The Effects of Different Sulfur Compounds on Jet Fuel Oxidation and Deposition

R. E. Kauffman

University of Dayton Research Institute,
Dayton, OH 45469-0161

This paper presents research that supports a proposed fuel oxidation/deposition mechanism involving acid:base reactions between "oxidizable" sulfur compounds, "basic" nitrogen compounds, and oxygen-containing polymers. The reported research presents experiments that study the effects of different sulfur compounds on the high-temperature (160–220°C) oxidation products and deposition tendencies of jet fuel. Surface analyses incorporating elemental analyses and depth profiles of deposits formed on steel surfaces were performed to identify the species involved in the initial stages of deposition by jet fuels. Experiments to study the effects of acid neutralizing compounds on the deposition tendencies of jet fuels are also presented.

Introduction

Future engine designs will utilize fuel recirculation due to higher operating temperatures and improved fuel efficiency. Fuel recirculation and higher operating temperatures will require fuels (1) to operate at higher temperatures, (2) to operate for longer periods of time at elevated temperatures in the presence of dissolved oxygen, and (3) to undergo numerous heating and cooling cycles prior to combustion. These increased fuel requirements will result in increased fuel deposition at heated surfaces and increased bulk particles causing valves to stick and filters to clog. Although hydrotreating and other fuel treatments can be employed to reduce deposition at higher temperatures, hydrotreating is expensive and may result in reduced stability toward dissolved oxygen, allowing fuel to oxidize during recirculation, leading to gum formation on valves and filters.

Therefore, a multidirectional research program is being sponsored by the U.S. Air Force to develop additive packages capable of increasing the upper temperature limits of straight-run jet engine fuels by 100°F and capable of stabilizing the fuel against oxidation and bulk particle formation during recirculation. One of the goals of the research program is to gain a better understanding of the fuel reaction mechanisms, which produce the compounds responsible for the surface deposits and bulk particles. Additive packages can then be designed to inhibit or alter the specific reactions that produce the surface deposits and bulk particle precursors.

It is well known that dissolved oxygen must be present for deposition to occur and that fuel deposits contain concentrated levels of sulfur and nitrogen in comparison to the heated fuel. It has also been reported that phenol-containing compounds present in jet fuel inhibit fuel oxidation at elevated temperatures (Kauffman, 1994) and increase the deposition tendencies of jet fuels (Hazlett et al., 1986). Further research in our laboratory (Heneghan and Harris, 1992; Heneghan et al., 1992; Kauffman, 1992) has shown that straight-run (>500 ppm S) and hydrotreated (<10 ppm S) fuels oxidize at different rates (hydrotreated fuels oxidize faster) at elevated temperatures to produce different type soluble and insoluble compounds. The straight-run fuels produce phenols and bulk particles containing concentrated (~2–4 percent) levels of sulfur and nitrogen. The hydrotreated fuels produce soluble hydroperoxides, organic acids, and

bulk particles with minimal levels (<0.2 percent) of sulfur and nitrogen. The bulk particles contain single carbon-to-oxygen bonds (ether type) for the straight-run fuels and contain both single and double carbon-to-oxygen bonds (carbonyl type) for the hydrotreated fuels.

Therefore, the reaction mechanism shown in Fig. 1 was proposed to explain the oxidation and deposition processes of hydrotreated and straight-run jet fuels.

Hydrotreated fuels that contain minimal levels of sulfur oxidize as detailed in reactions O1 through O4. Straight-run fuels that contain significant levels of sulfur oxidize as detailed in reactions O1 through O4, then deposit as detailed in reactions D1 through D5.

The proposed oxidation/deposition mechanism explains the need for oxygen to form deposits and explains the sulfur, nitrogen, and oxygen contents of deposits. The mechanism also explains the reported results (Hazlett et al., 1986) that phenols increase the tendency of fuels to form deposits. The proposed mechanism also predicts that the addition of sulfur compounds to hydrotreated fuels will decrease the hydroperoxide content and increase the phenol content of oxidized sulfur containing hydrotreated fuels. The sulfur-contaminated hydrotreated fuel should produce sulfur–nitrogen-containing bulk particles and deposits in which the sulfur compound is oxidized and should produce metal surface deposits that contain concentrated levels of the oxidized sulfur compounds. Also, the addition of sulfonic acids would be expected to increase deposits with minimal oxidation, as recently reported (Hazlett et al., 1991).

