

Reviews

The Development and Use of Metal Deactivators in the Petroleum Industry: A Review

J. Andrew Waynick

Southwest Research Institute, 6220 Culebra Road, P.O. Drawer 28510,
San Antonio, Texas 78228-0510

Received May 22, 2001. Revised Manuscript Received September 10, 2001

The development of metal deactivator additives for the petroleum industry is reviewed from the first additive used in gasoline to the present. The chemistry of how these additives are thought to work is detailed and related to chemical structure. Discussions of the three classes of action attributed to metal deactivators: chelation, surface passivation, and bulk phase reactivity, are provided. In this regard, special emphasis is given to the metal deactivator *N,N*-disalicylidine-1,2-propane diamine (MDA) in aviation turbine fuels. Previously reported work, especially work from 1991 to the present, investigating the impact of MDA on jet fuel thermal stability is reviewed. A discussion of the six classes of metal deactivators most commonly found in the literature is also provided.

Introduction

The tendency of cracked gasolines to form engine fouling gums was noted as early as 1914.¹ During the following 2 decades, it was determined that such fuel instability was due to oxidation. By 1932, it was also known that trace levels of certain metals in gasoline could greatly accelerate this oxidative gum formation.² This was especially a problem in gasolines sweetened by copper compounds where trace copper levels remained in the gasoline. Antioxidants could control gasoline oxidation in copper-free gasoline but often gave reduced performance when copper was present.³ In one study, the concentration of antioxidant in gasoline needed to provide a constant level of oxidation resistance increased 4-fold when 1 part per million (ppm) of soluble copper was added.⁴

Three methods of countering copper's adverse effects on gasoline stability have been proposed:³ increase antioxidant concentration, remove copper, or render copper innocuous without removing it.

The first method is usually costly and not always effective. The second method has been the subject of recent investigations,^{5,6} but overall economic viability in full-scale commercial and military applications has yet to be clearly demonstrated. The last method is the one usually chosen, and is accomplished by using additives known as copper (or metal) deactivators that form complexes with the copper, rendering it catalytically inactive.

Metal deactivators were first used in gasoline in 1939.⁷ Despite development of other metal deactivators claiming superior complexing ability,⁸ the most commonly used additive then³ is still the one most com-

(1) Hall, W. A. *J. Inst. Pet. Technol.* **1914–1915**, *1*, 102.
(2) Bridgeman, C. *SAE J.* **1932**, *30*, 207.
(3) U.S. Patent 2,181,121.
(4) Peterson, C. J. *Ind. Eng. Chem.* **1949**, *41*, 924–928.

(5) Puranik, D. B.; Guo, Y.; Singh, A.; Morris, R. E.; Huang, A.; Salvucci, L.; Kamin, R.; David, V.; Chang, E. L. *Energy Fuels* **1998**, *12*, 792.
(6) Morris, R. E.; Chang, E. L. *Pet. Sci. Technol.* **2000**, *18*(10), 1147.

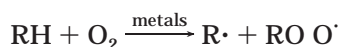
monly used now.⁹ That metal deactivator is also used in distillate fuels⁹ but has been shown to be less effective in other areas of the petroleum industry where contact with metals causes oxidative degradation. These areas of use include lubricants and polyolefin insulation for electrical wiring.¹⁰

The remainder of this review is divided into several sections. First, a general review of the chemistry of metal-catalyzed peroxidation is described. Second, three primary classes of action attributed to metal deactivators: chelation, surface passivation, and bulk phase reactivity, are discussed. In each of these sections, special attention is given to metal deactivator use in jet fuels since this is one of the most important and controversial areas of application. Third, a review of the synthetic development of metal deactivators is given that describes each of the six major structural classes described in the literature. Finally, a section including a summary and concluding remarks is provided.

Chemistry of Metal-Catalyzed Peroxidation

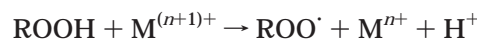
General Considerations. Metal ions, especially transition metal ions (copper, vanadium, nickel, lead, manganese, cobalt, etc.), can have a profound effect on the rate of hydrocarbon peroxidation.^{9,11} Some studies have shown that high levels of deliberately added copper salts (60–2000 ppm Cu) can suppress hydrocarbon peroxidation,^{12–15} possibly by complexing the peroxy radicals and interrupting the chain process.¹⁴ However, at the levels found in copper-contaminated fuels (usually 100 ppb or less Cu), hydrocarbon peroxidation is greatly accelerated. Other trace metals can cause similar accelerative effects, although the size of the effect is strongly dependent on the metal.⁹

Dissolved transition metals are thought to initiate hydrocarbon peroxidation by catalyzing the formation of free radicals.⁹



The above reaction is the net result of multistep reactions. The metals involved are catalytic metals such as copper.

Dissolved transition metals can also accelerate hydrocarbon peroxidation by catalyzing the decomposition of hydroperoxides. The mechanism usually cited is as follows:^{16,17}

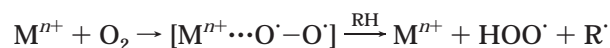


These oxidation–reduction reactions likely occur by first forming a metal–hydroperoxide complex followed by electron transfer to give the free radicals.¹⁶ The sum of these two reactions is a common decomposition reaction for hydroperoxides:¹⁷



If the metal involved is a strong oxidizing agent, such as tetravalent lead, the second reaction predominates. If the metal is a strong reducing agent, such as divalent iron, the first reaction predominates. However, the most damaging scenario occurs when the metal can convert between two oxidation states with comparable ease. Examples of such metals include copper, cobalt, and manganese. The ability of these metals to act as both an oxidizing agent (in its higher oxidation state) and reducing agent (in its lower oxidation state) allows a nonstoichiometric, catalytic process to occur where a very small concentration of metal can decompose large amounts of hydroperoxides. The greatly increased rate of free radical formation reduces the induction period, thereby accelerating the onset of rapid peroxidation.

Under some conditions, metals in hydrocarbons may complex with dissolved oxygen, thereby directly initiating the peroxidation process.^{18–22}



Metal Contamination in Jet Fuel. The copper sweetening process that resulted in the development of the first metal deactivator additive for petroleum gasoline has been almost entirely replaced by other processes that do not provide a potential source of copper contamination, such as Merox treating and hydrotreating.²³ However, copper and other transition metals can still become contaminants in jet fuel due to contact with copper-containing metal parts during transport and storage. One study reported in 1973 found JP-5 fuel on U. S. Navy aircraft carriers to contain as much as 1200 ppb copper.²⁴ However, a more recent and extensive study indicated lower values.²⁵ Of the 201 JP-5 samples tested, the highest copper level observed was 838 ppb, with 73 of the samples having copper levels above 50 ppb. Other metals such as iron, zinc, and nickel were also measured at various levels. However, copper is

(7) Downing, F. B.; Clarkson, R. G.; Peterson, C. J. *Oil Gas J.* **1939**, 38 (11), 97.

(8) U.S. Patent 4,749,468.

(9) Hazlett, R. N. *Thermal Oxidation Stability of Aviation Turbine Fuels*; ASTM: Philadelphia, 1991; Chapters 2, 6, 8, 9.

(10) Pospisil, J.; Klemchuk, P. P. *Oxidation Inhibition in Organic Materials*; CRC Press: Boca Rotan: 1990; Vol. 1, Chapters 3, 7.

(11) Por, Nahum *Stability Properties Of Petroleum Products*; The Israel Institute of Petroleum And Energy, The School of Petroleum And Energy Sciences: Tel Aviv, March 1992; p 30.

(12) George, P.; Robertson, A. *Trans. Faraday Soc.* **1946**, 43, 217.

(13) George, P.; Robertson, A. *J. Inst. Pet.* **1946**, 32, 382.

(14) Bernhard, R. A.; Marr, A. G. *Food Res.* **1960**, 25, 517.

(15) Klaus, E. E.; Wang, J. C. *Tribol. Trans.* **1992**, 35, 316.

(16) Scott, G. *Atmospheric Oxidation and Antioxidants*; Elsevier: New York, 1965.

(17) Reich, L.; Stivala, S. S. *Autoxidation of Hydrocarbon and Polyolefins, Kinetics, and Mechanisms*; Marcel Dekker: New York, 1969.

(18) Anderson, B. *Ark. Kemi* **1950**, 33, 451.

(19) Bateman, L. *Q. Rev.* **1954**, 8, 147.

(20) DeBoer, J. H.; Fortuin, J. P.; Waterman, H. I. *Koninkl. Ned. Akad. Wet.* **1958**, 61B, 170; C. A. **1959**, 53, 2144.

(21) Uri, N. *Nature.* **1956**, 117, 1177.

(22) Uri, N. *Chem. Ind. (London)* **1956**, 23, 515.

(23) Henry, C. P. Retention of Metal Deactivator Additive performance During Storage Of Aviation Fuels. In *Proceedings of the 6th International Conference on Stability and Handling of Liquid Fuels*, Vancouver, B. C., Canada, October, 1997; U.S. Department of Energy: Washington, DC; pp 51–59.

(24) Shertzer, R. H. Investigation of the Reduction of Thermal Stability of Fuel by Copper Contamination on Aircraft Carriers. Report NAPT-PE-14; Naval Air Propulsion Test Center, January, 1973.

(25) Cuellar, J. P., Jr.; Russel, J. A. Additive Depletion and Thermal Stability Degradation of JP-5 Fuel Shipboard Samples. Report NAPT-PE-141C, Southwest Research Institute on Contract with Naval Air Propulsion Center: Trenton, DE, June, 1985.

generally considered the most catalytically active of the metals typically found in fuels.^{4,7} In 1997, one source reported that copper will usually not exceed 100 ppb in jet fuels.²³

Effects of Metals on Jet Fuel Thermal Stability.

