Thermal Stability Testing**

The initial step of the additive analysis part of the program was to determine the breakpoint of the test fuels. Once the neat breakpoint was established, each candidate additive was evaluated at the respective breakpoint temperature for each fuel. While the program was bound by current methodology in determining the breakpoint, a concern arose that there might not be much differentiation with the standard visual tubercator (VTR) technique, so the ellipsometric tube rating (ETR) technique was designated as the performance arbiter. That worked very well, as can be seen from the following information.

#### **Basic Additive Effect Test Program**

1. To ensure accurate dosing, pre-dilute each additive to a 5% concentration by volume in the fuel being tested.
  - a. All of the samples dissolved without problem except for ES 3. With both fuels the dilution blend remained cloudy and, with time, the material would settle out. Since there was no replacement ester additive available, ES 3 was used as planned.
2. Run breakpoint (as described in ASTM D3241 Annex X2).
  - a. Determine breakpoint using the ASTM D1655<sup>[7]</sup> Specification pass/fail criteria:
    - i. VTR Color Code < Code 3
    - ii. No Peacock (P) Deposit
    - iii. No Abnormal (A) Deposit
    - iv. Differential Pressure (DP) < 25 mmHg
  - b. Evaluate the deposition on the tubes with the ellipsometer.
3. Test each additive at the breakpoint temperature (last passing temperature).
  - a. Successively, treat each test fuel with a candidate additive dosed at 200 mg/kg.

There is no known value for potential contamination but the consensus in discussions within the CRC Aviation Committee was that it might be as much as 50 mg/kg. Based on established additive evaluation principles<sup>[8]</sup>, this testing was set at 4X that estimate.
  - b. Run a single test at the appropriate breakpoint temperature.
  - c. Evaluate each test by the standard criteria and with the ellipsometer.
4. Compile data into tables:
  - a. Standard Criteria
  - b. Ellipsometer Depth

The VTR and ETR results for the two fuels are shown in Tables 1 and 2, respectively.

The yellow highlights in Tables 1 and 2 indicate the breakpoint, the last passing temperature for each fuel – 260°C for the Marginal fuel and 280°C for the Nominal fuel. To reiterate, the breakpoint is the last passing temperature in a series of D3241 tests run at increasing temperatures. Putting the additive in at the breakpoint temperature was the most direct way of determining if the additive has a significant effect on fuel thermal oxidative stability. In the above testing it is clear the additives can have a negative effect. It is also clear that the ellipsometric (ETR) results provide better discrimination between samples.

**Table 1: VTR Results for Test Fuels Neat and Additized**

Marginal Fuel		Additives at 200 mg/kg							
Temp, °C	Neat	MA 1	ES 1	AM 1	ES 2	MA2	AM 2 <sup>a</sup>	MA 3	ES 3 <sup>1</sup>
250	<1								
255	1								
260	2	2	<2	>4AP	<3	<3	>4*	2	<2
265	3								
270	4								
Nominal Fuel		Additives at 200 mg/kg							
Temp, °C	Neat	MA 1	ES 1	AM 1	ES 2	MA2	AM 2 <sup>a</sup>	MA 3	ES 3 <sup>1</sup>
280	<1	<1	2A	>4P	1A	<2A	1A	1	<1
285	2A								
290	3A								

**Table 2: ETR Depth Results for Test Fuels Neat and Additized**

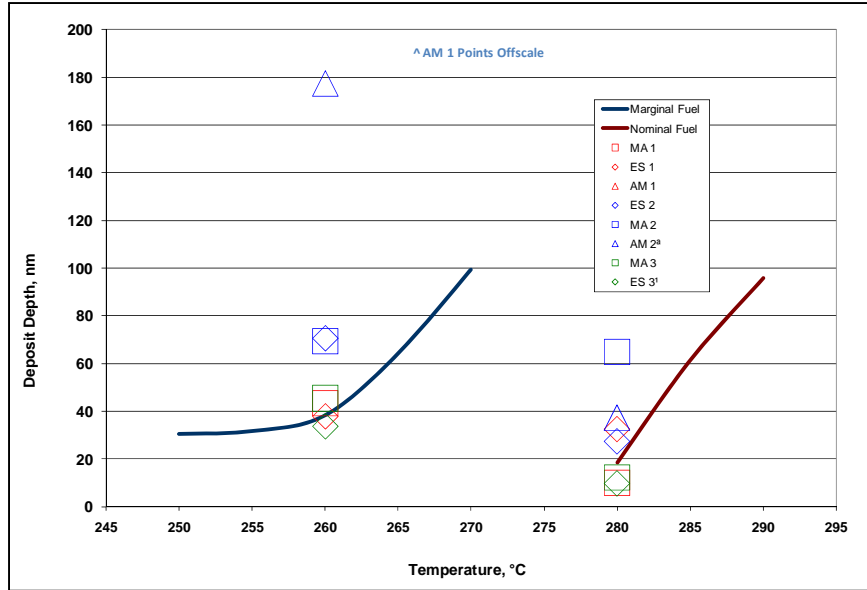
Marginal Fuel		Additives at 200 mg/kg							
Temp, °C	Neat	MA 1	ES 1	AM 1	ES 2	MA 2	AM 2 <sup>a</sup>	MA 3	ES 3 <sup>1</sup>
250	30.42								
255	31.61								
260	38.19	43.44	37.78	554.25	70.57	69.43	177.41	45.44	33.67
265	64.04								
270	99.24								
Nominal Fuel		Additives at 200 mg/kg							
Temp, °C	Neat	MA 1	ES 1	AM 1	ES 2	MA 2	AM 2 <sup>a</sup>	MA 3	ES 3 <sup>1</sup>
280	18.5	10.03	32.43	700	27.42	64.82	37.4	12.27	9.74
285	61.44								
290	95.77								

\* This sample also failed on DP and the deposit was Peacock above the rateable area

<sup>a</sup> after AM 2 run all hot seals on JFTOT were bad

<sup>1</sup> Does not dilute to clear with jet fuel at 5%

The ETR results, without sample AM 1 for clarity, are plotted in Figure 2.



