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THE ROLE OF A METAL DEACTIVATOR ADDITIVE IN IMPROVING
THE THERMAL STABILITY OF AVIATION KEROSENES:
ADDITIVE ADSORPTION STUDIES

By

R.H. Clark, K.M. Delargy and R.J. Heins
Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester CH1 3SH

INTRODUCTION

SCOPE OF PREVIOUS WORK

In an earlier paper¹, we reported studies that elucidated the mechanisms whereby MDA can affect the stability of jet fuel. The work not only investigated MDA in its claimed role as a metal chelating agent, but, more significantly, assessed the role of this additive within engine fuel system environments and within the thermal stability specification test (JFTOT). Thus the experimental work was on three parallel fronts:

- Realistic-large scale simulations of engine components
- Specification testing - the JFTOT
- Fundamental mechanistic studies

Glassware fuel oxidation studies clearly demonstrated the ability of MDA to act as a metal chelator, resulting in a near-unity chelation ratio. However, in the dynamic stability tests (i.e. fuel system simulators and the JFTOT), where fuel flows over a heated metal surface, the action of MDA was less clearcut. In particular, in spite of eliminating the metal chelation mechanism by using a metal-free fuel, benefits to fuel stability were still evident in our oil-cooler simulation² (Single-Tube Heat-Transfer Rig, STHTR) and the JFTOT. This improvement in fuel stability was attributed to MDA acting as a metal passivator and retarding the formation of lacquers on metal surfaces.

The passivating role of MDA was most evident on clean metal surfaces; once sufficient fuel lacquer had coated the metal surface, passivation ceased to be a factor controlling lacquer deposition. This differing response of a clean versus lacquered surface was of great concern for the specification test (JFTOT); given its short duration and low lacquer loadings, the JFTOT responds particularly strongly to the passivating action when compared with a more realistic rig (e.g. the STHTR) employing a longer test duration (25 - 100 hours). Thus, any improvement in fuel performance in the JFTOT obtained from the use of MDA may not necessarily be manifest in service. Figure 1, taken from reference 1, illustrates the different benefits of MDA on a low-metal-content fuel in a variety of systems.

CURRENT OBJECTIVE

Our use of a wide range of experimental systems has provided strong empirical evidence for the passivation mechanism of MDA, and, in particular, the overresponse of the JFTOT to MDA. Nevertheless, it was thought desirable to confirm such a mechanism by independent means. It was reasoned that a surface analysis technique would offer the opportunity of directly observing the adsorption of MDA molecules onto a metal surface. The chosen technique should be (i) sensitive enough to resolve a monolayer of MDA, and (ii) sufficiently discriminating to observe MDA in the presence of fuel or fuel lacquers. SIMS (Secondary Ion Mass Spectrometry) appeared a viable option, thus the overall aims became:

- To apply SIMS to observe directly the adsorption of MDA molecules onto aluminium surfaces, in particular JFTOT test specimens.
- To continue SIMS work to elucidate how MDA influences the lacquer patterns on a JFTOT test specimen

EXPERIMENTAL

SIMS

Secondary Ion Mass Spectrometry (SIMS) is a highly surface sensitive analytical technique (sampling depth = 0.5 - 1 nm) which involves the bombardment of a sample surface with a primary beam of energetic particles (normally ions or atoms). This results in the emission of a range of secondary particles, including positively and negatively charged ions. These secondary ions, both atomic and molecular species, are subsequently mass analysed to generate surface mass spectra similar to those obtained in conventional organic mass spectrometry. The technique, therefore, provides elemental analysis in addition to detailed and highly specific chemical structure information.

This study was carried out using a VG IX23S instrument equipped with a Poschenrieder time-of-flight analyser and a pulsed liquid metal ion source (Ga^+ , 30 KeV)³. For each sample, secondary ion spectra were recorded from an area of 0.5 mm x 0.5 mm. All spectra were generated under static SIMS conditions, where sufficiently low primary ion doses are used such that the samples are effectively undamaged throughout the course of the analysis. Both positive and negative ion spectra were recorded in the mass range 0 - 1500.