To evaluate the accuracy of the proposed oxidation/deposition mechanism, various sulfur compounds were dissolved in a hydrotreated jet fuel (Jet A-1). The neat Jet A-1 fuel, sulfur-contaminated Jet A-1 fuels, and a commercial straight-run fuel (Jet A) were heated in two different oxidation tests to determine the effects of the different sulfur compounds on fuel chemistry: soluble oxidation products (hydroperoxides versus phenols), bulk particles (S, N content of particulates), and initial deposits formed on steel wire surfaces (sulfur oxide content near metal surface). In an attempt to inhibit the deposition process of Jet A, various compounds with acid neutralizing capabilities were added to the Jet A fuel prior to oxidation to inhibit deposition reactions D3 and D5, which require acid/base reactions and acidic attack on metal surfaces, respectively. The results are reported herein.

Experimental

Sulfur Compounds. The sulfur compounds used in this study were 92–98 percent pure and were obtained from Aldrich

Oxidation Process

Fuel + O_2 → Fuel Radical + • O_2H (O1)

Fuel Radical + O_2 → Hydroperoxide Radical   (O2)

Hydroperoxide Radical + Fuel → Hydroperoxide + Fuel Radical   (O3)

Hydroperoxide → Aldehydes, Organic Acids, → Polymers   (O4)

Deposition Process

Hydroperoxide + Sulfur Compound → Phenol + Acidic Sulfur Oxide + Ketone   (D1)

Phenol + Hydroperoxide Radical → Phenol Radicals + Hydroperoxide   (D2)

Acidic Sulfur Oxide + Basic Nitrogen Compounds → S•N Compound   (D3)

S•N Compound + Phenol Radicals → Bulk Particles   (D4)

Acidic Sulfur Oxide + Metal Surface → Initial Deposition   (D5)

Initial Deposition + Bulk Particles → Surface Deposition   (D6)

Fig. 1 Proposed reaction mechanism for jet fuel oxidation and deposition processes

Table 1 Chemical properties of studied fuels

	Jet A Fuel	Jet A-1 Fuel
Hydrotreated	No	Yes
Aromatics, Vol %. (D1319)	19	19
Mercaptan Sulfur, Wt %	0.001	0.000
Sulfur, Total Wt % (D4294)	0.10	0.00
JFTOT Breakpoint, °C	282	332
Hydroperoxides, mmole/L [a]	0.03	0.01
Phenols, mmole/L [a]	2.6	0.4

[a] by cyclic voltammetry

Chemical Company, Milwaukee, WI. The dodecylbenzene sulfonic acid (90+ percent purity) was obtained from Conoco Petroleum, Conostan Standards Div., Hammond, IN.

Fuels. The jet fuels used in this study were a straight-run, commercial fuel (Jet A) and a hydrotreated, commercial fuel (Jet A-1) provided by U.S. Air Force Wright Laboratory, Aero Propulsion and Power Directorate. The fuels' chemical and performance characteristics are listed in Table 1. The sulfur-contaminated hydrotreated fuels were produced by dissolving (room temperature, shaken by hand) the selected sulfur compounds into different portions of the Jet A-1 fuel. The weight of each sulfur compound added to the Jet A-1 fuel was determined based on producing a Jet A-1 fuel with a sulfur concentration of 1000 ppm (sulfur level of Jet A fuel, Table 1).

Oxidation Tests

Flask Test. The flask test was used to evaluate the tendencies of the jet fuels and sulfur compounds to produce bulk particles. The flask test was performed by heating 20 mL of fuel in a 50 ml erlenmeyer flask placed on a hot plate (200°C surface temperature) with stirring capability. The fuel was added to the flask and was heated with stirring (magnetic stir bar). When the fuel temperature reached 100°C, the test time was initiated and an air flow (0.5 liter per hour) was initiated through a disposable glass pipette situated on the bottom of the flask. The test was stopped at 30 minutes (bulk temperature: 160°C), the flask was removed from the hot plate, and the heated fuel was allowed to cool to room temperature. The oxidized fuel was stored in a glass vial for subsequent hydroperoxide and phenol analyses. All of the fuels had reached their maximum hydroperoxide values by 30 minutes. The phenol concentrations increased with time for the entire test period.

