REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A103 486	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE EFFECTS OF ORGANOSULFUR COMPOUNDS UPON THE STORAGE STABILITY OF JET A FUEL		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT, 14 AUGUST 1981
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) CPT. FREDERICK C. HENEMAN		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS STUDENT, HQDA, MILPERCEN (DAPC-OPP-E), 200 STOVALL STREET, ALEXANDRIA, VA. 22332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS HQDA, MILPERCEN, ATTN: DAPC-OPP-E, 200 STOVALL STREET, ALEXANDRIA, VA 22332		12. REPORT DATE 14 AUGUST 1981
		13. NUMBER OF PAGES 75
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Document is a thesis to fulfill partial requirements for a Master of Science Degree in Chemistry at Colorado School of Mines, Golden, Colorado 80401.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Autoxidation of Fuels
Storage Stability of Fuels
Sulfur Compounds in Fuels
Basicity of Organosulfur Compounds
Jet Fuel Storage Stability

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This study examined the effect of sulfur-containing compounds on the storage stability of Jet A turbine fuel It was found that alkyl sulfides and disulfides increased the fuel stability while all thiols and thiophene derivatives tested decreased fuel stability (increased deposit formation) at temperatures and sulfur concentrations selected.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

The Effects of Organosulfur Compounds Upon the Storage Stability of Jet A Fuel.

Cpt. Frederick C. Heneman
HQDA, MILPERCEN (DAPC-OPP-E)
200 Stovall Street
Alexandria, VA 22332

Final Report, 14 August 1981

A thesis submitted to Colorado School of Mines, Golden, Colorado in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

Linear Arrhenius plots of sulfur-spiked fuel samples demonstrated that deposit formation decreased with increased slope for all alkyl sulfides, alkyl disulfides, thiols, and thiophene derivatives. A plot of insoluble deposit vs. concentration of added alkyl sulfide produces a negative slope. It appears that the inhibiting mechanism for alkyl sulfides is a result of the compound's reactivity with intermediate soluble precursors to deposit in the fuel.

A method of approximating the relative basicity of weak organo-sulfur bases was developed via measurement of their resonance chemical shifts in proton NMR. Linear plots of log gm. deposit vs change in chemical shift (shift differences between sulfur bases neat and complexed with I_2) were found for alkyl sulfides and alkyl thiols. This suggests the possibility that increased deposit formation is due to base catalysis with these compound classes.

T-2503

THE EFFECTS OF ORGANOSULFUR COMPOUNDS UPON THE STORAGE STABILITY OF JET A FUEL

By

Frederick C. Heneman

LIST OF FIGURES

ABSTRACT

This study examined the effect of sulfur-containing compounds on the storage stability of Jet A turbine fuel. It was found that alkyl sulfides and disulfides increased the fuel's stability while all thiols and thiophene derivatives tested decreased fuel stability (increased deposit formation) at temperatures and sulfur concentrations selected.

Linear Arrhenius plots of sulfur-spiked fuel samples demonstrated that deposit formation decreased with increased slope for all alkyl sulfides, alkyl disulfides, thiols, and thiophene derivatives. A plot of insoluble deposit vs. concentration of added alkyl sulfide produces a negative slope. It appears that the inhibiting mechanism for alkyl sulfides is a result of the compound's reactivity with intermediate soluble precursors to deposit in the fuel.

A method of approximating the relative basicity of weak organosulfur bases was developed via measurement of their resonance chemical shifts in proton NMR. Linear plots of log gm. deposit vs. change in chemical shift (shift differences between sulfur bases neat and complexed with I_2) were found for alkyl sulfides and alkyl thiols. This suggests the possiblity that increased deposit formation is due to base catalysis with these compound classes.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I am deeply indebted to the one individual who has assisted me above all others with this research project - Dr. Stephen R. Daniel. His help in every aspect of research for and preparation of this thesis has been the key factor in its completion. It has been an honor and a pleasure to have been his student and friend.