JFTOT

In essence, the JFTOT rig⁴ provides a system for passing a small sample of fuel (600 cm³) over a heated metal test section. The JFTOT assesses the stability of a fuel by its propensity to lacquer the test section and from the associated blockage of a downstream filter by decomposition products. For specification purposes, the hottest temperature on the test section (aluminium tube) is controlled to 260°C for 2.5 hours.

To pass the test, the tube lacquer must not be darker than the specified limit, and the filter pressure drop should not exceed 25 mm Hg. This results in a go/no go specification test. For research purposes, various refinements may be made to the procedure to allow fuel ranking.

TEST FUEL AND ADDITIVE

The test fuel was chosen so as to represent current refinery production. However, to minimise potential interference from other polar species within the SIMS analysis, the fuel was taken from commercial hydrotreated stock with a low intrinsic sulphur content. The fuel was pre-filtered to 0.45 μm before use. Two sources of the MDA concentrate were used:

- (i) 75% w/w MDA in xylene, proprietary name DuPont DMD No. 1.
- (ii) 50% w/w MDA in xylene, proprietary name DuPont DMD No. 2.

SAMPLE PREPARATION

Table 1 summarises the various sample preparation procedures. Samples comprised three basic types:

- (i) Sections of aluminium foil (approx 0.5 x 0.5 cm) for static/soaking experiments. These were pre-treated by ultrasonic cleaning with a trisolvent solution (an equivolume blend of toluene, isopropyl alcohol and acetone).
- (ii) Sections from JFTOT tubes (1.8 cm long) used in static/soaking experiments. The position of the sample along the tube was not critical.
- (iii) Sections from JFTOT tubes (1.8 cm long) used in a dynamic experiment, i.e. the uncut tubes had been run in the conventional JFTOT rig. These samples were taken to bracket the position on the test section corresponding to the hot spot (38.7 mm from the fuel inlet).

Except where indicated, all JFTOT tubes were used straight from the pack without any pre-treatment in compliance with the specification test conditions. Similarly, after exposure to the fuel or MDA solutions, the samples were rinsed with Analar grade heptane and allowed to dry (in accordance with the ASTM D3241 method⁷). The 1.8 cm samples were sectioned from the JFTOT tubes using a Beuhler saw. A stream of compressed air was used to remove any metallic debris from the sample surface.

RESULTS AND DISCUSSION

SIMS SPECTRUM - FRAGMENTATION PATTERN

Positive and negative ion spectra were taken in the mass range 0 - 1500; examples of spectra are given in Figures 2 and 3. The molecular weight (M) of MDA is 282, and ions corresponding to (M+H)⁺, at 283 daltons, and (M-H)⁻, at 281 daltons, were detected. A number of other ionic species were also observed but only in the presence of MDA; these are listed in

Table 2 together with the most probable assignments for molecular fragments arising from MDA. In addition to these characteristic ion fragments, a number of low-mass species were also detected in the positive and negative ion spectra, e.g. $C_2H_3^+$, Ph^+ , $PhCH_2^+$, C_n^- , C_nH^- , CN^- and PhO^- . Of all the fragments, the species at 118^- is considered to be, analytically, the most useful. The signal is of good intensity and is a highly characteristic indicator of MDA. Quasimolecular ions at 283^+ and 281^- are of limited use only: the intensity of the 283^+ signal is likely to be strongly dependent on the surface structure of MDA. Whilst the 281^- species is analytically more useful for assessing intact MDA molecules on a surface, it overlaps with a signal from an oleate-containing species. Consequently, any conclusions based on the 281^- signal alone are subject to some uncertainty. Thus for the purpose of comparison between samples the 118^- peak was used. As this peak lies adjacent to a characteristic reference peak for the substrate, $Al_2O_3H^-$ at 119^- , peak area ratios could be used with confidence to monitor the concentration of adsorbate. The relative surface concentration (C) of MDA was monitored using computed peak areas (A_{118} and A_{119}) in the following manner:

$$XC = \frac{A_{118}}{A_{118} + A_{119}} \times 100 \quad \dots(1)$$

The surface concentrations for each sample are shown diagrammatically in Figures 4 - 7. Interpretation of all results with equation 1 requires care, in that SIMS is considered only semi-quantitative. It is more important to consider trends within a series of specimens rather than absolute values.