The phenol and hydroperoxide contents of the cooled fuels were determined by cyclic voltammetry and the remaining fuel was filtered through a 0.4 μm filter to isolate the bulk particles

for elemental analysis by X-ray Photoelectron Spectroscopy (XPS). The isolated particles were washed with acetone/hexane (to remove residual fuel and soluble polymers) prior to XPS analysis. The filtered fuels were then heated under a stream of nitrogen to reduce the fuel volume causing the least soluble oxidation polymers to precipitate. The precipitated polymers were isolated by filtration and analyzed for elemental content by XPS.

Sealed Ampoule Test. The sealed ampoule test was used to evaluate the tendencies of the fuels and sulfur compounds to produce deposits on metal surfaces. The sealed ampoule test was performed by pippetting 3 mL of fuel into a 4 mL glass ampoule. A low-carbon steel wire was then placed inside each ampoule ($\frac{3}{4}$ of wire covered by fuel). The prepared ampoules were sealed under an air atmosphere. The sealed vials were $\frac{3}{4}$ fuel and $\frac{1}{4}$ air (allow for fuel expansion during heating). The ampoules were heated for 10 minutes in an oven set to 210°C (fuel at 210°C after 5 minutes). The ampoules were removed and allowed to cool for 10 minutes to room temperature or for 24 hours to enhance deposit formation. The ampoules were then broken open, the wires removed and cleaned with acetone/hexane (to remove fuel and soluble polymers), and the cleaned wires were analyzed by Auger spectroscopy to determine deposit thickness and to determine elemental depth profiles.

Bulk Particle and Deposit Elemental Analyses. Auger electron spectroscopy (AES) was used to perform depth profiles of the deposits formed on metal surfaces. AES depth profiles were obtained from a Varian scanning Auger spectrometer using an electron beam energy of 5 keV to obtain spectra and a 1 keV argon ion beam to sputter the samples. The sputter rate for the deposits that formed on the steel wires was estimated to be 2 nm min^{-1} based on measurements of a thin silicon nitride film whose thickness had been measured with ellipsometry.

Nomenclature

C = carbon
L = liter
mmole = millimole
ml = milliliter
N = nitrogen
nm = nanometers
O = oxygen
ppm = parts per million

S = sulfur
V = volt
Vol = volume
wt = weight

Abbreviations

AES = Auger Emission Spectroscopy
ASTM = American Society of Testing Materials

Jet A = commercial, straight-run jet fuel
Jet A-1 = commercial, hydrotreated jet fuel
JFTOT = Jet Fuel Thermal Oxidation Tester
XPS = X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to perform elemental surface analyses (top 3 nanometers of compound) of the bulk particles and deposits. XPS spectra were obtained with an extensively modified AEI ES-100 photoelectron spectrometer. Modifications to this instrument have included the addition of a 2001 s^{-1} turbomolecular pump and a 1101 s^{-1} ion pump for evacuation of the sample chamber. This instrument is equipped with a magnesium X-ray source.

Cyclic Voltammetric Fuel Tests

Introduction. The theory of cyclic voltammetry has been described in detail (see Kauffman, 1992). The cyclic voltammetric tests were performed with a commercially available voltammograph equipped with a glassy carbon disk (3 mm diameter) working electrode, a platinum wire (0.5 mm diameter) reference electrode, and a platinum wire (0.5 mm diameter) auxiliary electrode. The cyclic voltammetric procedure applies a small voltage ramp (0–1 V) to a platinum wire electrode and measures the produced current (μamp) at the active surface of a glassy carbon electrode. If a species in the diluted fuel sample undergoes oxidation in the applied voltage range, the oxidation of the species causes an increase in the current measured by the cyclic voltammograph. The quantity of current increase is directly proportional to the concentration of the species in the fuel. The voltage at which the current increase occurs is indicative of the type of species present in the fuel, e.g., dihydroxyaromatics (0.5–0.6 V), primary and secondary aromatic amines (0.7–0.8 V), substituted phenols (0.8–1.0 V), and so on.

Two cyclic voltammetric-based tests, the new hydroperoxide method and the phenol test, were studied.

Hydroperoxide Method. The hydroperoxide method (Kauffman, 1994) uses the same aqueous potassium iodide and acetic/hydrochloric acid solutions as prepared in the current standard hydroperoxide test, ASTM D3703-85. Hydroperoxide analyses performed using the new hydroperoxide and ASTM D3703-85 test methods have been shown to be in good agreement (Kauffman, 1994). The hydroperoxides in the fuel sample react with the acidic potassium iodide solution to produce iodine. Consequently, the concentration of iodine produced is directly proportional to the concentration of hydroperoxides in the reacted fuel sample. The hand-held voltammetric instrument used to measure the produced iodine was calibrated using blank (0 mmole) and standard (1 mmole) iodine solutions.

