DESIGN AND CURRENT STATUS OF DEVELOPMENT OF A JET FUEL THERMAL STABILITY ADDITIVE

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Abstract

An initiative led by the US Air Force concluded that advances in military fighter aircraft systems would require fuels with over 50% improvement in heat sink capability over conventional JP8 fuel. This led to the creation of the “JP8+100” program during which hundreds of commercial additives were tested for thermal stability enhancing characteristics. The program demonstrated that the thermal stability of jet fuels (particularly JP8) could be enhanced through the use of particular additives and additive blends used at relatively low concentrations. Additionally, flight testing highlighted a significant reduction in fuel-related maintenance costs, arising from cleaner combustion. One aspect of the incorporation of the most beneficial additives from a thermal stability viewpoint that has given some cause for concern, however, is the consequent effect on the water and solids separation from “JP8+100” fuel, a feature minimized by introduction of the “+100” additive as close to the skin of the aircraft as possible. Inspired by the USAF success, and anticipated consequential environmental benefits, we have conducted an experimental program for the design and development of a conceptually new multifunctional molecular species to enhance the thermal stability of jet fuels, without compromising other required essentials of jet fuel product quality. The philosophy behind the additive development is described in the present paper, as are results and conclusions of laboratory and large-scale tests conducted under this development program, which demonstrate (a) the activity of the new type of additive in enhancing the thermal stability of JP8 fuel, and (b) the compatibility of additized fuel with existing conventional filter/water separation systems.

Introduction

One of the major limitations to the development of more efficient gas turbine engines is effective thermal management. Since the fuel is used as the primary coolant for the engine as well as on-board avionics, environmental and hydraulic systems, the heat sink capability of the fuel has been subject to some scrutiny for many years.¹

Subjecting fuels to high temperature thermal-oxidative conditions leads to the formation of particulates, varnishes and gums, which clog valves and filters, and degrade injector nozzle performance.² In the extreme, coking can cause serious fouling in injectors and combustors, leading, for example, to re-light problems. Improvements in the thermal stability of “conventional”, eg JP8-type kerosene fuels of 100°F through the use of low-cost additive packages have been the subject of the US Air Force’s “JP8+100” program since 1989, on the basis that advances in military fighter aircraft systems would require fuels with over 50% improvement in heat sink capability over conventional JP8 fuel.³ During this program, hundreds of commercial additives were tested for thermal stability-enhancing or deposition-reducing characteristics. The program demonstrated that the thermal stability of jet fuels (particularly JP8) could indeed be enhanced through the use of particular additives and additive blends used at relatively low concentrations. Additionally, flight testing has highlighted a significant reduction in fuel-related maintenance costs, arising from cleaner combustion.

However, one aspect of the incorporation of the preferred thermal stability additives that has given some cause for concern, is the associated effect on the water and solids separation from “JP8+100” fuel, although, operationally, this is minimized through the introduction of the “+100” additive as close to the skin of the aircraft as possible.

Inspired by the successful USAF demonstrations of the increased thermal stability achievable through the use of additives, and the anticipated consequential
environmental benefits which could arise from reductions in emissions, we have conducted an experimental program in which the mechanisms of the thermal-oxidative stability of jet fuels have been used as the basis for the design and development of a conceptually new multifunctional molecular species that enhances the thermal stability of jet fuels, without compromising other required essentials of jet fuel product quality, namely water and solids separation.

**Basis of the Approach**

The objectives of the present development were three-fold:

- To understand how thermal degradation takes place, and how additives may interact in such processes;
- To understand the function of dispersant and antifoulant additives which show beneficial effects on thermal stability; and
- To identify and develop new, commercially-viable thermal stability additives without compromising other aspects of fuel quality.

**Fuel Thermal Degradation**

On the basis of our studies, we estimate that lacquers, gums and particulate deposits amount to approximately 0.01-0.05% (w/v) of the fuel, and it is probable that they are derived from the more polar fuel constituents, which undergo thermally-induced transformations depending on factors such as:

- fuel chemistry
- oxygen
- metals

which combine to form deposit precursors through polymerisation, oxidation or degradation reactions. The deposit precursor species lead to the formation of both bulk and surface deposits.

**Mechanisms of Additive Action**

In view of the above thermal deposition and degradation processes, various mechanisms can potentially improve fuel thermal stability, including:

- metal deactivation
- suppression of oxidation
- dispersancy
- detergency
- precursor stabilisation.