PRELIMINARY FINDINGS

Initial experiments made use of simple samples in the form of aluminium foil sections. With these, there was a close similarity between the SIMS spectrum of the foil wetted by an MDA solution (derived from a DMD No 2 concentrate) and that of foil exposed to the same solution and then rinsed in heptane. Those features common to these two spectra were not evident in the third spectrum, which corresponded to a foil sample that had not been in contact with MDA. In addition, differences between the samples could be seen in the surface concentrations of MDA as determined from equation 1.

However, there were various features of the SIMS MDA spectrum which corresponded to mass numbers higher than the molecular weight of the additive, suggesting that this sample of MDA had degraded or polymerised. This potential problem of storage stability accordingly led us to seek a fresh sample of MDA for the main body of experimentation.

JFTOT TUBE SAMPLES - STATIC PREPARATION

These preliminary findings having shown that SIMS had sufficient sensitivity to detect MDA adsorbed onto aluminium surfaces, subsequent samples were prepared to reflect more closely the reality of the

specification test:

- solutions of MDA were made up with commercial jet fuel
- aluminium samples were taken from JFTOT test sections

Whilst it was clearly desirable for all JFTOT tubes to be used without any surface pre-treatment (i.e. as ASTM D3241), there were concerns that residual cutting oils on the aluminium could interfere with the SIMS detection or alternatively reduce the number of surface sites available for additive adsorption. As a precaution, two similar sets of samples were prepared: one untreated and the other pre-cleaned. However, it was recognised that these various preparations suffered from the shortcoming of being static immersion tests at ambient temperature. SIMS spectra were recorded for the following untreated JFTOT tubes:

- (i) Fuel wetted and heptane rinsed
- (ii) Fuel + 5.7 mg/l MDA wetted and heptane rinsed
- (iii) Fuel + 64.8 g/l MDA wetted and heptane rinsed
- (iv) Neat MDA cast onto a JFTOT tube as a reference spectrum
- (v) Sample (ii) was then repeated using a pre-cleaned JFTOT tube.

The results in terms of MDA surface concentrations are illustrated in Figure 4. SIMS could detect MDA in all samples that had been exposed to the additive. Moreover, the concentration of additive within the original bulk solution had a strong effect on the resultant surface concentration; the 5.7 mg/l MDA solution gave a spectrum in which the additive was only just discernible, whereas the 64.8 g/l solution resulted in an MDA signal comparable to that of the neat additive. This effect of concentration suggests an equilibrium between the MDA in the fuel solution and the molecules adsorbed onto the metal, presumably following a simple adsorption-type mechanism (e.g. Langmuir isotherm). From this, it can be concluded that, at the specification MDA concentration, not all the surface sites will be occupied by the MDA molecule. Comparison of the pre-cleaned tubes and the as-received examples indicated better adsorption of the additive onto a cleaned tube, presumably because more surface sites have become available. However, the cleaned system is less relevant to the specification conditions.

JFTOT TUBE SAMPLES - DYNAMIC PREPARATION

Data from the first two sets of experiments gave the necessary confidence to dispense with the idealised model systems and to use samples actually generated within the JFTOT rig and covering a range of temperature and additive concentration. In particular, it was seen as crucial that at least one condition should reflect the current specification test conditions (260°C maximum tube temperature, 2.5 hours duration, MDA concentration 5.7 mg/l maximum).