I want to acknowledge the United States Army which has, for the most part, provided the funding and time for me to complete this thesis and Master's Degree in Chemistry.

I also want to acknowledge the financial support for research provided by the National Aeronautics and Space Administration Lewis Research Center under Grant # NSG-3122.

I want to thank Dr. Jonathan H. Worstell for his guidance and the research he has completed with organonitrogen heterocyclic compounds and fuel storage stability.

I also thank both Dr. George B. Lucas and Dr. Scott W. Cowley who, as members of my thesis committee, provided valuable suggestions and assistance.

I greatly appreciate Dixie Brough's most professional typing (and retyping) of this thesis, and Mary Durrett's excellent preparation of its graphics.

Finally, I thank my wife, Julia, and my children, Fritz and Marlene, for their continued patience and encouragement.

INTRODUCTION

Sulfur in Fuels

The current fossil fuel supply pattern has awakened a national recognition that coal and oil shale increasingly will become major suppliers of energy in the United States for at least the next several decades (1). Total sulfur content in oil shales is comparable to values measured in crude oils from many of the producing countries (2). Robinson and Dinneen list sulfur percent (by weight) in several typical shale oils, a few of which are reported in Table I (3). Also shown in Table I are several examples of coal syncrudes and their sulfur content. Lower percent sulfur values with coal syncrudes shown are primarily a result of the removal of sulfur by hydrotreatment processes (4,5). Crude oils vary in sulfur content from less than .05% to more than 14%. However, relatively few produced crude oils contain more than 4% sulfur, and most oils contain from 0.1% to 3% sulfur (6). Smith reports that the average sulfur content of crude oils based on 9347 samples 0.65% by weight, but that this would be considerably higher if many of the high sulfur crude oil (>1%) reserve supplies were included in his sampling (7). Indeed, ever since the discovery of "sour crudes" in Ohio during the

TABLE I: Sulfur Percent (by weight) in Shale Oils (2,3) and Coal Liquids (4,5)

Country	Locality, Type or Age	Sulfur %
USA	Colorado, Green River shale, Eocene	0.6-0.8
Australian	Glen Davis, Kerosene shale, Permian	0.6
Brazil	Tremembe-Taubate, Tertiary	0.7
France	Autun, St. Hilaire, Permian	0.5-0.6
West Germany	Messel, Eocene	0.6
USSR	Estonia, Kukersite, Ordovician	1.1
USA	Western Kentucky Coal Syncrude	0.08
USA	Utah Coal Syncrude	0.03

1880's an increased concern has been given to the serious problems caused by sulfur content.

Considerable research into the causes and effects of fuel deterioration at storage temperatures was initiated during the time period from the 1920's until after the Second World War. Hydrocarbon fuels were found to deposit gums that coated the walls of storage containers and also formed particles suspended in the fuel itself. Following the war, petroleum corporations were forced by demand to blend straight-run middle distillate fuel with catalytically cracked fuel. This led to problems resulting from the formation of sludge and deposit particularly in blends containing components derived from high-sulfur crudes (8).

In 1948 the American Petroleum Institute initiated Research Project #48 to study "The Production, Isolation and Purification of Sulfur Compounds and Measurements of their Properties." This study included analysis of the structures of organic sulfur compounds that comprise the sulfur in petroleum (9).

Sulfur's Participation in Fuel Stability

There has been an increasing interest in the participation of sulfur compounds in the "stability" of both petroleum and coal/oil shale derivatives. All uses of petroleum products as energy sources require combination with oxygen. Petroleum chemists spend considerable time developing methods to circumvent the attack of oxygen prior to combustion, i.e., increasing the stability of fuels. The degradation of fuel due to the attack of oxygen results in the production of insoluble gums, which in turn leads to numerous undesirable results. In the case of gasoline, carburator clogging, induction system deposits, valve malfunction, and piston/crankcase fouling are a few such results. Also the octane number of gasoline is reduced through the formation of peroxides, initial products of the reaction of fuel hydrocarbons with oxygen (10). In the field of lubrication, oxygen attack produces acids in lubricating oils and breaks down grease structure (10). A most vulnerable part of the jet turbine engine is its fuel system with its sensitive filters, nozzles and other regions of limited dimensional tolerance. Particulate matter in fuel resulting from fuel instability in these areas can be most detrimental to jet engine lifespan (10).

