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# JP-8+100: THE DEVELOPMENT OF HIGH THERMAL STABILITY JET FUEL

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## Abstract

Jet fuel requirements have evolved over the years as a balance of the demands placed by advanced aircraft performance (technological need), fuel cost (economic factors), and fuel availability (strategic factors). These challenges include: maintaining availability while minimizing the cost; maintaining flammability and heat content while minimizing fire and explosion hazards; allowing cold weather and high altitude operations by restricting flow characteristics, improving storage lifetimes, improving handling and improving refueling safety. To meet these evolving challenges, the Air Force over the years has developed fuels and fuel additive packages for both general (JP-4 and JP-8 fuels) and specialized (JPTS and JP-7) use. In a modern aircraft, the jet fuel not only provides the propulsive energy for flight, but also is the primary coolant for aircraft and engine subsystems. To address this particular requirement, the U.S. Air Force, industry, and academia have teamed to develop a new additive package for kerosene jet fuels that offers increased heat sink and thermal stability. This advanced additive package when added to jet fuels enables improved aircraft design and decreases fuel system maintenance due to fuel fouling/coking. This paper describes the development of an improved JP-8, named "JP-8+100", that offers a 55C (100F) increase in the bulk maximum temperature (from 325F to 425F), wetted wall temperature (from 400F to 500F) and improves the heat sink capability by 50%. Included are sections that detail the problem definition, the additive selection and design process, and flight and field-testing and evaluation. Field-testing in current front line Air Force aircraft has shown that an improvement in thermal stability of JP-8 fuel reduces fuel-related maintenance, reduces replacement parts requirements and increases aircraft readiness. In studies of the design of future advanced aircraft, JP-8+100 has been shown to reduce fuel system complexity and weight.

## Nomenclature

| | | | |
|---|---|---|---|
| **AFB** | Air Force Base | **JFTOT** | Jet Fuel Thermal Oxidative Tester |
| **CFDC** | Computational Fluid Dynamics with Chemistry | **JP** | Jet Fuels |
| **WRDC** | Wright Research and Development Center | **TAC** | Total Accumulated Cycles |

## Introduction

High performance aircraft use fuel as the primary coolant for aircraft subsystems (i.e. gearboxes, hydraulic systems, generators, and environmental control systems) and to cool the lubricating oils in the engine. High performance, high thermal efficiency engines currently being designed will operate at significantly higher temperatures than current engines. These advanced engines will require more fuel cooling to preserve component life and integrity and also will have less fuel available with which to manage and transfer that heat since they are more fuel efficient. The end result is that jet fuel will be exposed to significantly higher temperatures for longer periods of time causing the fuel to degrade and foul aircraft and engine components.

In 1990, an Aircraft Thermal Management Working Group of Wright Research and Development Center (WRDC) investigated the cooling requirements for current, next generation, and future aircraft.[1] Figure 1 illustrates the maximum estimated heat loads for various future aircraft and aircraft subsystems. Also, Figure 2 provides the worst case temperatures, pressures, and residence times experienced by fuel in various engine and airframe components. The WRDC working group reached an alarming conclusion: "*aircraft development in the near future will suffer performance penalties as tremendous quantities of ram air or excess fuel will be required to meet the heat sink requirements.*" To resolve the problem, the WRDC working group recommended the development of high thermal stability fuels, such as: (i) a high temperature thermally stable JP-8+100 fuel which provides a 50% improvement in heat sink capability over conventional JP-8 fuel, and (ii) a new fuel JP-900 that has a 482C (900F) thermal stability and could eliminate the need to recirculate fuel on-board an aircraft. Recent studies conducted by the Air Force have also identified the need for an intermediate heat sink fuel (between JP-8+100 and JP-900) identified as JP-8+225 and for fuels with more heat sink than JP-900 identified as endothermic fuels. All these advanced high heat sink fuels will be based on the additive building block philosophy of JP-8+100 and will undergo similar testing as outlined in this paper.[2]

This paper presents a brief overview of the development of JP-8+100, with emphasis on current flight testing and evaluation. Included are descriptions of the following:

1. Challenges faced in the development of JP-8+100 thermally stable fuel including, test development, additive testing, and materials interactions evaluation,
2. Test assessment and selection of an additive package from screening to flight tests,
3. Evaluation of additive performance based on flight data.

## JP-8+100 Program

In 1989, the U.S. Air Force initiated a research program to increase the thermal stability of JP-8 with the partnership of other government agencies, industry, and universities. Jet fuel development is the best compromise solution to engine performance requirements (technological needs), fuel cost (economic factors), and fuel availability (strategic factors). These same factors were key to the development of JP-8+100. The main goal of this program was to increase the heat sink capacity of current JP-8 fuel by 50 percent (i.e., a 55C increase in fuel operating temperature from 163C to 218C) by developing additives to blend with the fuel at a cost of $1 per 1000 gallons. This fuel will alleviate the need for using expensive specialty fuels such as JP-7 and JP-TS in future aircraft, and decrease maintenance costs for existing aircraft. To meet this goal, the following *five* major research tasks were identified and completed:

1. Identify and develop new fuel thermal stability test techniques.
2. Advance fundamental understanding of fuel thermal stability.
3. Develop global chemistry models and a thermal stability scale.
4. Formulate effective thermal stability improving additive packages.
5. Demonstrate, in actual aircraft flight time and maintenance records, the performance and cost savings produced by the use of new JP-8+100 fuel.

## Additives Testing

A prime goal of the "JP-8+100" development program was to find an additive or an additive combination that will improve the thermal stability of JP-8 fuel by 55C. Laboratory tests, while having significant advantages in assessing the development of an additive package, all have some inherent disadvantages. Not the least of which is that each test is limited as to the range of temperatures and times over which fuel heating (stressing) takes place. An initial analysis of showed that no one test (such as the accepted Jet Fuel Thermal Oxidation Tester, JFTOT) could replicate all of the temperature/times that fuels could undergo in a variety of airframes. Since little was known about modeling these effects, so as to extrapolate to other conditions, a variety of tests were planned. These tests have been grouped as screening tests, follow-on tests, and large-scale engineering tests (see Table 1.).

Since 1989, additive manufacturers have supplied over 400 additive candidates for testing. To accommodate such a large number of additives, a series of screening tests were used for initial additive evaluation. Tests were generally run at the manufacturer's recommended concentration. Screening tests are simple to operate; typically yielding results in less than a day. This allows many additives to be tested. However, these tests are operated under accelerated test conditions (i.e., excess oxygen or temperature). As a result, significantly more assumptions concerning the behavior of fuels and additives is needed to properly evaluate the test results. Those additives that performed "best" were tested in up to 12 fuels (see reference [3] for a description of the test fuels), and selected for follow-on testing including concentration optimization.

Follow-on tests more closely approach reality, but require significantly more time both in testing and turnaround thereby limiting the number of additives and fuel/additive combinations

## TABLE 1: SUMMARY OF THERMAL STABILITY TEST RIGS AND CONDITIONS

| Test | Temperature Range (C) | Miscellaneous |
|---|---|---|
| **Screening Tests** | | |
| Quartz Crystal Microbalance[8] | 140 | Closed system - measures surface deposits |
| Isothermal Corrosion Oxidation Test[9] | 180 | Bubbling air - measures bulk deposits |
| Microcarbon Residue Test[9] | 225 | Distillation - measures residual deposits |
| Hot Liquid Process Simulator[10] | 335 | JFTOT flow system |
| Jet Fuel Thermal Oxidative Tester | ~260 | JFTOT flow system |
| **Follow-on Tests** | | |
| Augmentor[11] | < 1000 | Vaporization flow system - simulates afterburner and nozzle soak back |
| Phoenix[12] | 200-300 | Constant wall temperature with on-line dissolved $O_2$ measurement |
| Near Isothermal Flowing Test Rig[4] | 140 - 210 | Isothermal flow system with on-line dissolved $O_2$ measurement |
| **Engineering Tests** | | |
| Extended Duration Thermal Stability Test[14] | 160-200 | Establishes fuel bulk and wetted wall temperatures |
| Advance Reduced Scale Fuel System Simulator[13] | | Configured to simulate F-22 |

that can be evaluated. Isothermal flowing tests[4] have been used to not only evaluate additives, but also to develop an understanding of the chemistry involved in autoxidation, deposition, and additive performance. Much of the chemistry involved in the autoxidation of jet fuels in static and isothermal flowing chemistry has been successfully modeled.[5] The chemistry models have further been incorporated into computational fluid dynamics with chemistry modeling codes.[6,7] These test rigs have been crucial in developing the models, and have been used to assess the effectiveness of nearly a dozen additives in up to 4 fuels. After testing, the candidate additives with the best likelihood of success were extensively tested in large-scale engineering rigs.

The large-scale engineering rigs are the closest to reality in temperature, flow conditions, oxygen level, and recirculation, but require significant time to evaluate an additive and often produce results that are hard to evaluate. However, this is the first level of test that can be used to assess the actual improvement in operating temperature achieved by the additives.[14] The difficulty of maintaining baselines and the large times scale required for a single test have limited the evaluation in large-scale test rigs to a few additives.

Concurrent with the large-scale test rigs, a series of materials compatibility tests were also run to identify/correct any adverse materials impact. To accomplish this compatibility tests, over

400 material/temperature combinations have been identified. Materials tested in this program span more than 50 years of technology from materials first used in the late 1950's and early 1960's on aircraft such as the KC-135 tanker and the B-52 bomber to aircraft materials planned to be used on aircraft after the turn of the century. In addition, many materials that are widely used on aircraft were never thoroughly tested with JP-8 such that baseline performance of all materials with JP-8 was required. Once the baseline for the large number of material and temperature combinations was established with JP-8 and the Betz Dearborn JP-8+100 additive, a shorter list was compiled for other additives. The performance of new additives needs be evaluated against only those materials that are most susceptible to chemical attack by an additive. A complete list of materials, material/fuel test results, and evaluations criteria are detailed in reference.[15]

Despite the fact that screening tests were followed-up with additional tests in up to 12 fuels, there remained a large variety of fuels in which the additive may be used. Therefore, in addition to and concurrent with the large scale testing, we verified that the additive package would work in most fuels by studying the effects in a world fuel survey. This survey comprised the baseline fuel tests and fuel plus additive package tests for the basic battery of screening tests.[16]

To date, one package has been qualified for flight. Field-testing has begun at a variety of military air reserve and national guard bases throughout the US. This package comprises an antioxidant (butylated-hydroxy-toluene) a metal deactivator (n,n'-disalicydene-1,2,- propane diamine) and ă detergent/dispersant (proprietary, Betz Dearborn Corporation). Details of the actual testing results, evaluations, chemistry models, model development, statistical analysis, and complete reference list for JP-8+100 development are listed in.[17] A second additive distributed by Shell International has recently been approved and will be available for use by US and foreign allies in Europe.

## Engine and Flight Tests

Although extensive laboratory testing of JP-8+100 was conducted, the true validation of the fuel is obtained by testing in actual aircraft hardware. Initial combustion tests of JP-8+100 were conducted in a CFM-56 combustor rig at Wright Laboratory. These tests showed excellent combustion behavior through a wide range of fuel to air ratios. Also, the fuel was tested in an F100-PW-200 engine in a 50 hour, 224 total accumulated cycles (TAC) test. The engine, prior to testing, was "dirty" with visible fouling typical of those found in the fleet. The JP-8+100 additive cleaned lightly fouled components, and improved overall engine performance by opening several small orifices such that the engine could operate at design conditions. Several other engines were tested (T63-A-700, F100-PW-200 (4000 TAC test), F100-PW-229 and in components of the F119-PW-100 engine) with similar improvements. Since these tests were successful, a flight test was conducted at Edwards AFB in September 1994. An F-16 with an F100-PW-220E engine was flown for 4.4 hours throughout the entire flight envelope including 28 engine restarts. This test found no problems, which cleared the fuel for use in other aircraft, and field-testing. In May 1997, Air Education and Training Command (AETC) facilitated a flight test of the Raytheon T-1A at the Raytheon facility in Wichita KS. Prior to the flight test, Pratt & Whitney Canada conducted a ground test of the JT15D engine. The test lasted 107 hours and showed a gradual small improvement in the specific fuel consumption. Raytheon conducted a complete evaluation of the performance of the aircraft with JP-8+100 and compared it to the performance of JP-8. Raytheon found no aircraft performance differences and cleared the T-1A for the use of JP-8+100, thus facilitating the conversion of T-1A aircraft at all AETC training bases. In March to May 1997, the Air Force Flight Test Center at Edwards AFB CA conducted a flight test of a C-141A aircraft with JP-8+100 to determine aircraft cruise performance, fuel quantity gauging effects, engine airstarts and engine smoke and soot production. Approximately 10 flight hours were conducted on JP-8+100. No differences were found with JP-8+100 when compared to JP-8 on aircraft cruise performance, fuel quantity gauging, and engine airstarts. The visual analysis of smoke and soot production was inconclusive, however, the engine showed reduced levels of soot upon post test inspection.

### Field Evaluation Results

Field evaluations are being conducted to quantify long term benefits of JP-8+100. Locations of the field evaluations, aircraft type, engine type and duration of the field evaluation are shown in Table 2. At all the bases except Westfield, all aircraft were converted to JP-8 + 100. At Westfield approximately one-half the aircraft were converted for the evaluation. The demographics of the aircraft numbers and types participating in the field evaluations are as follows: 73 F-16 aircraft, 70 F-15 aircraft, 97 T-37 aircraft, 114 T-38 aircraft, 30 C-130 aircraft, 16 helicopters and 8 OA-10 aircraft. Maintenance data for most locations was collected for a minimum of a 12 month period on JP-8+100 and compared to maintenance data collected during a prior 12 month period on JP-8. By analyzing data from a 12 month period, statistical sample size variations and season variations that effect engine performance are minimized. Results compared across several locations for the same aircraft and engine type also improve the statistical significance of the data collected.

Fuel fouling/coking was observed in fuel nozzles, fuel manifolds, augmentor sprayrings and spraybars on many of the engines that were using JP-8. The severity of the fouling/coking and the effect on engine maintenance varied from engine type to engine type and to a lesser extent from location to location. Some locations using JP-8 reported significant problems with augmentor no lights and bangs (augmentor turns on but doesn't light for a short period of time), engine stalls and flame-outs, premature failure of turbine blades and vanes, plugged manifolds, nozzles and augmentors, whereas others reported minor problems. Analysis of the problems with

JP-8 was complicated by variations between locations in maintenance trouble shooting procedures (within technical orders), maintenance practices to correct deficiencies, and data reporting into maintenance data bases. Because of these issues, data collected on the benefits of JP-8+100 required extensive manpower intensive analysis of the maintenance data to assure that maintenance reductions are carefully counted. Top level statistical analyses proved to be somewhat inconclusive since many non-fuel related factors (engine aging, non-fuel wetted parts failure, inspections etc.) can significantly effect maintenance actions and related costs.

**Problems with statistical analysis**

The statistical analysis of the occurrence of augmentor bangs presents an interesting problem. Because it is typically on the order of one to ten per 1000 hours of flight, The variation from one time period to the next can be large when compared to the average. If ordinary variance of analysis techniques (such as t-distributions) are used, the analysis shows real probabilities of negative rates of occurrence. That is, the analysis is not straightforward since the data set may not be large enough to use the central limit theorem, and a t-statistic may not be an appropriate distribution for analysis of the data. To correct this problem, a Poisson distribution can been assumed.

The Poisson distribution, $f(x) = \frac{\mu^x e^{-\mu}}{x!}$ for $x \geq 0$ and $x \subseteq$ integers ($x$ is the number of occurrences in a specified time period), has at least one very interesting property; the mean = $\mu$ and the variance = $\mu$. Even for small samples, the Poisson distribution can approximate a normal distribution fairly well. That is, the assumption that $\frac{\bar{x}-\mu}{\frac{\sigma}{\sqrt{n}}}$ is $n(0,1)$ is valid. However, the assumption that $\frac{ns^2}{\sigma^2}$ is independent of $\frac{\bar{x}-\mu}{\frac{\sigma}{\sqrt{n}}}$ (a necessary condition for t-statistics analysis) is not valid, since the variance $\sigma$ is equal to the mean $\mu$. The problem is self-correcting though since if we believe the central limit theorem holds then the z-statistic for a Poisson is just $\frac{\bar{x}-\mu}{\frac{\sigma}{\sqrt{n}}}$. This z-statistic does not suffer from the same problem as the normally distributed z-statistic in that there is but one unknown parameter in Poisson z-statistic (there is no $\sigma$) and therefore no need to use a t-statistic analysis. Therefore we can solve for the distribution of this statistic immediately, and determine a 95% ($1.96\sigma$) confidence limit from $n(0,1)$. That is, $-1.96 < \frac{\bar{x}-\mu}{\frac{\sigma}{\sqrt{n}}} < 1.96$.

## TABLE 2: SUMMARY OF FIELD TEST AIRCRAFT AND LOCATIONS

| Air Force Base | Aircraft type | Engine | Test Time (months)* |
|---|---|---|---|
| Kingsley Field ANGB OR | F-16A/B | F100-PW-200 | 36 |
| Fargo ANGB ND | F-16A/B | F100-PW-200 | 15 |
| Otis ANGB MA | F-15A/B | F100-PW-100 | 21 |
| Portland ANGB OR | F-15A/B | F100-PW-100 | 14 |
| Langley AFB VA | F-15A/B | F100-PW-100 | 4 |
| Burlington ANGB VT | F-16C/D | F100-PW-220E | 21 |
| Westfield ANGB MA | OA-10 | TF34-GE-100A | 20 |
| Sheppard AFB TX | T-37B,<br>T-38 | J69-T-25,<br>J85-GE-5 | 30 |
| Louisville ANGB KY | C-130H | T56-A-15 | 18 |
| Nashville ANGB TN | C-130H | T56-A-15 | 16 |
| Springfield ANGB OH | F-16A/B | F110-GE-100 | 15 |
| Kirland AFB NM | UH-1 | T400-CP-400 | 6 |
|  | MH-53 | T64-GE-7 | 6 |
|  | HH-60 | T700-GE-700C | 6 |
|  | MC-130 | T56-A-15 | 6 |

* As of Nov 97

This does not have a simple solution, but can be solved iteratively using an initial guess of $\mu = \bar{x}$ and calculating a new guess using $\mu = 1.96\sqrt{\frac{\mu}{n}} \pm \bar{x}$. The 95% confidence limits for a Poisson distribution are not evenly distributed about the mean, being truncated on the lower side, and as expected, as the number of flight hours increases, the interval for 95% confidence decreases. In these equations the "n" is the number of thousand hour flight intervals. We have checked our analysis and verified that the results do not depend on the size of this interval. The analysis has been shown to be robust except at extremely small n and $\bar{x}$, or $\bar{x} = 0$.

To verify a statistically significant decrease in occurrences as a result of JP8+100 usage, it suffices to show that the rate of failure with JP8, $\bar{x}_{JP8}$, is greater than the 95% confidence upper limit of the JP8+100 failure rate, $\bar{x}_{JP8+100}$. Or, conversely, that $\bar{x}_{JP8+100}$ is less than the 95% lower limit of $\bar{x}_{JP8}$. One can see from Figure 3 that there is a statistically significant decrease in the mean failure rate that is more than two per month. The decrease in the measured mean failure rate is nearly four per month.

### Additional field and laboratory observations

Other analyses have involved the careful analysis of each maintenance action comparing the initial pilot indication of problems to the actual maintenance action taken to correct the problem. Using this time intensive process, non fuel related maintenance actions can be sorted out and actual numbers determined. Due to the time intensity of this analysis, detailed quantitative results are not complete at this time, however the following qualitative results have been found: In F-15's and F-16's with the Pratt & Whitney F100 series engine, JP-8+100 reduces fouling/coking in augmentor manifolds and sprayrings. In laboratory experiments JP-8+100 has been shown to reduce deposition in these components by approximately 50% and in the field similar results have been found. In some applications, no new deposition was reported in up to 300 operating hours with the thermal stability additive package. By reducing the formation of deposits, augmentor anomaly rates have dropped 40 to 50% resulting in fewer unscheduled engine removals and reductions in maintenance man-hours and parts. Engine hardware appears to be cleaner with the use of the additive and reductions in smoke and soot in the engines has been note. In C-130 aircraft with the Allison T56 engine, the maintainers have had to replace fewer fuel nozzles and turbine assembles with JP-8+100. Inspections of hot section components have been made easier with reduced levels of soot on these components. Reductions in nozzle fouling have been observed in T-37 aircraft with the J69 engine and nozzle and augmentor fouling has been reduced in the J85 engine on T-38 aircraft. Both aircraft have experienced reduction in engine no-lights. In helicopters engines, preliminary results show reduced fuel nozzle coking and reductions in smoke and soot. In F-16 aircraft with the General Electric F110 engine, few problems were noted with JP-8 fuel. Hardware looks somewhat cleaner with JP-8+100 and some reduction in coking in the fuel nozzle swirler cups has been noted on engines with several hundred operating hours on the additive. The General Electric TF34 had an excellent track record of few problems on JP-8. After more than one year of analysis, no significant improvements were noted and no operational deficiencies were found. Overall, in engines with known fouling/coking problems, JP-8+100 reduces the problem and saves the Air Force scarce maintenance dollars.

The Air Force has developed an implementation plan to have all fighters and trainers use JP-8+100 by FY99. Twelve fighter and trainer bases were stood up in 1997 beyond the locations that participated in the field evaluation. Currently over 1000 aircraft are realizing the benefits of JP-8+100.

### Summary

This paper has discussed the development and field testing of a high thermally stability JP-8+100 fuel that provides a 50 percent improvement in the heat sink capability over conventional JP-8 fuel at an increased cost of less than a halfpenny per gallon. Some principle advances made towards achieving this goal are:

1. New techniques to test additives were developed and have been demonstrated to simulate the actual environment that fuel is exposed to in aircraft. Positive results in actual engines and aircraft in the field validated the testing process.
2. Fundamental global reaction mechanisms were proposed and used in CFDC computer models to predict oxidation and deposition processes in jet fuels. These models guided experiments and helped increase the understanding related to chemical and physical aspects of fuel deposition.
3. An additive package was developed for JP-8 fuel that increases thermal stability by 100F. The additive is now part of the JP-8 specification and is currently being used in over 1000 Air Force Aircraft
4. Statistical techniques to analyze the field-test data have been developed. These analyses combined with detailed maintenance data tracking validate the benefits of JP-8+100.
5. Field evaluation of the thermal stability additive package has been successful and the benefits obtained have paid for the increased effort associated with the tests. In many aircraft, significant maintenance savings have been achieved and reductions in smoke and soot noted.
6. Implementation plans have been established such that all fighter and trainer aircraft will be using the fuel by FY99. Plans to extend the use to all Air Force aircraft have been initiated.

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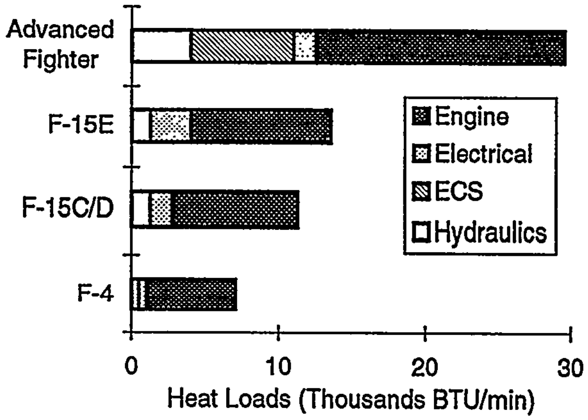
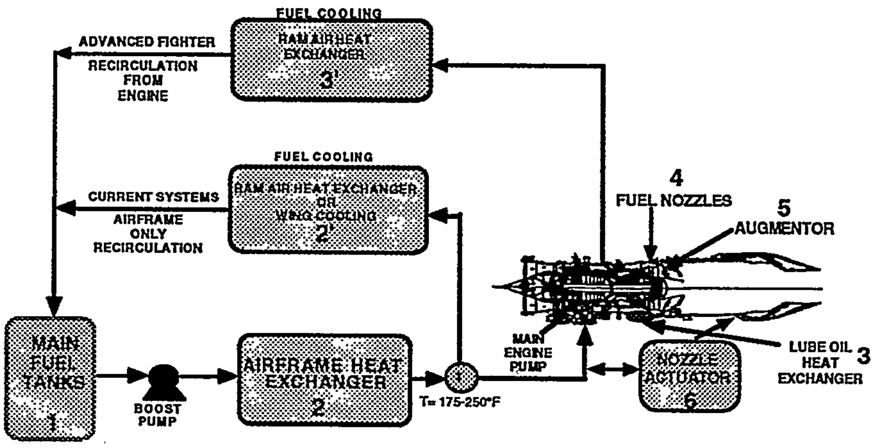


**Figure 1: Maximum estimated excess heat loads for various aircraft.**



| | 1 | 2 | 2′ | 3 | 3′ | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|---|
| TEMP | <70°C | <120 °C | <120 °C | 135 TO 163°C | <163 °C | 163 °C + | 260 °C + | <175 °C |
| PRESS | <25 PSI | <80 PSI | <80 PSI | 1200 TO 2000 PSI | <80 PSI | <40 PSI‡ | <40 PSI‡ | 1500 TO 4000 PSI |
| TIME | MIN TO HOURS | <15 SEC | <2 SEC | <3 SEC | <2 SEC | 2 SEC + | MIN ¤ | <20 MIN |

‡FLOW PRESS 1200 - 2000

¤ TIME <.1 SEC

**Figure 2: Worst case temperature, pressure, and residence time experienced by fuel in various airframe and engine components.**

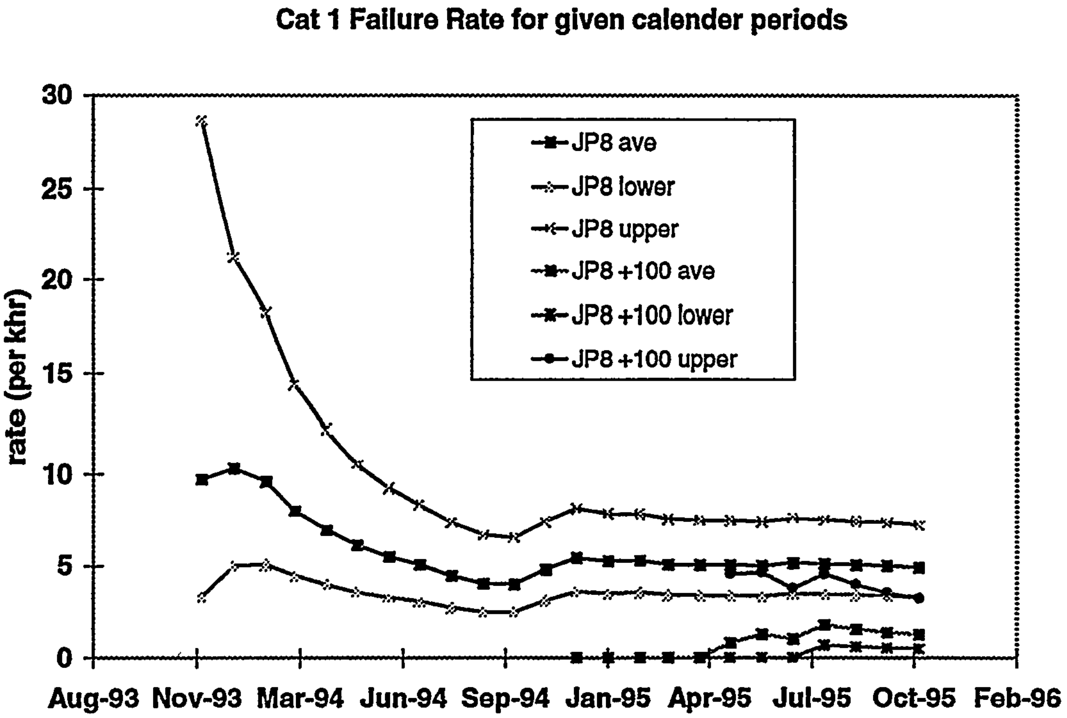


Figure 3: Mean rate of Category 1 failures with upper and lower bounds on the mean (2-sigma confidence limits) for JP8 and JP8+100 at Kingsley AFB.