(a) Concentration dependence

Figure 5 illustrates the amount of MDA present on the surface as a function of the original additive concentration for tests at ambient temperature. The results agree with those seen in the static experiments where the MDA adsorbed onto the surface increased with bulk additive

concentration. However, more detail can be derived by applying a simple Langmuir-type adsorption model. The surface concentration approaches a limiting value for the two highest bulk additive concentrations (570 mg/l and 57 g/l), indicating that the surface sites are approaching saturation. This further confirms that at the specification concentration (5.7 mg/l) only a small fraction of available sites are occupied by adsorbed MDA molecules.

(b) Effect of temperature

An increase in the surface concentration of MDA is observed with increasing temperature (Figures 6 and 7). A small increment accompanies the change from 25°C to 140°C, but a dramatic one results on further increasing the test temperature to 260°C. This temperature dependence of MDA adsorption is unexpected; one might predict an exothermic heat of adsorption, and thus a decreasing amount of MDA adsorbed with increasing temperature. This anomalous increase in surface MDA concentration coupled with the strong non-Arrhenius temperature response suggests that a simple adsorption mechanism is not occurring. A plausible explanation could be that, in addition to reaching the surface by an adsorption mechanism, the MDA molecules can also add to the surface by polymerising to form an MDA matrix on the surface. Alternatively, fuel lacquer could entrain MDA molecules on the surface.

A MODEL FOR MDA PASSIVATION

In our previous paper¹, we discussed how MDA could modify and passivate a metal surface. This latest work allows us to hypothesise as to the nature of the mechanism by which MDA passivates. It is doubtful that the passivation results solely from MDA molecules adsorbed onto the metal surface. A two-stage mechanism is proposed: firstly, the MDA molecules adsorb onto some of the available surface sites and then subsequently, under the influence of heat, the adsorbed MDA molecules crosslink with each other and those in solution to form an MDA matrix; alternatively, the MDA molecules could be entrapped within a fuel lacquer film. It is proposed that such a polymerised MDA layer presents a less favourable substrate for lacquer formation than a bare Al/Al₂O₃ surface. Since our previous work has shown that this passivation is short-lived, it is assumed that either the fuel lacquer grows thick enough on the surface to hide the passivating layer, or, alternatively, the passivating layer is metastable and is eventually displaced by fuel lacquer. Unfortunately, in its current form the SIMS approach is unable to confirm such a mechanism. If the MDA is undergoing reaction, one would expect a decrease in the parent ion signals at higher temperatures. In the event these signals are rather weak and obscured by other species. However, it has been noted that at higher temperatures there is an increase in the CN⁻ signal relative to the 118⁻ signal, which suggests breakdown of the MDA molecule.

CONCLUSIONS

SIMS offers the sensitivity and discrimination required to detect the MDA molecule on an aluminium surface. The surface concentration of adsorbed MDA is a function of the original bulk MDA concentration and

appears to reach a saturation for bulk concentrations of ~ 57 g/l, indicating a simple Langmuir-type adsorption model. A fuel doped with MDA at the specification limit (5.7 mg/l) when run in the JFTOT will result in MDA being adsorbed onto the aluminium test specimen. However, relatively few surface sites will be occupied at this lower concentration.

The strong influence of temperature and the non-Arrhenius behaviour of the MDA surface concentration indicate that more than an adsorption mechanism is in operation at elevated temperatures. This evidence indicates that MDA passivation of the JFTOT test section does not result solely from surface adsorption; the MDA molecule may well be present as a polymer or in a fuel decomposition matrix.