When measuring the thermal stability of aviation turbine fuels, the most common methods used involve the jet fuel thermal oxidative tester, JFTOT.⁹ The JFTOT involves passing fuel over the outer surface of an electrically heated metal tube and then through a 17 micrometer porosity filter.⁹ Although a wide variety of tube metallurgies have been used, the most common is an aluminum alloy. The fuel flow rate is laminar. In the most commonly used procedure, ASTM D3241, the fuel volume is 450 mL, the duration is 2.5 h, and the maximum tube temperature is 260 °C. During the test, the pressure drop across the post-tube filter is monitored as an indication of filterable material formed due to thermal stressing of the fuel. At the test's end, the outer surface of the tube is visually rated for signs of deposition. In another procedure, an ASTM D3241 test is repeatedly run at successively higher temperatures until an unacceptable tube rating or post-filter pressure drop occurs. This "breakpoint" temperature is used to define the upper limit of fuel thermal stability with respect to the JFTOT.⁹

The sensitivity of jet fuels toward the catalytic effects of copper is variable. In one study, as little as 1.32 ppb dissolved copper as copper(II) ethyl acetoacetate caused a 58% increase in fuel oxidation (as measured by oxygen consumption) compared to the same fuel without the added copper compound when stressed in the JFTOT at 260 °C.²⁶ However, higher levels are usually required to cause a failure in the ASTM D3241 when run at 260 °C. For instance, in the previously cited study of 201 JP-5 fuels, all of the 73 fuels with copper levels above 50 ppb failed the JFTOT at 260 °C; only several failed when copper was 25 to 50 ppb.^{9,25} Even so, in a more recent study when three jet fuel samples that each passed ASTM D3241 at 260 °C with a visual code 1 tube rating were doped with 50 ppb copper as copper naphthenate, only one fuel failed subsequent JFTOT testing at 260 °C. The other two jet fuels gave passing results that appeared unaffected by the copper.²⁷ In the same report, three other jet fuels were found to have JFTOT breakpoints higher than 300 °C despite the fact that each of the three fuels had copper levels between 26 and 29 ppb. When an effort was made to find jet fuel samples that would fail ASTM D3241 at 260 °C, eight such fuels were found. Analysis indicated that five of the eight fuels contained copper at 13–91 ppb.²⁷

The link between dissolved copper and jet fuel thermal stability problems may be more extensive and complex than previously thought. Kamin and Nowack²⁸ reported an instance when a large pipelined shipment

of JP-5 from Houston to Norfolk experienced significant degradation in JFTOT breakpoint during transit. The copper level was reported as 20 ppb. When a sample of the fuel was treated with benzotriazole to precipitate the copper, the JFTOT of the resulting fuel was not improved. The authors concluded that the 20 ppb copper was not a factor in the thermal stability degradation experienced by the fuel during transport.

However, more recent work by Pande and Hardy,^{29–34} using the gravimetric JFTOT, has shown that the combined effect of aging in the presence of dissolved copper is far larger than the sum of the individual effects of aging without dissolved copper and dissolved copper without aging. The gravimetric JFTOT is a modification of the JFTOT where the heated metal tube is replaced by a metal foil strip (usually stainless steel). The metal strip and the post-strip filter are weighed before and after the test to quantify the deposits. This gravimetric JFTOT work also showed that if the soluble copper dopant was added to the jet fuel after the aging process, the effect on gravimetric JFTOT performance appeared to be roughly equivalent to the sum of the aging effect alone and the copper effect alone. The importance of a similar synergistically antagonistic effect of jet fuel aging during transport and storage in the presence of adventitious copper on ASTM D3241 performance has not yet been clearly demonstrated. In this regard, interpretation of previously reported studies is often hindered by a lack of documentation of the inherent copper level and/or the age and storage history of the involved fuels. It remains to be determined to what extent such an effect plays a significant role in thermal stability problems such as the Houston to Norfolk incident reported by Kamin and Nowack.

The catalytic effect of metals on hydrocarbon oxidation is most commonly controlled by the use of metal deactivators. Data in the literature suggest three possible classes of action for metal deactivators: chelation, surface passivation, and bulk phase reactivity. Work done prior to 1991, especially with regard to jet fuels, has been previously reviewed.⁹ The following three sections of this paper deal with each of these three classes of action, emphasizing studies reported since 1991. It should be pointed out that the term "passivation" is used throughout this review to describe any effect that a metal deactivator has on a metal surface that affects stability-related properties. A better term may be "effects" since it correctly indicates that surface activity can modify fuel stability due to a wide variety

(29) Pande, S. G.; Hardy, D. R. The Effect of Copper, MDA, and Accelerated Aging on Jet Fuel Thermal Stability as Measured by the gravimetric JFTOT. In *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*, Rotterdam, The Netherlands, October, 1994; U.S. Department of Energy: Washington, DC; pp 195–209.

(30) Pande, S. G.; Hardy, D. R. *Energy Fuels* **1995**, *9*, 177–182.

(31) Pande, S. G.; Hardy, D. R. Comparison of the Effects of Storage Conditions, Type of Soluble Copper, and MDA on JP-5 Fuel Thermal Stability. In *Proceedings of the 6th International Conference on Stability and Handling of Liquid Fuels*, Vancouver, B. C., Canada, October, 1997; U.S. Department of Energy: Washington, DC; pp 211–230.

(32) Pande, S. G.; Hardy, D. R. *Energy Fuels* **1997**, *11*, 1019–1025.

(33) Pande, S. G.; Hardy, D. R. Effectiveness of MDA on Jet Fuel Thermal Stability as Determined Using the gravimetric JFTOT: Effects of Extended Duration Testing and Time of Addition of MDA. In *Proceedings of the 6th International Conference on Stability and Handling of Liquid Fuels*, Vancouver, B. C., Canada, October, 1997; U.S. Department of Energy: Washington, DC; pp 31–50.

(34) Pande, S. G.; Hardy, D. R. *Energy Fuels* **1998**, *12*, 129–138.

(26) Morris, R. E.; Turner, N. H. *Fuel Sci. Technol. Int.* **1990**, *8*, 327–350.

(27) Henry, C. P. Jet Fuel Thermal Stability And Metal Deactivator Additive. In *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando, FL, November, 1991; U.S. Department of Energy: Washington, DC; pp 692–702.

(28) Kamin, R. A.; Nowack, C. J. An Investigation of the Degradation of Aviation Fuel Thermal Oxidation Stability During Transit. In *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando, FL, November, 1991; U.S. Department of Energy: Washington, DC; pp 217–230.

of chemical processes only some of which involve the adsorption of a protective layer. However, "passivation" is nonetheless used throughout this review due to its common usage in the jet fuel literature. The wider implication of the term surface passivation should be remembered by the reader.

Chelation

Structure vs Performance. Since trace metals in fuels generate free radicals by first interacting with hydrocarbons and/or hydroperoxides, a logical approach to prevent such reactions is to strongly complex the entire inner coordination sphere of the metal ion with an innocuous molecule. Various chelating agents have been developed over the last 61 years that perform that function. All chelating metal deactivators have multiple donor atoms covalently connected by atoms that surround the complexed metal ion with several rings. The most common fuel metal deactivator used today is *N,N*-disalicylidene-1,2-propane diamine⁹ (also called *N,N*-disalicylidene-1,2-propane diamine): *N,N*-Disalicylidene-



1,2-propane diamine, commonly referred to as MDA, is one of the metal deactivators first developed for gasoline around 1939.⁷ As shown above, MDA is a tetradentate ligand, complexing the metal ion with two oxygen atoms and two nitrogen atoms.

A metal deactivator's ability to inhibit a given metal's catalytic effect on fuel peroxidation depends on two broad areas: metal deactivator structure and electronic properties of the metal.^{16,35} Factors pertaining to each of these areas include Lewis base strength, number of ligand–metal bonds, number of chelation rings, size of chelation rings, noncomplexing side chains, maximum coordination number of metal, and preferred ligand geometry. A brief discussion of each of these factors follows.

Coordinate covalent bonds formed in ligand–metal interactions are an example of Lewis acid–base reactions. Ligands that have stronger Lewis base properties will tend to form more stable complexes with the metals in the fuel, thereby reducing the level of peroxidation catalysis caused by the metal. Structural features that tend to increase electron density on the donor atoms of the ligand will increase coordinate bond stability.

The greater the number of donor sites in a metal deactivator (polydentate), the better the deactivation of the metal in the fuel. This is the so-called "chelate effect" and is related to entropy since it is less probable that all donor sites will simultaneously dissociate from the metal if the donor sites are connected by backbones within the same molecule.

As the number of donor sites increases within a single metal deactivator molecule, the number of chelation rings generally increases. This tends to increase the deactivation of a metal ion by more completely surrounding it, thereby better preventing the approach of hydrocarbons and hydroperoxides.

(35) Basolo, F.; Johnson, R. C. *Coordination of Chemistry*; W. A. Benjamin: Reading, MA, 1964; Chapter 5.

The number of atoms in the backbone of each chelation ring affects metal deactivator performance. Usually, maximum chelation stability occurs when ring backbones contain five to six atoms. Chelation rings with less than five atoms experience ring strain, while chelation rings with more than six become less stable because of reduced ring closure probability (entropy).³⁶

If a metal deactivator has a bulky side chain branching off near a donor site, the level of metal deactivation will be reduced. This is because the side chain hinders the close approach of metal and metal deactivator.

N,N-Disalicylidene ethylenediamine and related compounds effectively deactivate copper but have no effect on iron and have been shown to actually further activate cobalt.⁷ The likely reason is that copper(II) ions form tetradentate complexes, while iron and cobalt ions form hexadentate complexes.³⁵ The tetradentate MDA cannot completely saturate the maximum coordination number of iron and cobalt, thus allowing access to hydroperoxides. In the case where the supposed deactivators give further activation, shifts in metal d electron density are most likely occurring that provide more favorable electron transfer with hydrocarbons or hydroperoxides.

Coordination complexes of transition metal ions have specific geometric orientations that depend on the number of d electrons, the ligand field strength provided by the metal deactivator, and the distribution of d electrons within the ligand field-split set of d orbitals.³⁵ With maximum coordination number of six, the preferred geometry is invariably octahedral. Tetradentate complexes are either tetrahedral or square planar, depending on the factors mentioned above. A tetradentate metal deactivator, such as *N,N*-disalicylidene-1,2-alkylene diamine, has a square planar conformation of ligand sites, a good match for divalent copper ions (that form square planar complexes). However, monovalent copper ions form tetrahedral complexes. Thus, copper(II) complexes with *N,N*-disalicylidene-1,2-alkylene diamine will be stabilized against an oxidation state change on copper. This may be one reason such metal deactivators work well with copper.¹⁶

Effects on Jet Fuel Stability. The benefits, limitations, and general behavior of MDA as a chelant has been the subject of extensive investigations. In one often cited work by Clark,³⁷ a series of flask oxidation tests at 160 °C showed MDA to greatly reduce the oxidation rate in liquid phase reactions catalyzed by soluble copper(II) salts, and the 1:1 mole ratio of the Cu(II)–MDA complex was verified. In another study, when 50 ppb of synthesized Cu(II)–MDA complex was added to AVTUR 50, the JFTOT breakpoint was only slightly decreased.³⁸ This result was confirmed in much more recent work by Morris et al.³⁹ where 5.8 mg/L of Cu(II)–MDA complex was added to JP-5 and evaluated in

(36) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*; McGraw-Hill: New York, 1970; p 530.

(37) Clark, R. H. The Role of a Metal Deactivator in Improving the Thermal Stability of Aviation Kerosines. In *Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels*, London, England, September, 1988; Institute of Petroleum: London; pp 283–293.

(38) Amos, R.; Knight, J. Jet Fuel Therm-Oxidative Stability: Some Effects of Nitrogen Compounds and of Nitrogen Sulfur Interactions. Technical Report 83048; Royal Aircraft Establishment: Farnborough, Hants, U.K., May, 1983.

(39) Morris, R. E.; Hasan, M. T.; Su, T. C. K.; Wechter, M. A.; Turner, N. H.; Schreifels, J. *Energy Fuels* **1998**, *12*, 371–378.

JFTOT tests at 240–345 °C using stainless steel tubes. Deposits were measured using the carbon burnoff technique and compared to deposits obtained from the similarly tested neat JP-5. Only minor increases in tube deposits were observed for the Cu(II)–MDA additized fuel relative to the neat fuel when tested at 240, 260, and 300°. A slight decrease was observed at 345 °C.