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# ADDITIVE STABILITY IN JP8 – METAL ALLOY SYSTEMS AT ELEVATED TEMPERATURES

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## Abstract

We have developed a method to determine the concentration of the Betz/Dearborn 8Q462, know as SPEC-AID 8Q462, thermal stability additive in jet fuel samples. Betz 8Q405, the dispersant component, includes a proprietary amount of phosphorus. This technique utilizes the phosphorus content of Betz 8Q405 to estimate the concentration of the complete package in JP-8 +100. The precision depends on the availability of base fuel to correct for background and other matrix effects. If the base fuel is available the concentration can be measured with day to day or sample to sample variations less than 5%. Without the base fuel, but using a generic Jet-A or JP-8 as a standard, the sample to sample variations are within 17%. We have used this technique to study the effects of thermal aging in the presence of a variety of metallic materials. The change in additive concentration was studied over 28 day periods in three jet fuels, at 160F, 200F, and 350F, in the presence of Fe, Cu, Ni, Al and several stainless alloys. Preliminary results indicate that the concentration of BETZ 8Q405 remaining in solution is dependent on the storage temperature and type and condition of metal surfaces in contact with the fuel.

## Introduction

For several years the US Air Force has been sponsoring research to improve the thermal stability of jet fuels. One additive in particular, SPEC-AID 8Q462, has shown promise in significantly reducing fuel deposits and increasing fuel thermal stability. Before complete field implementation of the new additives occur, the airframe/fuel system engineers need to be assured that the new additives are compatible with all existing and/or proposed materials. At a minimum, it is necessary to identify all adverse effects. As part of the overall approval process, the Air Force initiated research into fuel/material interactions. In this paper, we focus on the effect of the materials on the additive concentration, and the development of a simple laboratory technique to estimate the concentration of additive in jet fuels.

To accommodate large numbers of samples (literally hundreds of materials have been identified and several base fuels and temperatures are used) and to be of use in evaluating unknown fuel additive concentrations, the analysis technique should have the following characteristics.

a. Minimal sample preparation

b. High sample throughput

c. Accurate analysis of field samples in the absence of base fuels for background correction

d. Environmentally benign (small sample size, minimal use of hazardous chemicals).

We have developed a technique using a Leeman Labs ICP-AES, (Inductively Coupled Plasma - Atomic Emission Spectrometer), to analyze fuels for phosphorus and scandium, Sc is used as an internal standard, to determine the concentration of BETZ 8Q405 in Jet-A or JP-8. We analyzed data obtained from ongoing fuel additive/material compatibility tests to describe additive stability during storage. These tests expose fuel system materials to neat fuel, normal additized fuel, and fuel additized at 4 times the normal concentration. The fuel soaked materials are stored at, 160F, 200F, and 325F for 4 weeks. Aged fuel is replaced each week and samples are analyzed from the first and last week. The fuel samples are analyzed for alloy metals and phosphorus while the metal test coupons are examined for evidence of corrosion. Smaller reductions in additive concentration on day 28 compared with day 7 are an indication of surface passivation. By analyzing alloy and additive concentrations from fuel/metal compatibility tests we hope to predict the interactions of additized fuel with the storage facilities and aircraft systems.

### Fuels and Chemicals

Chemicals used in the analysis are listed in Table 1. Each day of testing, (40 to 50 samples), consumes 100 mg of 300 ppm S-21 , (S-21 is a Conostan calibration standard comprised of 21 elements in an oil base), 7 mg of 500 ppm Sc, 200 ml of Kerosene, and 7,000 – 9,000 L argon. Fuels were supplied by the US Air Force Fuels Branch (POSF) and are identified by a unique four-digit number. The fuel identifiers and origin are given in Table 2.

### Instrumentation

A Leeman Labs ICP-AES is used to analyze test fuels for phosphorus and metallic corrosion products. This is an emission spectroscopy technique where the fuel sample is sprayed into an argon stream prior to its introduction into an argon plasma. Within the plasma the sample is completely disassociated into excited and ionized atoms. As the atoms regain their electrons and return to ground energy states they emit light at characteristic wavelengths. This light is collected by the collection optics and dispersed onto the detector by a dispersing prism and an Echelle grating (a grating designed to operate at very high orders). Dispersing by color and order provides very high resolution along with excellent signal thru-put. With the exception of Sn, all of the metals in S-21 are detectable in kerosene at 50 ppb or less. Single point calibration at 1,500 ppb yields errors on the order of +/- 50 ppb for measurements in the 5,000 ppb range.

The plasma conditions used for phosphorus measurements:

| | |
|---|---|
| Power | 1.0 KW |
| Argon coolant flow | 16 lpm |
| Auxiliary flow | 1 lpm |
| Nebulizer (V grove) | 34 psi |
| Sample | 1.3 ml/min |

### Method

Phosphorus, a constituent of the Betz package, is normally found at very low concentrations in Jet-A fuels (typically less than 20 ppb). Since phosphorus can be detected by several techniques, its concentration is commonly used as an indicator of SPEC-AID 8Q462 concentration in JP8+100. The background signal produced by the bulk solvent and the solvent's effect on sample transport (termed matrix effects) along with lot to lot variation in additive production, limit the accuracy of additive concentration determinations. In order to base concentration determinations on a pure measurement, we chose to quantify phosphorus directly and apply our conversion assumptions to arrive at an estimate of SPEC-AID 8Q462 concentration. We analyzed a number of JP8 and JP8+100 samples taken from various AF bases for phosphorus content In order to test the usefulness of this method.

Initially kerosene was used for background measurements and dilution of calibration standards as it produces very little signal at wavelengths used for metal detection. A 300 ppm (each metal) standard of S-21 was diluted with Kerosene to 2 ppm, the high range expected for most dissolved metals. Measurements were taken on two different days on ten Jet-A fuel samples containing Betz additive. Two additional unadditized fuels along with three in-house additized fuels were also analyzed. Figure #1 displays the concentration of phosphorus, normalized by the average phosphorus concentration. The phosphorus content of the survey had a fuel to fuel standard deviation of 19% and 13% on the two test days with an average 6% standard deviation in day to day measurements of the same fuel. Figure #2 shows the phosphorus content of 22 unadditized fuels taken from U.S. military bases throughout the United States and Europe. Clearly, an elevated level of phosphorus alone indicates the rough concentration of Betz 8Q405 where no other phosphorus containing additive is likely. However, the average phosphorus content measured was higher than the correct amount in a proper formulation. (The actual concentration constitutes proprietary information.)

A comparison of measured quantities of phosphorus in spiked samples of kerosene and Jet-A confirmed that some fuels delivered up to 60% more sample to the plasma than kerosene at the same sampling conditions. This was attributed to the different transport efficiency of kerosene as compared to JP8 or Jet-A. We then chose POSF-2926, (a particular Jet-A) as a background, or 'zero' standard, and to dilute the 300 ppm S-21 calibration standards to 1.5 ppm. Cobalt was added to each fuel sample at approximately 10 ppm to act as an internal standard for determining remaining transport effects. The percent recovery of Co indicated the net transport efficiency of the sample fuel compared with the standard fuel and was used to normalize the other metal concentrations.

Three fuel samples were prepared in the laboratory from Jet-A stock (POSF numbers 3250, 3272, and 3285). Each sample was mixed with the same amount of SPEC-AID 8Q462 and spiked with 100 µl of cobalt solution per 10 ml of sample. This produced three different Jet-A fuels with the same phosphorus concentration and 10 ppm Co. The samples were analyzed on Nov. 26 and 27 for P and Co. The phosphorus concentration was corrected by the percentage of Co recovered ($P_{measured}$ x $Sc_{spike}/Sc_{measured}$, see Figure #3) and normalized by the average phosphorus content. In addition to improving the day to day precision, the spike recovery (internal standard) technique helps to correct for sample transport property differences and environmental changes in the laboratory. While background differences (matrix effects) are still a problem whenever a neat fuel sample is not available for calibration, this method is sufficiently accurate to determine if a fuel has the Betz additive package in approximately the correct concentration.

Subsequent to this initial study we settled on the following method for metals and phosphorus measurements in standard fuel samples. Fresh standards are made up each day of 300 ppm calibration standard, S-21, diluted to 1 ppm with Jet-A (POSF 2926). For calibration, 20 ml of the 1 ppm S-21 in Jet-A is removed and spiked with 200 µl of 500 ppm Scandium (final concentration of 5 ppm Sc). Scandium was chosen for its large signal to noise ratio at 361.384 nm, its absence of interference with our normal metallic measurements and its scarcity in common jet fuels. Phosphorus is determined by its peak at 213.618 nm. Fuel samples are prepared by spiking 10 ml of sample with 100 µl of the same 500 ppm Sc solution. By mixing calibration standards by weight and spiking both the cal standard and sample by volume we are able to quickly evaluate and correct for most sample delivery variations in the system. The Sc spike also functions as an internal check standard where less than 90% spike recovery indicates an equipment or optical alignment problem and these results are rejected. On Sept. 3, 1997, the three sample fuels were sampled and analyzed using Sc as the internal standard. The results show good agreement with previous determinations, Figure #3. Using spike recovery we measured phosphorus content with 7%-12% std. dev. across the well mixed fuel types on the same day while the std. dev. of measurements of the same fuels on 3 different days was only 2% - 4%. On Sept. 3, '97 another survey of JP8+100 fuels was taken. Figure #4 summarizes the phosphorus content (normalized by the average P concentration) using scandium as the internal standard. In this case the average P concentration agreed with the predicted value while the standard deviation of results across all fuels remained at 0.17%. The remaining scatter is a result of possible mixing variations and uncorrected background noise.

**Material Compatibility Fuel Test Results**

Metal coupons, 1" x 2" x 0.06", were soaked in fuel at 160F, 200F, or 325F for 28 days with weekly fuel changes. SPEC-AID 8Q462, was added to the base fuel in both the normal (1X) concentration and in 4 times the normal concentration (4X). One JP8 base fuel was used for all of the tests reported here. At the end of 28 days the metals were examined for evidence of corrosion and weight change to indicate a pass or fail. Fuel samples taken during the test were analyzed for alloy components to correlate with corrosion evidence and, phosphorus was measured to track changes in the 8Q405 concentration.

In broad metallic categories, the amount of phosphorus (detergent component of the Betz package) remaining in solution after the first and last 7-day test segment is shown in Tables 3 and 4. The values reported represent averages over several alloys in each classification. Data on all alloys at all temperatures does not exist for this study since many materials were not tested at 160 F and a considerable number of alloys had been evaluated before the arrival of our ICP.

The most obvious trend is for higher phosphorus retention at lower temperatures. While copper appears to affect the phosphorus level the least, it also shows the highest dissolved metal content of any of these test metals. Copper concentrations, (though not reported here, 15 metals are quantified sequentially on each sample), indicate that much of the phosphorus measured is active in keeping copper in solution and may not be free to aid in dispersing additional material. Iron also appears in higher concentrations in tests of iron and stainless alloys when Betz is present to aid in keeping it in solution. Aluminum is known to have a surface affinity for phosphorus and since we do not see Al in measurable quantities in solution we believe the dispersant is binding to the surface. When we analyze the fuel from tests on predominantly nickel alloys we do not see any metals in measurable quantities and would expect to find the missing dispersant on the alloy surface.

## Conclusions

ICP-AES measurement of phosphorus content in jet fuels can provide a good indication of SPEC-AID 8Q462 additive concentration. Analysis of jet fuel field samples can be done without a true blank, however matrix effects can contribute more than 20% to measurement errors. The uniform addition of Scandium to calibration standards and to samples is a simple way to measure fuel to fuel variations in sample delivery efficiency and to monitor system performance. Preliminary results indicate that for fuel systems at elevated temperatures, Iron and Aluminum alloys have a significant effect on additive concentration, while alloys with high Nickel content have a minimum effect on Betz 8Q405.

## Acknowledgement

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**Table 1: Chemicals – Sources and Uses in this Study**

| | | |
|---|---|---|
| Kerosene | Fisher Scientific | Used to dilute 5000 ppm Sc standard to 300 ppm, also used as rinse fluid in ICP sample path. |
| Argon (liquefied) | Air Products | Primary constituent of the plasma 'flame' and carrier for sample mist. |
| S-21 | Conostan | Calibration standard containing 21 common metals at a concentration of 300 ppm by weight in oil matrix. |
| Sc | Conostan | Calibration standard containing 5000 ppm by weight of Scandium in oil matrix. |
| Co | Conostan | Calibration standard containing 5000 ppm by weight of cobalt in oil matrix. |
| Cobalt Solution | Locally Prepared | Internal Standard: 1Part cobalt Conostan standard, 10 parts Kerosene - nominally 500 ppm |
| Scandium Solution | Locally Prepared | Internal Standard: 1Part scandium Conostan standard, 10 parts kerosene - nominally 500 ppm |

**Table 2: Fuel Type and Origin**

| POSF # | Fuel | Date Rec. | Loc. |
|---|---|---|---|
| 2827 | Jet A | 5/16/91 | OH |
| 2890 | JPTS | 11/12/91 | OH |
| 2926 | Jet A | 5/21/92 | OH |
| 2928 | Jet A | 6/4/92 | OH |
| 2934 | Jet 50 | 9/21/92 | AK |
| 2962 | JP-5 | 6/1/93 | ** |
| 2976 | JPTS | 5/1/93 | OH |
| 2980 | Jet A | 6/1/93 | ** |
| 3000 | JP-5 | 9/1/93 | TX |
| 3049 | JP-8 | 3/1/94 | Greece |
| 3082 | JP-5 | 12/1/94 | NY |
| 3083 | JP-8 | 12/1/94 | HI |
| 3102 | JP-5 | 12/1/94 | HI |
| 3109 | JP-8 | 12/1/94 | VT |
| 3110 | JP-8 | 12/1/94 | DE |
| 3118 | JPTS | 12/1/94 | ** |
| 3119 | Jet A | 2/1/95 | OH |
| 3166 | Jet A | 1/1/96 | OH |
| 3285 | JP-8 | 7/1/96 | TX |
| 3325 | JP-8 | 11/19/96 | NM |
| 3334 | JP-8 | 1/7/97 | MD |
| 3389 | JP-8 | 4/9/97 | CA |
| 3396 | JP-8 | 4/21/97 | CA |
| 3413 | Jet A | 6/1/97 | IL |
| 3419 | JP-8 | 6/6/97 | NM |

**JP-8 +SPEC-AID 8Q462**

| POSF # | Date | Loc. |
|---|---|---|
| 3060 | 5/1/94 | TX |
| 3229 | 2/23/96 | VT |
| 3233 | 2/25/96 | MD |
| 3250 | 5/1/96 | OH |
| 3261 | 5/1/96 | KY |
| 3272 | 6/1/96 | OH |
| 3273 | 6/1/96 | OH |
| 3286 | 7/1/96 | TX |
| 3289 | 7/1/96 | OH |
| 3295 | 8/1/96 | OH |
| 3323 | 11/1/96 | NM |
| 3326 | 11/20/96 | NM |
| 3329 | 1/7/97 | MD |
| 3352 | 12/11/96 | NM |
| 3397 | 4/1/97 | CA |
| 3400 | 4/1/97 | CA |
| 3401 | 4/1/97 | CA |
| 3420 | 6/1/97 | NM |
| 3428 | 7/1/97 | OH |
| 3430 | 7/1/97 | TX |

**Table 3: Phosphorus Remaining of 1X Betz Concentration**

| | 325F | | 200F | | 160F | |
|---|---|---|---|---|---|---|
| | Day 7 | Day 28 | Day 7 | Day 28 | Day 7 | Day 28 |
| Aluminum | 60% | 40% | ** | 70% | ** | ** |
| Copper | 80% | ** | 80% | 80% | 90% | 70% |
| Iron | 50% | 60% | ** | ** | ** | ** |
| Nickel | 60% | ** | ** | 90% | ** | ** |
| Stainless | 40% | 60% | 70% | 90% | ** | ** |

**Table 4: Phosphorus Remaining of 4X Betz Concentration**

| | 325F | | 200F | | 160F | |
|---|---|---|---|---|---|---|
| | Day 7 | Day 28 | Day 7 | Day 28 | Day 7 | Day 28 |
| Aluminum | 70% | ** | 75% | 66% | ** | ** |
| Copper | 83% | ** | 88% | 98% | 100% | ** |
| Iron | 58% | 100% | ** | ** | ** | ** |
| Nickel | 79% | 100% | ** | ** | ** | ** |
| Stainless | 50 - 84% | 66 - 100% | 68 - 75% | 100% | ** | ** |

** Data unavailable.

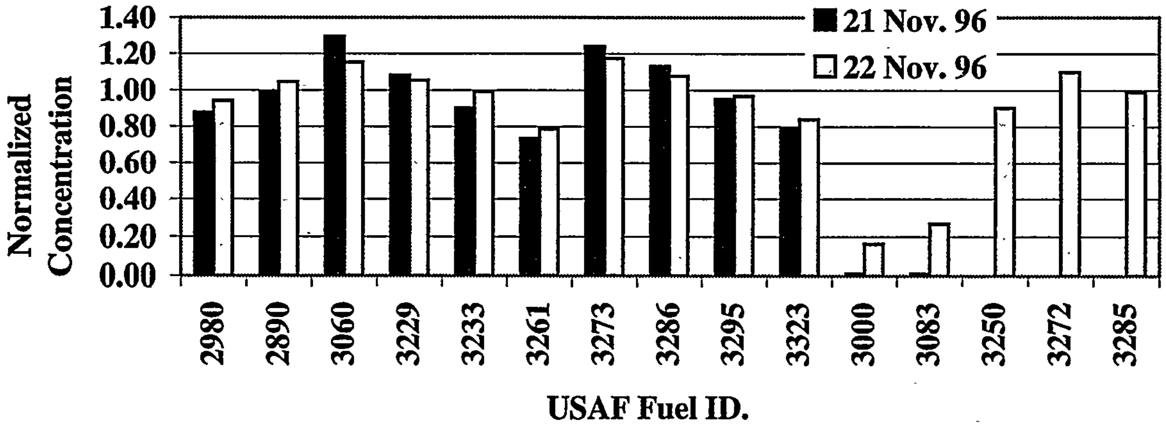

**Figure 1: Normalized phosphorus content in Table #2 fuels.**

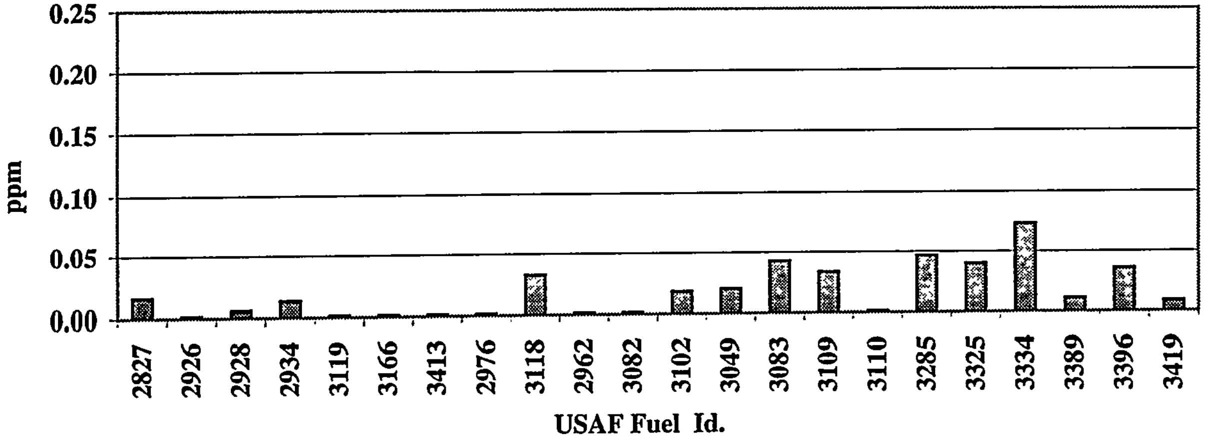

Figure 2: Phosphorus content of un-additized world survey fuels in Table #2.

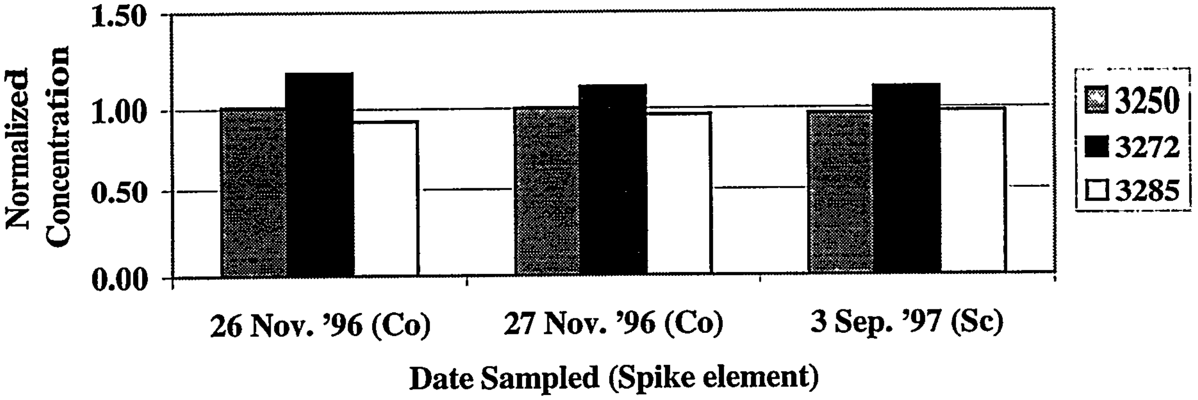

Figure 3: Normalized phosphorus content of laboratory additized fuels.

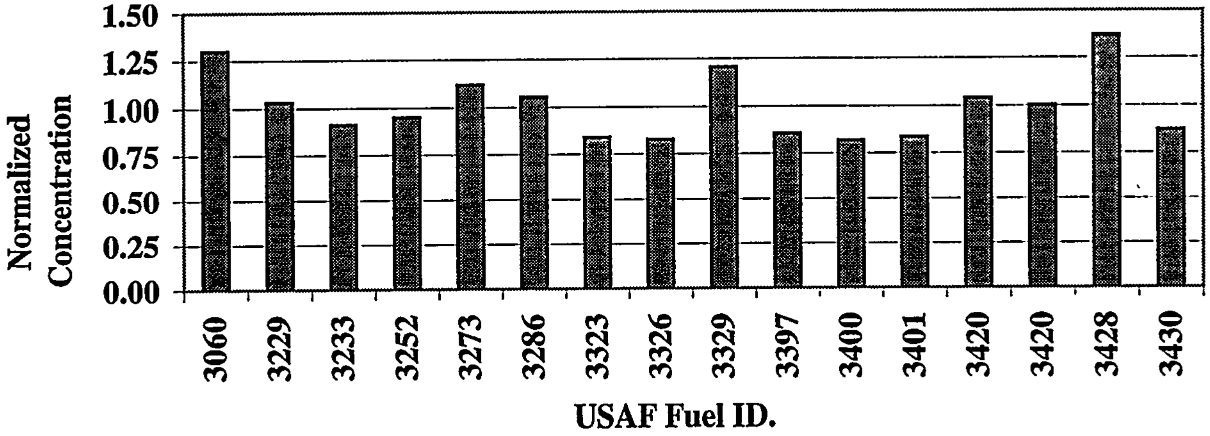

Figure 4: Normalized phosphorus content of Table #2 fuels containing SPEC-AID 8Q462.

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# HIGH REYNOLDS NUMBER THERMAL STABILITY (HiReTS) RIG FOR REALISTIC, RAPID EVALUATION OF DISTILLATE FUEL THERMAL OXIDATIVE STABILITY

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Shell Research Limited have developed a small-scale rig to evaluate jet fuel thermal stability under realistic test conditions. Pre-production prototypes of the HiReTS (High Reynolds number Thermal Stability) rig, known during its laboratory history as the Capillary JFTOT (C-JFTOT), have now been produced. Fuel passes through a stainless steel capillary tube at flow rates sufficient to ensure that turbulent conditions prevail. The tube is electrically heated and PC control ensures a fixed fuel outlet temperature. More power must be provided to maintain the fuel outlet temperature when deposits build up on the inner capillary surface. A non-invasive infrared thermometer monitors the tube outer surface during the, typically, two hour test. The more deposit produced, the higher the temperatures rise. The end-of-test result is the HiReTS or C-JFTOT number, the summation of final temperature rises at set scanning positions. C-JFTOT numbers have correlated well both with post-test carbon burnoff values and with results from large-scale rigs. 3-D displays of temperature changes provide dramatic pictures of temporal and positional differences in fuels' deposit-forming tendencies. HiReTS numbers for hydroprocessed fuels are up to an order of magnitude lower than those for specification-passing Merox fuels. Standard operating conditions were chosen to identify poor fuels, and differentiate between typical commercial fuels. Thermal stability improving additives can significantly lower HiReTS numbers and different flow/temperature/time conditions may be needed for the HiReTS to differentiate between high thermal stability fuels rather than to reject poor fuels. USAF are now evaluating a pre-production HiReTS machine, both as a possible specification test and as a research tool.

## INTRODUCTION

The JFTOT uses 600 mL of fuel per 2.5 hour test[1] to assess thermal stability properties. Jet fuels with poor thermal stability produce heavily lacquered test pieces and/or bulk insolubles that tend to block the filter downstream of the heated test piece. Features such as short test time, small sample size and ease of operation make the method acceptable for the routine qualification of fuels. However, the JFTOT, its variants and most small-scale rigs operate in the unrealistic laminar flow regime. Various studies have highlighted this and other limitations of the JFTOT including tube rating technique and the test heater metallurgy[2,3]. Operating under laminar flow conditions means that the JFTOT will always be sensitive to reactant mass transport effects[4]; it will suffer from the dominance of mass-transfer limitations on deposition, particularly for fuels of low radical initiation rate.

By contrast, large-scale rigs such as Thornton's Single-Tube Heat Transfer Rig (STHTR)[2], Mini-Injector Feed-Arm Rig (MIFAR)[5] and, formerly, Injector Feed-Arm Rig (IFAR)[6] require a specialist trained operator but provide realistic simulations of aircraft fuel systems. The STHTR test piece derives from a component of a fuel-cooled oil-cooler; the method monitors the loss of heat transfer efficiency, ΔHTC, as deposits build up on the test piece walls. Unfortunately, most large-scale rigs, whilst operating in (realistic) turbulent flow regimes, have large fuel appetites and long test durations; for the STHTR these would typically be 2000 litres and 100 hours, respectively. Such rigs tend to be "one-offs", totally unsuited for incorporation in jet fuel specifications.