The forerunner USAF programme concentrated on the operation of the first four mechanisms listed above, through the use of a proprietary detergent/dispersant species, formulated together with a commercial antioxidant [BHT; butylated hydroxytoluene (2,6-di-tert-butyl-p-cresol)] and the metal deactivator (N,N'-disalicylidene-1,2-propanediamine). In fact, it is the high degree of interfacial activity of the dispersant/detergent component in the formulation that is responsible for both the beneficial effects on reducing surface deposition as well as the undesirable effects on the performance of filter/water separators.

In addition to the four mechanisms described in connection with the USAF program, we have identified a further possibility by which deposit formation is arrested through preventing growth of the deposit precursor species. We envisaged at the outset of the work that a molecule with in-built multifunctionality could be developed, as conceptually depicted in Figure 1, with combined abilities to counteract many of the above thermal destabilisation mechanisms. Additionally, we were mindful of the need to restrict interfacial activity of any candidate additive for reasons indicated above.

**Additive Development and Testing**

The focus of this program was to identify the characteristic features required of an additive that exhibits beneficial effects on fuel thermal stability using proprietary dispersant additives from (the former) BP Chemicals' additives company, Adibis. This enabled "baseline" effects in laboratory tests to be established on the basis of the known chemistries involved.

**Identification of "Active Functionality"**

Figure 2 shows a schematic representation of the process of evolution of candidate additives on the basis

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American Institute of Aeronautics and Astronautics
of their effect on thermal stability. As shown, a two-pronged attack on the problem was undertaken. In parallel, a limited number of in-house proprietary additives, used commercially as dispersant additives in other fuel and lubricant systems, was assessed in tests for reduction of both bulk and surface deposition (see below). Simultaneously, the same testing program was carried out using selected small molecular species, designed to evaluate the effects of different chemical functional groups.

Additive Testing

Thermal Stability

According to Heneghan et al., the various test methods for assessing fuel thermal stability can be subdivided into three categories: static tests, flowing tests, and engineering tests. Following these authors, the various test methods used in the present study are summarized in Table 1.

Of the methods listed in Table 1, an in-house flask test was used as the main initial screening tool. This example of a "static test" involved heating (initially air-saturated) fuel at 140°C for typically 3 days, following which deposition on an immersed thin glass "coupon" enabled the extent and nature of the surface deposition on this substrate to be assessed, and the fuel coloration (measured by light absorption) and mass of filterable deposits enabled the effects on bulk deposition to be quantified. These tests were usually carried out in different fuels in order to identify the best candidates, which were subsequently subjected to the more well-established techniques, as listed in Table 1. Subsequent analyses of surface deposition, therefore utilized the quartz crystal microbalance (QCM) under the same temperature conditions as in the flask tests, and bulk deposition in the isothermal corrosion and oxidation test (ICOT; described in ASTM D4871) at the higher temperature of 180°C in order for additive effects to be quantified systematically.

The next stage involved determining surface deposition under quasi-dynamic conditions in the hot liquid process simulator (HLPS) on aluminum tubes at 335°C for 5 hours, followed by deposit thickness analysis using ellipsometry, as described elsewhere. Any candidate additive passing the laboratory screening tests would then progress into the extended test program, designed to evaluate the additive performance under representative operational conditions. In particular, courtesy of the USAF, additive characterization using Wright-Patterson laboratory's extended duration thermal stability test (EDTST) rig was generously conducted as an example of a larger-scale flowing evaluation. This test is shown in highly schematic form in Figure 3.

Figure 2. Schematic diagram of the evolution of thermal stability candidate additives.

Figure 3. Schematic diagram of the layout and operating temperatures of the extended duration thermal stability test.
Although the intricate details are not fully understood at the present time, fuel/water interfacial activity is inextricably linked to the propensity of the fuel to "disarm" filter/water separators, such that water and solids removal from the fuel is compromised. One measure of the activity of these systems is the fuel/water interfacial tension. We have used an approach which measures the dynamic interfacial tension of a fuel/water interface in assessing the effects of different additive classes. Using the nomenclature of the preceding section, this still constitutes a static test. Qualitatively, another static method, the water reaction test (ASTM D1094), provides an indication of the presence of surface-active material in a fuel. We have also used an industry standard flowing test intended to quantify the effects of surfactants on coalescer performance, namely the Microseparometer, ASTM D3948. Finally, and most significantly perhaps, the engineering test of commercial filter/coalescer elements has been undertaken on the preferred candidate material using a single-element test facility. A schematic of this test facility is shown in Figure 5.

Table 1. Summary of Thermal Stability Test Methods.