In the same report,³⁹ Cu(II) complexes of MDA and the *trans*-cyclohexane homologue of MDA were prepared. The thermal stability of the two complexes were measured in the gas phase using mass spectrometry (MS). The MDA complex dissociated at 295 °C into free copper and MDA, whereas the *trans*-cyclohexane MDA appeared stable until 385 °C, then dissociated at a rate much less than the MDA complex as temperature was further increased. Liquid phase thermal stabilities of the two complexes were measured using JFTOT runs at 350 °C for 2.5 h. Once again, the *trans*-cyclohexane MDA complex was more stable, although not by the 90 °C interval indicated in the gas phase work.

In another study,^{40,41} a series of six jet fuels of unstated age and storage history were tested in a near isothermal flow test rig (NIFTR). NIFTR tests consist of pumping test fuel through a narrow (i.d. = 0.216 cm), and long (81.3 cm), stainless steel tube held at 185 °C. In these tests, the NIFTR was run in a mode specifically designed to measure oxygen consumption of the test fuel during stressing. The stainless steel tube was silicosteel passivated to minimize any surface catalytic effects. Fuel flow rate was adjusted to vary fuel contact time with the hot tube. All test fuels were saturated with air before testing, and oxygen content of the fuel before and after entering the NIFTR was measured. The six fuels were tested with and without 2 mg/L MDA. On three fuels with negligible levels of metals, MDA had no significant effect on O₂ consumption. On the three fuels with moderate levels of metals (Cu = 34, 35, 7 ppb; Fe = nil, nil, 26 ppb), MDA noticeably reduced O₂ consumption.

However, MDA does have its limitations as a chelant. In another study by Morris and co-workers,²⁶ modified JFTOT tests at 280 °C were run on three aliquots of a Jet A additized with 1.32 mg/L (1,300 ppb) copper from three different fuel soluble organo-Cu(II) compounds. All three copper-doped fuels gave similar levels of tube deposits, as measured by the tube deposit rater (TDR). When 5.8 mg/L MDA was added to one of the copper-doped fuels and similarly tested, tube deposits as measured by the TDR were significantly reduced over the tube region corresponding to actual temperatures of 250 °C and higher. However, deposits on the tube corresponding to actual temperatures of 200–220 °C were not affected. X-ray photoelectron spectroscopy (XPS) of the tubes after testing revealed that copper-doped fuel without MDA gave deposits with copper distributed over the entire tube length, although most of it was in the area of the tube where actual temperatures were 200–220 °C. When MDA was added to this copper doped fuel, all copper in the tube areas corre-

Table 1. Effect of Copper, MDA, and Aging on JP-5 Thermal Stability as Measured by gravimetric JFTOT

MDA, ppm	Cu, ^a ppb	LPR, ^b aging	deposits, mg/L		
			strip	filter	total
0	0	no	0.049	0.24	0.29
0	0	yes	0.038	1.19	1.23
0	~400	no	0.048	1.28	1.33
5.7	396	no	0.016	0.15	0.17
0	400	yes	0.097	9.33	9.43
5.7	396	yes	0.024	0.20	0.23
5.7	0	yes	0.022	0.25	0.27

^a Added as copper(II) ethylacetoacetate. ^b 90 °C, 50 psig air, 24 h.

sponding to temperatures above 250 °C were no longer present, but copper levels in the lower temperature areas were not affected. These results suggest thermal decomposition of the fuel soluble, organo Cu(II) compounds at 220–220 °C. Also, MDA was effective in decreasing tube deposition caused by the copper doped fuel at 250 °C, but was ineffective at lower temperatures.

In work by Pande and Hardy,^{29,30} the effect of MDA on fuels that had experienced various combinations of copper contamination and aging were evaluated using the gravimetric JFTOT. Copper contamination was accomplished by addition of fuel soluble copper compounds. Aging was accomplished by simulating 6 months ambient laboratory aging by using the low-pressure reactor (LPR) that utilized 50 psig air overpressure at 90 °C for 24 h. When 5.7 mg/L MDA was added to jet fuels, the effect of subsequent doping with 400 ppb copper as copper(II) ethyl acetoacetate, or aging, or aging with the copper compound gave strip and filterable deposit weights similar to those of the neat nonaged fuel. Relevant data from this work are given in Table 1.

Similarly, a Jet A with 3 ppb natural copper was additized with 35 ppm MDA and 24 mg/L BHT and aged for 13 months ambient conditions while exposed to copper rods.^{33,34} At the end of the aging period, copper levels in the fuel were 4,000 ppb. Gravimetric JFTOT performance of the fuel was comparable to that of the neat aged fuel. Similar tests were performed on the same Jet A dosed with 400 ppb copper as Cu(II) ethyl acetoacetate and aged for 48 h in the LPR. When 5.8 mg/L MDA alone was added to the fuel before aging, gravimetric JFTOT deposits were not significantly increased. However, when 24 mg/L of BHT alone was added to the fuel before aging, gravimetric JFTOT filterable deposits were much higher. This agrees directionally with the original MDA gasoline work, which demonstrated the limited ability of antioxidants to control peroxidation due to soluble catalytically active metals.⁴ When a JP-5 was doped with 420 ppb copper as copper(II) ethyl acetoacetate, aged 24 h in the LPR, and then additized with 5.7 ppm MDA, strip deposits were not reduced and filterable deposits were only slightly reduced relative to the same copper-doped/aged fuel without MDA.^{29,30} The implication of this work is that the combination of aging in the presence of soluble copper can generate instability precursors or products.^{29–32} Once these precursors or products are formed, chelation of copper may be a moot point. The damage to fuel thermal stability may already be done.

(40) Balster, W. J.; Balster, L. M. Use of MDA, BHT, and Dispersant Singly and in Combination as Jet-Fuel Additives. Presented at the Symposium on Structure of Jet Fuels IV, 211th National Meeting of the American Chemical Society, New Orleans, LA, March, 1996.

(41) Jones, E. G.; Balster, W. J.; Balster, L. M. *J. Eng. Gas Turbines Power* **1997**, *119*, 830–835.

Table 2. JFTOT Performance of Jet A/A-1 Fuels and Effect of Added Copper and MDA

natural Cu, ppm	additive treatment	rating, ASTM code	ΔP	
			time	ΔP
10	as is	1	150	1
	80 ppb Cu	3A	150	69
	80 ppb Cu + 2 ppm MDA	<3A	150	3
<5	as is	1	150	3
	80 ppb Cu	1A	150	1
	80 ppb Cu + 2 ppm MDA	1	150	4
<5	as is	1	150	1
	80 ppb Cu	1	61	125
	80 ppb Cu + 2 ppm MDA	<2	150	2
6	as is	<2	150	0
	80 ppb Cu	3A	150	4
	80 ppb Cu + 2 ppm MDA	<2	150	0
5	as is	<2	150	0
	80 ppb Cu	3A	150	10
	80 ppb Cu + 2 ppm MDA	<2	150	2
34	as is	<2	150	0
	80 ppb Cu	3A	150	3
	80 ppb Cu + 2 ppm MDA	<3	141	125
<5	as is	2	150	1
	80 ppb Cu	<3	150	1
	80 ppb Cu + 2 ppm MDA			

Interestingly, several studies have reported MDA's inability to solve certain real world jet fuel thermal stability problems. One of those studies involved a fuel "stored several years."²⁷ The copper level of that fuel was not given. In yet another study,²³ seven Jet A/Jet A-1 fuels of unstated age, unstated transport/storage history, and varying inherent copper levels (<5–34 ppb) were evaluated by ASTM D3241 at 260 °C. All passed. When 80 ppb copper as copper naphthenate was added to each fuel, six failed; the seventh marginally passed. When the six failing fuels were also additized with 2 ppm MDA, two of the six fuels still failed. Interestingly, those two fuels had the highest inherent copper levels (10 and 34 ppb) of the original seven fuels. The MDA level was far in excess of the stoichiometric amount needed to complex both inherent and added copper. Relevant data from this work are given in Table 2.

These two studies underscore a common theme in much of the reported prior work: use of fuels that are either old or that have poorly defined or documented history. It may be difficult to obtain fuels that are either new or that have well documented storage and transport histories, especially if obtained by an organization that is not a fuel refiner/marketer. Nonetheless, if the effort to obtain such well-defined fuels is not taken, opportunities to answer long-standing technical questions and resolve apparent contradictions in the existing literature will likely continue to be lost.

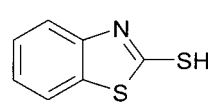
Recent work by Morris et al.³⁹ evaluated the effect of structure on relative metal deactivator effectiveness. Various analogues of MDA were synthesized and 5.8 mg/L of each were added to portions of a JP-5. Extended JFTOT tests at 260 °C for 5 h using stainless steel tubes were performed on each dry air-sparged, additized fuel, and tube deposits by carbon burnoff were measured. Results generally agreed directionally with the effects of structure on performance as discussed earlier in this review. However, the size of the effects as measured by JFTOT tube deposits were not as large as indicated in earlier O₂ consumption experiments, as indicated and cited by the authors. It should be noted that the JP-5 fuel contained 14 ppb copper. The authors concluded

that MDA's ability to control fuel peroxidation (via copper chelation) was not the only factor reducing JFTOT tube deposits.

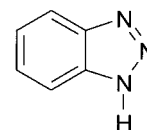
Information available in the literature suggests two additional classes of action by which MDA can affect fuel stability-related properties: surface passivation and bulk phase reactivity.

Surface Passivation

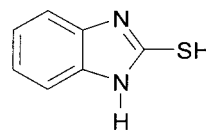
Structure vs Performance. Metal passivators have been primarily used in the lubricant industry. Commonly used metal passivators are generally heterocyclic materials, often polycyclic with at least one benzene ring. Alkyl groups are often present on either the benzene ring or on one of the heteroatoms to enhance solubility in the hydrocarbon. The basic structures (without alkyl groups) of four such metal passivators are shown below: Mercaptobenzothiazoles and mercap-



2-Mercapto-1,3-benzothiazole



1,2,3-Benzotriazole



2-Mercaptobenzimidazole



1,2,3-Thiadiazole

tobenzimidazoles not only form surface films, they can also trap corrosive sulfur.⁴² However, the effectiveness of these additives decreases at temperatures above 248 °F (120 °C). This is due to an oxidative dimerization, which produces a disulfide with no surface passivation properties. Benzotriazoles do not have the above problem,^{43,44} and depending on the oxidation state of the surface, can completely passivate copper with as little as 25% coverage.⁴²

One area within the petroleum industry that has received much attention with respect to metal deactivator surface effects such as passivation is jet fuels. Work concerning MDA surface effects in jet fuels is described in the next subsection.