This unsatisfactory position was the starting point for the current research, i.e. the designing of a small-scale rig using conveniently small samples, offering an accelerated test and yet incorporating the turbulent flow present in an aircraft fuel system. Initially, Kendall[7] examined the possibility of achieving a turbulent flow tester by modification of the JFTOT tube. His fluid dynamics calculations showed that the Reynold's number, $R_e$, for the JFTOT system under normal operations is about 11[8], assuming a bulk flow temperature of 170°C. This is clearly in the laminar flow regime since the minimum $R_e$ for turbulent flow is about 5,000. Kendall concluded that, even by altering gap sizes, it would be impossible to achieve high enough $R_e$ in a JFTOT for there to be turbulent flow. He then considered the design criteria for a capillary test section that would produce turbulent flow conditions. These covered: flowrate/diameter combinations necessary to achieve $R_e$ of about 5,000; estimates of the pressure drop within the test region; consequences of different diameter/length combinations; impact of capillary size/test regimes on the feasibility of measuring the resultant deposition. These estimates indicated that a large diameter capillary was required to: minimise the pressure drop; prevent blockage; ensure an adequate area for sufficient deposits to be generated for burn-off. However, these factors tended to conflict with the desire to use small flowrates and hence a small sample size. Also a larger capillary would make it more difficult to resolve small changes in heat-transfer data. The calculations favoured the use of a short capillary to enable a high wall temperature (300°C minimum, to produce higher levels of deposit) to be used in conjunction with a moderate, i.e. realistic, fuel temperature. Heat-transfer data are also seen as a route to measuring the degree of fuel degradation, i.e. the build-up of an insulating layer of lacquer will result in a rise in metal wall temperature.

Kendall's work provided the starting point for the development of a radically different small-scale tester, known during development stages as the Capillary JFTOT (C-JFTOT) and now, at pre-production prototype stage, as the High Reynolds number Thermal Stability (HiReTS) rig. The development work on the rigs, including preliminary statistical analyses and correlations with results from other thermal stability tests, form the bulk of this report.

## APPARATUS DEVELOPMENT

**Overview.** Early work concentrated on forming deposits under realistic conditions and detecting them properly; a prerequisite was that the device should distinguish between fuels of very different thermal stability. From the outset of the programme Shell aimed to assess deposition by monitoring the rise in tube outer wall (TOW) temperature as this method would not require any further equipment to analyse deposits. Early design work focused on the capillary test section; specifically, how to obtain the required fuel flow, the most efficient method of heating the capillary, how to control the test temperature and, not least, the best method of quantifying fuel stability. In Phase 1 of the development, the basic kit was assembled: a fuel supply system, a test piece, deposition monitoring facilities, and a test control system. Capillary diameters and lengths were varied to achieve suitable fuel outlet temperatures. During Phase 2, deposit monitoring methods were changed and developed. Some experiments were performed with a differential pressure transducer fitted across the test section. Correlations were used to check whether the C-JFTOT results bore any relationship to test data from other, particularly large turbulent flow, rigs. By the start of Phase 3 (mid-1991), a novel small-scale tester had been produced that was able to monitor fuel degradation and subsequently rank fuels. The basic operating conditions in the C-JFTOT device had been established: tests were set to run at a fuel outlet temperature of 290°C for 2 hours. The software and deposition monitoring protocols were optimised for these conditions. Work then concentrated more on automation of the system, removing its dependence on expensive and specialist external equipment, introducing more safety trips and cut-outs, and thereby making it more acceptable as a potential specification test. Fuels used in these early studies are detailed in Table 1; all were produced as Jet A-1.

A final phase of tests were run under "standard" conditions to generate a limited results database. Phase 4 used a different suite of (newer) Jet A-1 and related fuels: seven, some with additives, were derived from Merox treatment (from at least 3 locations); two were straight run; two were hydroprocessed (one with additives); a poor thermal stability JP-5 fuel ex US Navy (unknown processing); and there were 7 fuels containing 15 to 100% of Shell Middle Distillate Synthesis kerosine blended with conventional jet fuels or blending components. After further correlation and crude statistical exercises, these design and operation features were adopted as the base of a pre-production model, the HiReTS. The following sections summarise the evolution of certain components, through various stages, to the final configurations used in the C-JFTOT and HiReTS devices.

**Fuel supply.** Initially fuel was delivered to the capillary test section by using a pressurised reservoir that attached to a JFTOT apparatus. This was soon superseded by the use of a Gilson variable flow HPLC pump capable of delivering up to 50 mL/min at up to 2000 psi. Pulsations in flow were largely damped out by fitting a small accumulator immediately downstream of the pump. System pressure during a test was set to approximately 400 psi using an in-line relief valve downstream of the cooler. An adjustable over-pressure cut-out was incorporated to stop the pump should pressure exceed a preset value, 1000 psi. A high pressure water-cooled fuel-cooler was fitted downstream of the capillary test section to reduce the spent fuel temperature to ambient before the fuel went to waste at atmospheric pressure, thus preventing boiling.

Initially it was hoped to measure any build-up of deposits on a downstream test filter, much as is achieved by pressure drop (ΔP) measurements in the JFTOT. A differential pressure transducer was fitted, to measure ΔP across the test section. Unfortunately, it offered an easier electrical path than the capillary. When the transducer was insulated with high pressure Teflon tubing the bore was so narrow that the device had no sensitivity. Transducer and ΔP approach were rapidly dropped from the system.

**Test Piece.** Feasibility experiments used capillary tubing with outer and inner diameters (O.D and I.D) of 560 and 254μm, respectively. This was soon superseded with more robust commercially available 254 μm stainless steel capillary, with 1.59 mm O.D. Originally these capillary sections had sleeves silver-soldered to each end (to provide a large contact area for the electrical bus bars) and thermocouples spot welded at various points along the available test lengths. Thermocouples were abandoned when IR thermometry and carbon-burnoff approaches to deposit detection were introduced. Instead, test pieces were painted black to achieve better and uniform thermal emissivity.

**Heating control.** From the outset the capillary test section was heated electrically by applying power to bus bars that held the test section in place. Initially the operator adjusted the power of a simple transformer to produce a given initial tube outer wall (TOW) temperature at a given thermocouple on the test piece. A series of experiments were performed with 15 and 20 cm tubes, varying flow rates for different target TOW temperatures and measuring associated power, fuel outlet temperatures and capillary inlet pressures. 35 mL/minute, creating $R_e >> 10,000$ at the hottest part of the tube, produced the highest fuel outlet temperature for a given initial TOW temperature and was chosen as the "standard" flow condition. An off-grade Merox fuel W (see Table 1) was used in the capillary and fouling was monitored by pressure drop across the capillary and the rise in wall temperature for a constant fuel outlet condition. In the 6 hour test, ΔP was only 60 psi but the wall temperature rose by about 120°C. Tests with fuel W and with a very stable hydrotreated fuel, Y, soon showed that the intrinsic repeatability of this approach was poor.

The "start of test condition" was then redefined in terms of a fuel outlet temperature (FOT). Power was supplied to the bus bars until the capillary exit thermocouple reached a setpoint FOT. Initially, a 260°C FOT condition was used but 290°C produced more deposits. A Eurotherm 815 programmable temperature controller was introduced to automate this heating and was operated as a stand alone unit. Later, the controller was switched to operate in "Remote" mode from a PC which supplied the setpoint.

**Deposition Monitoring.** Earliest experiments used thermocouples to monitor deposits, much as was done for test sections in larger rigs (STHTR, MIFAR, etc.). Despite some promising results with a poor fuel, the approach had poor repeatability and was unable to distinguish between very different stability fuels W and Y. The thermocouples may have been distorting the capillary cross-section and acting as a considerable heat drain on the system because of their relatively high masses compared to that of the capillary tube.

The second phase of work introduced a novel, non-invasive approach to temperature detection, infrared thermometry. A separate rig was also constructed to measure the low levels of carbon on the test pieces, representing 70-80% of the lacquers produced at such temperatures. Post-test, the test pieces were placed in the rig and the carbon was burned off and measured (10-200 μg) in a controlled fashion; see details later.

An Ircon Ltd infrared thermometer was attached to a data logger, aligned on the test piece and used to record TOW temperatures at a single position. The IR system showed excellent repeatability in measured TOW temperature but no variation in results between fuels W and Y. However, end-of-test carbon deposit measurements indicated that a difference was present. Raising the fuel outlet temperature from 260 to 290°C produced a 100°C difference in TOW temperature between two fuels after two hours which was in accord with differences in post-test carbon deposit weights. These results suggested that rises in outer wall temperature during the test, caused by the need to apply more power to maintain the fuel outlet temperature as deposits built up inside the capillary and changed thermal resistance, could be used to monitor the increasing impact of fuel degradation with time. The differing gradients for these very different thermal stability fuels demonstrated an ability to distinguish and rank fuels. Further tests identified the position of maximum deposit formation along the test piece, 10 mm below the top bus bar (fuel exit point), and examined how sample pretreatment affected the levels of deposition. The pretreatment had no significant effect but these tests once again showed poor correlation between temperature changes and carbon measurements. These difficulties led to a period when "off-line", end-of-test carbon determination was used as the primary measure of deposition though "on-line" temperatures were still recorded.

**Early assessments.** A limited set of correlations were attempted between the average carbon burn-off values for the C-JFTOT at 290°C and other thermal stability predictors such as JFTOT variants (Carbon burnoff value, CBO, and JFTOT breakpoint), the radical initiation rate, $R_i$, (from the Thornton flask oxidation test[9]), fuel total sulphur content and data from large-scale rigs. The CBO value is the amount of carbon burnt off a tube tested at 350°C in a modified JFTOT apparatus, and the JFTOT breakpoint is the highest temperature at which the fuel still passes the visual tube rating (VTR) requirements of the JFTOT test. Table 1 lists data used in a STATGRAF linear regressions analysis program.

Figure 2 summarises data from the correlation of ΔHTC results from the STHTR with C-JFTOT carbon data. Neglecting intercept and gradient errors, the related fit using carbon burnoff values obtained after a 350°C test using a conventional JFTOT was: $\mathrm{Log}_{10}(\mathrm{HTC}) = 1.31{*}\mathrm{Log}_{10}(\mathrm{CBO}) - 2.49$, with 99.49% correlation confidence, F value 15.78 and $R^2 =$

0.6636. While a significant correlation clearly existed between STHTR and C-JFTOT, the C-JFTOT parameter was no better than other more traditional predictors of rig performance. A possible explanation was that the 290°C condition was too accelerated and may not have been reflecting reactions dominating under more realistic (lower temperature) conditions. Repeating the exercise at 260°C did not improve the correlation with STHTR. On the other hand, the C-JFTOT data correlated well with radical initiation rates measured in the flask oxidation test[10] i.e., the C-JFTOT responded to fuel chemistry (radical initiation) rather than mass transport effects. The STHTR response, which might have been expected to be similar, was probably reflecting the stages of pre-heating which simulate wing-tank heating (low grade but long residence time). The conventional JFTOT's moderate ability to predict STHTR performance may have been because the stagnant layer in the JFTOT's laminar system could be considered as equivalent to pre-heating the fuel.

A limited series of tests investigated the impact of sample preheating in the C-JFTOT. An "Off-the-shelf" Alcor heated reservoir was modified to tolerate the high pressures in the rig. Its capacity allowed a preheating residence time of 30 minutes. Correlations did not improve so the preheater was removed. Better simulation of the complex heat history of fuel in the STHTR, either by increasing the severity of preheat or by increasing the residence time, was not a viable option at that stage either because of safety reasons or the need to commission more new equipment.

Earlier work had already shown that Ri was a modest predictor of performance in the MIFAR, a rig usually run without tank heating[5]. The C-JFTOT was used to test a further five fuels all previously tested in the MIFAR. Ten fuels with MIFAR data (see Table 1) were then used in a second set of correlations. Figure 3 shows that the C-JFTOT was a better predictor of MIFAR than it had been of STHTR. The correlation results in Table 2 also showed that C-JFTOT was marginally better than the conventional JFTOT (breakpoint or carbon burnoff mode) in predicting MIFAR performance. By this stage the feasibility of the C-JFTOT technique had been demonstrated. However, the labour and skill levels required, combined with the use of external equipment to make the carbon measurements, made impossible its use as a specification test in that configuration.

Earlier single point IR thermometry had probably failed because of fuel-to-fuel variations in the position of the thickest point of lacquer on the capillary. (Sectioning of test pieces from other rigs - JFTOT, STHTR and MIFAR - has also shown that lacquer patterns are fuel-dependent.) Choosing a single point for temperature determinations without being able to see the inside of the rig was, at best, an optimistic approach. Now scanning was tried. Two-hour tests were performed with a fuel outlet temperature of 290°C, manually adjusting the detector position throughout the test. Temperature changes ($T_{final}$ - $T_{initial}$) were much larger for poor thermal stability fuels (high carbon burnoff) than for high stability fuels (very low carbon burnoff). Temperature profiling at six positions along the test piece provided good measures of the amounts of deposit produced by three fuels of significantly different thermal stability. These fuels produced completely different amounts and patterns of lacquering. Summing end-of-test temperature change values along the tube length ($\Sigma\Delta T$) produced a number with which to rank the fuels:

| | | |
|---|---|---|
| Hydrocrackate | ranking number 7.25 | ±25% |
| Merox AD | ranking number 475 | ±7.5% |
| Merox S | ranking number 745 | ±3% |

These numbers showed good repeatability and correlated well with the total mass of carbon deposited. Additionally, the pattern of fouling as time proceeded at any given position closely followed that seen in the MIFAR and other large-scale simulators, i.e. an induction period followed by constant deposition[5,6].

A PC was introduced to operate a mechanical scanner, collect and process the data, allowing the instrument to become "stand alone" and removing the need for "off-line" measurements of carbon weight. Scanning was fine-tuned. Standard conditions were chosen to provide adequate resolution in time and space in areas where there was significant deposition yet minimal distortion caused by heat drain from the upper bus bar. The change in outer wall temperature was an indication of the thermal resistance at that point and thus a representation of the lacquer thickness. Software was written to allow data to be captured continuously into an ASCII file for downloading into a spreadsheet at the end-of-test. The spreadsheet was set up to make an automatic search for the minimum recorded temperature at each position x, $T_{min}(x)$, which was not necessarily the first temperature recorded (see later). It then provided a 3-D display of a measure of deposition against position and time, and a numerical test result, the Capillary JFTOT number. This was the summation of the increase in surface temperature of the capillary at the n points of temperature recording (x =1 to n), on the last scan:

$$\text{C- JFTOT number} = \text{CJ\#} = \sum_{x=1}^{n} \Delta T(x), \ \text{where } \Delta T(x) = T_{final}(x) - T_{min}(x).$$

The C-JFTOT apparatus developed by this stage was as shown in Figure 1. The following sections describe the experimental conditions used with it in Phase 4 testing and the results obtained.

## EXPERIMENTAL

**Test pieces.** The test capillary consists of a commercially available[11] 152 mm length of HPLC stainless steel tube, with nominal 0.01" (254 μm) inner and 0.0625" (1.59 mm) outer diameters, respectively. To improve thermal emissivity for IR measurements the tubes are painted with two coats of high temperature matt black paint; spraying the capillary clamped stationary appears to give a consistent finish. Two commercially available paints, Rustolian B-B-Q Black and Wurth, have been used; the latter can degrade at high capillary temperatures.

The 20mm end sections, where the capillary is clamped in the bus bars, are masked off during this process. A batch of tubes are prepared in advance and then stored until needed. The capillaries are inspected prior to use for paint integrity and tube straightness. A "Swagelock" nut is then pre-swaged onto each end. The finished tubes are not cleaned with solvent but are flushed with test fluid prior to the main test.

**Fuels.** Fuels used in early development work are listed in Table 1. Phase 4 fuels were used to test the C-JFTOT in its "final" laboratory configuration. The first of these were chosen to cover a broad range of thermal stabilities; many were chosen because they already had full suites of analytical and test rig data, thus anticipating future correlation and checking exercises. Fuels with MDA, CI/LI or JP-8+100-type additives did not start to be tested until early 1995.

Most fuels are now routinely tested in the HiReTS unit, to establish a results database, irrespective of whether large rigs are run in parallel. Fuel for testing is sampled according to normal jet fuel testing protocols. About 5 litres are put into a clean stainless steel container, ready for testing. No pre-filtration is performed but the fuel passes through the HPLC pump's inlet sintered filter (20 μm pososity).

**Test protocol.** Figure 1 illustrates the complete C-JFTOT system. The test piece is electrically heated via bus bars, and fuel is passed through it via a 2000 psi HPLC pump. A dedicated IBM PS/2 40 controls the heating (via the Eurotherm unit) and temperature measurement protocols. It is interfaced to a "Time and Precision" stepper motor screw jack system to control the vertical tracking of the IR thermometer which records capillary wall temperatures at set positions and times. At the completion of the test, which is deemed to be the point at which the IR scanner returns to its start position following the recording of the final temperature on the last scan, power is switched off to the bus bars and the capillary is allowed to cool. Fuel flow is maintained until the fuel outlet thermocouple indicates the fuel temperature has fallen to 30°C or less. At this stage the HPLC pump is stopped and the disassembly of the test section can take place after a heptane flush. Post-test the data are presented in tabular and graphical formats using proforma spreadsheets. The C-JFTOT number is automatically calculated from these data. Most fuels are tested twice and the average C-JFTOT number is quoted.

The standard test protocol measures capillary wall temperatures every five minutes at 2.5 mm intervals 1 to 21 mm from the fuel outlet, for two hours. These nine positions are along the hotter section of the test piece. The fuel flow rate is 35 mL/minute; with pre-flushing and post-test cooling this means that the test requires just under 5 L of fuel.

**Safety Features.** High pressures and elevated temperatures have demanded that the machine has numerous safety cut-outs. Both in the final C-JFTOT and now in the HiReTS rigs, any safety trip operation stops heating to the capillary; fuel flow, etc. are continued until the conditions become safe. Almost all the HiReTS's safety features are under PC control.

**Carbon burnoff.** Post-test carbon burnoff values are usually established and also averaged. Pre-test cleaning and post-test rinsing of the capillary test piece are controlled to optimise the carbon burnoff method's sensitivity. The fuel inlet end of the used test capillary is connected to a low pressure oxygen (0.2 bar) supply, and the outlet is connected to a tube fed into the furnace of a Leco carbon analyser. The capillary, clamped between two electrical bus bars, is heated while oxygen is passed through it and the carbon dioxide evolved is measured. The amount of carbon in the deposit can then be calculated.

## RESULTS

Spreadsheet statistical packages have been used to analyse most Phase 4 results. C-JFTOT method repeatability itself has yet to be formally assessed but there seems to be an increase (worsening) in test repeatability as the fuel quality worsens. Figure 4 shows how average CJ# varies with average post-test carbon burn-off values. In all cases, the carbon and C-JFTOT results for the best fuels are at the limit of detection, and at the other extreme, the limited results for poor fuels may have an undue influence on the plots. When only non-additivated fuels (i.e. no metal deactivator, no corrosion inhibitor/lubricity improver or JP8+100 additive) are included, the fit improves slightly ($R^2 = 0.90518$). Similar plots for the non-averaged results still give quite reasonable regression coefficients for rig data, $R^2 > 0.8$. The corresponding results for additivated fuels alone are not included as the dataset is not large enough and the whole question of testing additivated fuels needs more consideration (see below). Nevertheless, the above correlations between CJ# and carbon weight are good enough to rely on CJ# alone when seeking correlations with other rigs, i.e. when establishing the predictive capabilities of the C-JFTOT.

**JFTOT and variants.** C-JFTOT and JFTOT-type tests should not be expected to correlate very well with one another or to provide similar predictions of larger rig performances because they examine fuels under different flow, temperature and metallurgy regimes. The C-JFTOT's acceptance as a candidate specification test, however, demands that the two approaches be compared. Figure 5 shows how average C-JFTOT results compare with the VTR in the standard, 260°C JFTOT test, for all Phase 4 fuels. There is a directional link between the two sets of results, albeit that the datasets do not include many poor fuels. Only one fails the existing 260°C pass with the JFTOT, which requires a non-peacock, non-abnormal VTR less than 3. A CJ# of about 1000 provides almost the same cut-off as the standard JFTOT test.

JFTOT breakpoint is established to within 5°C and therefore provides a statistic more amenable to correlation exercises than does the standard JFTOT result. However, the step size means that a very good correlation between JFTOT breakpoint and any other measurement is unlikely. Figure 6 again shows a correlation limited by the shortage of bad fuels. Whether for all the fuels or just those without additives, fits between breakpoint and

CJ# are poor, with $R^2 = 0.3288$ and $F = 9.3$ for the full set. (The F-test is more appropriate than $R^2$ for non-linear data.) These data were also transformed to give plots of a) $\mathrm{Log_e}$CJ# versus 1000/BP (in K) and b) 1000/BP (in K) versus CJ#. Of the three plots, 1000/BP versus CJ# gives the best correlation figure - $R^2 = 0.3819$ and $F = 11.7$ - but none provide convincing evidence for a good linear correlation.

Looking at Figures 6 and allowing for the scatter of the data, however, there appears to be some non-linear relationship between the two parameters. Since all fuels on or above the line at 260°C would pass the standard JFTOT test, the assumption that 1000 provides a reasonable pass/fail criterion still seems reasonable. (The 260°C JFTOT pass level has, historically, prevented obviously bad fuels being accepted despite the method's shortcomings, so this link-in has some justification.) Fuels which are destined to reach this level will have significant and measurable levels of deposits long before the end of the "standard" two hour test. Assuming that there is not much of an induction period before deposits build up, this suggests that a pass/fail specification test could be considerably shorter than the existing two hours and therefore require less fuel.

On the other hand Figure 6 also suggests that the C-JFTOT test may not discriminate adequately between very good fuels (say, breakpoints > 290°C). This was not, of course, what the C-JFTOT's standard operating conditions were chosen to achieve and does not mean that the apparatus cannot distinguish between very high thermal stability fuels. All that is required is a different set of operating conditions.

CBO experiments involve running a JFTOT test at 350°C and then measuring the amount of deposit created in terms of the weight of carbon that burns off. The condition is severe enough that practically all fuels produce deposit. Data are not shown here but there is not a straightforward relationship between CBO and the C-JFTOT results, either for the full set of fuels or for the fuels without additives.

**Large scale rigs.** Early correlations had suggested that the C-JFTOT was a good predictor of MIFAR performance. With a fuel appetite of at least 2000 litres, the MIFAR is not, however, used routinely for all fuels. The correlation between MIFAR and CJ# for just four fuels was good, as shown by Figure 7 which includes a regression line fitted to the points (R=0.9994). No very unstable fuels have been included; one could have been produced by deliberate doping of a good fuel but this approach might produce a systematic bias in the results. Figure 7 also shows results for a fifth fuel. Initially this Merox fuel had appeared too good for the ranking exercise - it had the same 290°C breakpoint as another Merox fuel already tested - but all the rig tests (STHTR, MIFAR and C-JFTOT) have shown it to be noticeably worse when tested under more realistic conditions. The two Merox fuels with the same breakpoint are shown. Including the fifth point in the regression fit decreases R slightly but the result remains very good compared with those for other correlation exercises, and is better than seen for the earlier Log(MIFAR) versus Log(C-JFTOT by carbon) fit listed in Table 2.

In the STHTR the loss of heat transfer efficiency per hour, ΔHTC, is measured at one or more fuel outlet temperature once steady conditions have been achieved. The one FOT always used is 225°C. When there is sufficient fuel, multiple measurements are made and results are fitted to a pseudo-Arrhenius model; this then allows a "best fit" ΔHTC value at 225 °C to be quoted. The actual (raw) and best fit (where available) results at 225°C are plotted against CJ# in Figure 8. Except at lower CJ# values, where results from both methods relate to very low deposit levels, there is some relationship between the two measurements. Figure 9 provides a log-log display of the same data, and includes the best fit to Log(best fit data) and Log(CJ#), omitting the lowest CJ# result. The value of $R = 0.9097$ ($R^2 = 0.8277$) and the F value of 24.021 show that this is a much more convincing correlation than previously observed between STHTR and C-JFTOT carbon (Figure 2). It is also better than the correlations between C-JFTOT and the JFTOT variants, but not as good as that seen between C-JFTOT and MIFAR. Some of this difference in correlations with MIFAR and STHTR correlation may relate to more data points being used in the latter case. However, there is also the possibility that the C-JFTOT still cannot fully model the heating effects (heated tank, in particular) of the STHTR.

**Additivated fuels.** Large scale rigs such as the MIFAR and STHTR can provide real time rates of change of temperature (not just post-test ratings) and results from these two rigs relate to periods of constant rates of change of heat transfer when the induction period has passed. Generally, the more stable the fuel, the longer the induction period and the lower the rate of heat transfer change (deposit build up) when the induction period has been overcome[5,12]. This only stops being the case when the fuel contains additives such as metal deactivator (MDA). Such additives increase the induction period but do not reduce the ensuing rate of heat transfer exchange; they may even increase the deposition rate and thus the rate of heat transfer loss[5,6]. These additives are thus able to "fool" instruments, such as the JFTOT, which only look at an end-of-test result and so are unable to tell if they are still operating within induction period conditions.

None of the C-JFTOT development work was explicitly targeted at whether the C-JFTOT would also be fooled by additives. Few Phase 4 fuels were additivated, although it was clear that JP-8+100 additives had a dramatic impact on the performance of poor thermal stability fuels[13]. The C-JFTOT does at least provide real time measurements as part of its standard operation and could be operated over longer periods, say 10 hours, to check that the induction period had ended.

A JFTOT-failing JP-5 fuel was received in April 1995, from the US Navy at Trenton. It contained just under 40 ppb metal (20.5 ppb Cu and 15 ppb Fe), a level that could cause many fuels to fail the thermal stability criteria of specifications. N.B. JP-5 fuel contains FSII and

CI/LI performance additives; the CI/LI is surface active and may already affect the deposit-forming tendencies of the fuel. There was just sufficient fuel to run two standard C-JFTOT tests and to run a single test where the fuel had been doped with 5.7 ppm MDA to the fuel (the maximum allowable amount and far in excess of the amount required to chelate the copper and iron). 3-D temperature rise versus position versus time plots are shown in Figures 10 and 11. The average result for the JP-5 is 1540. (The capillary tube was glowing red at the end of the tests.) This fuel would be rejected by a CJ# "cut-off" of 1000. Addition of MDA has caused a considerable reduction in the amount of temperature rise and the result is 495. The MDA-doped fuel seems to produce a more even deposit along the test specimen (the profile is flatter along the distance axis). Data for the hottest positions are replotted in 2-D format (see Figure 12); this figure illustrates the temperature dip effect noted with the C-JFTOT. (Temperature dips have been seen in all SRTCT's large-scale simulators - STHTR, MIFAR and IFAR - being most apparent with high stability fuels. One explanation for this is that the small amounts of deposit laid down in the capillary at the start of test effectively roughen the surface, increasing the turbulence of the fuel and hence increasing the initial rate of heat transfer. Another explanation is that the early deposit lay down fills surface crevices and thereby improves thermal conductance. Either has the effect of lowering the surface temperature. The C-JFTOT proforma spreadsheet automatically searches for this lowest temperature reading and uses it as the baseline from which all ΔT values are quoted at that particular measuring position.) It is not clear if MDA addition has prolonged the induction period as has been noted in MIFAR and STHTR experiments in the past. The temperature/time gradients for the MDA test are not very different from those at during the induction periods of the base fuel but rates of deposition are worsening as time progresses. A longer test or one with much less MDA in the system (had fuel supplies been sufficient) might have clarified the situation.