The general study of fuel stability is complex and many of the reactions that contribute to instabilty remain uninvestigated. When considering the stability of fuels, the term "storage stability" refers to a fuel's ability to resist autoxidative reactions while it is in a storage facility. "Thermal stability" may be defined as a given fuel's ability to resist chemical degradation while in the environment of an operating engine. Autoxidative reactions have been theorized to lead to the formation of deposits in fuel (10). During the early 1950's, a few investigations were made concerning the storage stability of diesel fuel and its relationship to the sulfur content of fuel. However, with the exception of the thiols, little is known about the actual contribution of sulfur compounds to fuel stability or instability (11,12,13,14,15).

Sulfur is the third most abundant atomic constituent of crude oil, following carbon and hydrogen (2). In most crude oils, hydrogen sulfide and elemental sulfur are very minor constituents of total sulfur content. Most sulfur is in organic combination (i.e., bonded to carbon). Although more than two hundred individual sulfur compounds have been separated and identified in crude oils, most are reasonably low molecular weight compounds. Many sulfur compounds in crude oil still remain unidentified. Figure I shows the general structural formula of several sulfur classes found in petroleum. Crudes that contain greater percentages of mercaptans/thiols are often referred to as "sour crudes". Thiols and disulfides are usually minor components except in some lighter oils. Oils are often classified as light or heavy

FIGURE I: Typical Aliphatic and Aromatic Sulfur Compound Classes in Petroleum

Class Name	Structural Formula	
Aliphatic Sulfides	R-S-R'	
Aliphatic Disulfides	R-SS-R'	R = alkyl chain
Aliphatic Polysulfides	$R-S_n-R'$	
Aliphatic Thiols	R-SH	
Aromatic Thiols	Ar-SH	Ar = aromatic
Thiophene		
Cyclic Aliphatic Sulfide		(Tetrahydrothiophene)

based on their viscosity index. Viscosity index expresses the variation of viscosity of an oil with temperature, generally ranging from zero to one hundred based on two reference oils (16). Thiols are more abundant in low boiling fractions than most other sulfur compound types. Most of the sulfur in crude oils occurs in C-S-C bonding in which the carbon atoms may be either saturated (aliphatic) or unsaturated (aromatic), and this three atom grouping may be either cyclic or acyclic. Thiacycloalkanes are usually more abundant than thiaalkanes. Ring systems containing sulfur occur as a variety of five and six membered ring derivatives. The aromatic thiophene ring is abundant as part of complex ring systems such as benzothiophene, dibenzothiophene, etc, but thiophene and simple alkyl thiophenes also occur. Most sulfur occurs in high boiling and/or residual fractions. Few compounds have been separated and identified from fractions boiling above 250°C (17,18).

Thompson, et al. found that free sulfur promoted instability in stored fuel oils (19). Additionally, it was found that thiophenes, aliphatic thiols and sulfides had little effect while disulfides, polysulfides,and particularly benzenethiol (thiophenol) were effective in forming deposits (19). The tert-aliphatic disulfides were determined to be more deleterious than normal aliphatic disulfides. For higher molecular weight compounds, n-aliphatic polysulfides were found to be more potent sediment producers than n-aliphatic disulfides. This was thought to be due to decreasing solubility of disulfides with increasing molecular weight (19). It should be pointed out that the results of these investigations on stored fuel oils were obtained by spiking samples with sulfur concentrations greater than 1000 ppm in an accelerated storage test at 100°F.