Effects on Jet Fuel Stability. Since the mid-1980s it has been known that MDA can often dramatically improve jet fuel thermal stability in ASTM D3241,²⁷ even in fuels with negligible levels of catalytic metals. Such thermal stability improvements are generally characterized by reduced surface deposits. The importance of reducing surface deposits in jet fuel systems is significant because such deposits in heat exchangers, injector nozzles, etc. have long been linked to potential jet engine performance problems.⁹ It should also be mentioned that the reduction in surface deposits (in real jet engines or large simulator rigs) or tube deposits (in smaller bench testers that use a tube configuration heated surface) attributed to MDA can be due to a surface effect or some other property of MDA that occurs

(42) Hamblin, P. C.; Kristen, U.; Chason, D. *Lubr. Sci.* 2, 287.

(43) Lewis, G.; Fox, P. G. *Corros. Sci.* 1978, 18, 645.

(44) Fox, P. G.; Lewis, G.; Boden, B. J. *Corros. Sci.* 1979, 19, 457.

in solution and then effects the fuels propensity to form deposits on the hot surface. Work that indicates surface effects are described in this subsection. The potential for MDA to affect a fuel's thermal stability in solution, both with respect to surface deposits and nondeposited insolubles (filterable insolubles), is discussed in the following section on bulk phase reactivity.

Morris and Hazlett evaluated the effect of MDA in a Jet A with less than 1 ppb copper using extended (5 h) JFTOT tests at 260–310 °C.⁴⁵ Five inch stainless steel tubes were used, and the fuel was sparged with air before testing. At MDA concentrations from 1.5 to 5.8 mg/L, tube deposit volumes as measured by the dielectric measuring device decreased by about 82% relative to the neat fuel. No further improvement was observed at 11.6 mg/L. The Jet A was diluted with an equal volume of Naval distillate (diesel) fuel, and similar JFTOT tests were run. MDA continued to reduce tube deposit volume relative to the neat fuel, although it was somewhat less effective at lower concentrations in the Jet A/Naval distillate blend compared to the Jet A. This demonstrated that the ability of MDA to reduce surface deposition in JFTOT tests was dependent on fuel composition. A similar report by the same authors using carbon burnoff measurements of JFTOT stainless steel tube deposits and a jet fuel with 4 ppb copper gave similar results.²⁶ Since negligible copper with respect to JFTOT performance was present in these fuels, the ability of MDA to reduce tube deposits did not appear to be due to chelation.

During 1988–1991, several studies,^{37,46,47} showed that MDA can significantly reduce surface deposits caused by fuels containing negligible copper when stressed in larger test rigs designed to more realistically simulate jet aircraft systems. However, the reduction in surface deposits relative to the neat fuel was generally less than the reduction in tube deposits observed in the JFTOT.³⁷ Also, it was noted that a somewhat higher concentration of MDA was required to reduce deposits in the large rigs compared to the JFTOT. More significantly, the MDA-induced reduction in deposit formation rate in the large test rigs appeared to exhibit an induction period beyond which little or no benefit was observed. The induction period was observed to vary directly with the MDA concentration.⁴⁷

It should be noted that in one of the above studies³⁷ copper and iron levels are given for test fuels, and in the other studies^{46,47} negligible metal levels in fuels are implied but measured values are not given. Similarly, in other studies cited throughout this review, test fuels are sometimes referred to as having negligible metals or negligible copper. Although actual measurement of

all metals should always be reported, such is not always the case. With respect to the presence of metals other than copper, as already mentioned and cited in this review, such metals usually have much less effect on jet fuel stability than does copper. Since MDA does not appear to be effective in deactivating these other metals through chelation, any improvement in surface deposits in MDA-treated fuels with such metals would most likely be caused by some other class of action.

These results were interpreted as evidence of a passivation of JFTOT tube and test rig surfaces by the MDA. Passivation and resulting resistance to deposits was thought to occur on clean surfaces.⁴⁶ Increased post-induction deposit formation rate was interpreted as an indication that the surface film was either stable for a limited time or provided less than perfect protection. The greater passivation effect in the JFTOT procedure was attributed to its shorter time and its laminar fuel flow compared with much longer times and turbulent fuel flow of the other more realistic test rigs.⁴⁸ This work generated a great deal of concern over the exact role of MDA in jet fuel thermal stability. As a result, numerous subsequent reports were published evaluating the effect of MDA on jet fuel thermal stability in various test environments.

Earlier in this review a report was discussed where a JP-5 had degraded in JFTOT performance during pipeline shipment from Houston to Norfolk.²⁸ This fuel had 20 ppb copper but did not improve in JFTOT performance when the copper was removed by precipitation with benzotriazole. This implied that the copper was not directly causing deposit formation during the actual thermal stressing in the JFTOT test. When 1 ppm MDA was added to this fuel, the JFTOT breakpoint increased from 243 to 304 °C. When this same MDA-treated fuel was tested in extended T700 injector tests at Southwest Research Institute, nozzle deposits were significantly reduced relative to the unadditized fuel for the first 100 hours. Beyond that time, the nozzle fouling rapidly increased.²⁸

In an Alcor hot liquid process simulator (HLPS) test at 335 °C, 5 h, and 3 mL/minute fuel flow rate, the effect of 7.5 mg/L MDA in three JP-8 fuels was evaluated.⁴⁹ Two of the three fuels were reported to have “no detectable copper.” The copper content of the third fuel was not given. All three fuels had been additized with BHT and a dispersant. The MDA reduced tube deposits in all three fuels relative to the fuels without MDA. When HLPS runs were extended to 30 h, no adverse effect of the MDA-treated fuels relative to the MDA-free fuels was observed. No indication of an induction period was observed in any of the additized fuels relative to the additive-free base fuel. Some of these data are presented in Figure 1a,b.

An earlier report used the HLPS in a “split run” procedure.⁵⁰ A jet fuel with 7 ppb copper was treated with 5.7 mg/L MDA and run for 75 min at 290 °C. Then

(45) Morris, R. E.; Hazlett, R. N.; McIlvaine, C. L., III Influences Exerted By Selected Stabilizer Additives on the Thermal Stability of Jet Fuel. In *Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels*, London, UK, Sept, 1988; Institute of Petroleum: London; pp 260–267.

(46) Clark, R. H.; Delargy, K. M.; Heins, R. J. The Role of a Metal Deactivator Additive in Improving the Thermal Stability of Aviation Kerosines: Additive Adsorption Studies. In *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, August, 1990; American Chemical Society: Washington, DC, 1990; pp 1223–1232.

(47) Clark, R. H.; Stevenson, P. A. The Thermal Degradation of Aviation Fuels in Jet Engine Injector Feed-Arms: Results from a Half-Scale Rig. In *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, August, 1990; American Chemical Society: Washington, DC, 1990; pp 1302–1314.

(48) Schreifels, J. A.; Morris, R. E.; Turner, N. H.; Mowery, R. L.; Hues, S. M. *Energy Fuels*. **1991**, *5*, 263.

(49) Anderson, S. D.; Harrison III, W. E.; Edwards, T.; Morris, R. W.; Shouse, D. T. Development of Thermal Stability Additive Packages For JP-8. In *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*; Rotterdam, The Netherlands, October, 1994; U.S. Department of Energy: Washington, DC; pp 255–273.

Table 3. Effect of MDA on Split Run HLPS Performance

run time, min.	MDA, mg/L	C/Al, max ^a
75	0	2.6
75	0.57	0
75	5.7	
75	0	0.15
75	0.57	
75	0	0.21
75	0	
75	5.7	0.5
75	0	
75	0.57	2.0

^a Deposits measured using electron beam of 4.0 kV.

unadditized fuel was run in the same test for another 75 min. Tube deposits were measured by scanning electron microscopy/energy dispersive analysis of X-rays (SEM/EDX) for carbon coverage on the aluminum tubes. Results of the 150 min split run indicated that MDA present only during the first half of the run greatly reduced the deposits compared to a 75 min run with the neat fuel. When the split run test was repeated with 0.57 mg/L MDA, deposits only slightly increased compared to when 5.7 mg/L MDA had been used. Relevant data from this work are given in Table 3. The authors concluded that under the conditions of the HLPS test, MDA continued to provide benefit even during the second 75 min of the "split run" (after it was no longer present in the fuel) because the surface passivating layer formed during the first 75 min did not desorb immediately. It is interesting to note that this is consistent with the results of the previously discussed HLPS work where no induction period was observed.⁴⁹

In a paper by Beal and Hardy,⁵¹ steel strips used in the gravimetric JFTOT were pretreated with various aqueous alkali metal hydroxides prior to use. When a JP-5 was evaluated by gravimetric JFTOT using each of those strips, strip deposit weight was decreased compared to an untreated strip. Furthermore, strip deposit reduction varied directly with the basicity of the hydroxide used. This behavior is consistent with other well-known facts. Magnesium migration to the surface of aluminum JFTOT tubes, known to have an inhibiting effect on jet fuel thermal deposit formation, will increase the tube surface basicity. Likewise, the chromium present in stainless steel JFTOT tubes will increase tube surface acidity, and the increased thermal deposits formed on stainless steel JFTOT tubes compared to aluminum tubes is well-known. Finally, MDA is a basic compound. The authors asserted that "some aspect of acid/base chemistry is involved in thermal deposition." It is interesting to note that MDA is a basic compound, although not as basic as alkali metal hydroxides.

In a series of papers by Pande and Hardy,^{29–34} the effect of MDA on jet fuel properties was measured using

(50) Baker, C.; David, P.; Hall, D.; Swatridge, R. Characterization of Degradation Products from Thermally Stressed Aviation Fuels and the Influence of MDA on Their Formation. In *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando, Florida, November, 1991; U.S. Department of Energy: Washington, DC; pp 316–328.

(51) Beal, E. J.; Hardy, D. R. The Effect of Temperature on Jet Fuel Thermal Stability Defined by Direct Gravimetric Analysis of both Surface and Fuel Insoluble Deposits. Presented at the Distillate Fuel Auto-Oxidation Chemistry Symposium. In *Abstracts of Papers*; 207th National Meeting of the American Chemical Society, Washington, DC, August, 1994; American Chemical Society: Washington, DC, 1994; pp 82–85.

the gravimetric JFTOT. A number of Jet A, JP-5, and JP-8 fuels were tested with ambient or accelerated aging, copper treating by dopant addition or natural uptake due to prolonged exposure to metallic copper and combinations of aging and copper. In every test documented involving MDA, no antagonistic effect was observed.

Antagonistic effects were observed in a recent study using the near isothermal flow test rig (NIFTR).^{40,41} As mentioned earlier in this review, the NIFTR consists of a long, narrow stainless steel tube through which the air-saturated test fuel flows at a very slow rate. When the NIFTR was used to measure tube deposits and bulk fuel insolubles, the tube was 183 cm long, the fuel flow rate was 0.20–0.25 mL/minute, the tube temperature was 185 °C, and total test duration was 72 h. These parameters were determined so as to ensure complete oxygen use during the stress period as the fuel traveled the length of the hot tube. After each test, the stainless steel tube was cut into 5.1 cm segments, and the deposits in each segment were determined via carbon burnoff. This allowed both total deposit weights and deposit formation rates as a function of fuel stress duration to be calculated. For all fuels tested, deposit formation rates dropped off approximately at the stress duration time (position along the tube) where previous O₂ consumption tests showed O₂ levels to approach zero. Four Jet A's were tested neat and with MDA. Two of the fuels contained negligible metals; two contained moderate levels (Cu = 35 ppb, Fe = nil; Cu = 7 ppb, Fe = 26 ppb). In the negligible metal fuels, MDA did not have a significant effect on tube deposit rate or total deposits. In the moderate metal fuels, either 2 or 6 mg/L MDA reduced tube deposit buildup initially by lowering the peak deposit formation rate achieved compared to the neat fuels. However, total deposits formed during the 72 h tests were higher for fuels with either 2 or 6 mg/L MDA compared to total deposits formed by the neat fuels.