**Figure 2: Additive Performance Evaluated by Ellipsometry**

The next step in the program was to down-select the additives to the best additive from each class. The ETR results for each fuel/additive combination were normalized based on the base neat fuel and then the sum of the Marginal and Nominal fuels was averaged for ranking.

$$Additive\ Value(n)_{Relative} = \left( \frac{ETR_{NF_1+A_n}}{ETR_{NF_1}} + \frac{ETR_{NF_2+A_n}}{ETR_{NF_2}} \right) \div 2 \quad [Eq. 1]$$

*ETR* = Ellipsometric Tube Rating

*NF<sub>n</sub>* = Neat Fuel, *n* = 1 or 2

*A<sub>n</sub>* = Additive, *n* = 1 to 8

The results are shown in Table 3.

**Table 3: Relative Additive Performance**

Additive Ranking	
ES 3'	0.7
MA 1	0.8
MA 3	0.9
Neat	1.0
ES 1	1.4
ES 2	1.7
MA 2	2.7
AM 2	3.3
AM 1	26.2

<sup>1</sup> Not Dispersable in Jet Fuel

While ES 3 performed well in this evaluation, the fact that it is not readily dispersible in jet fuel made it questionable as to whether it actually made it through the test filters. Based on this concern, ES 3 was passed over for the next best ester, ES 1. Choosing the amide to use also presented a quandary. AM 1 was by far the worst performer in the test but AM 2 had an unusually negative effect on the seals in the test.

The effect of AM 2 on the elastomers was to partially disintegrate the material. The D3241 test requires new elastomers for each test because the temperature cooks them and reduces their flexibility, but they are otherwise intact. An attack on the elastomeric material is clearly a compatibility problem. SwRI reasoned that at the lower initial concentrations the elastomer problem would be minimized and AM 2 was selected for the next phase.

Also of interest are the results for MA 2, as SwRI posited that the monoacids would be the best candidates. MA 2 ranked almost as poorly as the best amide, illustrating that expectation is no substitute for testing. The selected materials for the next step were MA 1, ES 1 and AM 2.

Once the additives were chosen, the next step was to take the chosen candidates and check the breakpoint performance with varying levels of additive to represent progressive amounts of contamination.

#### **Progressive Additive Effect Test Program**

1. Use the pre-diluted additives as previously prepared.
2. For each additive (MA 1, ES 1 and AM 2) in turn:
  - a. Run breakpoint with 20 mg/kg of additive.
    - i. Determine with standard criteria.
    - ii. Evaluate with ellipsometer.
  - b. If 20 mg/kg breakpoint  $\geq$  neat breakpoint, continue; if not, stop.
  - c. Run breakpoint with 75 mg/kg of additive.
    - i. Determine with standard criteria.
    - ii. Evaluate with ellipsometer.
  - d. If 75 mg/kg breakpoint  $\geq$  neat breakpoint, continue; if not, stop.
  - e. Run breakpoint with 200 mg/kg of additive.
    - i. Determine with standard criteria.
    - ii. Evaluate with ellipsometer.

If an additive made it to the 200 mg/kg dosage level, with either or both fuels, the next step would be to evaluate the potential interaction with a standard MIL-PRF-25017G corrosion inhibitor/lubricity improver (CI/LI)<sup>[4]</sup> additive. The evaluation would be made at the CI/LI additive's minimum effective and maximum allowable concentrations. (For the chosen additive the respective values are 9 and 22.5 mg/kg.) In the above tests the monoacid (MA 1) made it to 200 mg/kg in both fuels and the ester (ES 1) made it to 200 mg/kg in the Marginal fuel. In addition to not reaching the 200 mg/kg level with either fuel, AM 2 continued to have adverse effects on the elastomers in the method.

### CI/LI Compatibility Test

1. If 200 mg/kg breakpoint  $\geq$  neat breakpoint for either fuel, then check for compatibility with approved aviation CI/LI additive in both fuels.
  - a. Run breakpoint with 200 mg/kg of the selected DLA with 9 mg/l, the minimum effective concentration, of the CI/LI additive.
  - b. Run breakpoint with 200 mg/kg of the selected DLA with 22.5 mg/l+, the maximum allowable concentration, of the CI/LI additive.

The results are shown in Table 4. The yellow highlights indicate where the 5°C decrease in breakpoint stopped further testing on an additive.

**Table 4: Effect of Additive Concentration on Breakpoint**

Additive and Concentration	Test Fuel	
	Marginal Fuel	Nominal Fuel
No Additive	260	280
AM 2 @ 20 mg/kg	260	280
AM 2 @ 75 mg/kg	255	275
AM 2 @ 200 mg/kg	x	x
MA 1 @ 20 mg/kg	260	280
MA 1 @ 75 mg/kg	260	280
MA 1 @ 200 mg/kg	260	280
ES 1 @ 20 mg/kg	260	275
ES 1 @ 75 mg/kg	260	x
ES 1 @ 200 mg/kg	260	x
CI + MA 1 @ 9 mg/l CI conc.	260	280
CI + MA 1 @ 22.5 mg/l CI conc.	260	280
CI + ES 1 @ 9 mg/l CI conc.	260	275
CI + ES 1 @ 22.5 mg/l CI conc.	260	275

In addition to the tabulated data, it is instructive to review the actual deposition as measured by the ellipsometer, first for the monoacid DLA MA 1 (Figure 3) and then for the ester DLA ES 1 (Figure 4). Legend numbers are dosages in mg/kg.