The fuels were analyzed for hydroperoxide concentrations by dispensing 1 to 5 ml of fuel, 0.25 ml of aqueous potassium iodide solution, and 1 ml of acetic acid solution into a 10 ml vial. The vial was capped and shaken vigorously by hand for 30 seconds. The vial was opened, 1 ml of water added, the vial was recapped, and gently shaken for 2 seconds. The vial was allowed to sit undisturbed for approximately 10 seconds. The lower layer that formed was pipetted into a new vial. The iodine produced was determined by inserting the voltammograph electrode into the pipetted layer and scanning the voltage of the auxiliary electrode from 0.0 to −1.0 V (referenced to platinum reference electrode) at a rate of 0.1 V/s. The current produced by the glassy carbon electrode was compared against the blank and standard (1 mmole) to measure the produced iodine, and consequently, the concentration of hydroperoxide in the reacted fuel sample. The calculated concentrations of the hydroperoxides in the studied fuels are listed in Table 1.

Phenol Test. To determine the concentration of phenols present in the jet fuels, samples of the fuels (0.1 ml) were diluted with 3 ml of ethanol (fuel soluble) containing an inorganic base (potassium hydroxide: 0.25 percent) (Kauffman, 1994). The electrode was inserted into the diluted fuel and the voltage of the auxiliary electrode was increased from 0.0 to 1.0 V (referenced to the platinum reference electrode) at a rate of 0.05 V/s. The current produced by the glassy carbon electrode

was plotted versus scan voltage by a strip chart recorder interfaced to the voltammograph. The height(s) of the peak(s) produced by the fuels were measured and compared to solutions containing known concentrations of ethyl phenol and 1-naphthol. The calculated concentrations of phenols in the studied fuels are listed in Table 1.

Results and Discussion

Introduction. Research was performed to evaluate five predictions of the proposed oxidation/deposition mechanism:

1. Addition of oxidizable sulfur compounds will reduce hydroperoxide content and increase phenol content of oxidized Jet A-1 (hydrotreated) fuel
2. Jet A-1 fuel (in the absence of oxidizable sulfur compounds) will produce bulk particles and soluble polymers, which contain minimal amounts of sulfur and nitrogen and contain double carbon-to-oxygen bonds (aldehyde-acid polymers)
3. Addition of oxidizable sulfur compounds will produce bulk particles from Jet A-1 fuel, which contain sulfur oxides, nitrogen, and single carbon-to-oxygen bonds (phenol polymers)
4. Addition of oxidizable sulfur compounds will produce initial deposits on metal surface that have concentrated levels of sulfur oxides.
5. Addition of acid neutralizing compounds to Jet A (straight run) fuel will inhibit metal surface deposits and bulk particle formation.

The chemical and performance characteristics of the Jet A and Jet A-1 fuels used in this study are listed in Table 1. The sulfur compounds used in this study included hexadecyl mercaptan, diphenyl disulfide, benzyl phenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, and dodecyl benzene sulfonic acid. The acid-neutralizing compounds used in this study were laboratory grade and included ferric oxide powder (less than 0.1 μm particle size) and calcium oxide powder (less than 20 μm particle size).

Effects of Sulfur Compounds on Jet A-1 Oxidation Products. To test the effects of sulfur-containing compounds on the oxidation products of Jet A-1 fuel, Jet A-1 fuels containing the various sulfur compounds listed in Table 2 were oxidized for 30 minutes at a maximum temperature of 160°C using the flask oxidation test. Since the flask oxidation test is open to the air and a glass pipette is used to bubble air continuously through the heated fuel, oxygen is available for fuel oxidation during the entire test period. The hydroperoxide (reaction O3) and phenol (reaction D1) concentrations of the heated Jet A-1 fuels contaminated with the various sulfur compounds are listed in Table 2.