These results are interesting because unlike large jet fuel system simulator rigs where MDA performance limitations were observed, the NIFTR runs in laminar flow, just as does the JFTOT. However, interpretation of the NIFTR results in the light of other reported work is difficult for three reasons. First, the availability of oxygen in the fuel as it is thermally stressed along the hot surface will be different depending on the test equipment used. The NIFTR tests were designed to ensure oxygen was exhausted in a given portion of fuel before it exited the hot tube portion of the test device. Fuel flow in a JFTOT is much more rapid. However, JFTOT test fuels are typically not aerated before testing, as were the fuels in the NIFTR work. The oxygen availability of the jet fuel in large jet fuel system simulator rigs will also be different. Second, the ages of the fuels were not given. By the time this work had been done, several reports had indicated that MDA's ability to inhibit surface tube deposits can be greatly diminished or eliminated if the fuel is old,^{27,29,30} especially if the aging occurred in the presence of soluble copper.^{29,30} Third, others had already demonstrated that MDA may not provide any overall stainless steel tube deposit reduction (even in runs much shorter than 72 h) in fuels with copper when contact temperature is

below 220 °C.²⁶ The extent to which surface effects such as passivation show similar temperature dependency in the NIFTR test configuration may be different. However, reporting test work run only at 185 °C makes it difficult to interpret results in the light of other test data reported elsewhere. This is even further complicated by the uncertain effect of the inherent metals in at least two of the fuels. In fact, the authors of the NIFTR work acknowledged that different MDA behavior might have been observed at different temperatures.⁴¹ In hindsight, the NIFTR tests might have been more revealing if they had been repeated at several temperatures spanning a range including 280 °C. Also, the use of refinery fresh, metals-free fuels of varying ASTM D3241 performance would have been useful.

Surface Adsorption Dynamics. When it became clear that MDA was providing some additional benefit beyond chelation, reports began to be published investigating the adsorption behavior of MDA on various surfaces. In one of the earliest of these studies, secondary ion mass spectrometry was used to determine if MDA could be detected on aluminum surfaces after exposure to MDA-treated jet fuel.⁴⁶ Both aluminum foil and aluminum JFTOT tubes were used, and both static soaking tests and actual JFTOT tests at varying temperatures were performed. Results indicated that at ambient temperature, MDA was adsorbed at levels well below a monolayer when present in the fuel at 5.7 mg/L. As concentration increased, so did the amount of MDA detected on the surface. When JFTOT runs at varying temperatures were performed, surface MDA was found to dramatically increase as temperature increased from 140 to 260 °C. The authors concluded that MDA adsorption onto aluminum surfaces does not occur by a simple process. They proposed a possible mechanism whereby MDA polymerizes on the metal surface at high temperatures. Compositions of the proposed polymeric compounds were not given. In another paper, the presence of MDA was confirmed on aluminum and stainless steel when exposed to MDA-treated fuel or dodecane.⁵²

A series of subsequent papers by Schreifels, Morris, and co-workers have reported somewhat different findings. In one study,⁴⁸ various aluminum, stainless steel, and copper surfaces were exposed to solutions of 5.7 mg/L MDA in dodecane. A variety of spectroscopic techniques were used to measure MDA adsorption. Although MDA was detected on aluminum and stainless steel, it was at levels well below a full monolayer. No MDA was detected on copper. There appeared to be more MDA on stainless steel than aluminum. However, unless the dodecane was treated with silica gel prior to use, trace levels of dodecanoic acid displaced MDA in the experiments.

Gas-phase vacuum deposition experiments were conducted using stainless steel as the substrate and XPS and MS as the analytical tools.⁵³ Four chemi-adsorbed states and one physi-adsorbed state were observed. The physi-adsorbed state desorbed at about 30 °C, and the lowest chemi-adsorbed state was only weakly held

(Figure 2a,b). The higher chemi-adsorbed states may have had larger adsorption energies, but they could not be determined. In liquid-phase experiments using toluene as solvent, MDA was detected, and adsorption appeared to increase as steel surface temperature increased. However, coverage was estimated to be no more than 20%–30%.

Additional surface experiments detected the presence of a physi-adsorbed state and a chemi-adsorbed state on stainless steel surfaces exposed to MDA.⁵⁴ Under the conditions used, the chemi-adsorbed state began to form first, with the physi-adsorbed state initiating before the chemi-adsorbed state reached a monolayer of coverage. Temperature-programmed desorption experiments indicated that the chemi-adsorbed state desorbed at about 127 °C. Also, there was some indication that MDA may be decomposing on the surface. The authors suggested that since MDA did not appear to form a contiguous monolayer of coverage on metal surfaces, a surface passivation mechanism was not a likely reason for the deposit reduction behavior noted in MDA-treated jet fuels. Of course, the implicit assumption was that surface passivation can only occur if a complete monolayer occurs. As already mentioned, a complete monolayer coverage is known to not be required for complete surface passivation in the case of benzotriazoles.⁴²

In a follow-up study,⁵⁵ results indicated that MDA decomposed on stainless steel into two products. If the stainless steel was oxidized, evidence of two additional reaction products were noted. The authors proposed that the primary reaction products of MDA on stainless steel are formed by a Friedel–Crafts alkylation catalyzed by (Lewis) acid Fe sites on the stainless steel surface. Structures for the reaction products are proposed, and experimental evidence is given that these materials are more strongly bound to oxidized steel surfaces than the nonoxidized surfaces. The authors suggest that these reaction products will be present on steel surfaces of engine fuel systems at temperatures such as 450 K.

In a previously cited paper by Morris et al.,³⁹ the thermal stability of the Cu(II) complex of MDA was evaluated in the JFTOT using stainless steel tubes and a run temperature of 350 °C for 2.5 h. After the test, analysis of the deposits along the side of the tube revealed that the Cu(II)–MDA complex was dissociating at 340–350 °C and depositing copper on the steel tube surface. Further analysis of the copper revealed it to be zerovalent (elemental) copper. The absence of copper oxides led the authors to conclude that by the time the fuel got to the part of the JFTOT tube that was hot enough to dissociate the Cu(II)–MDA complex and deposit copper, oxygen in the fuel was exhausted. This, they concluded, was the reason carbonaceous deposits (from fuel thermal oxidative degradation) had not increased in that area of the tube despite the deposition of potentially catalytically active copper.

(53) Schreifels, J. A.; Gwynn, L.; Morris, R. E. Interactions of a Metal Deactivator with Metal Surfaces at Elevated Temperatures. In *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando, Florida, November, 1991; U.S. Department of Energy: Washington, DC; pp 661–675.

(54) Chusuei, C. C.; Morris, R. E.; Schreifels, J. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 3610–3617.

(55) Chusuei, C. C.; Morris, R. E.; Schreifels, J. A. *Appl. Surf. Sci.* **1999**, *153*, 23–34.

(52) Baker, C.; David, P.; Finney, R. Characterization and Quantification Of Deposits From Thermally Stressed Aviation Fuels. In *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, August, 1990; American Chemical Society: Washington, DC, 1990; pp 1233–1246.

At this point, the authors made an interesting observation. In turbulent test regimes such as the large scale rigs where MDA surface passivation effects are not as pronounced or long-lived as in the JFTOT, there will not be the temperature gradient that exists in laminar flow testers such as the JFTOT. At sufficiently hot test temperatures in those large rigs, any Cu(II)-MDA complex will dissociate to deposit copper on surfaces. This deposition will occur in areas where fuel O₂ will still exist. The authors suggested this as a potential explanation of the behavior of MDA-treated fuels in large test rigs. While this explanation bears additional investigation, it does not explain the behavior that MDA displays in fuels containing negligible metals.

Bulk Phase Reactivity

General Definition. As more work was reported on the effects of MDA on jet fuel thermal stability, data began pointing toward a third possible mechanism: bulk phase reactivity. Bulk phase reactivity as it applies to this review refers to any chemical activity of MDA (or other metal deactivators) other than chelation that changes fuel thermal stability and occurs in solution where reaction with metal surfaces does not occur. Examples of bulk phase reactivity would include homogeneous acid/base reactions such as neutralization of acidic reactants formed by fuel oxidation or other reactions, chain-breaking peroxidation inhibition, and hydroperoxide decomposition. No reports could be found in the literature which bulk phase reactivity of MDA was the central topic. However, a careful interpretation of data from various studies, many of which have already been cited herein, show that bulk phase reactivity is important.

Shorter Duration Testing. Clark³⁷ showed that in fuels with no metals present, MDA had no effect on fuel stability as measured by a flask oxidation test (400 mL fuel sparged with oxygen at elevated temperatures). This is consistent with the molecular structure of MDA, wherein no significant true antioxidant properties based on hindered phenal chemistry are expected.¹⁰ However, in two studies by Morris et al.,^{26,45} 5.8 mg/L MDA in jet fuels with negligible metals gave differing O₂ consumption results. In a Jet A fuel with less than 1 ppb copper, MDA gave large reductions in O₂ consumption compared to the neat fuel at 260 °C during a modified JFTOT test using stainless steel tubes and a 5 h duration. Hydroperoxides were similarly reduced. However, in another Jet A with 4 ppb copper, similar testing showed no significant reductions in hydroperoxides and only small reductions in O₂ consumption. Even so, the MDA caused dramatic reductions in the filterable insolubles formed during the JFTOT test.⁴⁵ From these data²⁶ it could not be determined if the benefits of MDA were due to a passivating effect on the hot steel tube surface, thereby reducing any heterogeneous oxidative catalysis, or due to some other reactive property of MDA.