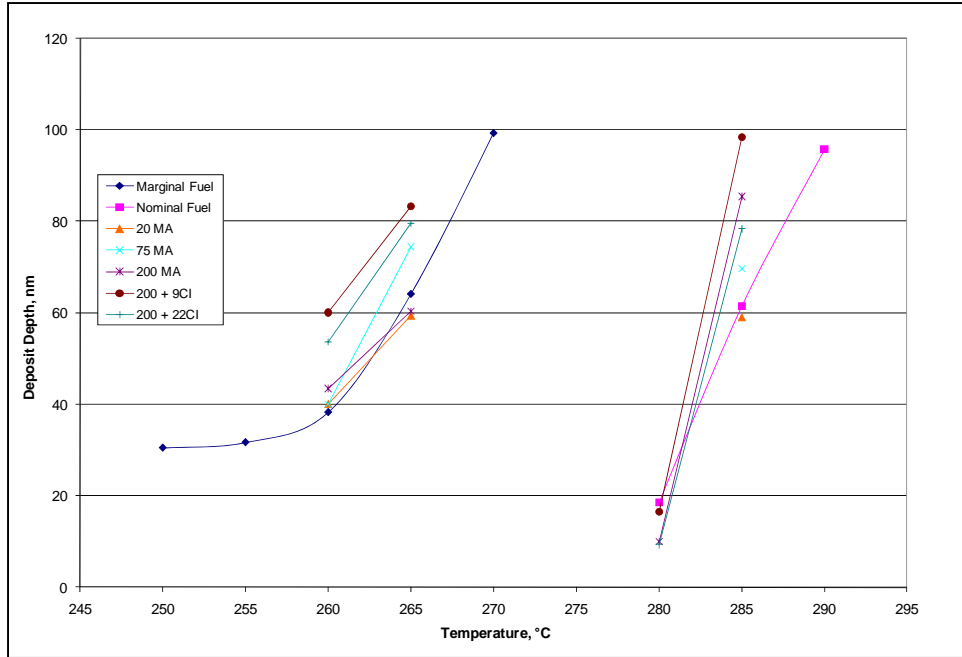


Figure 3: Evaluation of Monoacid DLA and CI/LI Effects

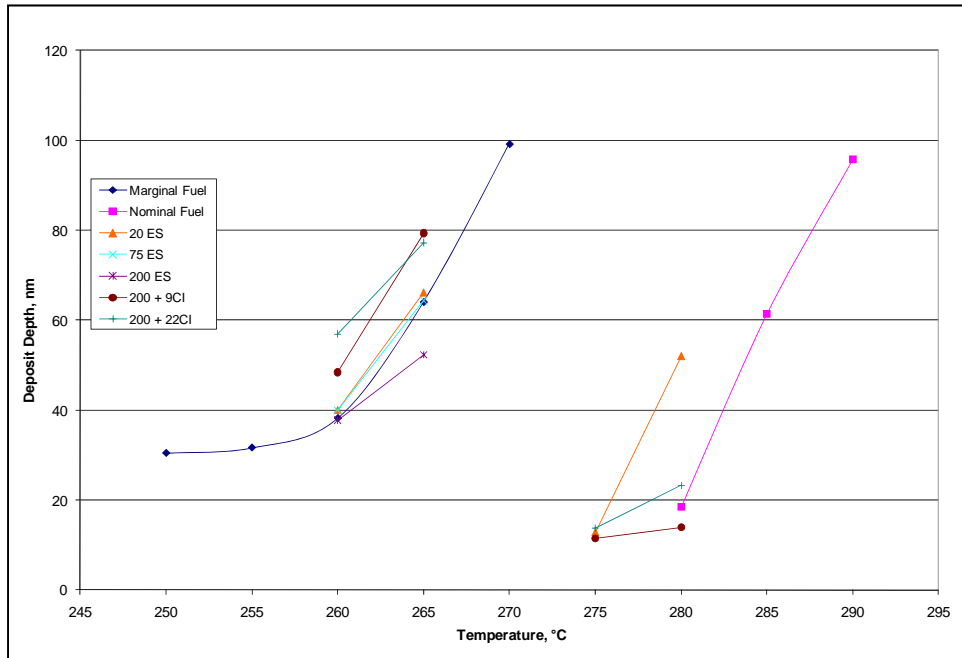


Figure 4: Evaluation of Ester DLA and CI/LI Effects



Several key points were apparent from the above testing:

- For the three additives selected only the monoacid, MA 1, does not affect the breakpoint at any tested levels, including those with corrosion inhibitor.
- While ES 1 reduced the breakpoint of the Nominal fuel at the lowest treat rate, the subsequent CI/LI testing suggests that the negative effect might be within the normal variation in breakpoint testing.
- The ellipsometer data indicates a significant increase of deposition but not VTR rating for three of the four fuel series in the presence of the CI/LI.
- The effect of the amide additive (AM 2) on elastomers was evidence that thermal stability is not the only potential fit-for-purpose<sup>[8]</sup> issue for additives.

## **DLA Testing – Conclusion**

This program started with two basic questions:

1. Is there a significant difference in additive effect?
2. Is there a path for minimizing the impact on aviation turbine fuel?

The data from the first part of this program shows there can be significant differences in additive effect. Of the collected additives, the amide based materials were clearly the least compatible with the selected jet fuels, with the better of the two averaging a 3.3X increase in deposition at the breakpoint value of the fuels. The monoacids and the esters both performed well in general but there were application issues with each, suggesting that a blanket class acceptance is not warranted.

Further testing of the best additives showed that breakpoint performance was reasonably stable from trace levels from 20 mg/kg up to this test's max treat rate of 200 mg/kg. Interestingly, on an absolute deposit depth basis, the fuels were more sensitive to much smaller doses of the standard CI/LI additive in the presence of the DLAs than to either of the DLAs by themselves. (It would be interesting to evaluate CI/LI separately but that was not in the scope of this program.) Since the industry has decades of experience with CI/LI without adverse thermal stability problems, this suggests that incidental amounts, up to 50 mg/kg, of a properly screened DLA would not necessarily be a problem.