The results shown in Table 2 indicate that the presence of certain type sulfur compounds affects the hydroperoxide/phenol ratios of oxidized Jet A-1 fuel. The neat (uncontaminated) Jet A-1 fuel oxidized to produce hydroperoxides and very little phenols (reaction O3 dominant) (Table 2). The addition of a mercaptan compound to the Jet A-1 fuel inhibited oxidation (reaction O2 and O3 inhibited) and produced low levels of phenols (reaction D1 activated) and undetectable (below 0.01 mmole/L of fuel) levels of hydroperoxide. The disulfide and sulfide compounds inhibited oxidation to varying degrees and produced high levels of phenols (reaction D1 activated) and low levels of hydroperoxides (Table 2). In contrast to the other sulfur compounds, the sulfoxide and sulfone compounds did not affect the oxidation products (reaction D1 inactive) and produced primarily hydroperoxides. In agreement with the sulfide and disulfide compounds, the Jet A fuel oxidized to produce primarily phenol type compounds (reaction D1 activated).

Table 2 Effects of different sulfur compounds on the oxidation products of Jet A-1 and Jet A fuels obtained from the flask oxidation test

Fuel	Sulfur Compound [a]	Initial Oxidation Products mmoles/L of Fuel		Bulk Particle XPS Analyses (% Atomic Wt)		
		Peroxides	Phenols	% O	% N	% S
A-1	---	5.5	0.75	11[b]	< 0.2[b]	< 0.2[b]
	Hexadecyl Mercaptan	< 0.01	3.3	25	1.8	4.4 (>98%)[c]
	Diphenyl Disulfide	1.5	7.5	22	1.0	1.7 (>98%)[c]
	Benzyl Phenyl Sulfide	2.0	6.0	18	0.4	0.8 (57%)[c]
	Diphenyl Sulfoxide	6.0	0.75	13[b]	< 0.2[b]	< 0.2[b]
	Diphenyl Sulfone	8.0	0.75	12[b]	< 0.2[b]	< 0.2[b]
A	---	0.4	4.6	20	1.9	2.8 (>98%)[c]

a Concentration 1000 ppm by sulfur. b Polymer obtained by evaporating fuel. c % oxidized sulfur

Effects of Sulfur Compounds on Jet A-1 Bulk Particles. To test the effects of sulfur-containing compounds on the bulk particles produced by oxidized Jet A-1, the stressed fuels obtained from the flask oxidation tests (Table 2) were filtered to isolate the bulk particles produced during the oxidation of sulfur contaminated Jet A-1 fuels. The oxidized Jet A-1 fuel had to be evaporated to isolate soluble material formed by oxidation. The XPS elemental analyses of the bulk particles and soluble material isolated from the oxidized Jet A-1 fuels are also listed in Table 2.

The results given in Table 2 show that the soluble material isolated from the oxidized Jet A-1 fuel contains minimal amounts of sulfur and nitrogen. Infrared spectroscopy determined the soluble material contained a large number of carbonyl (C = O) type carbon-to-oxygen bonds (polymer resulting from reaction O4). The oxidized Jet A-1 fuels contaminated with mercaptan, disulfide, and sulfide compounds produced bulk particles (Table 2) containing significant levels of sulfur oxide (reactions D1 and D3) and significant levels of nitrogen (reaction D3). Infrared spectroscopy determined the bulk particles mainly contained ether (C-O) type carbon-to-oxygen bonds (polymers resulting from reactions D2 and D4). The oxidized Jet A-1 fuel contaminated with sulfoxide and sulfone compounds produced soluble material similar to the material produced by the neat oxidized Jet A-1 fuel, i.e., minimal amounts of sulfur and nitrogen and high levels of carbonyl type carbon-to-oxygen bonds.

In agreement with the mercaptan, sulfide, and disulfide compounds, the Jet A fuel oxidized to produce bulk particles that contain sulfur oxides, nitrogen, and primarily ether type carbon-to-oxygen bonds. The addition of dodecyl benzene sulfonic acid to Jet A fuel produced visible bulk particles within 24 hours at room temperature. The isolated particles had a significant nitrogen content (reaction D3), ether type carbon-to-oxygen bonds (reaction D4) and produced elemental analyses similar to the particles produced by the oxidized Jet A fuel (Table 2).

Effects of Sulfur Compounds on Initial Metal Surface Deposits. To test the effects of different sulfur compounds on the thickness and composition of the initial deposits formed on metal surfaces, Jet A-1 fuels containing the various sulfur compounds listed in Table 2, Jet A-1 fuel and Jet A fuel were heated at 210°C for 10 minutes in sealed glass ampoules containing low-carbon steel wires. After cooling to room temperature (about 10 minutes), the heated glass ampoules were opened so that the exposed wires could be removed and rinsed with hexane and acetone prior to analysis by Auger emission spectroscopy. The removed wires appeared to be clean or slightly tarnished and the Auger depth analyses (performed by ion sputtering) determined the produced deposits to be less than 6 nm

in thickness (Fig. 2). Consequently, the thin deposits present on the metal surfaces represent the initial deposits formed by the heated fuels.