## DISCUSSION

The laboratory version of the C-JFTOT has been used in its existing format (see Figure 1) since early 1993 and appears to be a good predictor of large-scale rig, particularly MIFAR, performance. Shell Internationale Research Maatschappij B.V. has filed patent applications covering the basic design[14] (used in Phase 4 tests) and collaborated with a third party to produce a pre-production prototype, the HiReTS rig. The first machine was delivered in mid-1996 and a second was supplied at the end of 1996. Both machines have been commissioned and are producing results very similar to those obtained with the older C-JFTOT rig. Basic experimental details are similar to those already described for the C-JFTOT. Exact design details of the HiReTS rigs are proprietary, but the test section and its ancillaries are in a single unit (comparable in size to that of the JFTOT), with a PC controller system in a second unit. An on-screen display shows power readings and system pressure, as well as on-going temperature measurements. A video camera assures detector alignment. All system safety trips come under the control of the computer monitoring system and additional safety control test parameters are monitored by the computer. A "hard-wired" emergency stop system allows unattended running of the machine.

Machines are now about to be or are actually in the process of being evaluated by third parties (under loan), both to establish the inherent reliability of the HiReTS (repeatability and reproducibility of results) and to identify the best test protocols to adopt. There will be some tests performed on fuels with known engine performance data.

The existing test protocol was established with a commercial/civilian specification test in mind. This means discriminating between fuels with good and bad thermal stability so that the latter will be rejected. A CJ# or HiReTS number greater than 1000 appears to be found for most fuels that fail the standard JFTOT at 260°C. A detailed appraisal of the data is planned but it is probable that a shorter "specification" test could be adopted to achieve the desired pass/fail outcome. The HiReTS apparatus also has the potential to be developed for research activities and other specification tests; these applications are not mutually exclusive. In particular, it is becoming increasingly important to understand how additives affect deposition in turbulent flow environments. Such knowledge is relevant to another application that has arisen over the last few years, i.e. differentiating between fuels of good and excellent thermal stability. USAF are achieving thermal stability improvements through additivation.

Existing jet fuel specifications allow (or demand, for military applications) the use of metal deactivator and corrosion inhibitor/lubricity improver additives. The increased flexibility of the pre-production HiReTS should prove useful in studies to investigate the impact of these and JP-8+100 additives on aviation kerosine thermal stability. An increased range of additivated fuels have started to be tested under the current conditions to see if additivated and non-additivated fuels fall on different regression lines in correlations against JFTOT breakpoint, MIFAR performance, etc.. A number of systems have shown major discrepancies between HiReTS and JFTOT results. One case involves a poor Merox fuel with negligible levels of copper and iron that has been doped with MDA. The JFTOT breakpoint increases dramatically while the HiReTS number only drops marginally and is still much greater than the arbitrary cut-off (pass/fail) value of 1000[13]. Increasing the test time beyond two hours may help establish whether HiReTS numbers are always being quoted after the induction periods has passed; the original MDA/JP-5 result did not answer that question clearly. A longer test time and/or a higher FOT and/or a different flow rate might then allow a second test protocol to be adopted, aimed at differentiating between very good fuels rather than discarding poor ones. This would be particularly relevant for USAF's JP-8+100 programme. Preliminary results with such additives do suggest that the protocol will need to be altered when the object is not just to reject poor fuels

In its role as a research apparatus, the HiReTS may help investigate such effects as fuel recirculation. It may provide mechanistic insights far more readily and rapidly than is possible with large, fuel hungry rigs such as the MIFAR and STHTR and comparable rigs used at other locations. Additionally, the apparatus may be suitable for testing fluids other than aviation kerosine. Its short term development, however, will be directed towards ensuring that only reliably good thermal stability fuels are loaded onto aircraft.

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Table 1 - Test data for fuels used in first two correlation exercises using STATGRAF package

| | | *C-JFTOT* | *STHTR HTC* | *JFTOT CBO* | *JFTOT BP* | *Ri x $10^7$* | *Sulphur content* | *MIFAR deposit rate* |
|---|---|---|---|---|---|---|---|---|
| | *Units* | *µg* | *%/h* | *µg* | *℃* | *mol/L/s* | *%w* | mg/cm$^2$/h |
| | *STATGRAF coding =>* | *CAP* | *HTC* | *CBO* | *BP* | *RI* | *Sul* | MIFAR |
| *Fuel* | *Processing* | | | | | | | |
| I | Merox | 214 | 1.1 | 146.0 | 295 | 4.7 | 0.11 | |
| M | Merox | 457 | 7 | 228.0 | 275 | 10.7 | 0.13 | |
| O | Merox | 12 | 5.4 | 86.0 | 285 | 0.5 | 0.13 | 0.22 |
| Q | Merox | 44 | 1.3 | 143.0 | 285 | 2.5 | 0.03 | 0.33 |
| R | Hydrocracked | 8 | 1.9 | 90.0 | 290 | 4.9 | 0.01 | 0.15 |
| S | Merox | 122 | 0.6 | 138.0 | 265 | 5.8 | 0.10 | 0.27 |
| T | Merox | 97 | 1.28 | 307 | 250 | 12.30 | | 0.105 |
| V | Merox +LCCCO | 1277 | 12.3 | 553.0 | 245 | 4.9 | 0.30 | 0.41 |
| W | Merox | 699 | 28 | 714.0 | 210 | 25.5 | 0.10 | |
| Y | Hydrotreated | 7 | 0.19 | 54.0 | 285 | 0.93 | 0.002 | 0.049 |
| HC-1 | Hydrocracked | 8 | 0.58 | 31.0 | 270 | 2.55 | 0.004 | |
| HC-12 | Hydrocracked | 4 | 0.2 | 30 | 300 | 0.54 | | 0.046 |
| AD | Merox | 67 | 0.68 | 117.5 | 275 | 8.26 | | 0.166 |
| AL | Merox | 35 | 7.3 | 179 | 275 | 7.14 | | 0.137 |

where: HTC = STHTR loss of heat transfer efficiency at 225°C, CBO = Carbon burnoff value, BP = JFTOT breakpoint, Ri = Radical initiation rate, from flask oxidation test. C-JFTOT uses average carbon weight data recorded for 290°C fuel outlet temperature. MIFAR results quoted for fuels Q, S and T are the average of two determinations.

Table 2 - STATGRAF analyses of correlations. Large scale rigs versus carbon deposit weights from conventional and capillary JFTOTs, for fuels with MIFAR data in Table 1. All Logs are to base 10.

| Dependent | Log(MIFAR) | Log(MIFAR) | Log(MIFAR) | Log(MIFAR) | Log(HTC) |
|---|---|---|---|---|---|
| Independent | Log(CJFTOT) | Breakpoint | Log(BP) | Log(CBO) | Log(CJFTOT) |
| Mean square error | 0.0562 | 0.0890 | 0.0899 | 0.0612 | 0.3105 |
| Correlation confidence, % | 98.06 | 84.1 | 83.35 | 97.18 | 88.77 |
| F value | 8.5 | 2.41 | 2.32 | 7.15 | 3.17 |
| R-squared | 0.515 | 0.232 | 0.225 | 0.472 | 0.284 |
| Intercept +/-1 standard error | -1.3047+/-14% | 1.607+/-97% | 12.33+/-70% | -2.104+/-23% | -0.5599+/-77% |
| Gradient +/-1 standard error | 0.3103+/-34% | -0.0088+/-64% | -5.389+/-65% | 0.6134+/-37% | 0.4454+/-56% |

Figure 1. Laboratory Capillary JFTOT apparatus, used as basis of development of pre-production HiReTS machines.

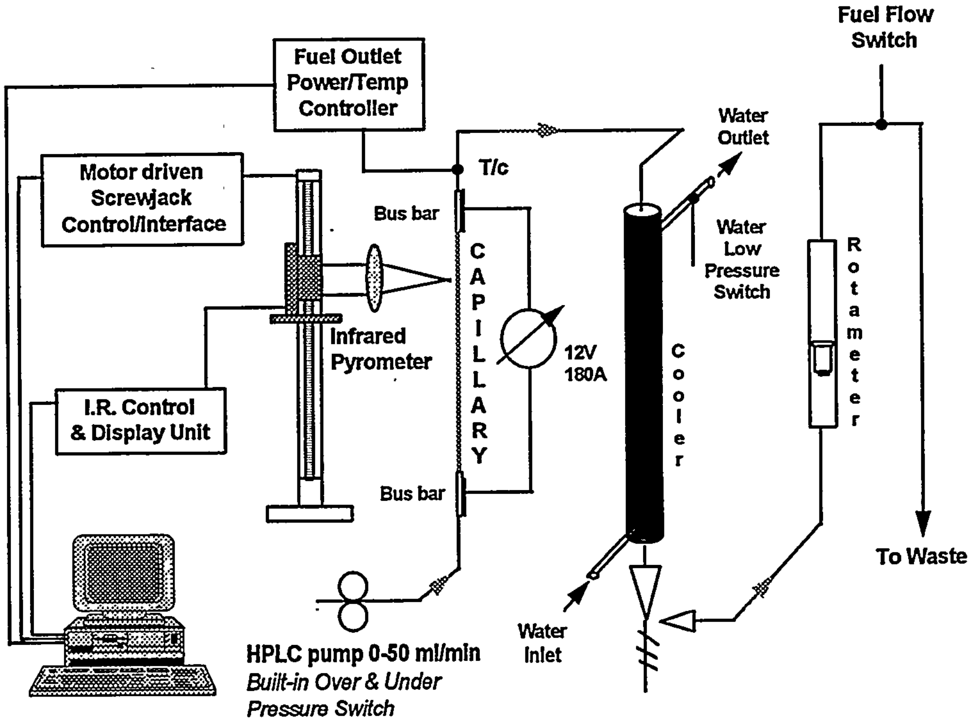


Figure 2. First correlation between fouling rate in the STHTR and carbon deposited in C-JFTOT at 290°C condition. $R^2 = 0.4507$, $F = 6.56$ and 95% confidence limits are shown.

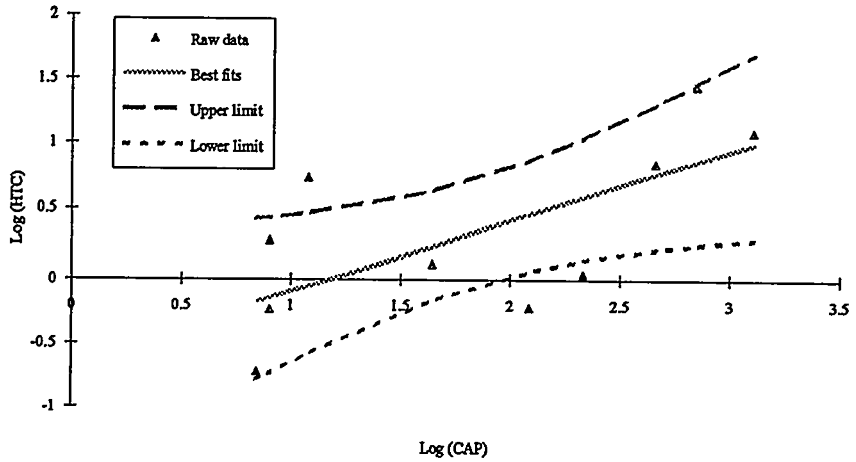


Figure 3. Correlation between deposition rate in the MIFAR and carbon deposited in C-JFTOT at 290°C condition, including 95% confidence limits. $R^2 = 0.5150$ and $F = 6.50$.

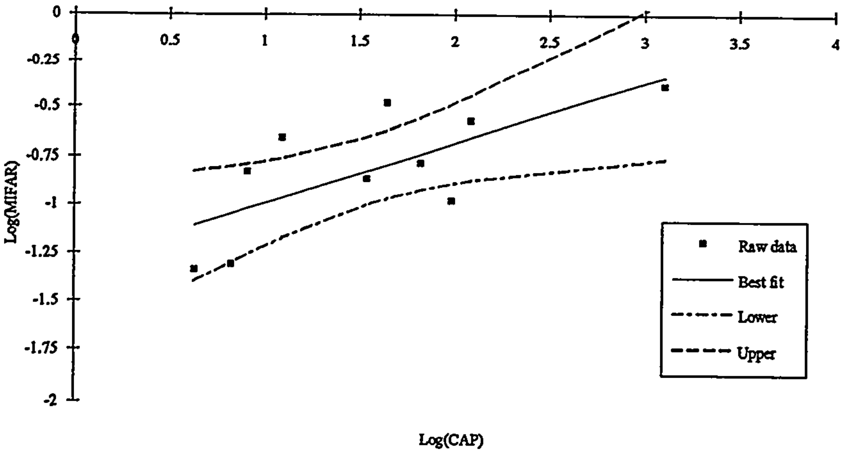


Figure 4. Average carbon deposit weight versus average C-JFTOT number (Phase 4 fuels).

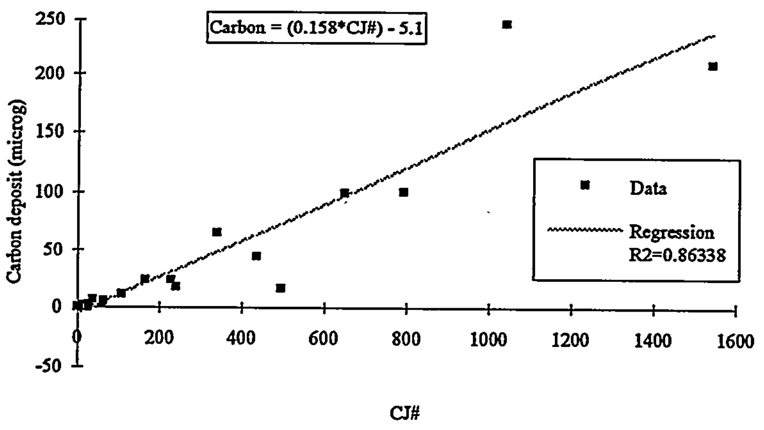


Figure 5. CJ# versus visual tube ratings from standard JFTOT tests for Phase 4 fuels.

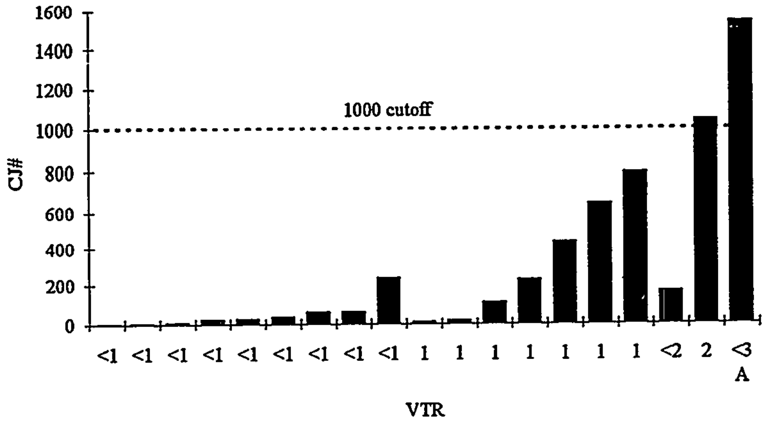


Figure 6. JFTOT breakpoint versus C-JFTOT number showing linear regression fit for Phase 4 fuels; omitting those with additives, Breakpoint = 292 - (0.0239*CJ#) with $R^2 = 0.4387$.

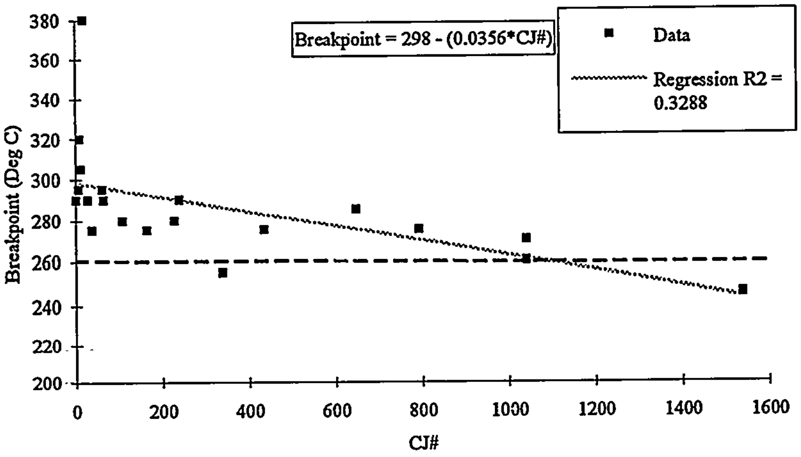


Figure 7. MIFAR deposit rate versus C-JFTOT number for Phase 4 fuels.

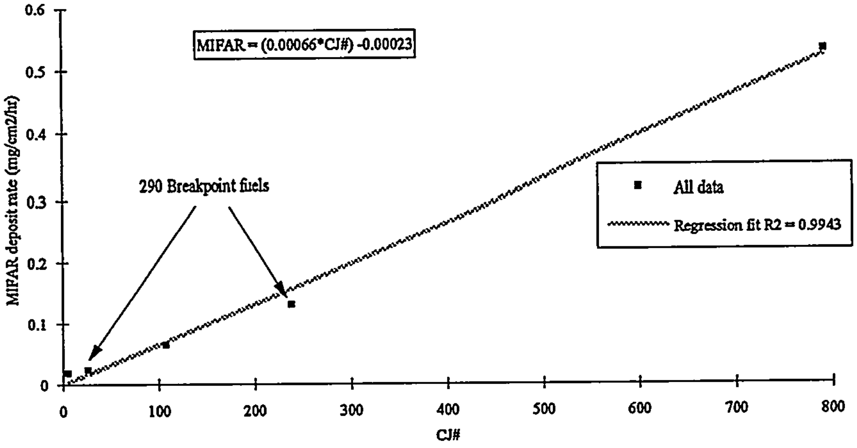


Figure 8. STHTR heat transfer coefficient ΔHTC at 225°C versus CJ# for Phase 4 fuels. STHTR data may be "raw" or from fitting data obtained at several temperatures.

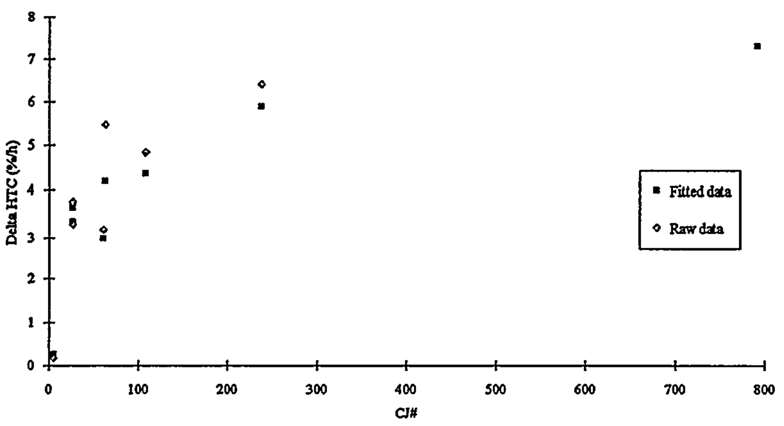


Figure 9. Log (ΔHTC) versus Log (CJ#), and regression fit (omitting lowest CJ# point).

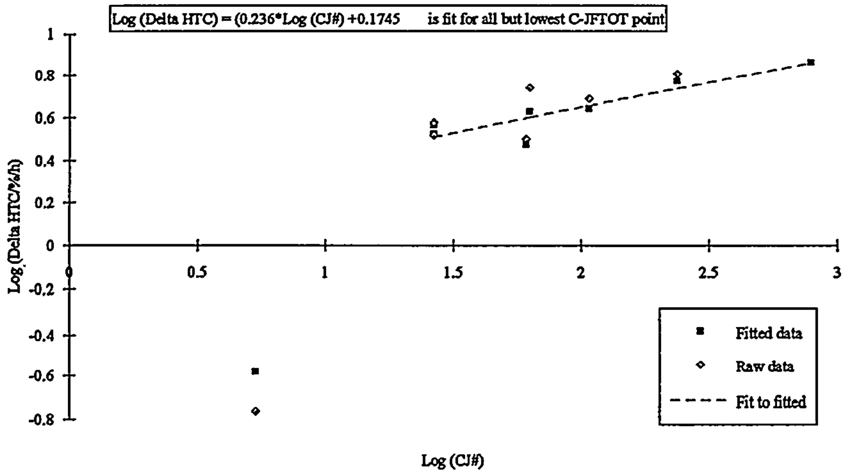


Figure 10. Trace for poor thermal stability JP-5 fuel received from US Navy, using C-JFTOT

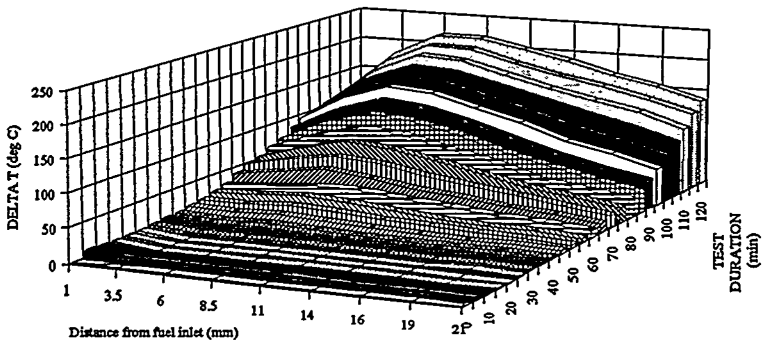


Figure 11. Same fuel with maximum allowable concentration of metal deactivator additive.

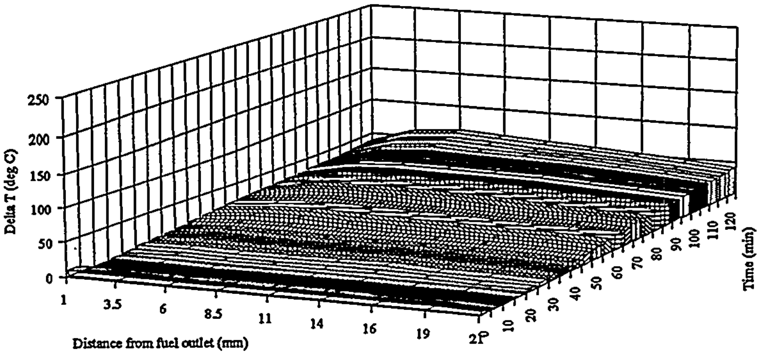
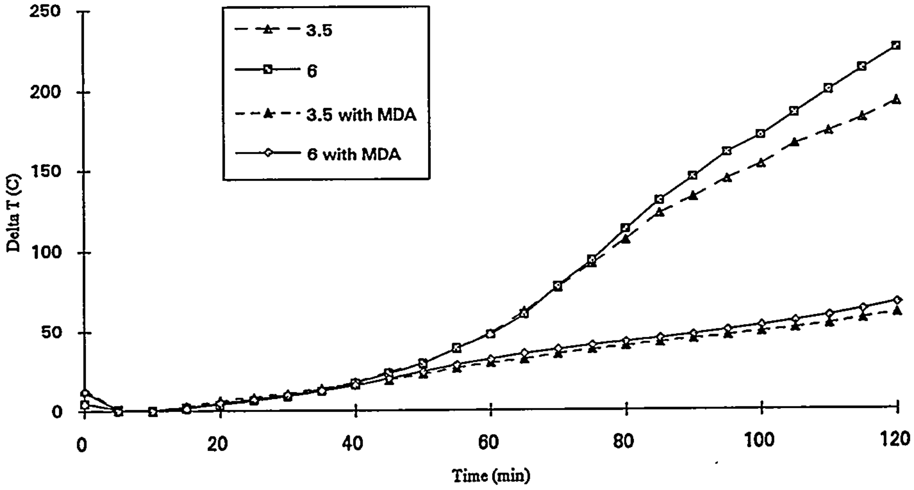


Figure 12. 2-D temperature change (Delta T) versus time at two hottest positions (3.5 and 6 mm from fuel outlet) for US Navy JP-5 fuel, as received and with 5.7 mg/L active matter MDA. Both show initial drop in Delta T followed by temperature rise.



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# ELECTRICAL CONDUCTIVITY OF HITTS ADDITIVE PACKAGES FOR THE JP8+100 PROGRAMME

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## ABSTRACT

The behaviour of two HITTS high temperature additive packages has been studied to examine possible interference with existing conductivity improver and also to assess their potential as conductivity improvers. The HITTS additives are shown to impart sufficient conductivity to fuels to meet certain fuel conductivity specifications without the addition of Stadis. Use of the HITTS additives with Stadis is shown to produce values of conductivity above the fuel specification. The conductivity performance of the HITTS additives is unaffected by the presence of phenolic or sodium salt impurities in the fuel which have been shown to have a detrimental effect on the performance of Stadis. The conductivity behaviour of the individual components of the HITTS additives is discussed. The dispersant is the main conducting component in the additive packages, but there are variations in the magnitude of the conductivity observed.

## 1. INTRODUCTION AND AIMS

The major objective of the JP8+100 programme is to improve the thermal stability of jet fuel using carefully selected additives. However, in this paper we examine the effects of such additives on properties which are unrelated to thermal stability characteristics, but which can have important consequences for the handling characteristics of the fuel.

In earlier papers[1,2,3] we examined the effects of a wide range of compounds, representative of naturally-occurring fuel components, on the performance of static dissipators (conductivity improvers). The work identified highly polar species capable of substantially reducing their effectiveness.

Certain HITTS packages are known to impart some conductivity to fuel. This work investigates the magnitude of this conductivity effect, on a model fuel and on three real fuels, for two Betz JP8+100 additives based on SPEC-AID 8Q405. SPEC-AID 8Q405, alone, at a concentration of

100mgl$^{-1}$, has been reported to produce an average conductivity increase of ~140pSm$^{-1}$ in three reference fuels[4].The spread of values in these fuels was not stated. The two fully formulated HITTS packages NB 345 S286 and SPEC-AID 8Q460 have been examined and components of the packages have been studied separately to identify components contributing to the conductivity.

The sensitivity of these HITTS packages to model impurities, phenols and sodium salts,has been determined and is compared with that of Stadis450. The effects of the HITTS additives on Stadis450 have also been measured.
Brief comments are made on the potential for the use of such additives as conductivity improvers.

## 2. EXPERIMENTAL

**2.1 Materials:** The composition of the HITTS additive packages NB 345 S286 and SPEC-AID 8Q460 are given in Table 1. The fully-formulated additives , SPEC-AID 8Q460 and NB234 S286A, the partially formulated package SPEC-AID8Q406 and the components SPEC-AID 8Q405(dispersant batch-1) and SPEC-AID8Q400(Betz metal deactivator) were supplied directly via Wright Patterson AFB by Betz Process Chemicals Inc. A second sample of SPEC-AID 8Q405 (batch-2), was supplied via British Petroleum. The additive BHT (2,6-diter-butyl-4-methyl phenol) was obtained from Aldrich Chemical Co Ltd., "conventional" metal deactivator (NN'disalicylidene 1,2-propane diamine - abbreviated to c-MDA) from Pfalz and Bauer Inc., m-cresol from British Drug Houses and octylamine from Fluka Chemica.
Stocks of the HITTs fuels were held by and supplied to us by Shell. These were, an additive-free Merox base fuel (Merox-AF), having a kinematic viscosity of 3.698 mm$^2$s$^{-1}$ at -20C, and two fuels produced from this to JetA1 and JP8 specification. These are designated Jet A1-MA1, which contains 1.87mgl$^{-1}$ reformulated Stadis450 and JP8-MA2 which contains 1.87mgl$^{-1}$ reformulated Stadis450 plus AL-48 to give a concentration of 1300mgl$^{-1}$ of FSII and 27mgl$^{-1}$of Nalco 5403. The sources and purification procedures employed for materials used previously, have been described[1,2,3].

**2.2 Equipment and measurements:** All measurements were made with the apparatus described previously[2,3] and made at 25C. The series of measurement was as follows:

**i)** time dependence of conductivity for NB 345 S286 and SPEC-AID8Q460 in dodecane.

**ii)** the conductivity of NB 345 S286 and SPEC-AID 8Q460 in dodecane and HITTS Fuels over a concentration range of 10 $mgl^{-1}$ to 800 $mgl^{-1}$.