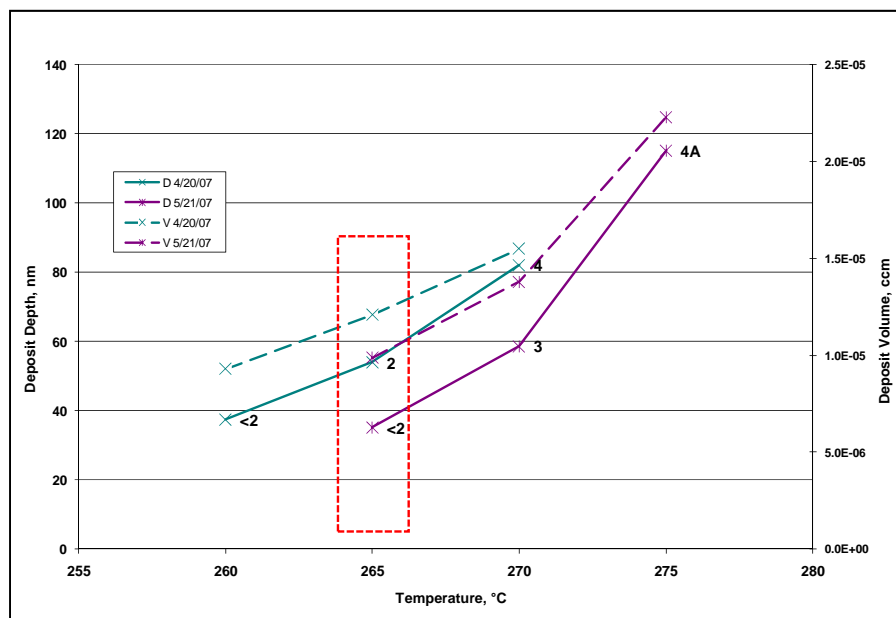
At a minimum it seems the best practice for any required use of DLAs in diesel fuel carried by common carrier pipelines, which also carry jet fuel, would be to select an additive that minimizes negative impacts on jet fuel thermal oxidative stability. A good first step would be to perform these same tests over a variety of jet fuels of varying crude source and process type. There should also be an appropriate analytical test to measure for contamination, and if contamination is found the fuel should be tested by ASTM D3241 to show that the thermal oxidative stability has not been compromised. The ultimate solution might be to qualify<sup>[8]</sup> a DLA for use in jet fuel; however, that would be an extraordinary effort.

## Supplemental Information Part 1: DLA-Energy Sponsored FAME Analysis

### Program Synopsis

In a parallel program funded by DLA-Energy, SwRI evaluated the effect of FAME on deposition. The program was intended as a supplement to the CRC DLA program and the data is provided by their courtesy. The purpose of the program was to investigate if FAME has any significant effect at trace levels\*. The test program was limited in scope: a breakpoint of the chosen jet fuel before and after the FAME tests and twenty-five (25) individual D3241 tests, five each with five FAME samples.

Typically, a program designed to evaluate contamination effects would evaluate a variety of fuels to find a fuel that showed an effect response to the property in question, but this exploratory program was limited to one fuel. The fuel used was the same Marginal fuel referenced above in the CRC DLA test program covered by the main body of this report. The chosen test fuel typically has a breakpoint in the 260–265°C range, as repeatedly demonstrated previously. Figure 5 is the chart of ellipsometric values for the results of the two breakpoints run on the test fuel in the DLA-Energy program.



**Figure 5: Marginal Fuel Breakpoint Variation over One Month**

In both test series the breakpoint was determined to be 265°C. While that is very consistent for this method, the ellipsometric results show a shift in absolute terms over the course of one month. Also note the breakpoint for this sample of fuel was better to start than the sample of the same fuel used in the CRC DLA program. All of the testing listed below was conducted between these two breakpoint tests.

\*As in the CRC DLA program, establishing a trace level is the subject of conjecture. The accepted detection limit is 5 mg/kg so it has to be higher than that. Since the material is so similar in nature to the DLAs, the same 50 mg/kg and 4X testing starting points were adopted.

Table 5 lists the five FAME samples used.

**Table 5: Biodiesels Used**

Code	Type
YGME	Yellow Grease (methyl ester)
SME	Soy
RME	Rapeseed
POME	Palm Oil
POME + AO	Palm Oil + Antioxidant

A detailed analysis of the test FAMES was not included in the scope of the project. The yellow grease and soy products were from a CRC Automotive Group FAME program. Shell Global Solutions provided the other samples.

In the interest of seeking out any significant effect of FAME contamination, the evaluation criteria were expanded beyond those in the standard specifications, as shown in Table 6.

**Table 6: FAME Effect Criteria**

Test Criteria	Limit
VTR	< 3, No A, No P
DP	< 25 mmHg
ETR, depth	< 60 nm
ETR, volume	< 1.25E-05 cm <sup>3</sup>

The VTR/DP criteria are as used in most specifications for pass/fail. The ETR values are based on this specific fuel. A general equivalence for a Code 3 VTR is a deposit depth around 85 nm. For this fuel it is consistently in the 55–65 nm range. Since the standard VTR deposit rating is a maximum apparent depth, < Code 3, over a minimum area (2.5 mm<sup>2</sup>), the ETR <60 nm level was chosen for this program for consistency between rating techniques. The relationship with volume is less clear but, in general, the typical volume at a failure is about 1.25E-5 cm<sup>3</sup>. Both the deposit depth and the deposit volume criteria were set based on the 4/20/07 breakpoint ellipsometer (Figure 4) measurements.

With only five available tests per FAME type, the traditional temperature-based breakpoint evaluation was not seen as the best approach. Instead this program uses a less frequent alternative, the additive breakpoint. In this type of breakpoint the test temperature is held constant and the level of additive is varied in a programmed fashion. The evaluation consisted of adding varying aliquots of FAME to the base fuel and performing a D3241 test at the characteristic breakpoint value, 265°C. The tests started at 200 mg/kg, the same screening level used in the CRC DLA program. A total of five (5) tests were performed per fuel using the simple hunting algorithm described below.