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Table 1
A summary of the sample preparation stages

Sample Group	Pre-treatment of specimen	MDA conc. (mg/l)	Heptane rinse after MDA exposure	Use of JFTOT	JFTOT test Temperature (°C)
(i) Aluminium foil (MDA No. 2)	Ultrasonic clean with trisol	0	✓	x	
		160,000	✓	x	
		160,000	x	x	
(ii) JFTOT test sections (MDA No. 1)	Ultrasonic clean with HPLC grade methanol. In addition duplicate set of uncleaned specimens.	0	✓	x	
		5.7	✓	x	
		64,800	✓	x	
		concentrate	x	x	
(iii) JFTOT test sections (MDA No. 1)	None	5.7	✓	✓	25
		57	✓	✓	25
		570	✓	✓	25
		57,000	✓	✓	25
		5.7	✓	✓	140
		5.7	✓	✓	260
		57	✓	✓	260

Table 2
Fragmentation of MDA in TOF SIMS:

ION MASS	FRAGMENT ION
107 ⁺	C ₆ H ₄ (OH)CH ₂ ⁺
120 ⁺	C ₆ H ₄ (OH)CNH ⁺
134 ⁺	C ₆ H ₄ (OH)CHNCH ₂ ⁺
148 ⁺	C ₆ H ₄ (OH)CHNCH(CH ₃) ⁺
162 ⁺	C ₆ H ₄ (OH)CHNCH(CH ₃) ⁺ CH ₂ ⁺
283 ⁺	(M + H) ⁺
118 ⁻	C ₆ H ₄ (CN)O ⁻
120 ⁻	C ₆ H ₄ (OH)CNH ⁻ OR C ₆ H ₄ (CHNH)O ⁻
281 ⁻	(M - H) ⁻

NOTES: (1) M = molecular species (mol. wt. = 282)
= C₆H₄(OH)CHNCH(CH₃)CH₂NCHC₆H₄(OH)

(2) ALSO DETECTED WERE: C_xH_y⁺, Ph⁺, PhCH₂⁺, C_n⁻, C_nH⁻, CN⁻, PhO⁻ ETC.

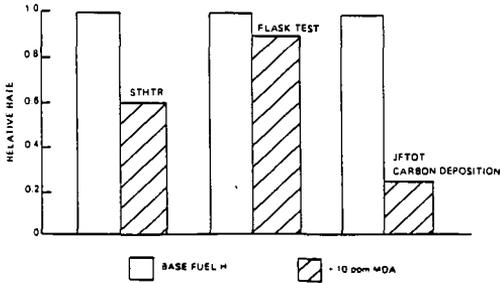


FIG. 1 - The influence of MDA on the behaviour of a sweetened fuel H. STHTR operated at 225°C condition, Flask at 160°C, JFTOT at 350°C to determine carbon deposit weight (Reference 1).

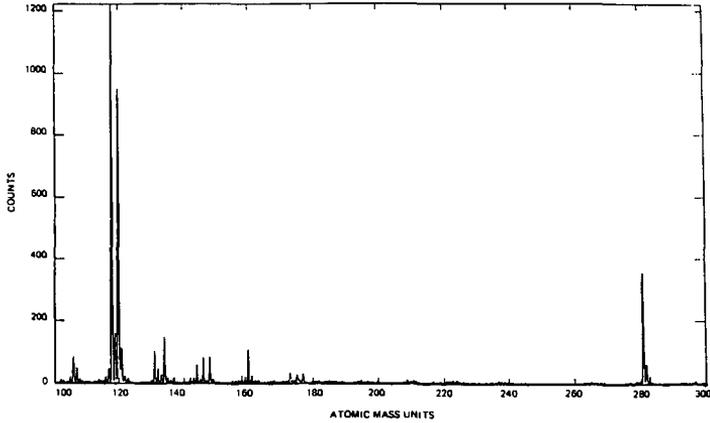
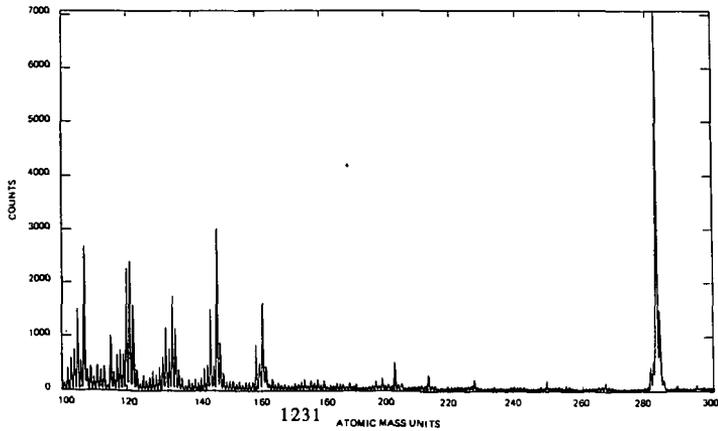