In a split run JFTOT procedure at 270 °C, it was shown that 0.57 mg/L MDA not only prevented further deposits on aluminum tubes when present during the second half of the 2.5 h run, it actually decreased deposits formed during the first half of the test.⁵⁰ This effect was observed in two different jet fuels. In a third jet fuel, the effect was less pronounced. Copper levels

Table 4. Effect of MDA on JFTOT Split Runs

	time, mins	level of MDA, mg/L	temp, °C	TDR			δP mmHg	visual rating ^a
				spun	spot	position		
I	70	0	270	14	14.5	44	0	3
I	150	0	270	14.5	16	34	0	4P
I	70	0						
I	80	5.7	270	12.5	13.5	44	0	3
I	70	0						
I	80	0.57	270	16	19	44	0	3
II	70	0	270	37	38	40	>25	4PA
II	150	0	270				>25	4PA
II	70	0						
II	80	5.7	270	18.5	19	42	>25	A
II	70	0						
II	80	0.57	270	17.5	19	40	>25	A
III	70	0	305	23	27	37	0.2	4
III	150	0	305	45	46	40	0.2	>4
III	70	0						
III	80	5.7	305	27.5	30	37	0.1	A
III	70	0						
III	80	0.57	305	15.5	18	43	0.3	A

^a P indicates peacock; A indicates abnormal.

for the three fuels were not reported. Relevant data from this work are given in Table 4. A second series of split run tests using the HLPS tester at 290 °C was performed using a jet fuel with 7 ppb copper and 27 ppb iron. A similar effect to that observed in the split run JFTOT tests was noted.⁵⁰ These data are included as part of Table 3. Also, some data were presented indicating that 5.7 mg/L MDA reduced filterable insolubles compared to runs using only neat fuel. This reduction in filterable deposits appeared to exist even when MDA was only used during the second half of the split run, after the HLPS tube had been covered with significant fuel deposits.

Therefore, these data suggest that the ability of MDA to reduce filterable insolubles may not be related to any surface passivation mechanism. Although it may be tempting to attribute this reduction in filterable insolubles to a detergency/dispersancy effect, the lack of a long hydrophobic tail in MDA's structure makes such an explanation unlikely.

In a similar paper, a split run technique was used with the JFTOT at 260 °C and 2.5 h as the total test duration.²⁷ The effect of 0.53 mg/L MDA was determined in two Jet A's with "no detectable copper." One was fresh, the other was 3 years old. Both fuels failed ASTM D3241 at 260 °C, and were therefore considered thermally unstable. Relevant data are presented in Table 5. The first segment of each split run test involved the neat fuel run for the duration just sufficient to produce significant (but not failing) levels of deposits. Deposit levels were measured by both visual and TDR methods. The second segment of the split run used the same aluminum JFTOT tube but MDA-additized fuel. For both jet fuels tested in this split run JFTOT procedure, final tube deposits were no worse (and perhaps slightly better) than after the completion of the first segment. This was interpreted by the author as an indication that surface passivation was not operative, since the surfaces were already fouled when MDA-treated fuel was introduced into the JFTOT. However, when one of the fuels was evaluated in another split run where the second stage was extended to double the total test time, tube deposits were marginally worse than a standard JFTOT on the neat fuel. The ability of MDA to maintain JFTOT

Table 5. Effect of MDA on Split Run JFTOT Performance at 260 °C

fuel ^a	run time, min	MDA, mg/L	tube rating	
			TDR	visual
A	80/70	0/0	15	4
A	30	0	4.5	2
A	60	0	17	<4
A	90	0	17	4
A	120	0	19	4
A	30/120	0/0.53	7	2
A	30/270	0/0.53	19	<4
A	150	0.53	0	1
B	150	0	12	4
B	150	0.53	2	1
B	70	0	5	<2
B	70/80	0/0.53	8	2

^a Fuel A was 3 years old; fuel B was "fresh".

tube deposits at an intermediate level was interpreted by the author as evidence of some "benefit other than by passivation."

The gravimetric JFTOT work of Pande and Hardy^{29,30} also provided significant data supporting a possible bulk phase reactivity for MDA. A JP-5 fuel with unstated copper level was additized with 1 ppm MDA, then aged for 24 h in the LPR (90 °C, 50 psig air) before testing in the gravimetric JFTOT. Filterable insolubles generated were reduced by 50% compared to the aged neat fuel. When the MDA level was increased to 5.7 mg/L, filterables were reduced to the level of the nonaged neat fuel. If the 5.7 mg/L MDA was added to the fuel after LPR aging, filterable insolubles were nearly reduced to the same level. It was not possible to determine if the MDA-induced reduction in filterable insolubles was due to surface passivation of the steel strip (preventing heterogeneous catalysis) or a bulk phase reaction.

Extended Duration Testing. However, this issue was clarified in subsequent papers,^{33,34} involving extended gravimetric JFTOT runs of 120 h at 260 °C with a refinery fresh Jet A containing 3 ppb copper. The separate and combined effects of adding BHT (24 mg/L) and MDA (35 ppm) to the fuel and then aging it for 13 to 16 months at ambient laboratory conditions were evaluated. BHT alone had negligible effect on gravimetric JFTOT performance; MDA alone significantly improved performance compared to that of the aged neat fuel, mostly due to reduction of filterable insolubles. Because of the 120 h duration of the test, the role of the steel strip in catalyzing filterable insolubles was probably minimal to nil over much of the test. This implies that the ability of MDA to reduce filterable insolubles is due to a bulk phase reaction. Furthermore, because BHT alone did not reduce deposits while MDA alone did, it follows that MDA's reduction in filterable insolubles was not due to chain breaking antioxidative reactions, at least based on any hindered phenol chain breaking chemistry. Data from this work are presented in Figure 3a–d.

However, it should be pointed out that hindered phenols are known to be less effective antioxidants at the temperatures used in these studies.^{9,10} The poor performance of BHT in these gravimetric JFTOT tests may simply reflect the limitations of hindered phenol antioxidants under such temperatures. One explanation for the performance of MDA in these tests and in the previously cited JFTOT oxygen consumption tests is a

chain breaking chemistry derived from the nitrogen-containing moieties. Aminic antioxidants such as alkylated diphenylamines and derivatives of phenylene diamine are well-known antioxidants, and their performance at higher temperatures is generally superior to hindered phenols.¹⁰ However, aminic antioxidant activity derives from the homolytically labile hydrogen covalently bound to the active nitrogen, and the ability of a properly attached aryl ring system to transfer radical electron density from the nitrogen. MDA contains none of those structural features. Therefore, it does not seem likely that MDA would possess chain breaking antioxidant activity from its basic nitrogen atoms. Furthermore, no conclusive work with adequate controls can be found that establishes such oxidation inhibiting performance for MDA.

Another possibility that may be more reasonable is that MDA is acting as a Bronsted base to neutralize acidic materials that contribute to peroxidation and other chemical reactions that are known to generate insolubles. As was discussed earlier in this review, work by Beal and Hardy⁵¹ indicated a relationship between acidity and surface deposits in the gravimetric JFTOT. Treatment by basic materials reduced such deposits. If insolubles formed by fuel contact with a hot acidic surface can be decreased by reducing the surface acidity, could a similar effect occur in solution away from the surface? Is the formation of bulk phase (filterable) insolubles promoted by acidic species either already present or formed during thermal/oxidative stressing of the fuel? Certainly, such behavior has already been shown to occur.⁹ The primary chemistry from a compound such as MDA can be expected to derive from its basic nitrogens. More work should be done to specifically investigate both the role of acids in the formation of both surface and bulk phase insolubles during jet fuel thermal/oxidative stressing, and the role of soluble bases to reduce insolubles.

The gravimetric JFTOT work of Pande and Hardy^{33,34} also demonstrated an interesting effect involving both BHT and MDA. When MDA (35 ppm) and BHT (24 mg/L) were both added to the Jet A before aging, reduction in filterable insolubles occurred relative to the aged neat fuel, but not as much reduction as occurred when MDA alone was used. However, when MDA at a lower concentration (15 ppm) was added to the BHT treated fuel after the 13 to 16 months aging, filterable insolubles were reduced by the same level as when MDA alone at 35 ppm was added before the aging (Figure 3a–d).^{33,34} These results strongly imply that an adverse interaction occurred between MDA and BHT during the aging process that reduced MDA's effect on filterable insolubles generated during the gravimetric JFTOT test. Care must be used when interpreting these data. The gravimetric JFTOT is a much more discriminating procedure than ASTM D3241.⁵¹ All the neat fuels used by Pande and Hardy were stable in the ASTM specification test for thermal stability. Therefore, the trends observed in the gravimetric JFTOT would likely not be seen if D3241 was used. Also, the amounts of filterable insolubles generated during the gravimetric JFTOT are much larger than the amounts of surface (strip) deposits. However, within the context of the gravimetric JFTOT procedure, the effects of MDA appear valid.

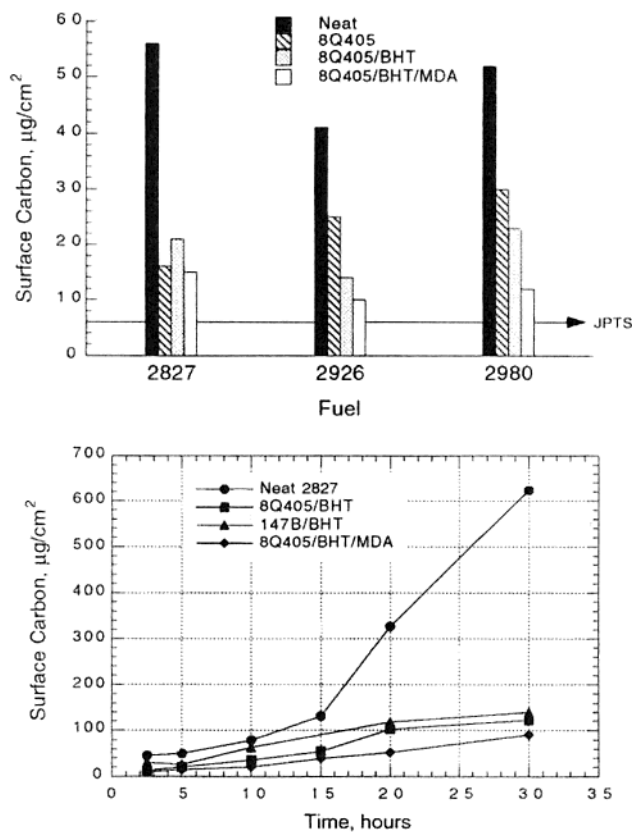


Figure 1.

Further work using fuels of known metal levels and a more widely varying performance on D3241 would be very useful in further defining the effects of MDA on filterable insolubles, and its potential interaction with BHT during prolonged storage. Also, the potential adverse interaction of BHT and MDA during prolonged storage should be further examined using other thermal stability test methods.

Another study⁴⁹ used the Isothermal corrosion/oxidation test (ICOT), a flask oxidation test run at 185 °C for 5 h with 1.3 l/hr. air sparge, to evaluate three JP-8 fuels that had been additized with BHT and a dispersant (Figure 4a,b). Each of the fuels gave significant levels of filterable insolubles in the ICOT; when 7.5 mg/L MDA was added to each fuel, filterable insolubles were eliminated (Figure 4a). Two of the fuels had “no detectable copper.” The copper content of the other fuel was not reported. The same three fuels were also evaluated using the quartz crystal microbalance (QCM) run at 140 °C for 15 h. MDA increased deposits on two fuels and had no significant effect on the third, relative to the deposits formed from the fuels without MDA (Figure 4b). These results illustrate the importance of test conditions in determining an additive’s performance.