**iii)** the conductivity of NB 345 S286 and SPEC-AID 8Q460, over a range 10$mgl^{-1}$ to 800$mgl^{-1}$, in dodecane containing 3$mgl^{-1}$ Stadis450

**iv)** *m*-cresol and 2,6-di-*tert*-butyl-4-methylphenol were added separately over the concentration range 50-1000 $mgl^{-1}$ to solutions of 135$mgl^{-1}$ NB 345 5286 in dodecane and HITTS Fuels and 127$mgl^{-1}$ SPEC-AID 8Q460 in dodecane and HITTS Fuels. The conductivity was measured after each addition of the phenol.

**v)** sodium naphthenate was added, over the concentration range 0.3 to 18 $mgl^{-1}$, to solutions of 135$mgl^{-1}$ NB 345 S286 in dodecane and 127$mgl^{-1}$ SPEC-AID 8Q460 in dodecane. Conductivity measurements were made after each addition of sodium naphthenate.

**vi)** components of the additive packages namely SPEC-AID8Q405, SPEC-AID8Q400 and c-MDA were added separately to HITTS Fuels and the conductivity measured.

**vii)** test of the variability of samples of SPEC-AID8Q405 dispersant between batches (where impurity levels could be different) by measurement of the conductivity of batch 2 SPEC-AID,8Q405 in the three HITTS fuels to compare with similar results from batch 1.

**viii)** neutralisation of possible acidic impurities using SPEC-AID 8Q406 ( SPEC-AID8Q405 + BHT antioxidant) was shaken for five minutes with finely divided $CaCO_3$ diluted with hexane, then separated and the solvent removed by evaporation. A control sample was treated in a similar way but without the $CaCO_3$.

Acid and Base Additions: In a preliminary attempt to investigate ion production mechanisms we have examined the effects of an amine and an acid on the conducting species. Octylamine, diluted in toluene, was added to a solution of 100$mgl^{-1}$dispersant SPEC-AID 8Q405 in the Merox-AF and the conductivity was measured after each addition. Similar measurements were made using dodecylbenzenesulphonic acid.

## 3. RESULTS AND DISCUSSION

### 3.1 The Time dependence of the Conductivity of Fully-Formulated Additives, NB345 S286 and SPEC-AID8Q460 in Dodecane Solutions

The time dependence of conductivity has been examined in a limited series of measurements over a three-hour period. These measurements were required in order to see if any large drifts in conductivity occurred during the time-scale of the experiments. The conductivity of the NB345 S286 solution(135$mgl^{-1}$) increases slowly with time whereas that for SPEC-AID8Q460 (127$mgl^{-1}$)

shows a slow decrease. However in neither case were the changes sufficient to warrant detailed corrections to data obtained during the period of the experiments-normally about an hour.

### 3.2 Effect of Concentration of Fully-Formulated Additives on the Conductivity of Dodecane Solutions

Data in dodecane were required to provide a baseline for comparison with behaviour in real fuels. In these experiments only the the fully-formulated HITTS additive packages SPEC-AID 8Q460 and NB345 S286 were examined.

Figure 1 shows the effect of these packages on dodecane and demonstrates their ability to impart conductivity. We note also that the conductivity varies approximately linearly with concentration of the additive package, with the NB345 S286 giving a larger gradient than SPEC-AID8Q460. The recommended in-fuel concentrations of these additives are 135mgl$^{-1}$ for the former and 127mgl$^{-1}$ for the latter .

The behaviour of these packages in dodecane containing 3mgl$^{-1}$ of original Stadis450 is shown in figure 2. The results of repeat runs, undertaken after an interval of nineteen months show a measurable change in behaviour. The fact that the stadis450/dodecane solution had a conductivity close to that in the original experiments suggests that the observed changes are due to ageing effects in the Hitts additives. The cause of the low concentration behaviour is not yet clear, however at concentrations >200mgl$^{-1}$ the variation of conductivity with concentration for each package is similar to that observed in the absence of Stadis450. These low concentration effects are reminiscient of the effects of salts on Stadis450.

### 3.3 Effects of Polar Fuel Components on the Conductivity of Hitts Additives in Dodecane

Figure 3 shows the influence of m-cresol concentration on the conductivity of solutions containing given concentrations of (i) original-Stadis450, (ii) NB345 S286 and (iii) SPEC-AID8Q460. The concentrations chosen are recorded on the figures and correspond approximately to those used in jet fuels.

We previously reported on the influence of m-cresol on original-Stadis450[3] and this is also further discussed in an accompanying paper[5]. For SPEC-AID8Q460 we observe a small decrease in conductivity with concentration which is probably insignificant from a user viewpoint. For NB345 S286 conductivity appears to increase gradually with m-cresol concentration and the increase, after allowance for a small time correction, would be ~ 30pSm$^{-1}$ at 1000mgl$^{-1}$ m-cresol. For comparison figure 4 shows the effects of a highly hindered phenol of the type employed as antioxidants. This is a good example of an almost complete lack of any antagonistic interaction with any of the three additives.

Earlier results on the effects sodium salts of a naphthenic acid, a phenol and dodecylbenzenesulphonic acid, on the behaviour of original-Stadis450, showed strong antagonistic effects on conductivity response[3] and these were qualitatively similar for all three types of salt. Sodium naphthenate was chosen as representative of these and its influence on the additive packages is shown in figure 5. For each HITTS package the concentration dependence of conductivity is quite different from that of Stadis solutions. There is no minimum, the conductivity remains approximately constant up to a concentration of ~ 2mgl$^{-1}$ and then increases with concentration. We note that sodium naphthenate alone imparts some conductivity[3] , but this cannot account for the total observed increase. However, in this case, because the concentration of such compounds in fuels is likely to be low-probably <1mgl$^{-1}$, the practical effect of this will be very small.

### 3.4 Effects of Fully-Formulated Additives on the Conductivity of Hitts Fuels

We note that the conductivities of Jet A1-M1A and JP8-M2A, measured at the start of the study, are very similar, having values of ~ 500 pSm$^{-1}$. However , during the period of the work conductivity is seen to decrease for each fuel, with that for JP8 showing a fall of ~34% and for JetA1 a fall of ~20% over 250 days. This is taken into account in our comparisons of behaviour. The only difference between these fuel solutions is the presence of AL-48 in JP8-M2A. We know that in short-duration experiments AL-48 has no measurable effect on the performance of Stadis450[6]. No long-duration experiments ie up to ~250 days have yet been done.

Figure 6 shows the response of HITTs fuels to NB345 S286. This is represented by the increase in conductivity over the initial conductivity of the fuel. Dodecane data are shown for comparison. Clearly there are differences in response which follow the order : JP8 > Jet A1 > Merox-AF > Dodecane. Likewise figure 7 shows the response of HITTs fuels to SPEC-AID8Q460. In this case the differences in response are much less clear cut, though JP8 and Jet A1 again show greater resonse than Merox-AF and Dodecane. ie JetA1 ~ JP8 > Dodecane ~ Merox-AF. The lower viscosity for Merox-AF(1.45mm$^2$s$^{-1}$) compared with dodecane(1.86mm$^2$s$^{-1}$) at 25C would lead us to expect a higher conductivity in Merox-AF. Mixtures of aromatic and alkane liquids of a given viscosity are expected to promote a higher conductivity than an isoviscous pure alkane at the same temperature. Therefore the presence of aromatic components in Merox-AF(19%) will raise the conductivity[6]. To these effects must also be added those due to interactions between additives. The net result on ion production is seen in the measured conductivity. Paradoxically the low concentration behaviour observed with these additivesin Stadis/dodecane mixtures is not observed in the more complex real fuel systems. In these cases however, the ageing effect has not yet been examined.

A practical point is that, at the recommended dosing concentration for HITTs additives in JP8 and JetA1, the total conductivities, as shown in table 2, are above the upper limit specification values of 600pSm$^{-1}$ and 450 pSm$^{-1}$ respectively. We also note that the conductivity of Merox-AF, containing the recommended concentrations *is* within the specification conductivity range for JetA1 without the addition of Stadis 450, but 8Q460 falls slightly short of the minimum value for JP8. However we feel that more data is required on batch-to-batch variations and on fuel composition effects.

### 3.5 Effect of Model Phenolic Impurities on the Conductivity of HITTS Additives in HITTS Fuels

Figure 8 shows that the total measured conductivities of SPEC-AID 8Q460 in Merox-AF are *insensitive* to the presence of *m*-cresol "impurities". Results for NB345 S286 are similar. The apparent sensitivity to *m*-cresol in the JP8 and JETA1 fuels can therefore be attributed to the interaction of the *m*-cresol with the Stadis450 in these fuels and not to any interaction of the *m*-cresol with NB 345 S286 or SPEC-AID8Q460.

### 3.6 Effects of Additive Components on the Conductivity of HITTS Fuels

Work on a range of phenol types[5] in dodecane has shown that highly hindered phenols have little or no effect on the conductivity of hydrocarbons nor do they adversely affect the performance of Stadis450. We have confirmed that BHT does not contribute to the conductivity of the additive package in any of the HITTS fuels.

Earlier measurements on conventional-MDA in dodecane showed it had no effect on conductivity[1] Figure 9 shows that this is also true for solutions in Merox-AF and JP8. For Jet A1 a small decrease of ~10% is observed in the concentration range 0 to 100 mgl$^{-1}$.

In marked contrast, the Betz MDA, see figure 10, although it contributes only a small amount to the conductivity of Merox-AF, nevertheless has a considerable enhancing effect on the conductivity of Jet A1 and causes a modest reduction in the conductivity of JP8. These effects are clearly indicative of interaction between this MDA and components present in these fuels.

Repeat runs with this additive, after an ageing period of eighteen months, demonstrated an increased response. However, during this period the USAF decided not to consider a new MDA but to continue with conventional MDA. For this reason work on Betz MDA was discontinued. Figure 11 shows that the dispersant SPEC-AID8Q405 imparts significant conductivity to each of the fuels and conductivity varies linearly with concentration above ~50mgl$^{-1}$. We note the response follows the order JP8 > Jet A1 > Merox-AF as observed for the fully-formulated additive packages. In view of the results for BHT and c-MDA discussed above, it is clear that SPEC-AID8Q405 is the only conducting component in SPEC-AID8Q460 and is the main, but not the sole conducting component in NB345 S286.

### 3.7 Effect of Batch Variation on the Behaviour of SPEC-AID 8Q405

Figure 11, also demonstates batch to batch variation on the conductivity-improving ability of SPEC-AID 8Q405 with Batch 2 giving generally lower conductivity values. At a concentration of 100mgl$^{-1}$, batch-1 in Merox-AF meets the Jet-A1 and JP8 conductivity specifications, without Stadis, whereas batch-2 meets that for Jet-A1 only. Either batch added to Jet-A1 fuel causes the conductivity to be out of specification. This is also the case for addition of batch-1 to JP8 fuel. The magnitudes of some of the observed effects seems also to be influenced by ageing of the fuels and we hope to examine this further.

### 3.8 Preliminary Investigation of the Conducting Species

The conductivities of both carbonate-treated and untreated SPEC-AID8Q406 samples (see para 2.2 ) are identical. This suggests that participation of acidic species in the conduction process is unlikely.

Figure 12 shows that both dodecylbenzenesulphonic acid n-octylamine interact to increase the conductivity. Repeat experiments after an interval of sixteen months show, that apart from some small apparent differences at very low concentrations, the behaviour is generally unchanged within the experimental uncertainty. In the case of the sulphonic acid the effect is partly due to the acid itself[1,3]. However, this cannot be the explanation for the effect of the amine which alone has no effect on the conductivity[6]. More information is required before much speculation can be justified.

# 4. SUMMARY AND CONCLUSIONS

## 4.1 CONDUCTIVITY BEHAVIOUR OF HITTS PACKAGES

### 4.1.1 In Model Fuel (Dodecane) with Model Impurities

1 Both the HITTS packages impart conductivity which shows a small time dependence.

2 Both the HITTS packages can impart conductivity to fuel, without the use of Stadis450.

3 The conductivity response of both the HITTS packages is insensitive to phenolic impurities.

4 The conductivity response of both the HITTS packages is insensitive to sodium salts.

5 The HITTS packages have the advantage of imparting the required conductivity to fuels without the sensitivity to fuel impurities, such as phenols and sodium salts, which is detrimental to Stadis450.

### 4.1.2 In HITTS Fuels

1 Both the HITTS additive packages used at the recommended concentration in the HITTS fuels JP8 MA2 and JETA1 M1A, gave conductivities *above* the fuel specification.

2 The conductivity of the MeroxA-F containing the recommended levels of both HITTS packages was within the fuel conductivity specification for Jet-A1 *without* the use of Stadis450. For JP8 with the additive 8Q460, conductivity falls slightly short of the minimum conductivity specification

3 There is a simple linear relationship between conductivity and the concentration of the HITTS additives.

4 Both the HITTS additive packages appear to be unaffected by the presence of phenolic impurities in fuel.

5 Reduction in conductivity in the HITTS JP8 and JET A1 with the HITTS additives in the presence of phenolic impurities is attributed to interaction of the phenol with the Stadis 450 in these fuels.

6 The HITTS additives show potential as conductivity improvers. Additional work is required on batch-to batch variation, ageing effects and on the temperature dependence of conductivity before these additives can be given serious consideration as sole conductivity improvers.

## 4.2 CONDUCTIVITY BEHAVIOUR OF *INDIVIDUAL COMPONENTS* OF HITTS ADDITIVES

1 The c-MDA contributes little to the conductivity of the HITTS additive.

2 The contribution of the Betz MDA to conductivity is complex. In the Merox-AF the Betz MDA contributes a small increment to the conductivity. In the JP8 it produced a reduction in conductivity and in the JETA1 it produced an increase in conductivity. The reasons for the variations could be due to interaction with Stadis450 and/or water in the fuels. Recently the Betz MDA has ceased to be of interest to USAF.

3 The BHT antioxidant does not contribute to the conductivity of the HITTS additives.

4 The dispersant SPEC-AID8Q405 is the main conducting component in the HITTS additives. At 100mgl$^{-1}$ in the presence of Stadis, conductivity will generally exceed the specification upper limit. In the absence of Stadis it is likely that the Jet-A1 specification will be met but there is uncertainty with respect to JP8.

## 5. ACKNOWLEDGEMENTS

The authors wish to thank additive manufacturers and oil companies, in particular BP, for their constructive cooperation and for supplies of additives and fuels. Especially they would like to thank BP and DRA for many helpful and enjoyable discussions during the course of this work. They also wish to express their thanks to the DRA for its funding support provided under DRA Contract LSF/E 20093.

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6.Dacre,B.; Hetherington, J.I. Preliminary unpublished work.

| Commercial Additive | Description | Concentration Added to Fuel | Comments |
|---|---|---|---|
| BHT | Antioxidant<br>2,6-di-*tert*-butyl-4-methylphenol | 25mgl$^{-1}$ | |
| MDA (conventional) | Metal Deactivator<br>NN'disalicylidene-1,2-propanediamine | 10mgl$^{-1}$ | |
| 8Q405 | Dispersant<br>BETZ<br>(proprietory) | 100mgl$^{-1}$ | |
| Spec Aid 8Q400 | Betz Metal Deactivator | 10mgl$^{-1}$ | Different chemistry from conventional DuPont MDA |
| Spec Aid 8Q406 | 8Q405 / BHT<br>dispersant / antioxidant | 125mgl$^{-1}$ | |
| NB 345 S286A | Experimental<br>8Q405/BHT/8Q400<br>Dispersant / Antioxidant / Betz MDA | 135mgl$^{-1}$ | Assumed composition:<br>8Q405 100mgl$^{-1}$<br>BHT 25mgl$^{-1}$<br>MDA 10mgl$^{-1}$ (Betz) |
| Spec Aid 8Q460 | 8Q405 / BHT /MDA<br>Dispersant / Antioxidant / MDA (conventional chemistry) | 127mgl$^{-1}$ | Assumed composition:<br>8Q405 100mgl$^{-1}$<br>BHT 25mgl$^{-1}$<br>MDA 2mgl$^{-1}$ (conventional) |

**Table 1** Composition of HITTS High Temperature Additive Packages

| FUELS | SPEC AID8Q460<br>127mgl$^{-1}$ | NB 345 S286<br>135mgl$^{-1}$ |
|---|---|---|
| Merox-AF | 123 | 221 |
| Jet-A1 | 666 | 817 |
| JP8 | 668 | 864 |
| Dodecane | 132 | 200 |

**Values taken from data in figures 7 and 8.**

| **Specification Conductivity ranges:** | **Jet-A1** | **50--450pSm$^{-1}$** |
|---|---|---|
| | **JP8** | **150--600pSm$^{-1}$** |

**Table 2 Measured Conductivities (pSm$^{-1}$) in HITTS Fuels**

| Fuel | Batch-1<br>100mgl$^{-1}$ | Batch-2<br>100mgl$^{-1}$ |
|---|---|---|
| Merox-AF | 158 | 115 |
| Jet-A1 | 689 | 584 |
| JP8 | 671 | 557 |

**Values taken from data in figure 11.**

**Table 3 Measured Conductivities (pSm$^{-1}$) of 8Q405 in HITTS Fuels**

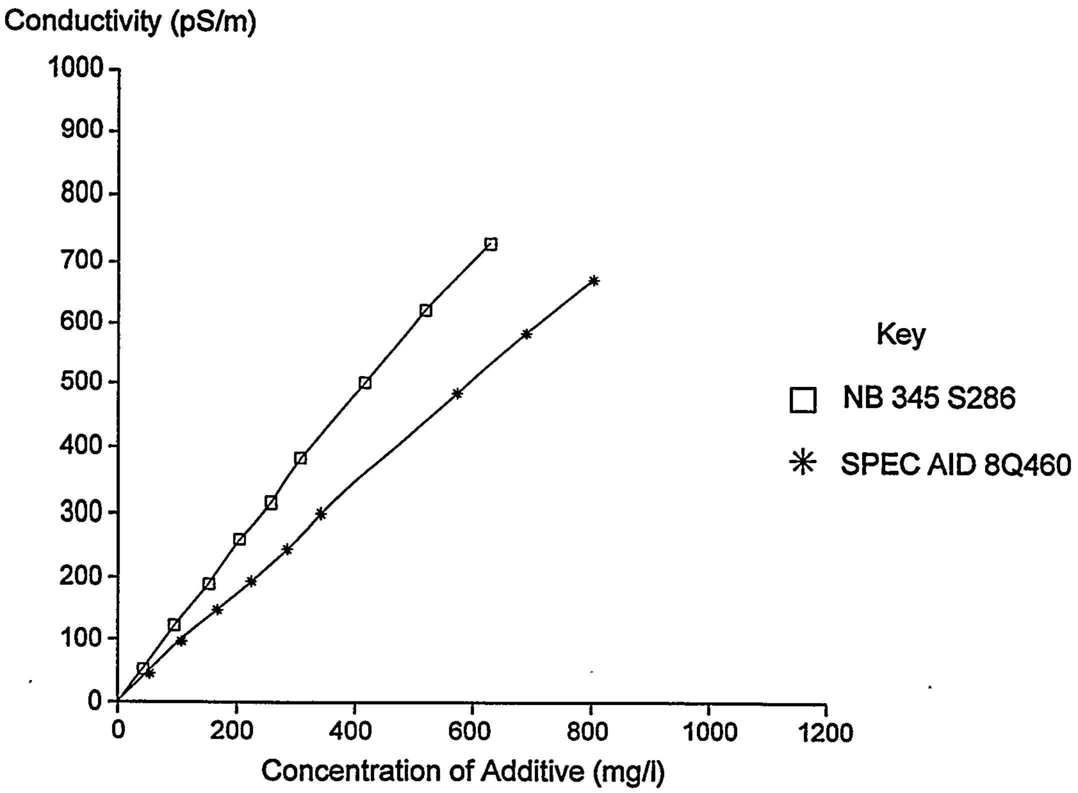

Fig. 1 Conductivity vs. Concentration for High Temperature Additive Packages in Dodecane

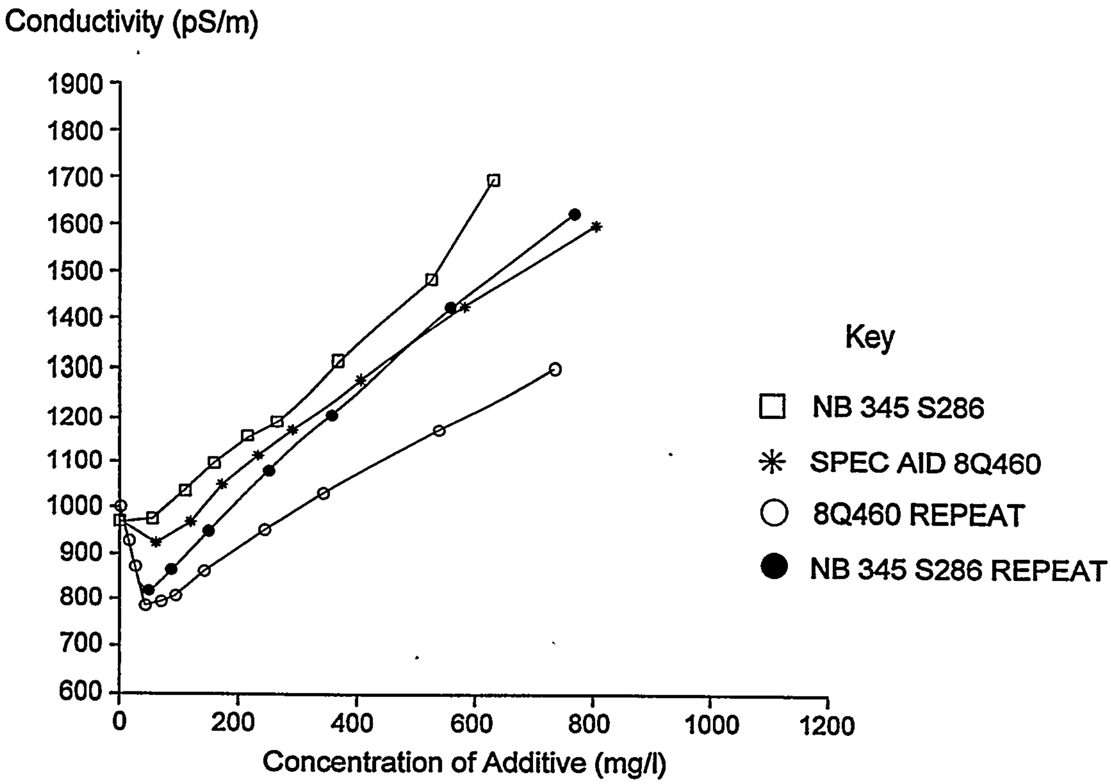

Fig. 2 Effect of High Temperature Additive Packages on Conductivity of 3mg/l STADIS 450 in Dodecane

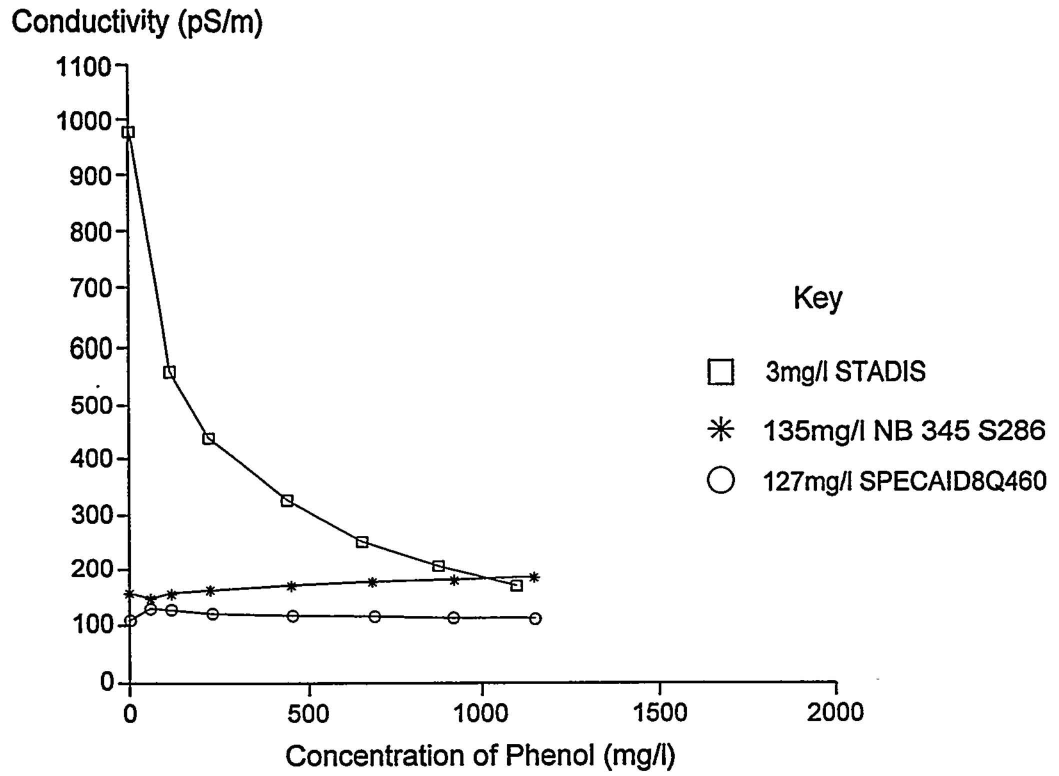

Fig. 3 ffect of m-Cresol on Conductivity of Stadis 450 and High Temperature Additive Packages in Dodecane

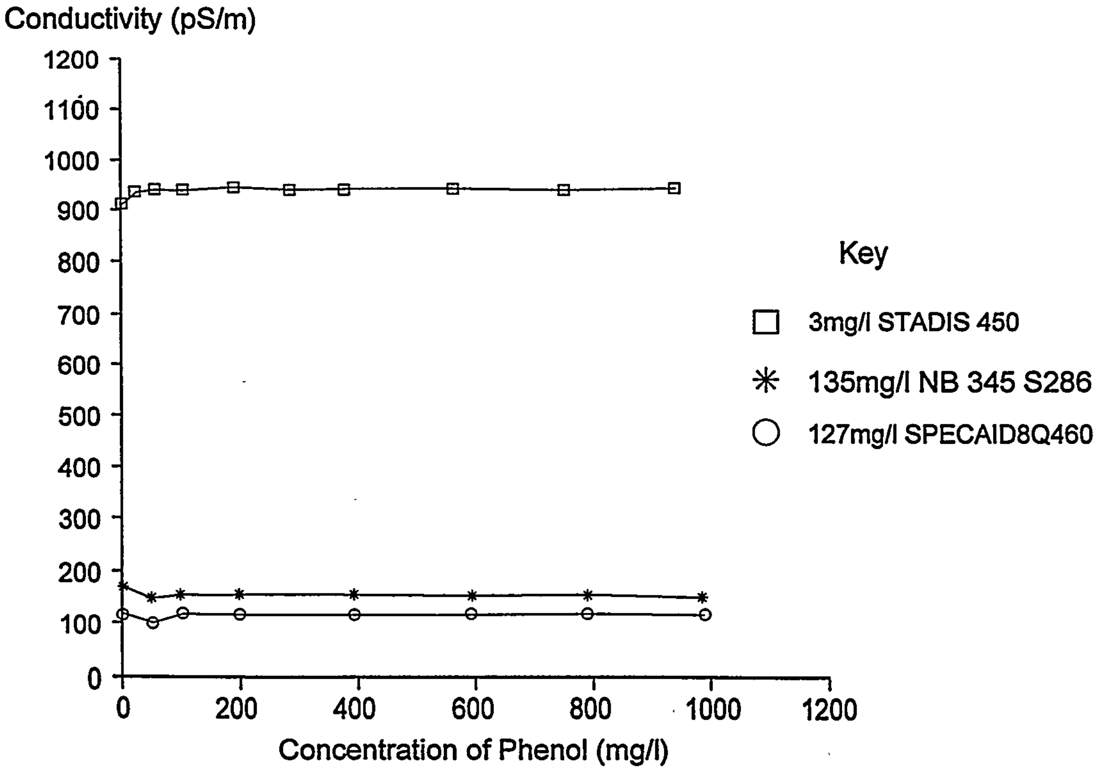

Fig. 4 Effect of 2,6di(tert)butyl-4-methylphenol on Conductivity of Stadis 450 and High Temperature Additive Packages in Dodecane