FIG. 2 - Negative ion TOF SIMS spectrum of MDA concentrate cast onto aluminium JFTOT tube.



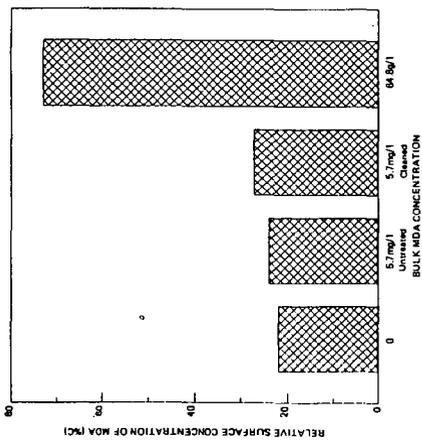


FIG. 4 - The influence of MDA bulk concentration on the resulting MDA surface concentration of JFTOT test specimens. Samples generated within a static experiment.

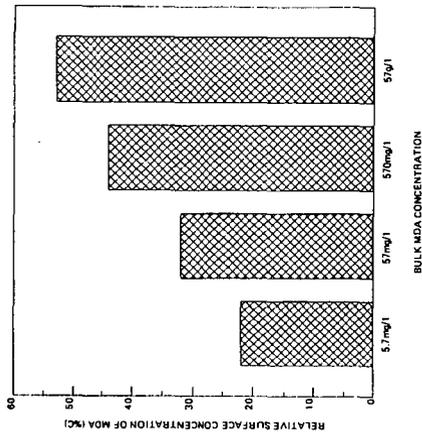


FIG. 5 - The influence of MDA bulk concentration on the resulting MDA surface concentration of JFTOT test specimens. Samples generated within a JFTOT rig at ambient temperature.

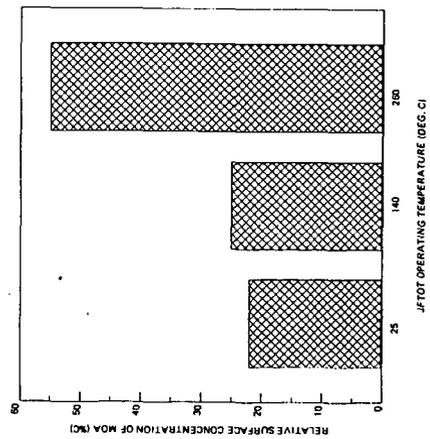


FIG. 6 - The influence of JFTOT operating temperature on the resulting MDA surface concentration of JFTOT test specimens (MDA bulk concentration 5.7 mg/l).

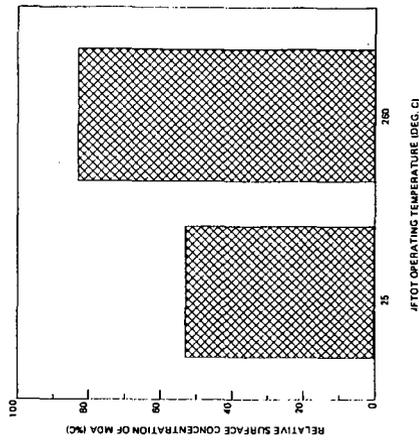


FIG. 7 - The influence of JFTOT operating temperature on the resulting MDA surface concentration of JFTOT test specimens (MDA bulk concentration 59 μg/l).