The Auger elemental analysis and depth profiles of the wires heated in the presence of neat Jet A-1 fuel (Fig. 2) indicate that the metal surface is covered by a thin oxide layer with minimal amounts of nitrogen and sulfur present. The Jet A-1 fuels containing mercaptan, sulfide, and disulfide compounds produced deposits 2–4 nm in thickness, which contain from 9 to 16 percent sulfur and less than 1 percent nitrogen (Fig. 2). The Jet A-1 fuels containing sulfoxide and sulfur compounds produced wires with metal oxide layers containing less than 1 percent nitrogen and sulfur (similar to Jet A-1 in Fig. 2). In agreement with the Jet A-1 fuels containing mercaptan, sulfide, and disulfide compounds, Jet A fuel produced a deposit 2 to 4 nm in thickness, which contained a maximum of 9 percent sulfur and 1 percent of nitrogen (Fig. 2).

For the fuels producing deposits in Fig. 2, the sulfur content of the deposit is at its maximum at the metal oxide surface of the steel coupon as predicted by reaction D5. XPS analyses determined the fuel deposits produced by the sulfur-contaminated Jet A-1 fuels and the Jet A fuel contained sulfur, which was >90 percent sulfur oxides as predicted by reaction D5.

Effects of Acid Neutralizing Compounds on Fuel Deposition. To study the effects of acid-neutralizing compounds on fuel deposition, Jet A fuels containing varying amounts of superfine iron oxide and calcium oxide powders were heated at 210°C for 10 minutes in sealed glass ampoules containing low-carbon steel wires. To increase the thickness of the deposits, the heated ampoules were allowed to cool for 24 hours prior to opening. The wires were removed from the opened ampoules, rinsed with hexane then acetone to remove residual fuel, and analyzed by Auger emission spectroscopy. The measured thicknesses of the produced deposits are listed in Table 3.