<table>
<thead>
<tr>
<th>Test</th>
<th>Temperature (°C) / duration</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static tests</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flask test</td>
<td>140 / 3 days</td>
<td>-</td>
<td>Closed system with limited air; surface deposition on glass and bulk filterables</td>
</tr>
<tr>
<td>QCM*</td>
<td>140 / 5-15 hours</td>
<td>4</td>
<td>Closed system; measures surface deposits and headspace O₂ concentration in real time</td>
</tr>
<tr>
<td>ICOT</td>
<td>180 / 5 hours</td>
<td>5</td>
<td>Continuous air supply; measures bulk insolubles</td>
</tr>
<tr>
<td>Flowing tests</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JFTOT</td>
<td>240-340 / 2.5 hours</td>
<td>-</td>
<td>Non-isothermal flow system using Al tubes; breakpoint analysis</td>
</tr>
<tr>
<td>HLPS + Ellipsometry</td>
<td>335 / 5 hours</td>
<td>6</td>
<td>Ellipsometric deposit thickness measured; USAF use stainless-steel tube and carbon burn-off</td>
</tr>
<tr>
<td>NIFTR*</td>
<td>140-210 / 6 hours</td>
<td>8</td>
<td>Isothermal flowing system with online O₂ measurement</td>
</tr>
<tr>
<td>Engineering tests</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDTST*</td>
<td>190-260 / 96 hours</td>
<td>7</td>
<td>Simulates bulk fuel and nozzle wetted wall conditions</td>
</tr>
<tr>
<td>AFTSTU†</td>
<td>250-400 / 25-200 hours</td>
<td>9</td>
<td>Simulates nozzle wetted wall temperatures</td>
</tr>
</tbody>
</table>

*Conducted at Wright-Patterson AFB, OH/University of Dayton/ISSI
† Conductor at Rolls-Royce, Derby
An API 1581 (4th edition) single-element test protocol suitable for category M (military) and M100 (thermal stability enhanced military) fuels was adapted for testing 3rd edition-qualified filter/coalescer elements (C in Figure 5) with the present additive. A Merex fuel was initially clay-treated to remove any residual surfactants, as confirmed by a resultant Microseparometer reading of 96 and conductivity of 2 pS m⁻¹. The category M fuel was prepared by adding a military additive pack, comprising:

- 2.0 mg l⁻¹ Stadis 450 antistatic additive
- 15 mg l⁻¹ DCI-4A corrosion inhibitor/lubricity enhancer
- 0.4 mg l⁻¹ Petronate L surfactant replacement additive
- 2.0 mg l⁻¹ fuel system icing inhibitor (diethylene glycol monomethyl ether).

The M100 fuel contained 25 mg l⁻¹ of the new thermal stability additive. A fuel flow-rate of 29 US gal was used throughout in a single-pass configuration. The procedure consisted of four stages:

- Element conditioning
- Water coalescence test on the clean element
- Solids holding test
- Water coalescence test on the solids-containing element.

The solids holding capacity of the elements was tested by introducing the "dirt" (90% ISO 12103-1 Ultrafine test dust + 10% R9998 Copperas red iron oxide) as a fuel slurry at 133 mg per USgal per minute for 75 minutes. Residual free water content of the fuel was determined at W in Figure 5 by Aqua-glo (ASTM D3240) and Karl-Fischer analysis, and residual solids, after a stop/start procedure, by collection at point S on pre-weighed 0.8 µm Millipore filters (ASTM D 2276). Pressure drop across the element and treated fuel conductivity (not presented herein) were also monitored.

**The Designed Additive**

The parallel thermal stability testing process described above led to the identification of a specific chemical functional group which appeared to reduce the
level of fuel degradation over and above the performance of in-house proprietary dispersants. This suggested to us that mechanisms other than dispersancy/detergency route may be appropriate to meet our objectives. However, a balance needed to be struck between the introduction of specific functionalities into a fuel-based additive, and its solubility characteristics (Figure 6).

Two factors are important to consider when introducing functional groups into a "carrier" molecule that has inherent fuel solubility. Firstly, the molecular weight of the molecule will inevitably increase. Secondly, groups which possess thermal stability activity are also likely to be polar in nature. Not only do each of these conspire against fuel solubility, but the increased polarity of the resultant molecule will also have an enhanced water reaction effect.

In order to reduce the surface activity of the product, sacrifices were necessary in terms of the resultant dispersancy/detergency. A "classical" surfactant structure was therefore avoided when building in the appropriate functionality to a suitable "host" molecule. Antioxidancy and the possibility for metal chelation were also available in the host. The result was a molecule that conferred very good thermal stability on different JP8 base fuels, but resulted in little degradation of their water reaction characteristics. Scale-up and optimization of the synthetic route was then necessary to achieve the best performance. Figures 7 and 8 illustrate the variations in product efficiency on bulk and surface deposition levels depending on the synthesis conditions.