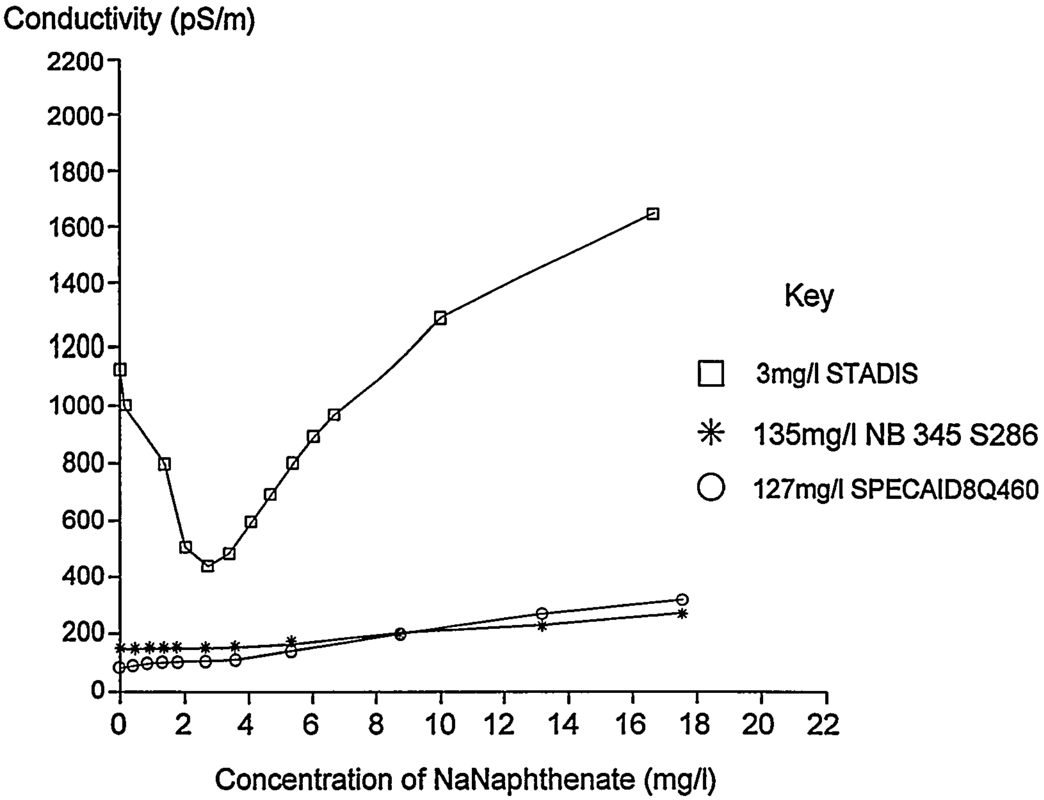

Fig. 5 Effect of Sodium Naphthenate on Conductivity of Stadis 450 and High Temperature Additive Packages in Dodecane

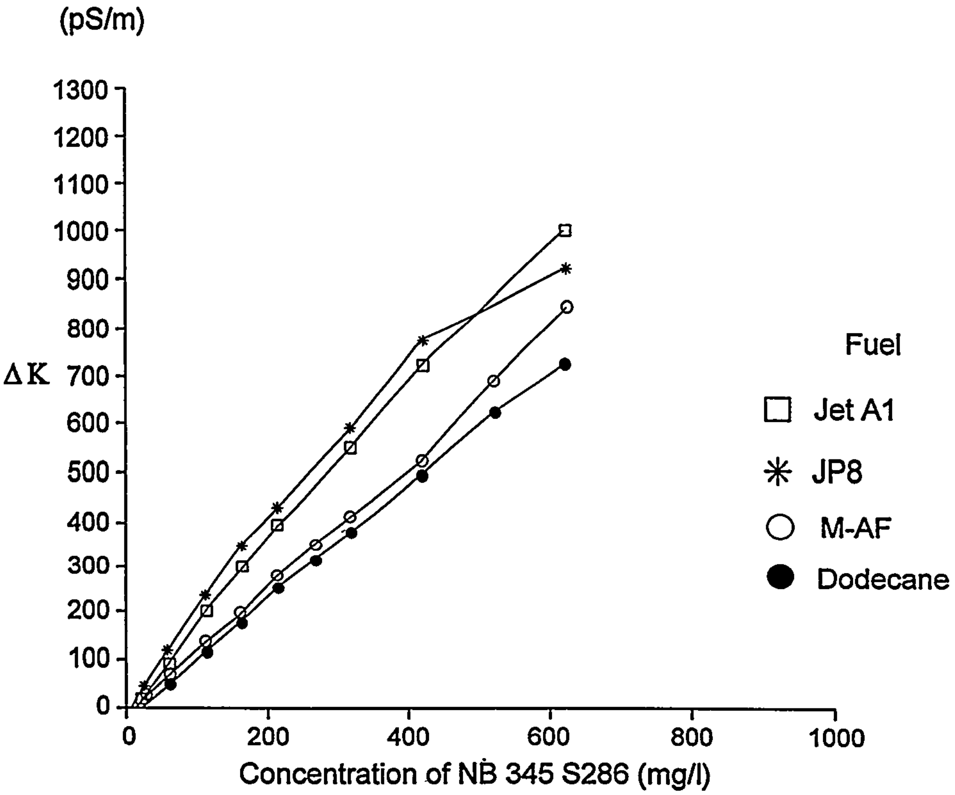

Fig. 6 Effect of NB 345 S286 on the Conductivity of HITTS Fuels

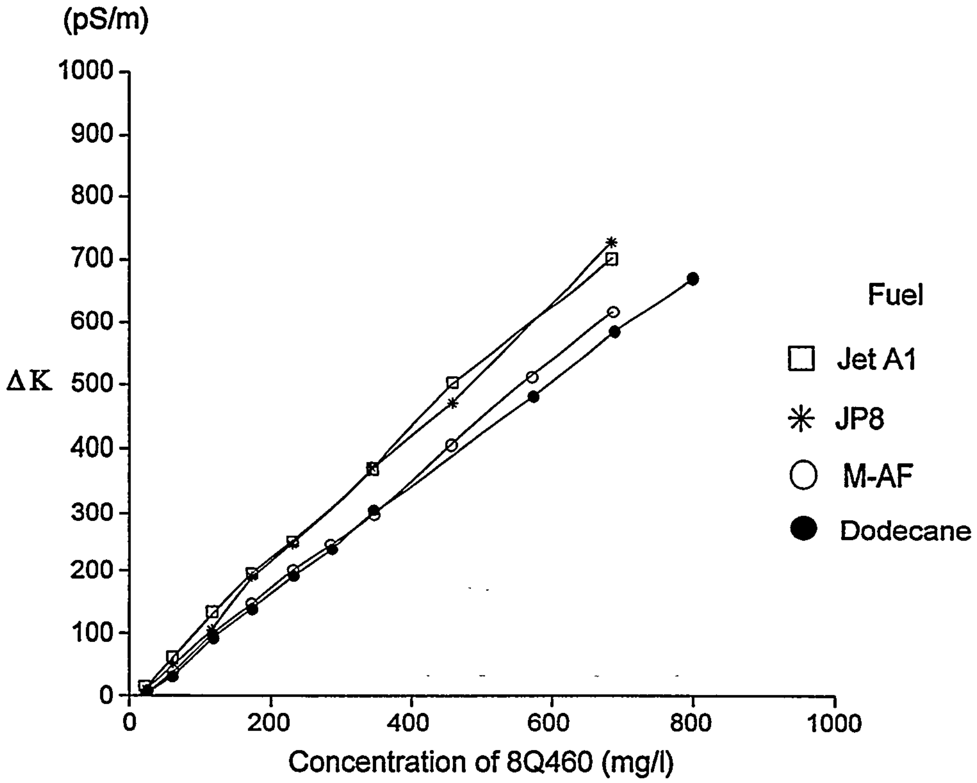

Fig. 7 Effect of 8Q460 on the Conductivity of HITTS Fuels

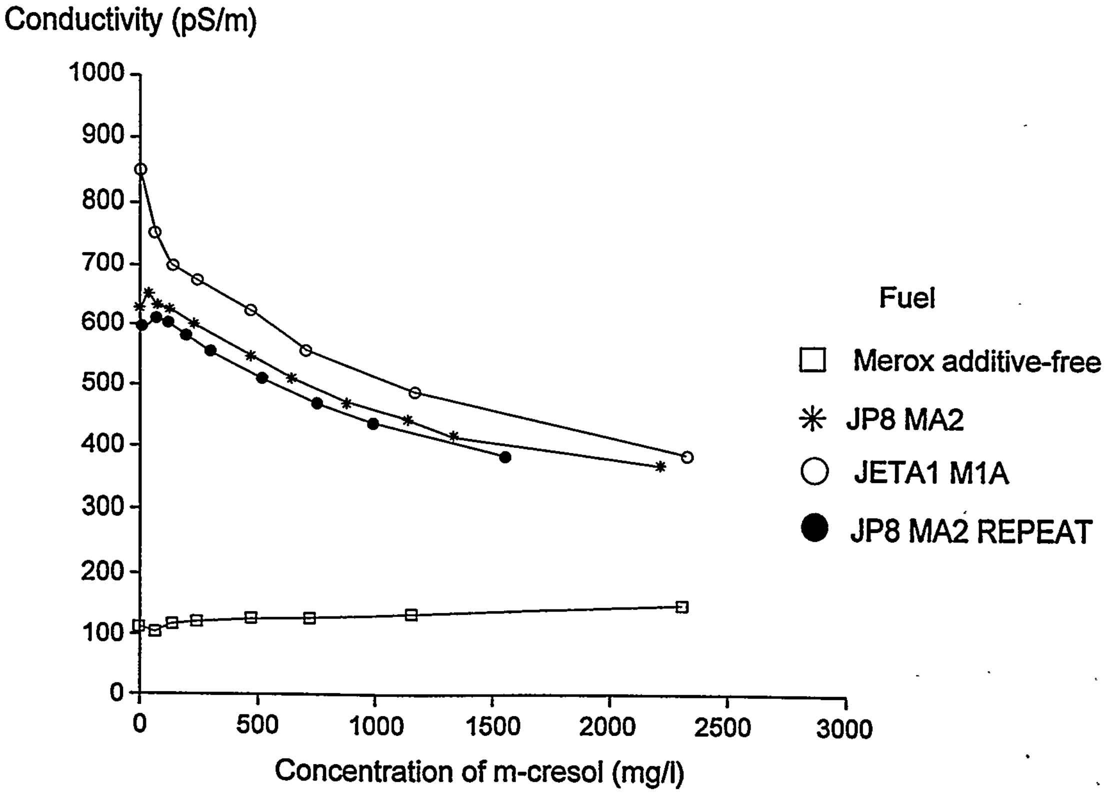

Fig. 8 Effect of m-cresol on Conductivity of 127 mg/l SPECAID 8Q460 in HITTS Fuels

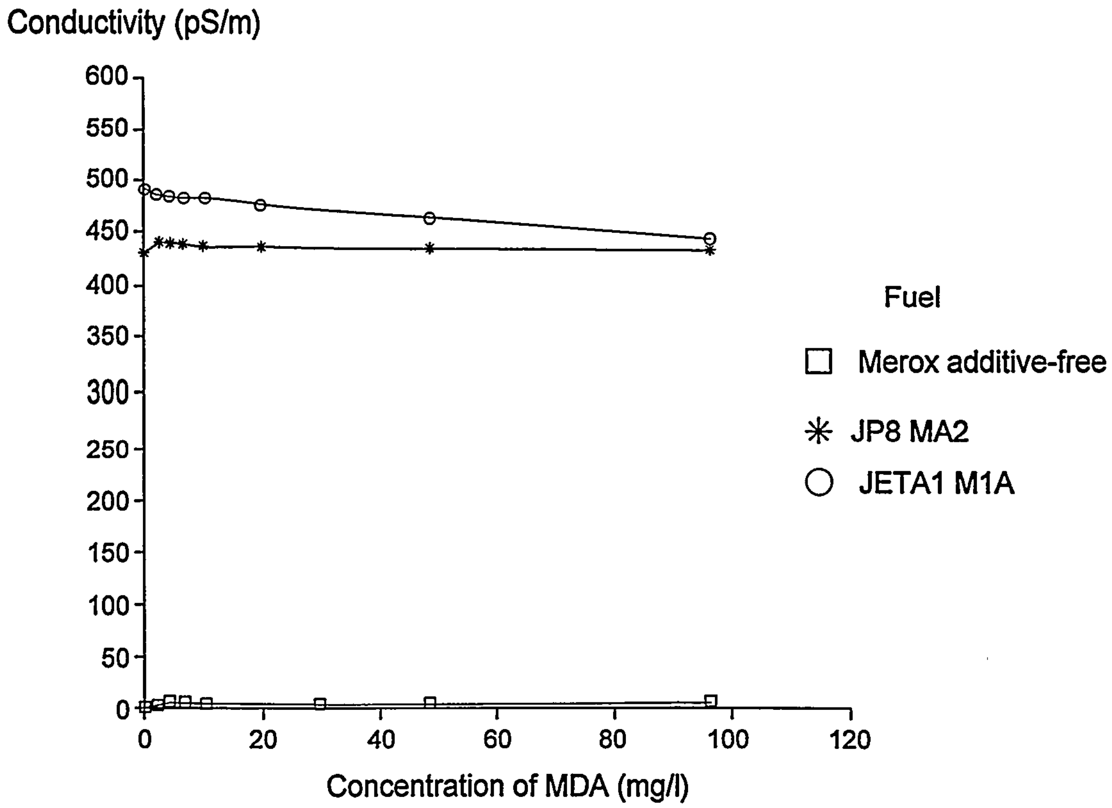

Fig. 9 Effect of MDA (conventional) on Conductivity of HITTS Fuels

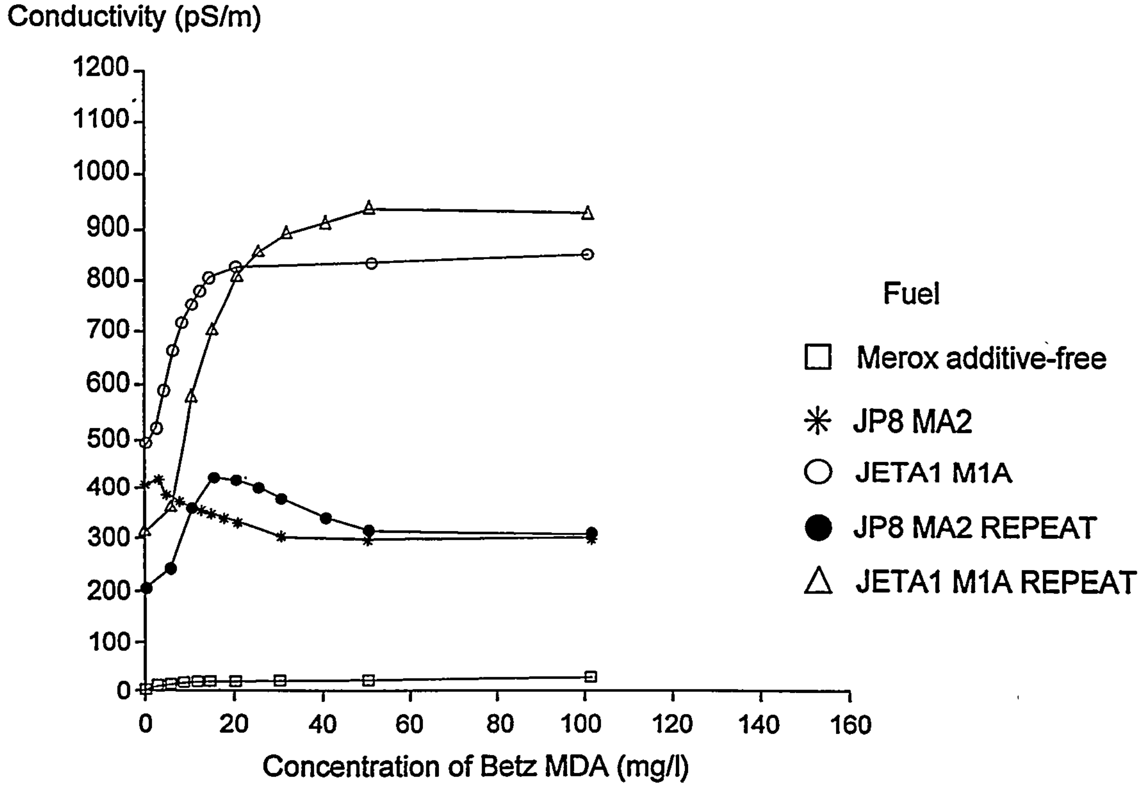

Fig. 10 Effect of Betz MDA on Conductivity of HITTS Fuels

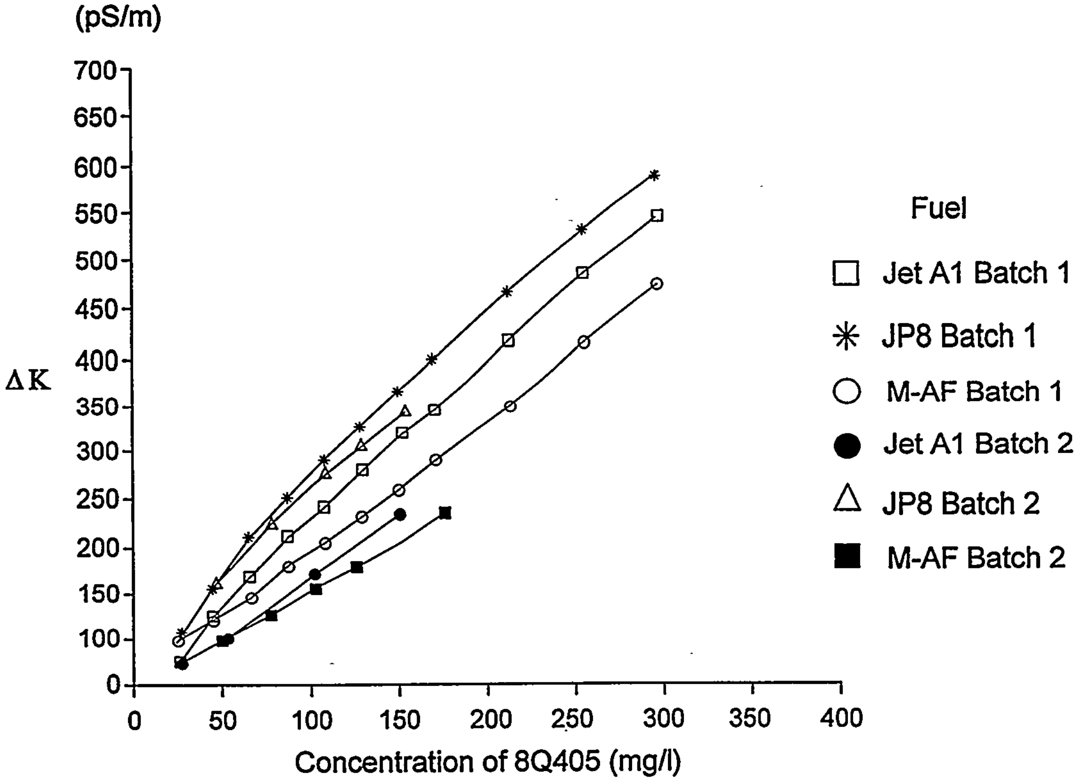

Fig. 11 Effect of 8Q405 and Batch Variation on the Conductivity of HITTS Fuels

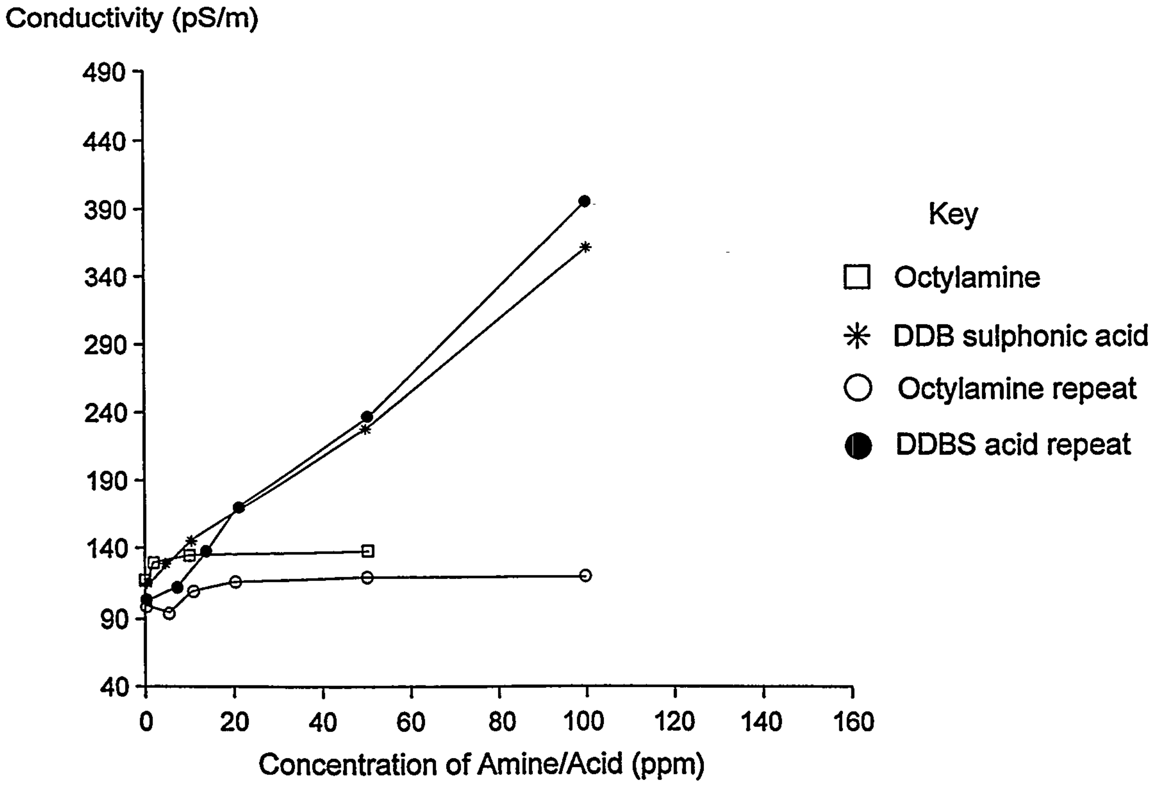

Fig. 12 Betz Dispersant 8Q405(Batch 2) 100mg/l in HITTS Additive-free Merox Effect of Acid or Amine on Conductivity

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# TESTING JP-8+100 PACKAGES IN EUROPEAN JET FUELS - EVALUATING AND UNDERSTANDING BENEFITS AND DRAWBACKS

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The UK's Ministry of Defence (MoD) has instigated a European extension of the JP-8+100 programme, testing front-runner USAF additive packages and other additives from UK companies in European-sourced jet fuels. Shell Research Ltd have provided Jet A-1 fuels and upgraded them to military specifications (JP-8 = NATO F-34) by the use of fuel system icing inhibitor and corrosion inhibitor/lubricity improver (CI/LI) additives. Fundamental, analytical, small-scale and large-scale rig tests have been used to examine how and if the additives improve thermal stability performance. A Flask Oxidation Test investigates the first stages of fuel oxidation and indicates that none of the additives has a significant impact on this step. Later stages in the fuel degradation are affected as evidenced by higher JFTOT breakpoints, lower levels of deposit in a carbon burn-off version of the JFTOT, and lower levels of deposition in Shell's new HiReTS (High Reynolds number Thermal Stability) rig. Fuels containing both CI/LI and JP-8+100 additives produce the greatest apparent improvements in thermal stability performance. Other performance characteristics have been tested in parallel: lubricity, handling (e.g. water shedding), low temperature and storage stability. CI/LI additives alone improve fuel lubricity (JP-8 better than Jet A-1) but lead to a drop in handling performance. None of the JP-8+100 additives significantly affects lubricity performance but results for water shedding tests are further worsened. Low temperature behaviour is insensitive to the presence of the additives while accelerated storage tests indicate that the JP-8+100 additivated fuels produce higher levels of gums than the base fuels.

## INTRODUCTION

The United States Air Force and its collaborators have established that the thermal stability performance of military jet fuels can be improved by using additive packages. Many papers and presentations have been made in the last six years, for instance, at the last conference in this series[1]. In the UK, the Ministry of Defence (MoD) has instigated a European extension of USAF's JP-8+100 programme, managed by the Defence Evaluation & Research Agency (DERA), Pyestock. Additives have been tested in fuels, produced from a different slate of crudes to those used in North America, and which are supplied as Jet A-1 to DEF STAN 91-91 specification (or to the AFQRJOS "Checklist"). Such fuels must contain a static dissipator additive (SDA) and, if hydroprocessed, an antioxidant (AO).

Testing "same batch" additives in a common set of fuels is allowing MoD-sponsored companies to maximise the read across between experimental results. Experiments range from small-scale fundamental tests to specification tests to large-scale rig operations. Various in-house methods have been used thereby providing new insights into how and if particular additives affect performance. Shell Research Ltd have been concentrating on small-scale tests covering not only thermal stability performance but also side-effects and storage stability evaluations. The performances of Jet A-1 and JP-8 fuels with additive packages or single components are now compared with those of the baseline fuels.

## EXPERIMENTAL

**Reagents.** Large volumes of three fuels have been procured for the MoD programme: JPTS (provided by USAF via RAF Killingholme); a deliberately marginal thermal stability Merox base fuel (AT); and a hydroprocessed Jet A-1 (HT-1A). JPTS is the "target" fuel whose thermal stability performance JP-8+100 fuels are intended to approach. Two tanks of AT have been upgraded to Jet A-1 (M-1A), by the addition of 2 mg/L of new formulation Stadis 450 static dissipator, the dosage level having been advised by S.D. Anderson of USAF Dayton. Table 1 lists additives and additive packages used to upgrade or modify the fuels. It includes mandatory and JP-8+100 performance and component additives such as DMD-2, a 50% active matter metal deactivator additive (MDA). Samples of both Jet A-1 fuels, in 200-litre epoxy-lined steel drums, have been further upgraded to JP-8 fuels by the addition of mandatory fuel system icing inhibitor (FSII) and corrosion inhibitor/lubricity improver (CI/LI) additives (Table 1). Originally this conversion was achieved by adding AL-48 to the Jet A-1 but the concentration chosen led to 20% overdosing of the CI/LI component so all subsequent blends have been made by adding FSII and CI/LI separately. Unless otherwise indicated non-mandatory and "performance" additives have been doped singly or as packages directly into 25 to 50L batches of Jet A-1 and JP-8 fuels at the levels indicated in Table 1. (Most of the work relates to fuels treated with some or all of the components of the Betz Spec Aid 8Q462 package that has formed the basis of most JP-8+100 field trials by USAF.) BHT blends have been prepared by first dissolving the BHT powder in a small portion of fuel before making up to the final volume. M-1A has also been used to prepare a 200L stock of 2 mg/L active matter MDA, WF, to match the 8Q462 concentration of MDA. Aliquots of this stock have been diluted to produce the 25L blends WG and WH described in Table 4. BP have supplied four fuels (based on AT) that they have doped with their candidate additives A to D.