#### Additive Breakpoint Hunting Algorithm

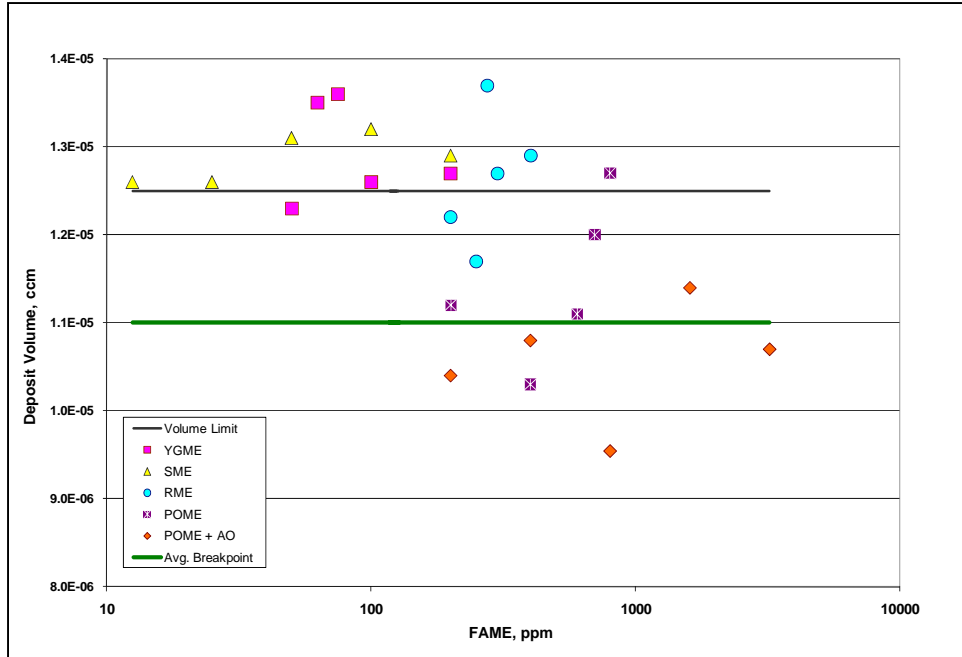
1. Run D3241 test at 265°C (start with 200 mg/kg of selected additive).
  - a. If the test passes all four criteria in Table 6, double the additive and go back to step 1.
  - b. If the test fails any of the four criteria in Table 6, halve the additive and go back to step 1.
2. Run a total of five tests with each additive.

Starting at 200 mg/kg, the above algorithm could lead to a FAME concentration as low as 12.5 mg/kg and as high as 3200 mg/kg. In fact, both extremes were reached in this testing. In the course of testing these FAMEs the only differentiation factor turned out to be a variation in deposit volume. Table 7 gives the results for the five test series.

**Table 7: Relative Effect on Volume of FAME Contamination**

Additive Concentration, mg/kg	YGME	SME	RME	POME	POME + AO
<b>12.5</b>		1.01			
<b>25</b>		1.01			
37.5		-			
<b>50</b>	0.98	1.05			
62.5	1.08				
75	1.09				
87.5					
<b>100</b>	1.01	1.06			
112.5					
125					
117.5					
150					
162.5					
175					
187.5					
<b>200</b>	1.02	1.03	0.98	0.90	0.83
225					
250			0.936		
275			1.096		
300			1.016		
325					
350					
375					
<b>400</b>			1.032	0.824	0.86
500					
600				0.888	
700				0.96	
<b>800</b>				1.016	0.76
1200					
<b>1600</b>					0.91
<b>3200</b>					0.86

As noted above, in this particular exercise with this approach the volume criteria provided the only way to separate the results. The additive numbers in bold font cover the standard steps. The table shows how the additive breakpoint level was found for each FAME. For the above table the data was converted to deposit relative to the limit ( $E_{vol}/Limit_{vol}$ ) for clarity. Figure 6 is a graphical representation of the same data.



**Figure 6: FAME Effect on Deposit Volume**

Based on the criteria for this test, the results were as shown in Table 8.

**Table 8: FAME Additive Breakpoint**

Type	Additive Breakpoint @ 265°C
YGME	50 mg/kg
SME	< 12.5 mg/kg
RME	250 mg/kg
POME	600 mg/kg
POME+AO	> 3200 mg/kg

The FAME test series were conducted in the order noted in Figure 6 and Table 8. The results were constrained by the test design. As shown by ellipsometry in Figure 5, the fuel improved (though the standard breakpoint did not change) over the course of the program. This change may have affected the absolute results allowing the latter tests to pass the volume criteria. Also note that in the regular breakpoint tests illustrated in Figure 5 the volume at the first failing test is about 25% larger than at the breakpoint. Most of the failures in this test are an order of magnitude lower in percentage change. The effect on deposit volume was measurable but, in SwRI's experience, a long way from truly significant. The DLA-Energy charge was to find any evidence that FAME affected the deposition. If SwRI had used only the standard visual and differential pressure ratings for the D3241 testing, the testing might have gone up to 3200 ppm of FAME for all the tests.

## **FAME Analysis – Conclusion**

Overall, there is some effect from trace levels (12.5 to 3200 mg/kg) of FAME. These effects, however, are not significantly different from effects seen with the better DLAs or DLA-CI/LI blends in the CRC DLA program. Practically any surface active agent will have some deposition effect. A review of the second round of DLA testing shows that specification-allowed amounts of CI/LI have more effect on the deposit than the better DLAs, and that was also true for the FAMEs in this testing. In practical terms, the definition of 'adverse effect' is fairly simple: whether the FAME makes the fuel fail the D3241 test.

Deposit volume is not used in the standard method for evaluating fuel performance. A fuel with a normal visual rating < Color Code 3 will pass the test regardless of how much area is at that level. The fact that the ellipsometer shows that the D3241 method does respond to the addition of FAME should give some assurance that it would respond appropriately to excessive contamination. This program also shows that the ellipsometer can provide a finer level of differential data in fuel analysis, while there is no effect on the visual evaluation.