Wallace claims that the most deleterious sulfur compounds are elemental sulfur, thiols, disulfides and polysulfides. Disulfides reportedly form intermediate free radicals that decompose to more reactive sulfur derivatives such as thioaldehydes (18). The participation of thiols in the instability of petroleum fractions appears to be the best understood reaction. Thiols are readily oxidized to thiyl radicals (see Reaction #1, Figure II). These radicals in turn form disulfides, add to diolefins and monolefins to form hydroxy sulfoxides, and initiate olefinic polymerization reactions. These reactions are accelerated by light, heat, hydroperoxides, and trace metals (18,20,21,22,23,24).

The processes in which diesel fuels form deposits during storage have been explained from two points of view. Elmquist claims that stability is affected by the presence of easily oxidizable aromatic thiols, hydrocarbons, and oxygen. This theory is based upon Kharasch's mechanism for the cooxidation of olefins and sulfur containing compounds (See Figure II) (21,25). Clinkenbeard theorizes that instability is due to autoxidation products formed from the hydrocarbon components in the fuel and their resulting reaction with sulfur, oxygen, and nitrogen compounds (26).

Schwartz, et al. reported the effect of sulfur compounds on deposit formation in cracked gasoline. It was determined that compounds including benzenethiol, 1-hexanethiol, n-butyl sulfide, and n-butyl disulfide accelerated the formation of deposit. In these tests, 0.5 volume percent radioactive-labelled sulfur compounds were utilized at a storage temperature of 110°F for periods of up to sixty-four days. It was noted in these tests that sulfur levels were higher in the deposit than in the fuel sample (27,28).

Storage Stability of Jet Fuel

Little work has been done on the storage stability of jet fuel. Elemental analysis of jet fuel deposit formed during storage indicates an increase in weight percent nitrogen, oxygen, and sulfur as compared to their concentrations in the original fuel solution. Taylor reported that jet fuel insoluble deposit formed in the presence of oxygen had a sulfur content of 0.49 weight% as compared to 0.076 weight% in the parent fuel (29). It is suspected that due to the large increase in oxygen content that the fuel probably undergoes oxidation as an initial step toward deposit formation. Carbon to hydrogen ratios determined by elemental analysis suggest that many aromatics (or other unsaturated compounds) are being concentrated in the deposit (29,30,31).

Johnson, et al. (32) tested the storage stability of JP3 and determined a relationship between fuel stability and the refining process. It was found that the fuel stability increased in the order: thermally-cracked, catalytically-cracked and straight-run. Furthermore, tests were run by adding polylsulfides, aliphatic mercaptans, and benzenethiol to JP3, and a relative order of increased rate of deposition was found to be in agreement with Thompson's findings (19,32). Since jet fuels overlap the boiling range of both gasoline and distillate fuels, it would be expected that the influence of composition on storage stability would assume some of the characteristics of both. The sulfur distribution (%weight) in various types of gas oils were found by Nixon to be: straight-run - .39%, catalytically-cracked - .78%, and thermally-cracked - .98% (33). Thus it appears that increased sulfur content generally corresponds to de-

FIGURE II: Kharasch's Mechanism for Co-oxidation of Olefins with Sulfur-Containing Compounds (21)

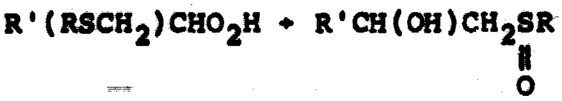
1) $RSH + O_2 \rightarrow RS^{\cdot} + HO_2^{\cdot}$

2) $HO_2^{\cdot} + RSH \rightarrow RS^{\cdot} + H_2O_2$

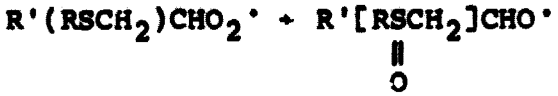
3) $RS^{\cdot} + R'CH = CH_2 \rightarrow R'(RSCH_2)CH^{\cdot}$

4) $R'(RSCH_2)CH^{\cdot} + O_2 \rightarrow R'(RSCH_2)CHO_2^{\cdot}$

5a) $R'(RSCH_2)CHO_2^{\cdot} + RSH \rightarrow R'(RSCH_2)CHO_2H + RS^{\cdot}$

6a)