**Apparatus and Procedures.** Four classes of tests have been performed on the fuels: Certificate of Quality, CoQ, or specification tests; industry standard tests not required by specifications; non-industry tests using specification apparatus in non-standard modes; in-house (IH) analytical or "rig" tests using non-specification apparatus. All CoQ tests are performed according to the ASTM and/or IP methods required by, e.g. DEF STAN 91-91 Issues 1 & 2. Most industry tests are performed according to the indicated ASTM or IP method. Particulate contaminants have been measured using a modified version of ASTM D2276/IP 216; only 1L of fuel is filtered through a 0.22 μm filter. Low temperature flow properties have been measured by an in-house variant upon ASTM D 4305-83 that uses a Mark I Setapoint apparatus modified to automate some of the heating and cooling stages.

*Analytical.* Copper and iron contents of fuels have been measured by an in-house quantitative ICP-MS method which compares signals with those from a standard solution of the two metals in metal-free Jet A-1. Other metal contents are measured using a semi-quantitative ICP-MS method which relies on a S21 Conostan mixed element standard diluent doped into Jet A-1. This gives approximate elemental concentrations in the sample to within a factor of three of the true value but results are only reported if the isotope signals are significantly above fluctuations on a blank solution.

*Thermal stability.* Two more quantitative versions of the JFTOT test have been performed using standard model 203 or 240 apparatus. JFTOT breakpoint has been established by identifying, to the nearest 5°C, the highest temperature at which the fuel still passes the rating and pressure drop restrictions of ASTM D3241/IP 323. The JFTOT carbon burn-off (CBO) method uses stainless steel test pieces and operates the JFTOT at 350°C. A Leco analyser measures the carbon content of the resultant deposit. A flask oxidation test[2] has been used to investigate the very early stages of fuel degradation that precede deposit formation. Oxygen uptake is measured as air is passed through samples held at 160°C, and the oxidation rate versus time profile allows induction periods and/or radical initiation rates to be calculated. A new apparatus, the High Reynolds number Thermal Stability rig, HiReTS,[3] (or its laboratory forerunner, the Capillary JFTOT (C-JFTOT)) has been used to measure the amount of deposit formed under turbulent flow conditions. Standard two hour tests have been performed, with a 290°C fuel outlet temperature condition. Quoted HiReTS (or C-JFTOT) numbers and, where appropriate, end-of-test carbon weights in the capillary test pieces refer to averages of duplicate determinations unless otherwise indicated. (C-JFTOT numbers can be compared from table to table, but at this stage, it is only appropriate to compare HiReTS results obtained in a restricted series of tests, invariably displayed in a single Table.)

*Lubricity and water shedding tests.* The Thornton Aviation Fuel Lubricity Evaluator (TAFLE) establishes the highest load a fuel can bear before a cylinder-on-cylinder contact starts to break down because of scuffing wear. The rig operates in a one-pass mode and measures the friction and wear generated as contacts are made with progressively higher loads between two different hardness EN31b steel discs, one fixed and one rotating. Unless indicated otherwise, TAFLE loads are the average of duplicate determinations. WASP, an in-house test[4], involves preparing a fine 1000 ppm water-in-fuel emulsion then measuring the water content at a fixed depth after a 45 minute settling period. The lower the water content the better the water shedding properties, and experience shows the fuel is less likely to cause problems such as coalescer disarming.

*Storage stability.* Two 5L portions of each fuel have been stored in epoxy-lined cans in a thermostatically controlled cabinet held at 45°C to accelerate processes that might occur in sample storage at ambient conditions. Cans have been removed after 6 or 12 weeks of storage and certain small-scale (CoQ, analytical and rig) tests have been repeated to check for product degradation. (These conditions are not as severe as those required for the JPTS specification, MIL-T-25524D.) Where a particular fuel has been stored in more than one large tank, samples from each have been taken for storage tests.

## RESULTS

**JPTS**. CoQ tests have confirmed that the JPTS sample meets MIL-T-24424D. Its freeze point is -63.5°C, well within the specification. Several properties have changed slightly after storage: Saybolt colour, total acidity and the level of filterable particulates. Its behaviour in non-standard tests is summarised in Table 2. Poor WASP and MSEP test results are consistent with the high levels of surfactant additives in the fuel and which are at least partially responsible for the excellent thermal stability performance. The flask oxidation test induction period is about twice the length observed for normal hydrotreated fuels indicating excellent resistance to the first stages of oxidation. Those tests that look at the later stages of degradation, when deposits are laid down, show the fuel to be very stable. Whether this is wholly because of reduced radical initiation rates or whether it is because the additives prevent adhesion of fuel deposits (in the bulk or on surfaces) is not clear. Figure 1 shows a trace for JPTS in the laboratory C-JFTOT apparatus; with the standard operating conditions, the result is at the lower limit of deposit detection.

**Merox Jet A-1**. Table 3 records key CoQ and other test results for the base fuel, AT, and the Jet A-1 produced from it, M-1A. AT meets the Jet A-1 specification except in the area of conductivity; there had not been any SDA addition to this moderately high sulphur content fuel at the refinery. It is borderline on flash point and smoke point performance, with quite low IBP and FBP. Metals contents, except lead, are fairly insignificant. M-1A, with SDA, passes the conductivity requirements of DEF STAN 91-91 but its water shedding properties have degraded; the fuel would be expected to have borderline handling properties. The first breakpoint measured for AT was 270°C. Breakpoints measured for M-1A started at a similar level but, as with those for AT, have degraded over time; samples now give results of 260±5°C. A TAFLE failure load of 102.5 kg for AT is very good, consistent with the fuel's moderately high total sulphur content though perhaps better than one might first have anticipated from its BOCLE result. Previous work at Thornton, however, has shown that scuffing resistances of high sulphur fuels are underestimated by the BOCLE which operates under a different, milder wear regime.

*Approved additives (WF, WG, WH & WI).* Fuels have been tested that just contain MDA or BHT, two already approved components in the USAF front-runner 8Q462 package. MDA is an additive with a reputation for "fooling" the JFTOT$^5$. BHT would normally only be added to hydroprocessed fuel on run down at the refinery, to provide antioxidancy at ambient temperatures. Preliminary results are in Table 4 as are results for the base fuel, M-1A, retested in parallel. Few of the simple analytical tests show any significant change upon the additivation and none of the additives affect BOCLE performance. Thermal stability tests do respond to the additives, though differently. HiReTS numbers for WF and WI are only slightly lower than those for M-1A. By contrast, the JFTOT breakpoint for WF is at least 340°C.

*Jet A-1+100 (VX, VY and WW).* M-1A (not from same tank as above) has been doped with 8Q405 and 8Q406 to produce fuels VX and VY, respectively. WW has been produced by doping another M-1A tank sample with the "full" 8Q462 package. Table 5 lists the current status of analytical and small-scale tests. BOCLE results for these three fuels and M-1A are not significantly different. Additivation notably worsens performances in the handling tests - MSEP, WASP and water reaction - consistent with the presence of the dispersant/detergent additive that makes up 8Q405. Conductivities of all three fuels exceed the limits for Jet A-1. All three additives or packages also produce significant (approximately 30°C) rises in JFTOT breakpoint; the presence of antioxidant in VY has not produced any further improvement over the performance of VX but MDA in WW provides a 5°C increase. The appropriate M-1A was tested in the HiReTS before and after the two additivated fuels; before, the average HiReTS result was 840 while a single run at the end of the series gave a result of 621. Results for VX and VY are very low, at the limit of detection of the apparatus, suggesting excellent thermal stability improvements have been achieved. Storage stability results for VX, VY and M-1A are in Table 6 and show that the fuels have deteriorated slightly with respect to Saybolt colour and MSEP (albeit that this last test is of dubious worth for additivated fuels). Conductivities have decreased in every case, more markedly for the base fuel than the additivated ones, and now all are within Jet A-1 specification limits. WASP ratings and water reaction test results for VX and VY have remained bad, and existent gum levels have worsened. None of the fuels have deteriorated in JFTOT or corrosion tests.

**Merox JP-8 (M-2A).** Table 3 includes test results for an early (i.e. CI/LI overdosed) batch of M-2A. Compared with the base and Jet A-1 fuels there are slight increases in thermal stability performance and a worsening with respect to existent gum, total acidity and water shedding properties. These changes and the improved lubricity (BOCLE) performance are directly ascribable to the addition of the acidic CI/LI component which is a surfactant designed to adsorb onto metal surfaces. The first flask oxidation test result for M-2A indicated that the radical initiation rate for JP-8 was lower than for the base fuel, AT. A second FOT result, about a year later, was greater for M-2A than for AT. The later result indicates fuel deterioration has taken place and/or that the original difference in radical initiation rate was not significant. M-2A has a breakpoint 5°C higher than that first measured for AT and M-1A; bigger differences are apparent in the C-JFTOT. AT has a single test result of 1040 while the average result for M-2A is 434. Figure 2 shows one of the C-JFTOT traces for M-2A.

*JP-8+100 (VO and M-4A).* Table 7 lists test results for the CI/LI overdosed JP-8 doped with 8Q405 and 8Q406. MSEP, WASP and water reaction results are very bad for both fuels, again consistent with the presence of a highly surface active dispersant/detergent additive. As expected from work at Thornton and elsewhere[6] the additives further boost the fuel conductivities, in this case above the Jet A-1 maximum limit of 450 pS/m; one of the VO results would also fail the F-34 (JP-8) specification[7] limit of 600 pS/m maximum.

Flask oxidation test results for the two fuels are similar, and only slightly lower than the latest result for JP-8, suggesting that the additives have no significant impact on the early stages of fuel oxidation. Breakpoints for both fuels, however, are significantly increased over the JP-8 result of 275°C. M-4A shows a further dramatic improvement in C-JFTOT number over that seen for M-2A (Figure 3), with the average C-JFTOT number being very similar to that obtained for JPTS. CBO deposit weights are much lower for these fuels than for the JP-8; differences between the results for VO and M-4A are not very large. These suggest that the apparent thermal stability improvements are achieved mainly by dispersant/detergent action and not by antioxidant action.

Lubricity results for VO and M-4A are similar but may just be significantly different from the JP-8 BOCLE result of 0.53 mm. There may be some interaction in the bulk fuel or at the metal surface between the dispersant/detergent and the CI/LI or the results may be an indication of the BOCLE's sometimes dubious response to additives. Storage stability tests have been completed for a new, second batch of JP-8 fuels, with and without Betz additives (Table 8). Saybolt colour and conductivity results have changed for the JP-8 but all fuel handling related test results have stayed similar, all pointing towards a fuel with high surfactant content and poor water shedding properties. Corrosion and thermal stability test results have remained satisfactory. VO and M-4A have shown less dramatic decreases in Saybolt colour and have slightly higher existent gum levels than M-2A.

**Hydrotreated Jet A-1.** CoQ, simple analytical test results and additive details for a sample from one of the three HT-1A tanks are in Table 9. These data show that the fuel meets all specification requirements for Jet A-1, with freeze point close to the maximum acceptable value. Table 9 also includes JFTOT breakpoint values, metals contents and WASP results. Breakpoints have varied slightly from tank to tank (results are shown for all three tanks in this case) and are at the low end for hydrotreated fuels. They still indicate a more thermally stable fuel than the Merox fuel in the programme. All UK participants have noted problems in rating the JFTOT tubes for this fuel and some derived from it; unusual white deposits have been observed. Oxidation rate profiles in the flask oxidation test have also been unlike those seen for most hydroprocessed fuels. After an induction period, the oxidation rate increases (as normal) but then falls again suggesting that the system has produced its own antioxidancy. (This may or may not have some link to the odd JFTOT deposits and rising breakpoints, and to the fuel's relatively high sulphur content compared with previous samples from the same refinery). The behaviour warrants investigation, but in the meantime the traces have been analysed according to normal rules for hydroprocessed fuels: induction times have been measured and radical initiation rates have then been calculated given known antioxidant dose rates. The radical initiation rates are about an order of magnitude lower than those for the Merox fuels, consistent with the better JFTOT performance of HT-1A. HT-1A also produces much lower levels of deposit in the HiReTS; Figure 4 provides an example of a typical trace. The fuel does not deteriorate significantly in 12 weeks of accelerated storage, indicating that the mandatory antioxidant has been effective. WASP ratings for HT-1A are moderate rather than good; the fuels are not excellent water shedders but one would not anticipate undue handling problems with them. MSEP values, though not required because of the added SDA, are satisfactory. BOCLE results for the two samples taken are similar to those of the Merox base and Jet A-1 fuels and, taken on their own, do not indicate that any lubricity problems should be experienced. The TAFLE results, however, show the fuels to have considerably less lubricity than the Merox fuels.

*Jet A-1+100 (VT and VU).* Table 9 shows small-scale and storage stability test results for fuels derived from one of the HT-1A tanks. Rig tests show that the performance additives have no significant impact on lubricity performance. JFTOT breakpoints have improved by 20 to 25°C on the Jet A-1, and limited HiReTS test results show the additives give about half as much deposit as HT-1A (see Figure 5). Neither test shows a significant difference between the 8Q405 and 8Q406 packages. CBO deposit weights for VT fuels are, if anything, greater than a Jet A-1 result of 38 μg; maybe at 350°C the deposit is a combination of fuel and additive. After storage, changes in Saybolt colour, acidity, JFTOT and peroxide number are small. All fuels still produce poor MSEP and water reaction test results. WASP results have improved numerically (though not significantly) but still show all the fuels to have poor handling characteristics. All have acceptable thermal stability and conductivity performance, though the latter test values have decreased.

*JP-8 (HT-2A).* HT-2A has a breakpoint significantly higher than that of the Jet A-1, and higher than that achieved by using Betz additives; see Table 10. The impact of CI/LI additive is also shown by the higher total acidity and improved BOCLE performance; the fuel has marginally worse lubricity performance than the CI/LI overdosed Merox-based JP-8 but both results are still "good". A single TAFLE result confirms the improvement in fuel lubricity. The WASP result is worse than that for the Jet A-1 and indicates a fuel of borderline handling properties. Conductivity is well within specification. Storage stability results for the JP-8 are given in Table 11. MSEP and WASP ratings worsen, though water reaction results remain unchanged. Black fibres (not analysed) have been seen in the aged product, consistent with the unusually high levels of filterable deposits.

*JP-8+100 (VZ and WA).* Most tests results for the two additivated JP-8s are different from those for the JP-8 (Table 10). Existent gum levels are higher, WASP and MSEP ratings are worse, and both fuels exhibit increased conductivity. Breakpoints are significantly higher than those for the JP-8, and are higher than for the additivated Jet A-1s and corresponding

Merox-based fuels. HiReTS test numbers show a small reduction with the additives but the differences are probably not significant for these already thermally stable fuels. The same is true for the BOCLE results for the additivated fuels; all give good performances. Storage stability test data in Tables 11 show few significant changes for the additivated fuels. Saybolt numbers appear to cycle with time. Water reaction test results worsen, with no clear trend for the already poor MSEP and WASP performances of the two fuels.

**Assessment of BP candidate additives.** Small samples of Merox base fuel, M-1A, additivated with candidate BP additives A to D have been tested as a small suite in the HiReTS production prototype unit 1. A sample of M-1A fuel was also included in the test suite; it has given borderline performance in the JFTOT (260°C breakpoint at best). There was insufficient fuel to perform other tests. Results from duplicate tests are summarised in Table 12, and Figures 6 and 7 are examples of the HiReTS profiles. One test ended prematurely so the result for additive C is not the average of duplicate tests. All four candidates produce very significant improvements in the thermal stability of the Merox fuel. The HiReTS repeatability at these levels means, however, means that the additives cannot be considered as having significantly different thermal stability improving properties.

## DISCUSSION

The two base fuels chosen for the programme have considerably less thermal stability than the target JPTS, and are amenable to showing thermal stability improvements produced by additives. The Merox fuel has been consistently less stable than the hydrotreated fuel. Thermal stabilities and lubricities of both improve in at least one test just with the addition of JP-8 packages though these same packages then worsen fuel handling properties; this is not surprising since CI/LI additives are strong surfactants. Addition of Betz additives to the Jet A-1 and JP-8 fuels improves thermal stability and tends to further worsen handling properties; the dispersant/detergent component is the most potent component in this respect. BHT and MDA additions make, at best, small improvements in thermal stability and none of the additivated fuels match the JPTS fuel in terms of JFTOT performance.

A full suite of fuels have yet to be tested in all the pertinent rigs, and new types of performance additives are currently being tested. Nevertheless, some trends or features are clear and findings can be carried forward. Certain CoQ categories are unaffected by the presence of the additives. None has yet affected corrosion, combustion or volatility properties. Likewise, none of additives tested has affected the low temperature performance features - low temperature viscosity, freeze point, Setapoint flow temperatures - of the Jet A-1 or JP-8 into which they are doped. This means that most JP-8+100 fuels will not match the low temperature performance of JPTS, for which maximum freeze point requirement is -53°C, 6°C lower than Jet A-1 specifications demand. If JPTS-like low temperature performance is needed for a particular application, the operator either will have to use JPTS or will have to specially procure lower freeze point Jet A-1/JP-8 fuels. Only fuels derived from naphthenic crudes or produced by hydrocracking are likely to meet these criteria. Storage stability tests have not identified any unexpected or particularly worrying or trends; handling properties have tended to worsen and the additive packages have not obviously slowed down fuel degradation processes.

Conductivity data for the additivated Merox fuels may be misleading. The performance additives (directly or indirectly) boost the conductivities significantly, to above specification levels. The Jet A-1 already had a high conductivity because of the high SDA dope rate; refinery dope rates are typically 1 to 1.5 mg/L SDA and the performance additives might not cause failures if added to a Jet A-1 with an optimised SDA dosage. Corresponding hydrotreated fuels, with 1.0 mg/L of SDA, do not give such high conductivities and the Jet A-1 has a higher conductivity than the JP-8, the reverse of the Merox fuel cases. This may be because of the lower additive levels or because the old Stadis 450 and the CI/LI may have interacted in a different manner in the hydrotreated JP-8 to that seen between the new Stadis 450 and CI/LI combination in the Merox JP-8. There may be some interesting fuel:additive, CI/LI:additive, SDA:CI/LI:additive combinations to investigate in more detail. Conductivity and lubricity studies could be performed in parallel; lubricity data do not yet show signs of any significant synergies or antagonisms between the components. None of the Betz additives provide Merox or hydrotreated Jet A-1 with a boost in lubricity performance or significantly degrade the performance of the JP-8 fuels. This suggests that the CI/LI additives are more strongly adsorbed to the metal surfaces than the Betz additives over the range of temperatures experienced in the BOCLE's ball-on-cylinder contact zone. BOCLE data have yet to be obtained for Jet A-1 or JP-8 with MDA in the full 8Q462 package to see if MDA might be another additive that can affect lubricity performance. The mean wear scar diameter of 0.66 mm for JPTS, while good, is higher than one might have anticipated for a fuel with mandatory CI/LI additives. This may indicate some interaction between the many additives in JPTS which include the multi-component JFA-5 additive, which itself contains MDA.

Only in the area of prime interest, thermal stability, are there any large issues to be sorted out. The HiReTS rig, operated in its standard format, certainly appears to differentiate between fuels of different thermal stability. (Without longer time data, it is not possible to establish whether the system may have been fooled by CI/LI and other additives, i.e. whether effects are only short-lived.) As performances improve, the scope for differentiation becomes smaller; the deposits approach the IR camera's limit of detection of temperature changes. Used with a poor fuel, the HiReTS can certainly identify additives which can improve other fuels' performances. The protocol should probably be altered to produce a more severe test if it is to rank performances of "good" additives, e.g. to differentiate between the various BP additives or to compare the BP additives with the Betz packages.

In its standard mode, the HiReTS rig has been a good predictor of at least one large rig simulator. Some of the additivated systems are now starting to be ranked differently in the

HiReTS to the way the JFTOT tests would rank them. Planned large-scale rig tests may clarify why this is happening but in the short term it suggests that traditional measurements of thermal stability should be treated with caution when additives are introduced into fuels. One case to illustrate the problem is the work with MDA-doped M-1A which, though not yet complete, shows that 2 mg/L MDA significantly improves JFTOT breakpoint whereas the HiReTS result is only marginally improved. The effect of the same level of MDA in the full 8Q462 package in the same Jet A-1 is nowhere near as dramatic - the breakpoint is 295° rather than >340°C. Has the HiReTS been responding, correctly, just to a slightly reduced radical initiation rate caused by the chelation of low levels of copper and iron in the fuel while the JFTOT test piece responds to differing levels of MDA adsorption from the two fuels?

Discussions with USAF and other MoD-sponsored companies suggest that the bulk of the findings of the Shell work do not contradict results obtained with other rigs and fuels. There are fuel-to-fuel variations in the performances of additivated fuels, and fuel handling properties are invariably degraded as thermal stability properties are improved. If the differences and new findings in this report can be resolved, real progress will have been made.

## ACKNOWLEDGEMENTS

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## TABLE 1 - Additives for HiTTS/JP-8 programme and Fuels containing them

| *Additive name (type)* | *Type* | *Dope rate* | *Main blends:* |
|---|---|---|---|
| "New" Stadis 450 | SDA | 2 mg/L | M-1A (& VX,VY,WW,WF, WG,WH,WI) and M-2A (& VO,M-4A) |
| AL-48 Type 6 (see DEF STAN 68-150/Issue 1) | FSII + CI/LI (Nalco 5403) | 0.13%vol | M-2A, 1st blends (& VO,M-4A 1st blends) |
| AL-41 (NATO code S-1745) (see (Interim) DEF STAN 68-252/Issue 1)<br>Nalco 5403 | FSII<br>CI/LI | 0.13% vol<br>22.5 mg/L | M-2A, 2nd blends (& VO,M-4A 2nd blends); HT-2A (& VZ,WA) |
| DMD-2 (50% Active matter) | MDA | 2 mg/L max, AM (see Table 4) | WF, WG, WH |
| BHT = 2,6-di-tert-butyl-p-cresol | AO | 25 mg/L | WI |
| Betz Spec Aid 8Q405 | "Dispersant/detergent" | 100 mg/L | VX, VO, VT, VZ |
| Betz Spec Aid 8Q406 = 8Q405 + BHT | Disp/det + AO | 125 mg/L | VY, M-4A, VU,WA |
| Betz Spec Aid 8Q462 | (Disp/det + AO + MDA) + Aromatic solvent = 1:1 | 254 mg/L | WW |

## TABLE 2 - In-house tests on JPTS[1]

| *Specification Description* | *Method* | *Units* | *Value* |
|---|---|---|---|
| **CONTAMINANTS** | | | |
| WASP rating | SMS 2772 | (mg/kg) | 1080 |
| Metals | PT/71:GM08 | | |
| Copper | | (ppb) | 6 |
| Iron | | (ppb) | <3 |
| **(THERMAL) STABILITY** | | | |
| Breakpoint | SEM/004 | (°C) | ≥ 380 |
| Flask oxidation test | SEM/008 | | |
| Induction time | | (minutes) | 137.5 |
| Capillary JFTOT | Under dev | | 17.8 |
| CBO Deposit weight | SEM/003 | (µg/C) | 21.1 |
| **LUBRICITY** | | | |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.66 |

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[1] *In this and following tables: * = Not a specification test; RT = retest; (xw) = test result after x weeks accelerated storage at 45°C; # = Retest on 2nd blend.*

## TABLE 3 - Progress on tests with Merox-based fuels for HiTTS

| **Fuel Code:** | | | AT (Base) | M-1A(Jet A-1) | M-2A (JP-8) |
|---|---|---|---|---|---|
| **PT/A Test Results:** | Method | Units | Value | Value | Value |
| **APPEARANCE** | | | | | |
| Appearance | UK 1636 | | B&C | Satisfactory | Satisfactory |
| Saybolt Colour* | D 156 | | 28 | | 26 |
| **COMPOSITION** | | | | | |
| FIA Aromatics | D 1319/IP 156 | (%V) | 19.3 | | |
| Mercaptan sulphur | D 3227/IP 342 | (%m/m) | 0.0008 | | 0.0009 |
| Total sulphur | D 1266/IP 107 | (%m/m) | 0.18 | | |
| | D 2622/Inhouse | (%m/m) | 0.170 | | 0.175 |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | <0.001 | 0.004 | 0.004 |
| **VOLATILITY** | | | | | |
| Distillation (partial) IBP/FBP | D 86/IP 123 | (°C) | 144.0/245.0 | | |
| Flash point, Abel | IP 170 | (°C) | 38.5 | | |
| Density @ 15°C | D 1298/IP 160 | (kg/m3) | 792.2 | 792.6 | 793.0 |
| **FLUIDITY** | | | | | |
| Freezing point | D 2386/IP 16 | (°C) | -52.0 | | -50.5 |
| Viscosity @ -20°C | D 445/IP 71 | (cSt) | 3.698 | | 3.710 |
| **COMBUSTION** | | | | | |
| Specific energy | D 4529/IP 381 | (MJ/kg) | 43.339 | | |
| Smoke point | D 1322 | (mm) | 25 | | |
| **(THERMAL) STABILITY** | | | | | |
| JFTOT - Pressure drop/VTR | D 3241/IP 323 | (mm Hg/-) | 0.0/2 | <1/1 | <1/1 |
| **CORROSION** | | | | | |
| Copper Corrosion (2h/100°C) | D 130/IP 154 | | 1A | | 1A |
| Silver Corrosion (4h/50°C) | IP 227 | | 0 | | 0 |
| **CONTAMINANTS** | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | 1 | | 4 |
| Particulate contaminant* | D 2276/IP 216 mod | (mg/L) | 0.8 | 0.4 | 0.30 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 1B | 1B |
| MSEP | D 3948 | | 98 | 93 | 49 |
| WASP rating* | SMS 2772 | (mg/kg) | 220 | 720 | 1200 |
| Metals* - Copper, Iron | PT/71:GM08 | (ppb) | <8, 5.5 | 4, 6 | 3, <4 |
| Other (semi-quantitative) | | (ppb) | Pb 164 | Pb 124 | Pb 200, Zn 7 |
| **OTHER TESTS** | | | | | |
| Peroxide number* | D 3703 | (ppm) | 1 | 1 | <1 |
| Conductivity | D 2624/IP 274 | (pS/m @ °C) | 3 @ 20.5 | 325 @ 21.0 | 430 @ 23.0 |
| **IH FLUIDITY** | | | | | |
| Flow/No-flow temp (Setapoint Mk 0) | SEM/024 | (°C) | | -48.7/-51.4 | |
| **IH (THERMAL) STABILITY** | | | | | |
| Breakpoint | SEM/004 | (°C) | 270 then 260 | 270, 260, 260 | 275 |
| CBO Deposit weight | SEM/003 | (µg/C) | 77.2 | 146 | 102.6 |
| Total acidity (inc retests) | TMS 448/93 | (mg KOH/g) | 0.0009 | 0.0018, 0.0021 | 0.0036, 0.0042 |
| Flask oxidation test, Ri | SEM/008 | (Mol/L/s) | 3.82E-7 | | 2.66E-7, 5.26E-7 |
| C-JFTOT number | Under dev | | 1039.6(1) | | 434.15 |
| **IH LUBRICITY** | | | | | |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.75 | 0.74 | 0.53 |
| Failure load (TAFLE) | SEM/013 | (kg) | 102.5 | | |