![Figure 6. The "Performance by Design" balance between molecular functionality and fuel solubility.](image)

![Figure 7. Variation in product effectiveness based on the performance in ICOT tests (180°C; 5 hours).](image)

It was often found that the candidates performing well at reducing bulk deposits (using ICOT or flask tests) also performed well in the surface deposition tests. Although gratifying, this is somewhat surprising, since the respective test conditions are significantly different.

![Figure 8. Variation in performance of the candidate additive produced by different synthetic procedures based on HLPS (335°C; 5 hours) followed by ellipsometric analyses. The corresponding base fuel level is 700 ppb.](image)

The thermal stability performance tests identified the preferred synthetic procedure to obtain the active material, and this was successfully scaled up from bench-scale, through pilot-plant, to full-scale conditions. Based on the results of static and flowing tests, an active concentration of 25 mg/l shows consistently high levels of insolubles reduction in different fuels, as illustrated in Figure 9, with NIFTR results also suggesting increased antioxidant activity.
Figure 9. Product effectiveness at 25 mg/l in ICOT tests on different fuels.

At this concentration of active material, interfacial tension measurements confirmed limited activity at the water/fuel interface. This property is consistent with Microseparometer data shown in Figure 10, in which only a very small effect is seen within the "working concentration" range (boxed).

"Active" concentration (mg/l)

Figure 10. Effect of "active" additive concentration on the Microseparometer value.

From the foregoing, it is evident that, as a result of fuel thermal stability considerations, an additive which confers improved thermal stability properties on JP8-type fuels has been demonstrated in the laboratory. The remainder of this account deals with the results of engineering tests.

Results of Engineering Tests

Thermal Stability

Performance of the laboratory-optimized additive has been carried out using the EDTST and AFTSTU at Wright-Patterson AFB, OH, USA and Rolls-Royce, Derby, UK, respectively.

The EDTST measures deposition in heated stainless-steel tubes, simulating bulk fuel temperature (typically 190-204°C) and burner wetted-wall effects (260°C). Both effects are measured as surface deposits on the inside of stainless-steel tubes, which are sectioned and the deposit quantified by carbon burn-off.

Data from tests using the present additive (at 25 mg/l unless otherwise indicated) [formulated throughout with the antioxidant BHT (25 mg/l) and metal deactivator N,N'-disalicylidene-1,2-propanediamine (2 mg/l)] are shown in Figures 11 and 12. Figure 11 contains deposit profiles for the pre-heater section, representing a bulk fuel temperature of 190°C. The two fuels investigated, POSF-3219 and POSF-3166 (USAF fuel designations) had very different thermal stabilities, as determined by JFTOT breakpoint and HLPS analysis. Their behaviour is compared with POSF-3219 containing an un-optimized version of the present additive, which had marginal effect on base fuel thermal stability.

Corresponding data for the heater region, representing a wetted wall temperature of 260°C are shown in Figure 12. The POSF-3219 data indicate the considerable improvement in thermal stability resulting from the inclusion of this additive at 25 mg/l; results from the corresponding test at double this concentration reduced the deposition to JPTS levels. Very recent results (not shown) indicate that this performance level...
has also been achieved for a bulk fuel temperature of 204°C.

Following the very promising EDTST results, larger-scale AFTSTU testing at Rolls-Royce was undertaken. This unit operates with a single-pass fuel flow rate of 23 l/h. Direct comparisons were made between additized and unadditized base fuel at different wetted wall temperatures. The JP8 fuel used in this test was purported to be "borderline" in terms of its JFTOT breakpoint (265°C, based on a "streak" deposit), although it behaved as a more stable fuel in the AFTSTU itself. In Figure 13 are shown AFTSTU data obtained for the base fuel at 270, 300 and 340°C, and for the additized fuel at 300 and 340°C, since at the lowest temperature, the fuel was stable even in the absence of additive. The results in Figure 13 indicate an increase in the inner wall temperature as a thermally-insulating layer of deposit builds up with time, preventing heat transfer. As is usual in analyzing AFTSTU data, the deposition is quantified as the rate of temperature increase when near-linear steady-state conditions are reached, i.e. after approximately 50-60 hours as seen in Figure 13. Comparative deposition rates calculated in this way are shown in Figure 14, from which the effect of the present additive is clearly apparent.

The results of laboratory tests, described above, indicated to us that the present additive should have relatively little effect on water and solids removal from fuel. Single element tests were therefore undertaken in order to confirm this.