## Supplemental Information Part 2: FAA Red Dye Program Sponsored Nozzle Testing

### Program Synopsis

When the question about potential contamination with DLA and then FAME became important, the nearly-decade-long FAA-sponsored study on the effect of Red Dye on jet fuel was nearing an end. The program advisory council for that program recommended that the final monies in that program be used to make an initial evaluation of the effects of DLA and FAME on fuel nozzle deposition.

In the 1990s the IRS and the EPA combined to require that some diesel fuels be dyed red if they were untaxed or high sulfur. The dye was to be used at either 11 mg/l for tax purposes or 4 mg/l for sulfur discrimination. These levels were referenced to Solvent Red 124, a tinctoral standard, but the actual dyes used were the ones used for aviation gasoline, alkyl derivatives of azobenzene-4-azo-2-naphthol. A concern about potential cross contamination led to a laboratory test program which showed that the dye could have substantial effects on thermal stability. The Red Dye program was developed to determine if there was a safe level of dye contamination. The results of that effort are contained in the program report but the use of that program to evaluate the potential effect of DLA and FAME is also covered here.

Figure 7 is an example of the effect of Red Dye on a specific jet fuel nozzle. The Red Dye report graphs are presented in the form and units as published by FAA.

The data format, log fouling rate versus  $1000/^\circ\text{K}$ , is the standard for nozzle evaluations. The fuel flow rate and pressure drop across the test nozzle were monitored continuously so that the instantaneous flow number (FN) of the nozzle could be determined. The rate of degradation of FN is called the fouling rate and is the metric used for quantifying nozzle fouling and to evaluate the effect of contamination.

$$\text{Fouling Rate, FR} = \frac{d(\text{FN})}{dt} \quad [\text{Eq. 2}]$$

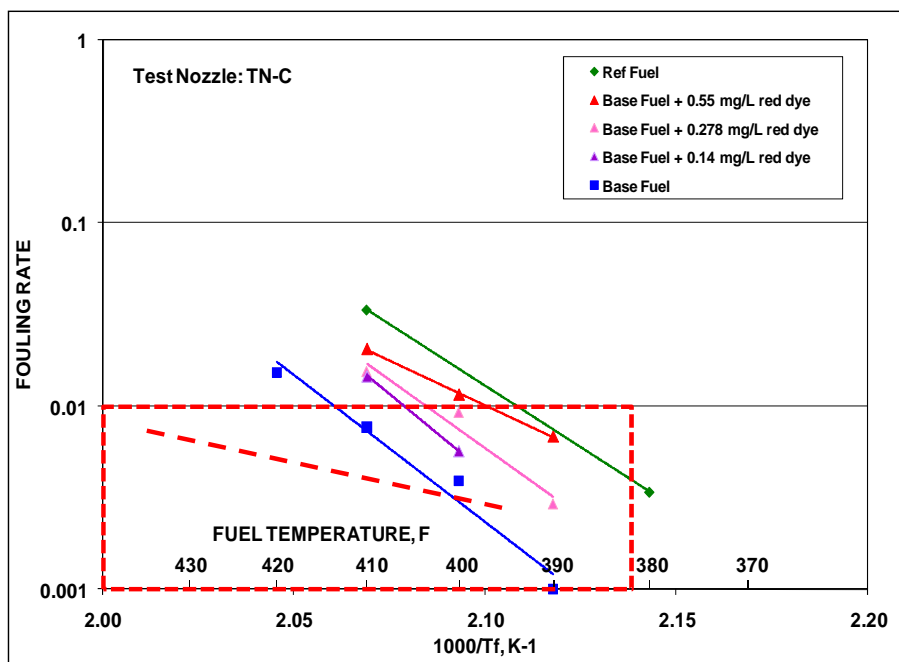
$$\text{where FN} = \frac{m_{\text{fuel}}}{\sqrt{\Delta P}}$$

and  $m_{\text{fuel}}$  = fuel flow rate

$\Delta P$  = pressure drop across the nozzle

The fouling rate is presented as a unitless quantity since the mass flows and differential pressures are proprietary but consistent throughout the testing.

Displaying the test fuel temperature as  $1000/^\circ\text{K}$  is a historical preference for nozzle testing and is a typical format for engineering evaluations. The  $^\circ\text{F}$  data was included for quick reference to show that the temperature goes from hotter to cooler, left to right. The use is archaic but is what was used in the original report. The  $370^\circ$  to  $430^\circ\text{F}$  range is the same as  $188^\circ$  to  $221^\circ\text{C}$ .



**Figure 7: Effect of Red Dye Contamination on Fouling Rate of TN-C Fuel Nozzle**

The Base fuel for this project was acquired in truckload batches over the course of a decade. The typical breakpoint of this fuel was 285–290°C. The Reference fuel had a breakpoint value of 260°C. The latter is the same fuel that was used as the Marginal fuel in the CRC DLA program and the sole fuel in the DLA-Energy FAME program. Some reviewers have noted that the dye-driven fouling rates are still better than that for the Reference fuel, which just met specifications. While true in this instance, the Red Dye could be a serious issue for a reactive fuel that was at the specification D3241 limit. Note also the level of Red Dye reported in Figure 7. At a range of 0.14 to 0.55 mg/l there is a distance of three to four orders of magnitude between the Red Dye additive and the DLA and FAME evaluation levels.

D3241 breakpoint data is not directly transferable to nozzle testing except in relative ranking. The laboratory test works in a low-flow, non-turbulent regime and emphasizes surface deposition effects. Actual nozzle performance is dominated by the operational effects of the equipment design in a turbulent flow system. Experience has shown that nozzles respond in the same order as fuel breakpoints but with varying effect. Part of the Red Dye program was to evaluate multiple nozzle designs to find one that was sensitive to the dye and had sufficient differentiation between the Base and Reference fuels to allow proper evaluation of the dye effect.