## TABLE 4 - Analytical & small scale test results for approved additives in Merox Jet A-1

| Fuel Code/Additive: | | mg/L: | M-1A<br>0 | WF/MDA<br>2 | WG/MDA<br>1 | WH/MDA<br>0.5 | WI/MDA<br>25 |
|---|---|---|---|---|---|---|---|
| *Specification Description* | *Method* | *Units* | *Value* | *Value* | *Value* | *Value* | *Value* |
| **COMPOSITION** | | | | | | | |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.001 | 0.001 | | | 0.001 |
| **(THERMAL) STABILITY** | | | | | | | |
| JFTOT- Pressure drop/VTR | D3241/IP 323 | (mm Hg)/- | <1/1 | <1/1 | | | <1/1 |
| Breakpoint | SEM/004 | (°C) | ~260 | ≥340 | 325 | 305 | 260 |
| CBO Deposit weight | SEM/003A | (μg/C) | 146 | | | | |
| HiReTS | "Standard" | | | | | | |
| HiReTS number (start/end) | | | >1697/<br>>1617 | 1468.5 | | | 1418.1 |
| Carbon burn-off (start/end) | | (μg) | 238/229 | 103 | | | 173 |
| **CONTAMINANTS** | | | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | <1 | 1 | <1 | <1 | 1 |
| Particulate contaminant | D2276/IP 216 | (mg/L) | | 0.4 | | | 0.6 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 1B | 1B | 1B | 1B |
| MSEP | D 3948 | | 63 | 54 | | | 71 |
| WASP rating* | SMS 2772 | (mg/kg) | 350 | 480 | 440 | 770 | 540 |
| **OTHER TESTS, LUBRICITY** | | | | | | | |
| Conductivity @ 20°C | D 2624/IP 274 | (pS/m) | 253 | 298 | 300 | 314 | 285 |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.74 (4) | 0.76 (4) | 0.76 (4) | 0.755 (5) | 0.755 (4) |

## TABLE 5 - Main small scale & analytical test results for additivated Merox Jet A-1 fuels

| **Fuel Code/Additive:** | Method | Units | VX/8Q405 | VY/8Q406 | WW/8Q462 |
|---|---|---|---|---|---|
| **APPEARANCE, COMPOSITION** | | | | | |
| Saybolt Colour* | D 156 | | +20 | +20 | +18 |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.004 | 0.004 | 0.007 |
| **FLUIDITY** | | | | | |
| Freezing point | D 2386/IP 16 | (°C) | -51.5 | -51.0 | |
| Viscosity @ -20°C | D 445/IP 71 | (cSt) | 3.736 | 3.792 | |
| **COMBUSTION, CORROSION** | | | | | |
| Specific energy | D 4529/IP 381 | (MJ/kg) | 43.371 | 43.368 | |
| Copper Corrosion (2h/100°C) | D 130/IP 154 | | 1A | 1A | 1A |
| **(THERMAL) STABILITY** | | | | | |
| JFTOT- Pressure drop/VTR | D 3241/IP 323 | (mm Hg) | 1/1 | <1/1 | <1/1 |
| **CONTAMINANTS, OTHER TESTS** | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | 1 | 2 | 2 |
| Particulate contaminant | D 2276/IP 216 | (mg/L) | 0.5 | 0.4 | 1.1 |
| Water reaction, interface rating | D 1094/IP 289 | | 2 | 2 | 4 |
| MSEP | D 3948 | | 55 | 54 | 49 |
| WASP rating* | SMS 2772 | (mg/kg) | 920 | 812 | 560 |
| Peroxide number* | D 3703 | (ppm) | 0.2 | 0.2 | <0.1 |
| Conductivity | D 2624/IP 274 | (pS/m @ °C) | 587 @ 18 | 475 @ 19 | 458 @ 22 |
| **IN-HOUSE TESTS** | | | | | |
| Flow/No-flow temp (Setapoint Mk 0) | SEM/024 | (°C) | -51.55/-51.8 | -51.35/-51.65 | |
| Breakpoint & CBO Deposit weight | SEM/004/003 | (°C)/(μg/C) | 290 | 290 | 295/58.0 |
| HiReTS number/Carbon burn-off | "Standard" | - (μg C) | 18.8(3)/1.48 | 11.95/0.8 | |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.7275 | 0.7525 | 0.76 |

## TABLE 6 - Storage stability tests - Merox Jet A-1 and with Betz additives.

| | Fuel: | | M-1A | | | VX 8Q405 | | VY 8Q406 | |
|---|---|---|---|---|---|---|---|---|---|
| *Test* | *Method* | *Units* | *Initial* | *6 wk* | *12 wk* | *6 wk* | *12 wk* | *6 wk* | *12 wk* |
| **APPEARANCE** | | | | | | | | | |
| Saybolt Colour* | D 156 | | +21 | +19 | +11 | +14 | +14 | +18 | +14 |
| **COMPOSITION** | | | | | | | | | |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.002 | 0.003 | 0.002 | 0.002 | 0.002 | 0.004 | 0.002 |
| **(THERMAL) STABILITY** | | | | | | | | | |
| JFTOT Presure drop/VTR | D 3241/IP 323 | (mm Hg)/- | <1/1 | <1/1 | 1/1 | <1/1 | <1/1 | <1/1 | <1/1 |
| **CONTAMINANTS** | | | | | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | 2 | 3 | 2 | 6 | 6 | 7 | 5 |
| Particulate contaminant | D 2276/IP 216 | (mg/L) | 0.8 | 0.8 | 1.9 | 0.4 | 1.1 | 0.4 | 0.5 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 1B | 1B | 2 | 1B | 2 | 2 |
| MSEP | D 3948 | | 88 | 60 | 46 | 0 | 46 | 0 | 0 |
| WASP rating* | SMS 2772 | (mg/kg) | 685 | 480 | 1040 | 1005 | 1100 | 935 | 1070 |
| **OTHER TESTS** | | | | | | | | | |
| Conductivity | D 2624/IP 274 | | | | | | | | |
| Conductivity | | (pS/m @ °C) | 478 @ 21 | 380 @ 18 | 111 @ 17 | 430 @ 18 | 440 @ 15 | 450 @ 18 | 410 @ 17 |
| Conductivity | | (pS/m @ °C) | 380 @ 16# | | | | | | |
| Peroxide number* | D 3703 | (ppm) | 1, 0.3# | 1.4 | 0.9 | 1.5 | 0.6 | 0.8 | 0.5 |

## TABLE 7 - Small scale and analytical test results for additivated Merox JP-8 fuels

| *Fuel code/ mg/L Additive:* | | | VO (100 8Q405) | M-4A(125 8Q406) |
|---|---|---|---|---|
| *Test Description:* | *Method* | *Units* | *Value* | *Value* |
| **APPEARANCE, COMPOSITION** | | | | |
| Saybolt colour* | D 156 | | +24 | +24 |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.006 | 0.007 |
| Total sulphur | PT/71:IH09 | (%m/m) | | 0.175 |
| **FLUIDITY** | | | | |
| Freezing point | D 2386/IP 16 | (°C) | -51.0 | -50.5 |
| Viscosity at -20°C | D 445/IP 71 | (cSt) | 3.755 | 3.659 |
| **(THERMAL) STABILITY** | | | | |
| JFTOTPressure drop/VTR | D 3241/IP 323 | (mm Hg)/- | <1/1 | <1/1 |
| **CONTAMINANTS, OTHER TESTS** | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | 3 | <1.0 |
| Particulate contaminant | D 2276/IP 216 | (mg/L) | 1.8 | 0.9 |
| Water reaction, interface rating | D 1094/IP 289 | | 2 | 4 |
| MSEP | D 3948 | | 43 | 0 |
| WASP rating* | SMS 2772 | (mg/kg) | 1210 | 1225 |
| Metals* - Copper/Iron | PT/71:GM08 | (ppb) | 4/<6 | 4/10 |
| Other (semi-quantitative) | | (ppb) | Pb 133, Zn 40, Mn 6 | Pb 95.5, Zn 15 |
| Conductivity | D 2624/IP 274 | (pS/m @ °C) | 734 @ 26.5 | 540 @ 21 |
| Conductivity (pre-storage) | D 2624/IP 274 | (pS/m @ °C) | 476 @ 17 | 457 @ 17 |
| Peroxide number | D 3703 | (ppm) | 0.9 | |
| **IH (THERMAL) STABILITY** | | | | |
| Breakpoint/CBO Deposit weight | SEM/004/003 | (°C)/(μg/C) | 300/53 | 305/35.75 |
| FOT, radical initiation rate | SEM/008 | | 4.45E-7 | 4.32E-7 |
| C-JFTOT number | Under dev | | | 11.95 |
| **IH LUBRICITY** | | | | |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.595 | 0.575 |

## TABLE 8 - Storage stability tests - Merox JP-8 and JP-8+100 fuels.

| | | Fuel: | M-2A | | 8Q405 VO | | 8Q406 M-4A | |
|---|---|---|---|---|---|---|---|---|
| *Test* | *Method* | *Units* | *6 week* | *12 week* | *6 week* | *12 week* | *6 week* | *12 week* |
| **APPEARANCE** | | | | | | | | |
| Saybolt Colour* | D 156 | | +14 | +7 | +18 | +12 | +19 | +14 |
| **COMPOSITION** | | | | | | | | |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.005 | 0.006 | 0.003 | 0.015 | 0.004 | 0.006 |
| **CORROSION** | | | | | | | | |
| Copper Corrosion (2h/100°C) | D 130/IP 154 | | 1A | 1A | 1A | 1A | 1A | 1A |
| Silver Corrosion (4h/50°C) | IP 227 | | 0 | 0 | 0 | 0 | 0 | 0 |
| **(THERMAL) STABILITY** | | | | | | | | |
| JFTOT Pressure drop/VTR | D 3241/IP 323 | (mm Hg)/- | <1/1 | <1/1 | | | | |
| **CONTAMINANTS** | | | | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | 5 | 2 | 3 | 3 | 3 | 4 |
| Particulate contaminant | D 2276/IP 216 | (mg/L) | 1.2 | 2.7 | 0.5 | 0.6 | 0.9 | 0.3 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 1B | 2 | 2 | 2 | 4 |
| MSEP | D 3948 | | 48 | 57 | 45 | 0 | 0 | 41 |
| WASP rating | SMS 2772 | (mg/kg) | 960 | 1110 | 900 | 410 | 935 | 975 |
| **OTHER TESTS** | | | | | | | | |
| Conductivity | D 2624/IP 274 | (pS/m @ °C) | 283 @ 18 | 155 @ 22 | 544 @ 20 | 550 @ 18 | 503 @ 20 | 412 @ 18 |
| Peroxide number* | D 3703 | (ppm) | 2.1 | 0.6 | 3.5 | 1.6 | 3.3 | 1.1 |

## TABLE 9 - CoQ, Small-scale & storage tests for Hydrotreated Jet A-1 &/- additives

| Fuel/additive | | | HT-1A | VT/8Q405 | VU/8Q406 |
|---|---|---|---|---|---|
| *Test Description* | *Method* | *Units* | *Value* | *Value* | *Value* |
| **APPEARANCE, COMPOSITION** | | | | | |
| Appearance | UK 1636 | | Satisfactory | | |
| Saybolt Colour * (0,6,12 weeks) | D 156 | | 27, 23, 22 | 27, 23, 21 | 26, 22, 22 |
| Total acidity (0,6,12 weeks) | D 3242/IP 354 | (mg KOH/g) | 0.002, 0.002, 0.003 | 0.003, 0.001, 0.003 | 0.003, 0.001, 0.002 |
| FIA Aromatics | D 1319/IP 156 | (%V) | 17.1 | | |
| Mercaptan sulphur | D 3227/IP 342 | (%m/m) | 0.0002 | | |
| Total sulphur (also ran IP 336) | IP 373 | (%m/m) | 0.0175 | 0.0152 | 0.0148 |
| **VOLATILITY, FLUIDITY** | | | | | |
| Distillation (partial), IBP/FBP | D 86/IP 123 | (°C) | 153/256 | | |
| Flash point, Abel | IP 170 | (° C) | 44 | | |
| Density @ 15°C | D 4052/IP 365 | (kg/m3) | 793.4 | 793.5 | 793.4 |
| Freezing point | D 2386/IP 16 | (°C) | -48 | -47 | -47.5 |
| Viscosity @ -20°C | D 445/IP 71 | (cSt) | 4.000 | 4.023 | 4.021 |
| **COMBUSTION, CORROSION** | | | | | |
| Specific energy, net | D 4529/IP 381 | (MJ/kg) | 43.403 | 43.394 | 43.395 |
| Smoke point | D 1322 | (mm) | 26 | 24 | 24 |
| Copper Corrosion (2h/100°C) | D 130/IP 154 | | 1A (0&12w) | 1A (0&12w) | 1A (0&12w) |
| Silver Corrosion (4h/50°C) | IP 227 | | PASS (0) | | |
| **(THERMAL) STABILITY** | | | | | |
| JFTOT at 260°C | D 3241/IP 323 | | | | |
| Pressure drop/VTR | | (mm Hg)/- | <1/1 | <1/1 | <1/1 |
| Pressure drop/VTR | | (mm Hg)/- | <1/1 (6w) | <1/1 (6w) | <1/1 (6w) |
| Pressure drop/VTR | | (mm Hg)/- | <1/1 (12w) | 2/1 (12w) | <1/1 (12w) |
| **CONTAMINANTS** | | | | | |
| Existent gum (0,6,12 weeks) | D 381/IP 131 | (mg/100mL) | <1, <1, 1 | 2, 6, 2 | 2, 2, 2 |
| Particulate contaminant* (0,6,12 weeks) | D 2276/IP 216 | (mg/L) | 0.5, 0.7, 0.4 | 1.6, 0.4, 1.0 | 1.2, 0.6, 0.8 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 2 | 2 |
| MSEP | D 3948 | | 93 | 44 | 43 |
| WASP rating* (0,6,12 weeks) | SMS 2772 | (mg/kg) | 570,615, 470 | 860, 975, 870 | 925, 1020, 920 |
| Metals* - Cu/Fe&Sn(Semi-Q) | PT/51:GM08 | (ppb) | 4/2 & 6(SQ) | | |
| **OTHER TESTS, ADDITIVES** | | | | | |
| Conductivity | D 2624/IP 274 | | | | |
| Conductivity & temp | | (pS/m @ °C) | 345 @ 20 | 321 @ 22 | 278 @ 22 |
| Conductivity & temp | | (pS/m @ °C) | | 340@20# | 300@20# |
| Conductivity & temp (12weeks) | | (pS/m @ °C) | 380 @ 17 | 267 @16 | 238 @17 |
| Peroxide number* (0,6,12 weeks) | D 3703 | (ppm) | <1, 0.3, 0.3 | <1, 0.5, 0.2 | <1, 0.3, 0.2 |
| Antioxidant | RDE/A/609 | (mg/L) | 22.7 | 22.7 | 22.7 |
| Static dissipator additive | RDE/A/621 | (mg/L) | 1.0 | 1.0 | 1.0 |
| **IH FLUIDITY** | | | | | |
| Setapoint Flow/no-flow temp | SEM/024 | (°C) | -46.65/-49.3 | -46.95/-49.5 | -49.1/-40.55 |
| **IH (THERMAL) STABILITY** | | | | | |
| Breakpoint* (2nd figure is repeat) | SEM/004 | (°C) | 280, 275 | 300 | 300 |
| CBO Deposit weight | SEM/003A | (µg Carbon) | | 72.9 | |
| HiReTS number/Carbon burn-off | "Standard" | - /(µg) | 64.0/0.2 & 62.8/0(1) | 17.25/0 | 33.7/0 |
| FOT - Induction period & Radical initiation rate | SEM/008A | (min) & (Mol/L/s) | 65.2 & 5.96E-8 | | |
| **IH LUBRICITY** | | | | | |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.76 | 0.76, 0.81# | 0.76 |
| Failure load (TAFLE) | SEM/013 | (kg) | 30 | | |

## TABLE 10 - Analytical data and small scale tests on hydrotreated JP-8 and blends

| MOD Code:<br>Fuel & additive type: | | | HT-2A<br>JP8 | VZ<br>JP8+8Q405 | WA<br>JP8+8Q406 |
|---|---|---|---|---|---|
| *Specification Description* | *Method* | *Units* | *Value* | *Value* | *Value* |
| **APPEARANCE** | | | | | |
| Appearance | UK 1636 | | Satisfactory | | |
| Saybolt Colour* | D 156 | | +21 | +23 | +23 |
| **COMPOSITION** | | | | | |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.006 | 0.005 | 0.005 |
| Mercaptan sulphur (potentiometry) | IP 342 | (%m/m) | 0.0004 | | |
| Total sulphur (also ran IP 336 - 0.02) | IP 373 | (%m/m) | 0.0160 | 0.0145 | 0.0149 |
| **VOLATILITY** | | | | | |
| Density @ 15C | D 4052/IP 365 | (kg/m3) | 793.7 | 793.8 | 793.8 |
| **FLUIDITY** | | | | | |
| Freezing point | D 2386/IP 16 | (Deg C) | -48 | -48.5 | -48 |
| Viscosity | D 445/IP 71 | | | | |
| Viscosity @ -20°C | | (cSt) | 4.018 | 4.055 | 4.043 |
| Viscosity @ 40°C* | | (cSt) | 1.243 | 1.242 | 1.238 |
| Flow temperature (Setapoint Mark 0)* | SEM/024 | | | | |
| Flow temperature (endpoint) | | (Deg C) | -47.45 | -47.65 | -47.35 |
| No-flow temperature | | (Deg C) | -49.90 | -49.85 | -49.65 |
| **CORROSION** | | | | | |
| Copper corrosion (2h/100°C) | D 130/IP 154 | | 1A | | |
| **(THERMAL) STABILITY** | | | | | |
| JFTOT at 260C | D 3241/IP 323 | | | | |
| Pressure drop | | (mm Hg) | <1 | <1 | <1 |
| Visual tube rating | | | 1 | 1 | 1 |
| Breakpoint* | SEM/004 | (Deg C) | ~310 | 325 | 320 |
| HiReTS* - HiReTS number | "Standard" | | | | |
| HiReTS number | | | 25.55 | 15.5 | 14.4 |
| Carbon burn-off | | (µg C) | 0.15 | 0.05 | 0 |
| **CONTAMINANTS** | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | <1 | 3 | 3 |
| MSEP | D 3948 | | 85 | 46 | 43 |
| Particulate contaminant* | D 2276/IP 216 | (mg/L) | 0.6 | 1.1 | 0.7 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 2 | 2 |
| WASP rating* | SMS 2772 | (mg/kg) | 743 | 965 | 925 |
| **OTHER TESTS** | | | | | |
| Conductivity | D 2624/IP 274 | (pS/m@ °C) | 168@22 | 250 @ 17.5 | 230 @ 17 |
| Peroxide number* | D 3703 | (ppm) | <0.1 | <0.1 | <0.1 |
| **LUBRICITY*** | | | | | |
| Wear scar diameter (BOCLE) | D 5001 | (mm) | 0.57 | 0.57 | 0.605 |
| Failure load (TAFLE) | SEM/013 | (kg) | 60(1) | | |

## TABLE 11 - Storage stability test results for hydrotreated JP-8 and JP-8+100 variants. See also Table 10.

| | | | HT-2A | | 8Q405 VZ | | 8Q406 WA | |
|---|---|---|---|---|---|---|---|---|
| *Test* | *Method* | *Units* | *6 week* | *12 week* | *6 week* | *12 week* | *6 week* | *12 week* |
| **APPEARANCE** | | | | | | | | |
| Appearance | UK 1636 | | Satis | Black fibres | Satis | Satis | Satis | Satis |
| Saybolt Colour* | D 156 | | +25 | +16 | +9 | +14 | +13 | +18 |
| **COMPOSITION** | | | | | | | | |
| Total acidity | D 3242/IP 354 | (mg KOH/g) | 0.005 | 0.004 | 0.003 | 0.006 | 0.004 | 0.005 |
| **(THERMAL) STABILITY** | | | | | | | | |
| JFTOT at 260°C | D 3241/IP 323 | | | | | | | |
| Pressure drop | | (mm Hg) | <1 | | <1 | <1 | <1 | <1 |
| Visual tube rating | | | 1 | | 1 | 1 | 1 | 1 |
| **CONTAMINANTS** | | | | | | | | |
| Existent gum | D 381/IP 131 | (mg/100mL) | <1 | 3 | 7 | 3 | 5 | 3 |
| Particulate contaminant* | D 2276/IP 216 | (mg/L) | 0.6 | 8.6 | 0.5 | 0.4 | 1.2 | 0.5 |
| Water reaction, interface rating | D 1094/IP 289 | | 1B | 1B | 2 | 4 | 2 | 4 |
| MSEP | D 3948 | | 59 | 48 | 46 | 0 | 47 | 49 |
| WASP rating* | SMS 2772 | (mg/kg) | 645 | 970 | 930 | 960 | 965 | 1110 |
| **OTHER TESTS** | | | | | | | | |
| Conductivity | D 2624/IP 274 | (pS/m @ °C) | 75 @ 23 | 212 @ 17 | 324 @ 21 | 320 @ 20 | 301 @ 20 | 280 @ 19 |
| Peroxide number* | D 3703 | (ppm) | <0.1 | <0.1 | 1.8 | 3.8 | 1.6 | 0.2 |

## TABLE 12 - Results for BP HiTTS candidates in HiReTS unit 1

| **Fuel code** | **HiReTS numbers** | **Carbon burn-off (μg C)** |
|---|---|---|
| Merox Base fuel, AT, ex tank 248 | Test 1 - 1100.48<br>Test 2 - 1006.7<br>Average 1055.8 | Test 1 = 102<br>Test 2 = 74.4<br>Average 88.2 |
| A | Test 1 - 10.7<br>Test 2 - 28.1<br>Average 19.4 | Test 1 = 0<br>Test 2 = 0.2<br>Average 0.1 |
| B | Test 1 - 18.7<br>Test 2 - 29.1<br>Average 23.9 | Test 1 - 0<br>Test 2 - 0<br>Average 0 |
| C | Test 1 - 4.1 - Stopped early<br>Test 2 - 17.7<br>Report: 17.7 (1) | Test 1 = NA<br>Test 2 = 1.89<br>Report: 1.89 (1) |
| Base fuel - check run | Test 3 - 1040.3 | Test 3 - 112 |
| D | Test 1 - 11.6<br>Test 2 - 20.1<br>Average 15.9 | Test 1 = 0.3<br>Test 2 = 0.75<br>Average 0.53 |

Figure 1. 3-D C-JFTOT trace for JPTS, the JP-8+100 "target" fuel.

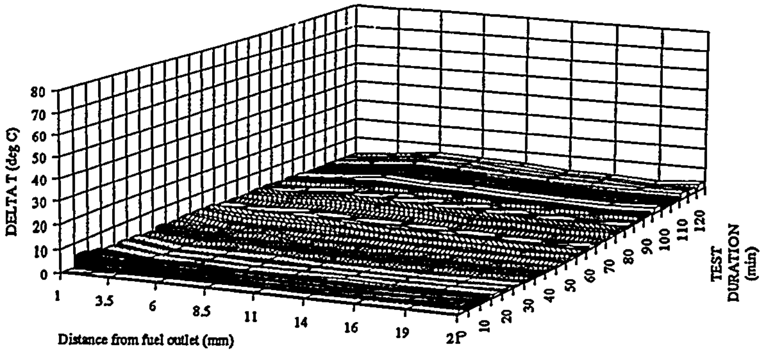

Figure 2. On same scale, trace for Merox JP-8 (M-2A).

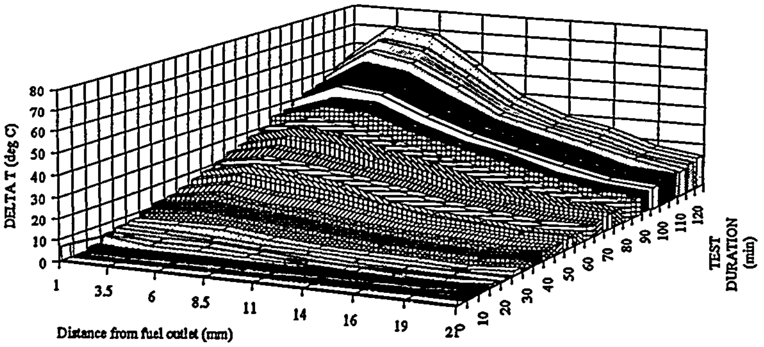

Figure 3. M-2A plus 125 mg/L 8Q406, = M-4A, again on same scale.

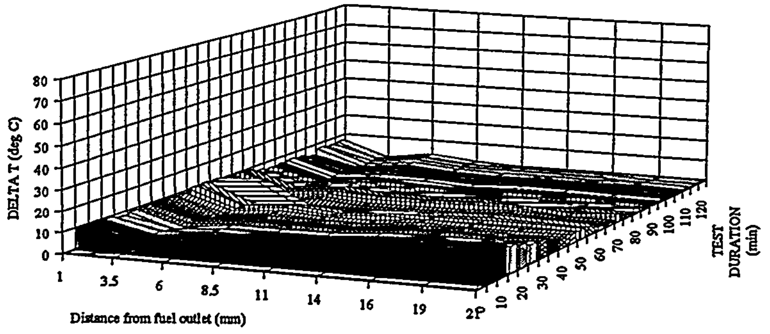

Figure 4 - HiReTS trace for Hydrotreated Jet A-1, HT-1A

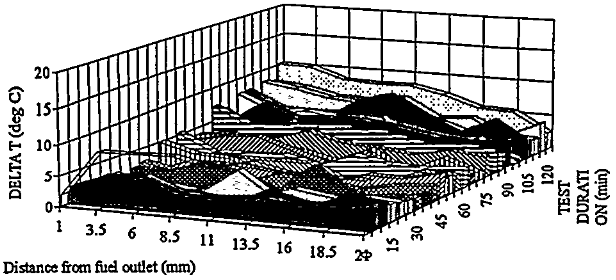

Figure 5 - HiReTS trace for above Jet A-1 plus Betz 8Q405 = VT.

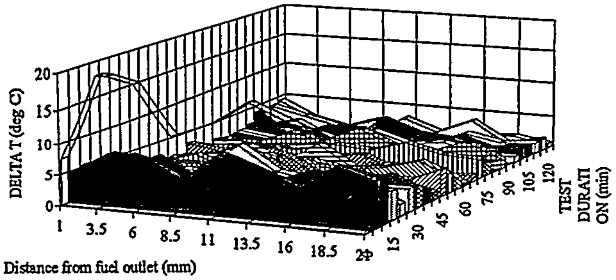

Figure 6 - A HiReTS 3-D profile for the base fuel used in the BP additive tests

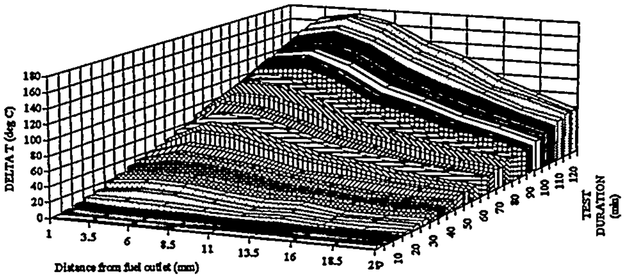

Figure 7 - Same base fuel with BP additive A, on the same scale as Figure 6