Figure 15 shows single element test results for a trial using the 4th Edition API 1581 protocol, as described above. Pressure drop across the element, and solids and water hold-up in the fuel are indicated throughout the duration of the test. It is evident that, at no time do the solids and water levels exceed the specification limits (indicated). Visually, coalescence seemed to be only slightly influenced by the presence of the additive, with marginally smaller droplets exiting the coalescer element. Coupled with this, the lack of any significant pressure increase demonstrates the tolerance of the coalescer element to the additive, i.e. there was no evidence of coalescer disarming, consistent with the results of the laboratory tests.
Figure 15. Pressure drop and water and solids concentration profiles for 4th edition API 1581 testing of a 3rd edition element in the presence and absence of the thermal stability additive. Regions A through E indicate, respectively: 0.01% (v/v) water injection; 3% (v/v) water injection; solids injection at 133 mg per USgal per minute; 0.01% (v/v) water injection; 3% (v/v) water injection.

**Specification Conformance**

A commercial sample of Jet-A1 fuel was additized at an “active” concentration of 25 mg/l, and each subjected to full specification testing. The majority of the results were identical, with specific comparisons summarized in Table 2. For this Jet-A1 fuel example, it can be seen that no adverse effects result from the inclusion of the additive at 25 mg/l.

**Future Developments**

The current development programme includes further large-scale testing, both for thermal stability and water/solids separation. Limited engine trials have been possible to date, but where undertaken, beneficial effects on engine cleanliness have been observed. Further data analysis is required before firm conclusions can be drawn as far as emissions are concerned. Tests are currently in progress to assess additive-additive compatibility, as well as any effects on fuel system and engine materials. The additive is based on carbon, hydrogen and oxygen, and its structure is considered unlikely to cause significant metallurgy-related problems.

We believe that modifications to the specific molecular design of the present additive offer the ready opportunity to reach beyond the “+100” target, thereby improving the prospects for fuels such as JP8+225.

**Summary**

The present paper describes the development of what is believed to be the first additive specifically-designed to enhance the thermal stability of jet fuels, yet with minimal effect on water and solids separation. Improvements in the thermal stability of JP8 fuels meeting original USAF targets have been demonstrated, on both performance and cost grounds.

**Acknowledgements**

Support for the initial research on this initiative from the UK Defence Evaluation and Research Agency is gratefully acknowledged. Continued support from Air BP has been essential in achieving the challenging objectives, with particular thanks to John Cooper for his initial encouragement. Finally, we acknowledge the contributions made during the development phase by many external organizations, some of whom are mentioned herein.
Table 2. Some specification test results comparing additized with unadditized Jet-A1.

<table>
<thead>
<tr>
<th>Test</th>
<th>Base fuel (Jet A1)</th>
<th>Base fuel + additive</th>
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<tbody>
<tr>
<td>IP 354</td>
<td>Total acidity (mg KOH/g)</td>
<td>0.002</td>
</tr>
<tr>
<td>D1319</td>
<td>FIA aromatics (%vol)</td>
<td>18.9</td>
</tr>
<tr>
<td>D4294</td>
<td>Sulphur (% mass)</td>
<td>0.00</td>
</tr>
<tr>
<td>IP170</td>
<td>Flash point (°C)</td>
<td>40.0</td>
</tr>
<tr>
<td>IP16</td>
<td>Freezing point (°C)</td>
<td>-64.5</td>
</tr>
<tr>
<td>D3338</td>
<td>Specific energy net (MJ kg⁻¹)</td>
<td>43.266</td>
</tr>
<tr>
<td>D1322</td>
<td>Smoke point (nm)</td>
<td>25</td>
</tr>
<tr>
<td>D1840</td>
<td>Naphthalenes (%vol)</td>
<td>0.3</td>
</tr>
<tr>
<td>IP154</td>
<td>Copper corrosion</td>
<td>1A</td>
</tr>
<tr>
<td>IP227</td>
<td>Silver corrosion</td>
<td>0</td>
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<tr>
<td>IP323</td>
<td>JFTOT pressure difference (mm Hg)</td>
<td>0</td>
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<tr>
<td>D381</td>
<td>Existent gum (mg/100 ml)</td>
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<tr>
<td>IP289</td>
<td>Water reaction interface rating</td>
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<tr>
<td>D3948</td>
<td>WSIM (Microsep)</td>
<td>98</td>
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<tr>
<td>IP274</td>
<td>Conductivity (25°C) (pS m⁻¹)</td>
<td>245</td>
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<td></td>
<td>Interfacial tension (25°C) (mN m⁻¹)</td>
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References