$R'(RSCH_2)CHO_2H \rightarrow R'CH(OH)CH_2\underset{\underset{O}{\|}}{S}R$

and/or

5b)

$R'(RSCH_2)CHO_2^{\cdot} \rightarrow R'[R\underset{\underset{O}{\|}}{S}CH_2]CHO^{\cdot}$

6b)

$R'[R\underset{\underset{O}{\|}}{S}CH_2]CHO^{\cdot} + RSH \rightarrow R'CH(OH)CH_2\underset{\underset{O}{\|}}{S}R + RS^{\cdot}$

(hydroxylated sulfoxide)

creasing storage stability, although it must be noted that olefins also follow the same order as the listed sulfur distribution.

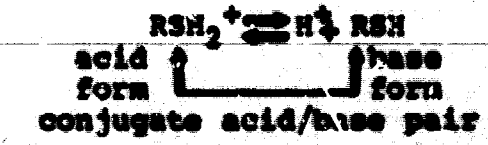
More current studies have been concerned with the effects of organosulfur compounds on the stability of jet fuels. However, again, it must be noted that investigatons have been restricted to high concentrations of added sulfur compounds in samples, and in the following cases, tests made of thermal stability. In 1967 Taylor and Wallace reported that 1000 ppm sulfur concentrations of pure organosulfur compounds markedly influenced the rate of deposit formation from essentially sulfur-free hydrocarbons at ~450°F in the presence of oxygen. They found that the selected thiols, sulfides, disulfides and condensed thiophenes which increased the rate of deposit formation decomposed into radical fragments under the conditions studied. These radical fragments initiated complex, free-radical autoxidation reactions that led to the formation of deposits (34). During the mid 1970's Taylor published additional findings of the effects of trace impurity sulfur compounds on the rate of deposit formation in deoxygenated jet fuel. One of his experiments, run with 3000 ppm sulfur added at ~540°C in the presence of less than 1 ppm O_2, resulted in higher formation rates with sulfides, disulfides, polysulfides and a thiol.

Added condensed thiophene compounds did not increase the deposit rate. Taylor suggested that two distinct mechanistic processes occur in saturated and deoxygenated fuels. One mechanism is predominant in a low temperature air-saturated environment, and the other in a high temperature deoxygenated condition (35,36).

Base Catalysis and Fuel Stability

One important consideration in understanding the effect of individual organosulfur compounds on deposition rate is whether there exists a dependence of deposit formation upon the base strength of the compound. Worscell concluded that many nitrogen compounds accelerated the formation of deposit in Jet A and diesel fuel through base catalysis (37). It would therefore be significant to determine whether similar results might occur with certain organosulfur compounds since they can function as Lewis bases via sulfur nonbonding electron pairs.

The organic sulfides, disulfides, thiols, and thiophenes are extremely weak bases. The basicity of such compounds is normally measured in terms of the Ka or pKa of their conjugate acids. For example, in the case of thiols, the conjugate acid/base pair is shown as follows:



$$RSH_2^+ \rightleftharpoons H^+ + RSH$$

The pKa in this case equals -log Ka = -log $[RSH][H^+]/[RSH^+_2]$. Tabulated values of Bronsted basicity (ability of the compound to accept a proton) in aqueous medium of many weak organonitrogen bases are available. However, such data are not available for the weaker organosulfur bases.

An attempt to measure the basicity (a measure of sulfur's non-bonding electron pair donating ability) of some of the thiols and disulfides was made by Arnett, et al. via solvent extraction and gas chromatography, and by Scorrano, et al. using nuclear magnetic resonance techniques (38,39). Unfortunately, virtually all results have been affected by the fact that the compounds often decompose during protonation (40). Scorrano, et al. studied the decomposition reactions extensively and it is his current belief that it is not possible to determine realistic absolute pKa values for mercaptans and disulfides (41,42,43). In 1973 Arnett et al. developed a plot of calorimetrically determined heats of protonation (ΔH_i) in HSO_3F versus the few reliably known aqueous pKa values previously determined for specific sulfides. A fair linear correlation exists between ΔH_i and pKa over the range of 40 kcal/mole for enthalpies and twenty-two pKa units. However, it was suggested, that such a relationship would disperse into a series of different lines for different classes of compounds (44,45).