The results in Table 3 indicate that the iron oxide powder (<1 μm particle size) at 50 ppm and the calcium oxide powder (<20 μm particle size) at 100 ppm are capable of inhibiting the formation of deposits on the steel surface. The results in Table 3 also indicate that the deposition-inhibiting capabilities of the oxide powders decrease as the concentrations of the oxides decrease. Additional tests with other metal and oxide powders demonstrated that only powders with acid neutralizing capabilities were able to inhibit the deposition process. For instance, superfine alumina and silicon dioxide powders (unreactive toward sulfur containing acids) had no effect on the deposition process of Jet A even at concentrations of 1000 ppm powder. The addition of cyclohexane amine (a strong organic base) inhibited the deposition process in agreement with reported research (Hazlett et al., 1986).
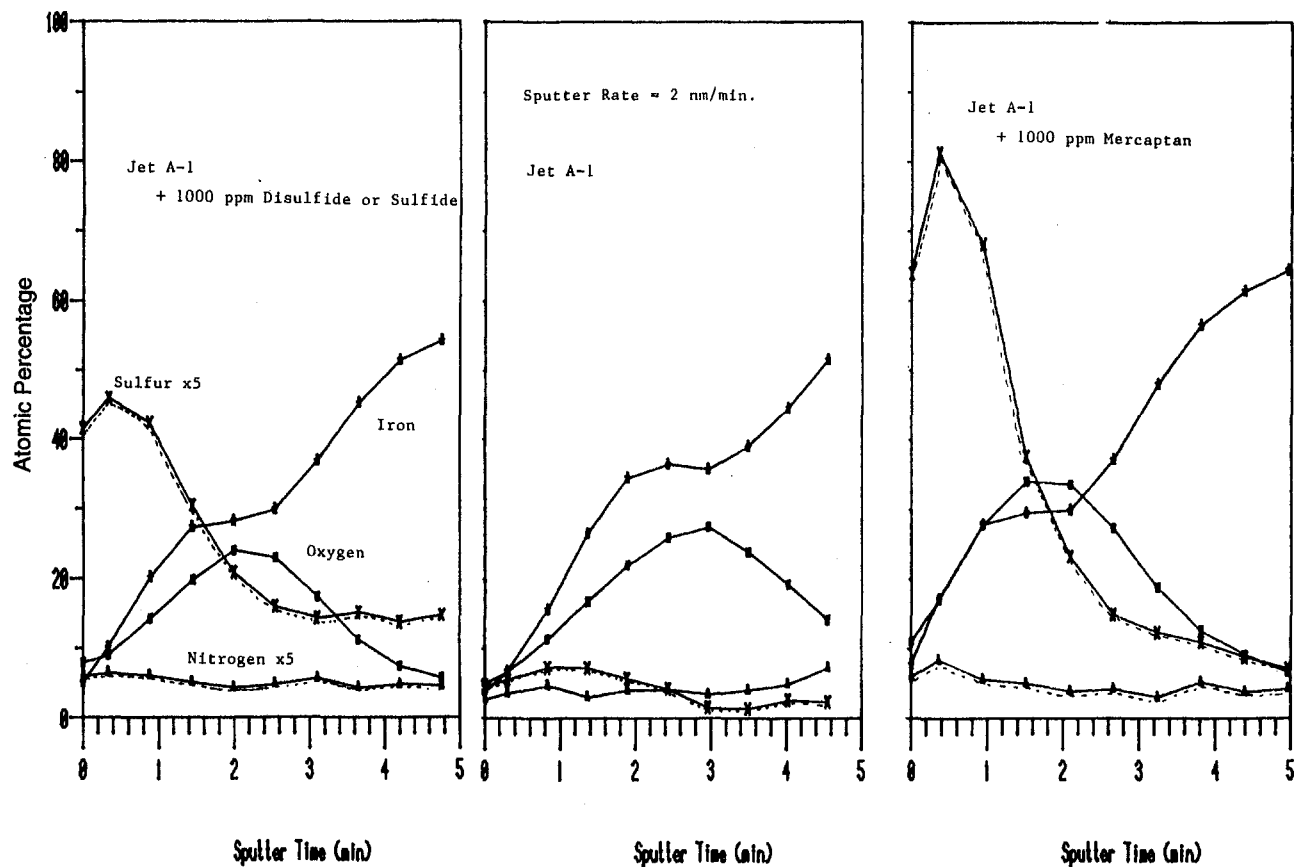
Fig. 2 Auger emission spectroscopic depth profiles of deposits formed on steel wires during sealed ampoule testing (ten minute cool down) at 210°C by Jet A-1 fuels containing different sulfur compounds (1000 pm sulfur)

The fact that the deposits are much thicker for the 24 hour cooled steel wire than the 10 minute cooled wires, indicate that bulk particles are responsible for the thickness of the deposition

Table 3 Thickness measurements by AES depth profiling for deposits formed on steel surfaces by Jet A fuels with and without acid neutralizing powders

POWDER	Concentration (ppm)	Deposit Thickness [a] (nm)
Ferric Oxide	12	900
	25	300
	50	80
Calcium Oxide	50	400
	100	80
Aluminum Oxide	1000	1700
Silicon Dioxide	1000	1600
None	-	1800

a Sealed Ampoule Test (cooled 24 hours), Jet A-1 deposit thickness 70 nm

(reactions D5 and D6). The fact that acid neutralizing powders are able to inhibit deposition thickness indicates that acid–base reactions are important in the formation of bulk particles (reaction D4). The acid-neutralizing powders heated in the Jet A fuel were isolated by filtration and analyzed for sulfur and nitrogen. All of the isolated powders contained significant levels of sulfur oxides and nitrogen, further indicating the powders had reacted with acidic sulfur compounds.

Summary

The results presented herein strongly support the oxidation (reactions O1–O5)/deposition (reactions D1–D6) reaction scheme proposed for jet fuels. The results show that the "oxidizable" sulfur compounds (mercaptan, sulfide, and disulfide) inhibit hydroperoxide production, increase phenol production, increase bulk particle formation, and increase surface deposition for sulfur contaminated Jet A-1 fuel. The "nonoxidizable" sulfur compounds, sulfoxide and sulfone, have very little effect on the oxidation/deposition processes of sulfur contaminated Jet A-1 fuel (in agreement with Mushrush et al., 1994). The results also show that the addition of "oxidizable" sulfur compounds to Jet A-1 fuel cause the contaminated Jet A-1 fuel to undergo oxidation/deposition processes similar to those of Jet A fuel. Consequently, the results herein demonstrate that "oxidizable" sulfur compounds have a very strong effect on the oxidation/deposition processes of jet fuels.