In Figure 7 the dashed red box and line represent the area in which all of the data on the DLA and FAME tests would be found and is intended to aid the evaluation of the data presented below. As seen by the dashed line, the fouling rate for the last batch of the Base fuel was lower than that for the previous batches. The primary result of that is that the DLA and FAME tests were conducted under significantly harsher conditions than most of the Red Dye evaluations.

Based on the industry concern about contamination and a general desire to set a ‘no harm’ allowance at 100 ppm in the field, this testing was conducted at 100 mg/l. While this is lower than the current understanding that the desired 100 ppm limit is in fact 100 mg/kg, it is in the same order of magnitude.



While laboratory testing is typically conducted at 4X the proposed limit, nozzle testing is considered a full-scale component test and thus additive testing is conducted at use limits.

Though the identity is not stated in the report, the DLA testing was conducted with best DLAs, MA 1 and ES 1, from the CRC DLA program. The best performing DLAs (i.e., the ones with the least impact on breakpoint) were chosen based on the concept that DLA selection for common use systems could be limited to those materials with demonstrated minimum thermal stability impact. The FAME testing was conducted with the worst examples, SME and YGME, from the DLA-Energy FAME program. The worst performing FAMEs (i.e., the ones that showed the greatest increase in deposit volume), from the available samples, were chosen based on the fact that any qualified FAME might be used in diesel fuel.

The DLAs were tested first, with the following results (Figure 8).

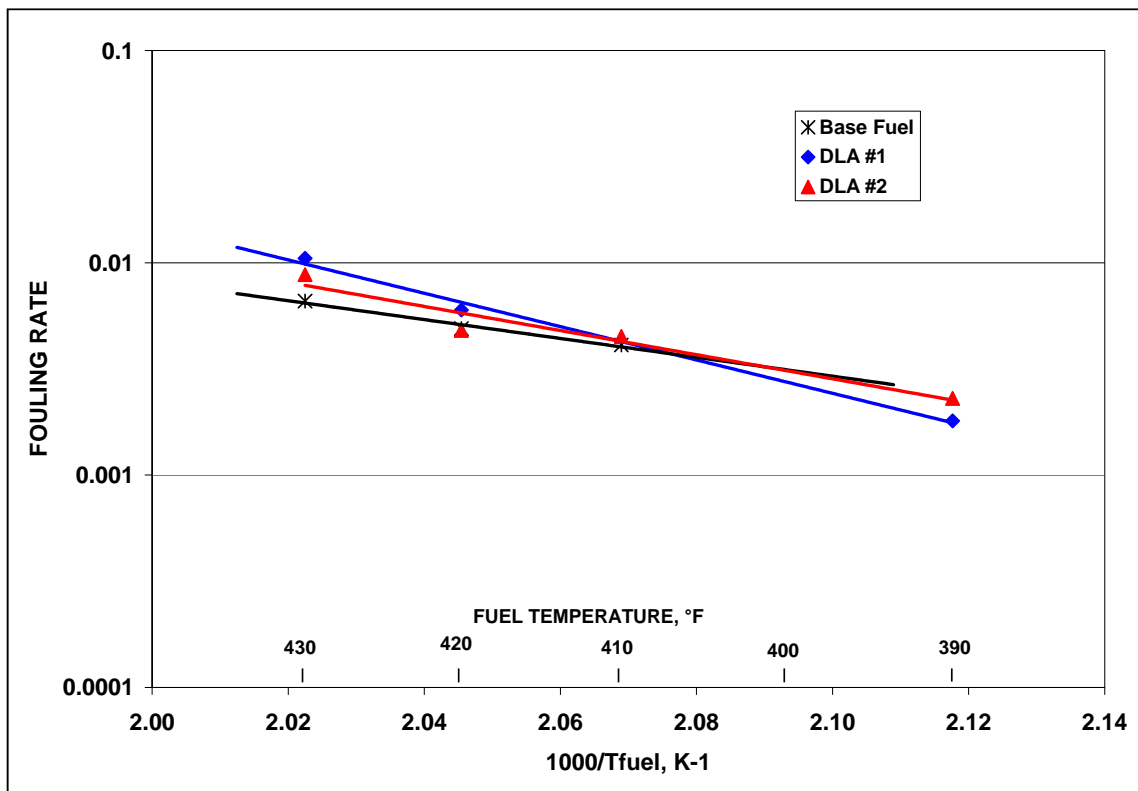
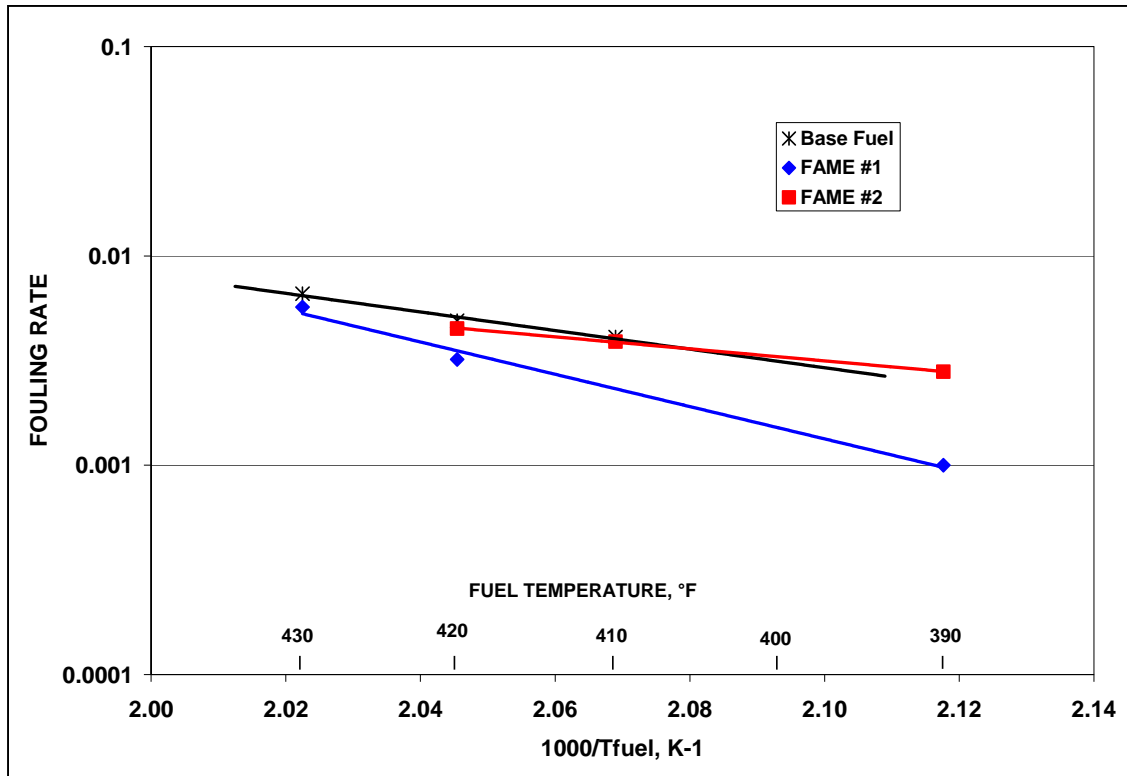