In another paper,⁵⁶ more QCM tests were performed on eight fuels. Test temperature and duration were the same as in the previous study. All fuels had been additized with BHT and a dispersant. When 7.5 mg/L MDA was added to each of the fuels, QMC test insolubles increased in five of the fuels, decreased in two

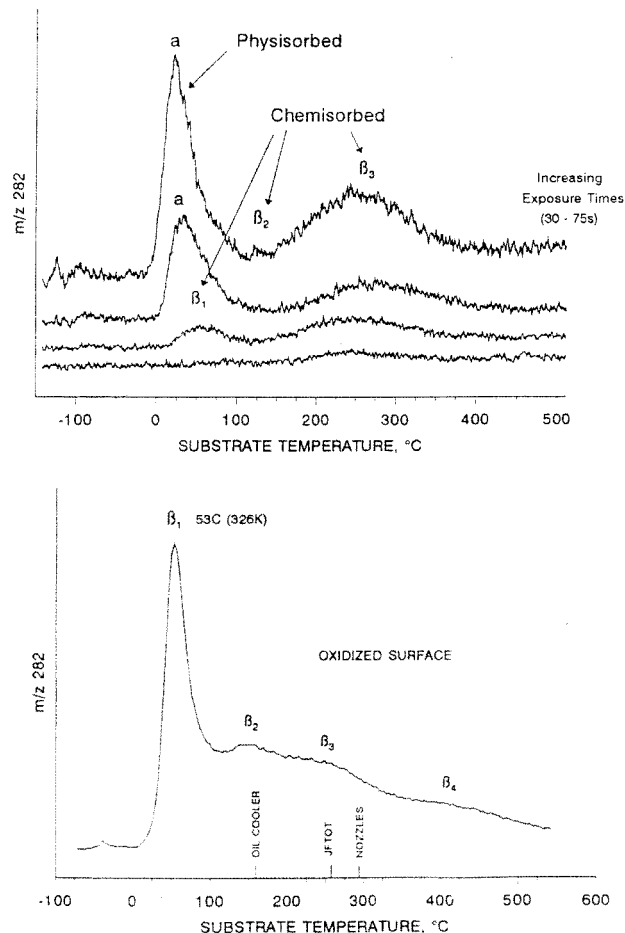


Figure 2.

of the fuels, and remained unchanged in the remaining fuel. The authors cited unpublished results run at higher temperatures where MDA gave significant improvements in insolubles. The reason for using such a low temperature in the published QCM tests was not given. It had long been established that MDA performance was strongly a function of temperature. Additional QCM tests using refinery-fresh fuels of known metal levels at temperatures including the 260–280 °C range typically used in other reported tests would be very useful. Such information would help to explain the differences that exist between some of the QCM test data and previous reports using other methods.

Additional QCM work was reported where the effect of MDA on jet fuel stability was measured over runs lasting 10 or more hours.⁵⁷ A JP-5 with 285 ppb added copper was stressed in the QCM unit at 140 °C while deposition mass, oxygen concentration, and MDA concentration were measured at various times during each test run. Runs were done with the copper-doped fuel without MDA and with MDA concentrations at 3, 5.8, and 12.0 mg/L. The authors noted that 1.1 mg/L MDA was the concentration required to completely chelate the 285 ppb copper. Test results showed that for all fuels the rapid onset of deposition was just preceded by the rapid consumption of available headspace oxygen. The copper-doped fuel without MDA exhibited a deposition induction period of about 3 h. With 3 mg/L MDA that

(56) Zabarnick, S.; Grinstead, R. R. *Ind. Eng. Chem. Res.* **1994**, *33*, 2771–2777.

(57) Zabarnick S.; Whitacre S. D. *J. Eng. Gas Turbines Power* **1998**, *120*, 519–525.

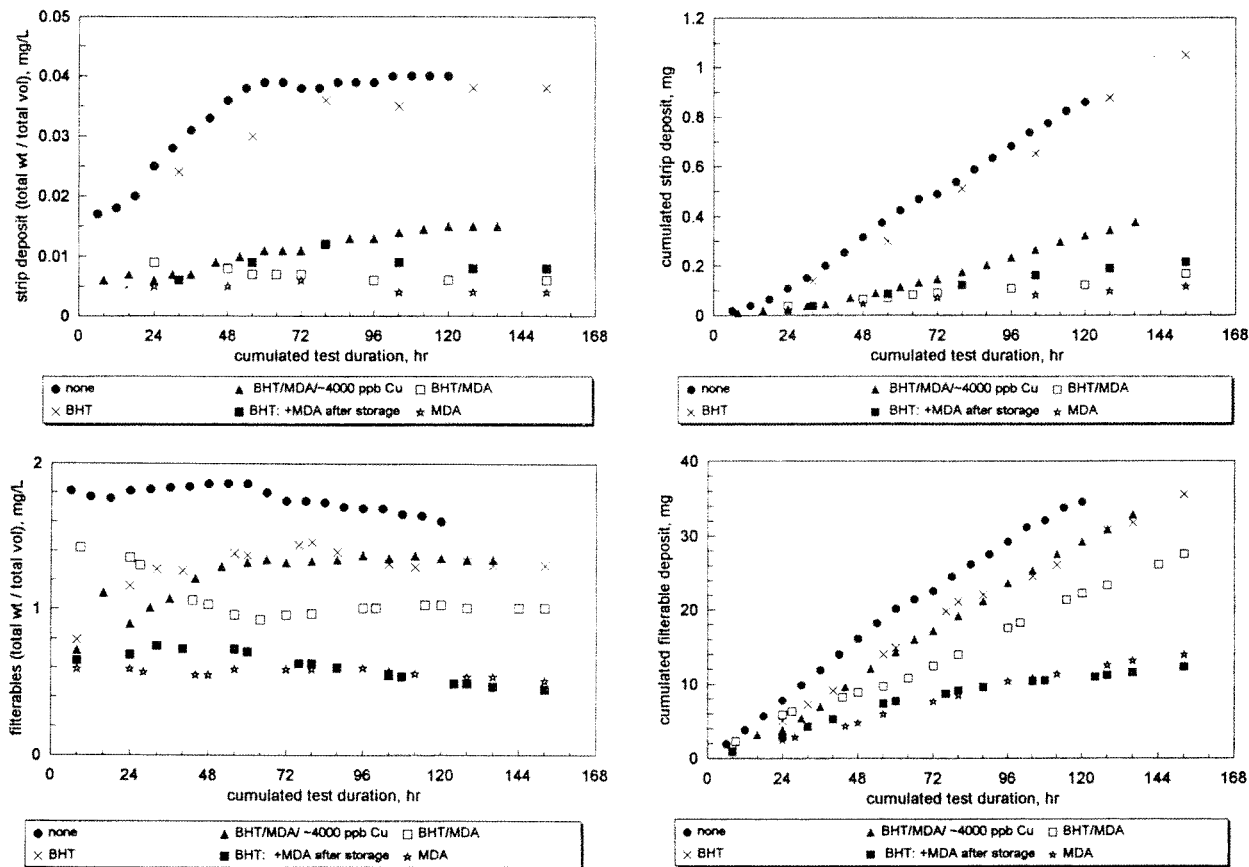


Figure 3.

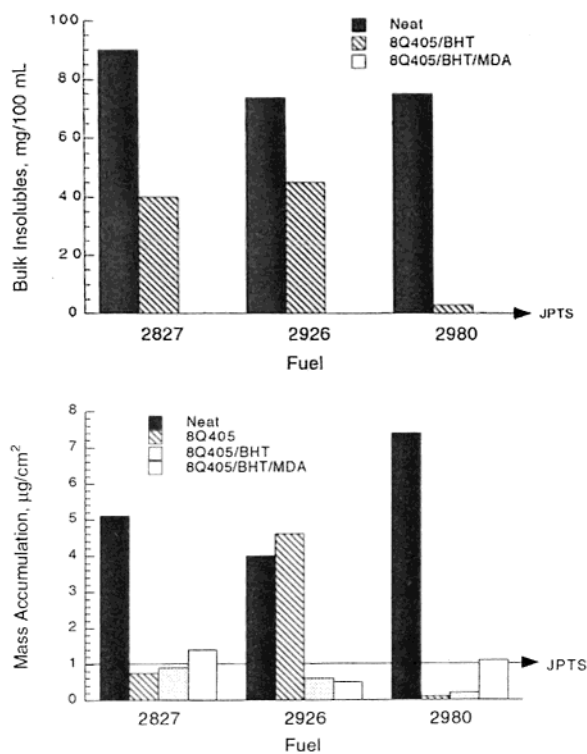


Figure 4.

induction period was increased by about 1 h, with 5.8 mg/L MDA the induction period was increased by about 5 h, and with 12.0 mg/L MDA the induction period was lengthened by about 10 h. Since all three MDA levels are well above the amount needed for complete copper

chelation, the added benefit to thermal stability as measured in these QCM tests must be due to some other mechanism. In these experiments, the QCM electrode surface upon which deposition occurred was gold. Assuming that exposed quartz surfaces did not affect the chemical processes occurring during the tests, the additional benefit provided by MDA had to be due to either a surface effect on the gold electrode or due to some bulk phase reactivity.

MDA concentrations fell during each test run, and the authors noted that rapid consumption of headspace oxygen and deposition occurred when MDA levels fell below the 1.1 mg/L required for complete copper chelation. The implication as noted by the authors is that when MDA was consumed to the point that copper-bound MDA was consumed, the released copper would catalyze fuel peroxidation.

The mechanism by which MDA was consumed during the QCM test runs is one of the most interesting aspects of this work. The authors admitted that this mechanism was "uncertain". While chain breaking oxidation inhibition was mentioned as a possibility, this seems unlikely for reasons already discussed in this review. The authors also mention "complexation of acidic reaction products" as a possible mechanism. The basic properties of MDA are well-known, as already mentioned herein. If acidic products are being generated as fuel components oxidize, these acids would be expected to protonate the most basic, available species also present in the fuel. Depending on the presence of other more basic fuel components, noncomplexed MDA would be a potential base for such a proton transfer reaction. Once the noncomplexed MDA was protonated, the complexed

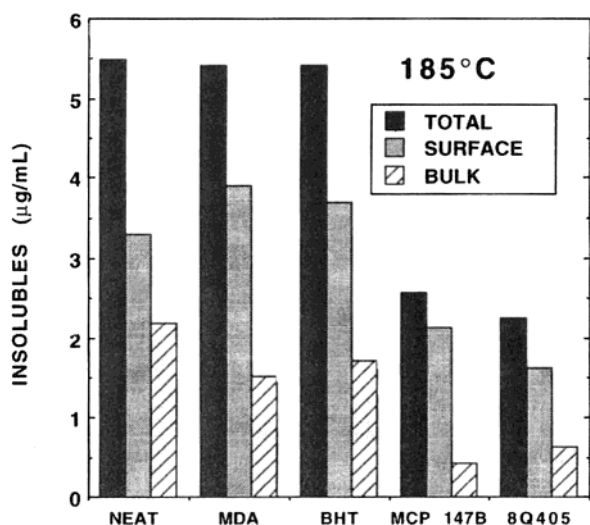


Figure 5.