The exact identity of the oxidizable sulfur compounds responsible for the deposition processes cannot be assigned from this initial study due to the low purity levels (92–95 percent) of the mercaptan, disulfide, and sulfide compounds. However, XPS analyses were used to confirm that the sulfur contents of the "oxidizable" compounds were below 0.3 percent oxidized sul-

fur prior to use. Since the oxidized sulfur contents of the produced bulk particles were 57–98 percent (Table 2), the "oxidized" sulfur content was produced during the fuel oxidation reaction (reaction D1).

The fact that acid-neutralizing powders such as iron oxide and calcium oxide effectively inhibit surface deposition and the addition of sulfonic acid promotes bulk particles supports the acid (sulfur)/base (nitrogen) reaction proposed herein and previously (Hazlett et al., 1986) as an initial step of the deposition process. Dispersants or soluble compounds with acid-neutralizing capabilities will be studied in future work for inhibiting bulk particle formation as well as surface deposition.

Further research is also planned for identifying the "basic" nitrogen compounds, e.g., alkyl amines, aromatic amines, indoles, pyrroles, substituted pyridines, etc., which combine with the oxidized sulfur compounds to produce bulk particles and surface deposits. It is interesting to note that all of the "oxidizable" sulfur compounds produced bulk particles with significant nitrogen contents. An initial assessment of the XPS bulk particle analyses (Buckley, 1994) indicate that pyrrole and pyridine type nitrogen compounds are present. The XPS analyses also indicate that ionic type nitrogen compounds (salt from acidic sulfur: basic nitrogen reaction) are also present in the bulk particles, especially the particles from the Jet A fuel oxidation tests. The XPS analyses are in agreement with deposit-causing nitrogen compounds identified by other researchers (Hazlett et al., 1991).

The role of phenols in the bulk particle and deposition processes is more complicated than the roles of the "oxidizable" sulfur and "basic" nitrogen compounds. The phenols can act as both oxidation inhibitors (reaction D2) and deposition promoters (reaction D4). The high oxygen contents (12–17 percent) of the bulk particles and the ether type (C–O) carbon-to-oxygen bonds strongly indicate phenols or other type oxygenated compounds are involved in the deposition processes. Other researchers (Hazlett et al., 1986) have also proposed a role for phenols in the deposition process.

References

Buckley, A. N., 1994, "Nitrogen Functionality in Coals and Coal-Tar Pitch Determined by X-Ray Photoelectron Spectroscopy," *Fuel Processing Technology*, Vol. 37, pp. 165–179.

Hazlett, R. N., et al., 1986, "The Chemistry of Deposit Formation in Distillate Fuels," Report No. MRL-R-986, Materials Research Laboratories, Victoria, Australia.

Hazlett, R. N., et al., 1991, "Distillate Fuel Insolubles: Formation Conditions and Characterization," *Energy and Fuels*, Vol. 5, pp. 269–273.

Heneghan, S. P., and Harrison, W. E., 1992, "Antioxidants in Jet Fuels: A New Look," *Proc. 203rd National Meeting of the American Chemical Society, Division of Petroleum Chemistry, Symposium: Structure of Jet Fuels III*, pp. 404–411, San Francisco, CA.

Heneghan, S. P., Martel, C. R., Williams, T. F., and Ballal, D. R., 1992, "Studies of Jet Fuel Thermal Stability in a Flowing System," ASME Paper No. 92-GT-106; ASME JOURNAL OF ENGINEERING FOR GAS TURBINES AND POWER, Vol. 115, 1993, pp. 480–485.

Kauffman, R. E., 1992, "New Techniques to Predict and Evaluate the Effectiveness of Antioxidants in Jet Fuels," *Proc. 203rd National Meeting of the American Chemical Society, Division of Petroleum Chemistry, Symposium: Structure of Jet Fuels III*, San Francisco, CA, pp. 412–419.

Kauffman, R. E., 1994, "New, Rapid Techniques for Determining the Hydroperoxide Content, Oxidation Stability, and Thermal Stability of Jet Fuels," ASME Paper No. 94-GT-346.

Mushrush, G. W., et al., 1994, "Liquid Phase Oxidation of Organo-Sulfur Compounds by Tert-butyl Hydroperoxide and Fuel Instability Reactions," *Fuel*, Vol. 73, No. 9, pp. 1481–1485.