Figure 8: Effect of Two Diesel Lubricity Additives at 100 mg/l on Fuel-Nozzle Fouling Rate

With this slight variation in slopes it would take considerably more effort to prove there is any difference in performance. This is consistent with the data generated in the DLA evaluation discussed earlier in this report. The FAME results are shown in Figure 9.



**Figure 9: Effect of Two Fatty-Acid Methyl Esters at 100 mg/l on Fuel-Nozzle Fouling Rate**

While the FAA Red Dye program authors noted the interesting fact that in this testing the Base fuel dosed with 100 mg/l of FAME #1 performed better than the neat fuel, they did not suggest it as proof that FAME could provide deposition protection. Since this nozzle was used previously for the DLA work there is a chance that this represents an effect of the previous DLA that was overcome by the time FAME #2 was tested.

### **Nozzle Testing – Conclusion**

The following paragraphs are the conclusions of the FAA Red Dye program authors.

*“The results on the effect of the diesel lubricity additives (DLA) and fatty-acid methyl esters (FAME) contaminations are to be considered preliminary, and no conclusions should be drawn. Over 100 tests have been conducted on the effects of red dye. This is the first data produced on the potential effects of DLA and FAME on fuel nozzle fouling. Also, there is effectively only one red dye, whereas there are several chemical types of DLA and several products of each type on the market. Furthermore, there are several different FAMEs available.*

*Thus, not only is the chemistry involved in these additives and blending materials significantly different than the hydrocarbon chemistry of the fuel, there is a wide variety of chemistry involved within the various products marketed as DLA and for the various FAMEs available.*

*Further evaluations of the different DLA and FAME chemistries must be investigated with basic tests, such as the JFTOT as a screening tool, to be followed by a comprehensive evaluation with fuel nozzle fouling tests.”*

The program authors further recommended caution:

*“It is recommended that further tests be conducted on several candidate chemistries of both DLA and FAME in one or more fuel nozzles that allow fouling rates to be measured at lower fuel temperatures than tested here. The design of fuel nozzle TN-C is such that the fuel temperatures necessary to get measurable fouling rates in test times of the order of 10 to 30 hours are much higher than most of the other nozzles tested. Since the presence of DLA and FAME infer potentially different chemical mechanisms leading to deposition, the results would be more meaningful if the fuel temperatures were closer to operational fuel temperatures, perhaps in the range of 300° to 350°F.”*

## Summary Conclusions

These programs, in combination, have shown that it is possible to have DLA or FAME in an aviation turbine fuel with no adverse effect on thermal oxidative stability. The CRC DLA program has also shown that some forms of DLA do have significant impact on fuel thermal oxidative stability. However, as the authors of the FAA Red Dye report noted, there is not enough evidence yet to give blanket approval to either DLA or FAME. What has been shown, however, is that a reasonably cautious plan should allow the industry to function in the presence of low levels of contamination, in the range of 5 to 100 mg/kg.

For the diesel lubricity additives the CRC-sponsored testing indicated, and the FAA nozzle testing supported, the idea that it was possible to have such contaminate materials present and have little effect on the thermal oxidative stability of jet fuel. The DLA testing also showed there was no specific class of DLA that was without a problem in these trials. It gave strong negative contra-indications to using an amide DLA for both thermal oxidative stability and materials compatibility reasons.

If diesel lubricity additive is to be used for multi-product pipeline transport of diesel fuel, it needs to be tailored to minimize the potential effect on aviation turbine fuel. Ultimately, it might be wise to have a DLA that is qualified for use in aviation turbine fuel by the ASTM D4054 path. This might also be good for aviation, as the continued changes in aviation turbine fuel chemistry may reduce the efficacy of the existing CI/LIs. That would take years to achieve, if desired. In the interim, the responsible path would be to evaluate candidate additives for no-harm effect, on thermal oxidative stability, with a diverse group of fuels and develop methodologies to detect them at contamination levels. For this latter approach, DLA contamination with a tailored additive would still require confirmation of suitability by running the D3241 test at the level appropriate for the specification in question.

The DLA-Energy FAME testing, though not extensive, combined with the nozzle testing shows there is no fundamental thermal oxidative stability issue with having FAME in jet fuel at trace levels ( $\leq 100$  mg/kg). This is consistent with other industry studies, such as those being conducted by the Energy Institute Joint Industry Program on FAME (EI JIP). Any surface active material, including the allowed CI/LI as demonstrated in the CRC DLA program, can affect the absolute deposition in the D3241 test. The important issue is whether it increases deposits sufficiently to fail the specification criteria. The testing associated with this program reinforces the principle that if an aviation turbine fuel is found to be contaminated with FAME then performing a D3241 test to evaluate if it is suitable for use would be a prudent course.

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\*This Practice was revised substantially with the 2009 edition, so the date is necessary for the context of the reference.

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