MDA would be protonated, first on the phenolate oxygens and then on nitrogen. This protonation would destroy the MDA–Cu complex, thereby releasing catalytically active copper. Also, the neutralization of acidic species as they formed during fuel oxidation might explain the increased deposition induction period exhibited by fuels with higher levels of MDA.

If this theory is correct, one would expect to find an increasing level of protonated MDA in the fuels during each test run. The MDA was measured by using a silica gel column to remove it from the fuel and then elute it.⁵⁷ The MDA was then measured using a GC/MS procedure where the 161 au fragment ion and 282 au parent ion was measured. A singly protonated MDA would yield a parent ion of 283 au. The authors did not report any measurement of such species. Without further information, it cannot be determined if protonated MDA was generated during the test runs. If no protonated MDA was present, then either MDA was not acting as a Bronsted base, or the protonated MDA reacted further upon being formed.

Work using the near isothermal flowing test rig (NIFTR) also provided some data concerning MDA bulk phase reactivity.⁵⁸ A silicosteel passivated tube heated at 185 °C was used, and test duration was 72 h. The base jet fuel had a JFTOT breakpoint of 266 °C and no detectable copper. This fuel was one of the fuels that had been evaluated in the ICOT flask test discussed earlier in this section. When 2 mg/L MDA was added to the fuel, bulk insolubles were reduced by 25% compared to the neat fuel (Figure 5). Oxygen consumption measurements were also taken for the base fuel with MDA, and for the base fuel with BHT. Neither additive altered O₂ consumption relative to the neat fuel. Once again these data suggest that the ability of MDA to reduce filterable insolubles is not related to chain breaking oxidation inhibition, but that some other reactivity is involved.

Similar NIFTR tests at 185 °C were done using the longer (183 cm) stainless steel tube.^{40,41} The effect of 2

mg/L MDA was determined. The results of tube deposits were discussed in an earlier section of this review. MDA increased filterable insolubles in a fuel with 35 ppb copper, but decreased filterable deposits by 50% in a fuel with 7 ppb copper. The ages of the fuels were not given. It is interesting that the fuel with the lowest copper content was the one where MDA provided a significant benefit. Further work using refinery-fresh fuels with known and documented metal levels at higher test temperatures would be useful.

Development of Metal Deactivators

Overview. Development of metal deactivators has been reported primarily in the patent literature. The driving force behind this work has been a need for metal (usually copper) deactivation primarily in three areas: fuels, lubricants, and polymers. Metal deactivators are used in the first two areas because of trace metal contamination or contact acquired during manufacture, transport, storage, or use. The third area usually involves polypropylene insulation for copper wiring. The first commercial metal deactivators were developed in 1939 for fuels.³ They were found to be not sufficiently effective for copper wire insulation, and other metal deactivators were developed.¹⁰

Metal deactivators can be categorized by chemical structure into six broad classes: Schiff's bases (imines), hydrazides, oxalyl amides (oxamides), oxalo-hydrazides, heterocycles, Mannich bases.

Schiff's Bases (Imines). A Schiff's base or imine is usually formed by condensation of an aldehyde or ketone with a primary amine: The oldest fuel metal deactivator,



N,N-disalicylidine alkylene diamine, is a symmetrical Schiff's base, and is formed by condensation of salicylaldehyde and alkylene diamine.,^{3,59–63} The 1,2-ethylenediamine homologue was originally the most commonly used compound. However, it was found to be of limited solubility in fuels, especially at low temperatures,⁶⁴ and its copper complex was fuel insoluble, causing fuel filter plugging.⁶⁵ The 1,2-propane diamine compound replaced it and continues to be the prevalent fuel metal deactivator today.⁴² The most notable deficiency of the first symmetric Schiff's base metal deactivators is their inability to deactivate a wide range of metals.^{10,42} Numerous other Schiff's base metal deactivators have been proposed to incorporate various structural modifications to improve low-temperature solubility,^{64,66,67} increase polydentancy,^{68–71} or impart intrinsic antioxidation properties.⁷²

(59) U.S. Patent 2,181,122.

(60) U.S. Patent 2,282,513.

(61) U.S. Patent 2,284,267.

(62) U.S. Patent 2,285,259.

(63) U.S. Patent 2,285,260.

(64) U.S. Patent 3,071,451.

(65) U.S. Patent 4,022,835.

(66) U.S. Patent 2,533,205.

(67) U.S. Patent 2,813,080.

(68) U.S. Patent 2,426,206.

(69) U.S. Patent 2,461,894.

(70) U.S. Patent 2,462,668.

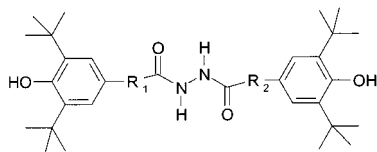
(71) U.S. Patent 2,843,536.

(72) U.S. Patent 3,706,802.

(58) Anderson, S. D.; Jones, E. G.; Gross, L. P.; Balster, W. J. Effect of Additives on the Formation of Insolubles in a Jet Fuel. In *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*, Rotterdam, The Netherlands, October, 1994; U.S. Department of Energy: Washington, DC; pp 291–301.

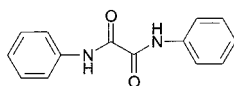
Hydrazides. Hydrazides are acylated derivatives of hydrazine. They were developed to provide metal deactivation in polypropylene insulation used in electrical (copper) wiring. The first hydrazide metal deactivator was a combination hydrazide and Schiff's base.⁷³

N,N-Dihydrazides of a single hydrazine unit were developed later.^{74–76} Many variations have been proposed. The structure illustrated below is an obvious attempt to incorporate oxidation inhibiting properties into the hydrazide: Additive concentration suggested for



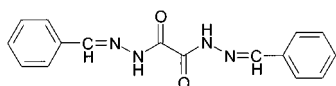
hydrazide metal deactivators in polypropylene is about 0.5%, about 100 times more than the concentration range usually used for Schiff's base metal deactivators in fuels. This difference in concentration is most likely due to the much greater level of exposure of copper in polypropylene copper wire insulation, and the very low diffusivity of solid polypropylene.

Oxalyl Amides (Oxamides). At nearly the same time that the first hydrazide metal deactivator was being developed, oxalyl amides (oxamides) were also proposed as metal deactivators for polypropylene insulation used in copper wiring.^{77,78} One of the earliest and simplest is given below:⁷⁷ At best, oxamides are weak



metal deactivators. The original data indicated that the best oxamides were able to restore only 25% of the oxidation life of antioxidant-containing polypropylene when exposed to copper. Oxamide concentration was 0.5%.

Oxalo-Hydrazides. Oxalo-hydrazides have also been proposed as metal deactivators for polypropylene used in copper wire insulation. This is a natural progression from the previous two classes of metal deactivators. The oxalo-hydrazides are formed by the condensation of the appropriate aldehyde or ketone with oxalyl dihydrazide, and the resulting structures contain Schiff's base groups. The first and most basic oxalo-dihydrazide metal deactivators are the ones where the aldehyde is either benzaldehyde or salicylaldehyde.^{79,80} Further ring substituents are claimed, but performance data for such compounds is not given. The dibenzyl additive gained widespread use in the 1970s as a metal deactivator for polypropylene:¹⁰



(73) U.S. Patent 3,110,696.

(74) U.S. Patent 3,772,245

(75) U.S. Patent 3,993,622.

(76) U.S. Patent 4,043,976

(77) U.K. Patent 974,274.

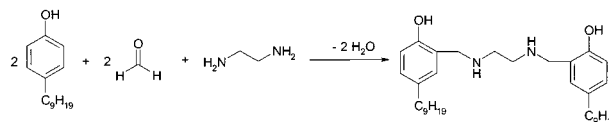
(78) U.S. Patent 4,154,723.

(79) U.S. Patent 3,357,944

(80) U.S. Patent 3,440,210

Heterocycles. Various heterocyclic compounds, usually containing nitrogen, have been proposed as metal deactivators for fuels, lubricants, and polypropylene wiring insulation.⁸¹ This class of additives include the benzotriazoles and other heterocyclic compounds discussed earlier in the surface passivation section of this review.

Mannich Bases. Mannich bases have been used for many years as dispersants and detergents. Recently, Mannich bases have been developed as metal deactivators for fuels.^{8,82–84} Mannich bases are condensation products of aldehydes (or ketones), amines, and compounds such as activated phenols that have labile hydrogen.⁸⁵ The formation and likely structure of one Mannich base metal deactivator is given below:⁸ The



advantage of the claimed Mannich base metal deactivators is that they are effective against a wider range of metals including cobalt, nickel, manganese, and iron.

Summary and Conclusions

Metal deactivators have been used in the petroleum industry for over 60 years. The first metal deactivators were developed specifically for copper-sweetened gasoline, and were then used without further modification in other fuels, especially jet fuel. Metal deactivators are also used in lubricants and in copper wire insulating polymers. The compounds preferred in each of these areas are different than the one that is usually used in fuels. Use of the metal deactivator MDA in jet fuels has become controversial due to its ability to improve JFTOT results even when deleterious metals are not present in significant levels. Further investigations appear to indicate properties other than chelation exist for MDA. These additional properties, surface passivation and bulk phase reactivity, continue to be less than adequately defined despite various efforts by numerous researchers.

To continue to improve the level of understanding of the chemistry of MDA in jet fuel, certain procedural aspects in future work would be helpful. Use of refinery fresh fuel instead of fuel stored for various times over various conditions would allow more control over experimental design. It is understandable that many of the researchers working in this area of endeavor do not have easy access to such fuels. Nonetheless, use of a "stock fuel" that has been sitting on a shelf or in a storage room for months or years introduces a variable into all resulting data that cannot be adequately defined. Also, all test fuels should be carefully and thoroughly analyzed for all relevant properties. Complete metals analysis is a good example of a test

(81) U.S. Patent 3,367,907

(82) U.S. Patent 4,810,354.

(83) U.S. Patent 4,847,415.

(84) U.S. Patent 4,883,580.

(85) Tramontini, M.; Angiolini, L. *Tetrahedron* **1990**, *46*, 1791–1837.

property that should be done without exception. When designing experimental programs, care should be taken to include test conditions that will allow the greatest chance of informative interpretation with respect to data already in the open literature. Finally, it is interesting that MDA, originally developed for gasoline in the 1930s, appears to have other beneficial attributes for a different fuel, jet fuel, while other more recent and potentially superior metal deactivators are not being significantly investigated and reported in the open literature for their ability to have the same or even superior attributes. This is an area of research that deserves attention in the future.

Acknowledgment. The author thanks Dr. Seetar G. Pande, Geo-Centers, Inc., and Dr. Dennis R. Hardy, U.S. Naval Research Laboratory, for their encouragement in preparing this paper. Also, thanks to Ms. Wendy Mills and Ms. Cathy Gomez for their assistance in preparing the manuscript. All tables and figures are used with the kind permission of Harry N. Giles, U.S. Department of Energy, and the International Association of Stability and Handling of Liquid Fuels. Finally, thanks to Southwest Research Institute for their support during the writing and revision process.

EF010113J