Comparative absolute values of pKa's measured between gas phase and in solution show striking differences. The current absence of any means for directly determining the hydration energy of the sulfonium ion prevents obtaining an exact quantitative accounting for pKa's in terms of relative solvation energies of the base versus its conjugate acid (44).

EXPERIMENTAL

Preparation of Chemicals and Reagents

Jet A turbine fuel was acquired during previous research from the National Aeronautics and Space Administration Lewis Research Center. All accelerated storage tests were made from the same originally acquired sample of fuel stored at 4°C. n-Ethyl sulfide, n-butyl sulfide, n-pentyl (amyl) sulfide, n-butyl disulfide, n-pentyl (amyl) disulfide, isopentyl (amyl) disulfide, 1-propanethiol, 1-butanethiol, 1-pentanethiol, benzenethiol (thiophenol), p-toluenethiol, 1-naphthalenethiol, toluene-3,4-dithiol, 1-benzothiophene (thianaphthene), dibenzothiophene, and tetrahydrothiophene were purchased from Eastman Organic Chemicals of Rochester, New York. Tetrahydrofuran (THF) and iodine were acquired from the J.T. Baker Chemical Company of Phillipsburg, New Jersey. Tetramethylsilane was purchased from Norell, Inc. of Landisville, New Jersey. All chemical compounds were utilized as received in unopened containers as purification was not found necessary.

Jet A fuel was filtered through a fine sintered glass funnel prior to use. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride ($LiAlH_4$) prior to use.

Measurement of Insoluble Fuel Deposit

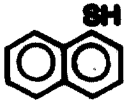
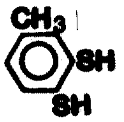
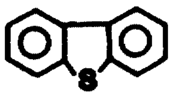
The "slip" technique developed by Worstell during his studies with heterocyclic organonitrogen compounds was utilized to determine the amount of insoluble fuel deposit formed with each tested sample of Jet A fuel (46). Aliquots of 10 mls of Jet A fuel were volumetrically pipeted into standard 4-ounce Flint-glass containers of 147 ml capacity. Although these containers were in fact a soft glass, and soft glass has been shown to have an inhibiting effect on the degradation of many fuels, experimental design of this research was oriented toward the measurement of relative fuel degradation of samples. Thus, the inhibiting effect may be considered non-consequential within the framework of these experiments (46,47). All glass containers were cleaned for 48 hours at room temperature in a chromic acid bath and then placed in sodium bisulfite solution for 24 hours. Containers were then rinsed repeatedly with deionized water and dried prior to use. Worstell experimentally verified that this cleaning process has no siginificant effect upon the accelerated storage test aging process of Jet A fuel (46).

Glass microscope coverslips of 324 mm^2 area were tared and one placed in each container with the fuel sample. Standard THF solutions of the various sulfur-containing compounds were prepared. These compounds were for the most part selected because they have boiling points greater than the temperature at which accelerated storage tests were conducted (Table II). The volume of organosulfur compound corresponding to 10 µg sulfur/ml fuel was chosen for kinetic experiments because it provided a reasonable amount of deposit being formed within the temperature and time conditions selected. Liquid sulfur compounds were added neat, except in cases where spiking amounts were less than one microliter. In these cases, a solution of the compound in the THF was utilized to increase spiking reproducibility. Previous research by Dahlin demonstrated that THF in Jet fuel in a ratio of 1:10 has no effect upon the rate of deposit formation. As mentioned previously, the formation of peroxides is felt to be an intermediate step toward the formation of gums and deposits in fuel. Although THF is easiy oxidized to it's hydroperoxide, its rapid volatilization from fuel solution at temperatures tested probably accounts for the lack of effect (46,48). The amount of THF utilized in sample preparation of organosulfur compounds was considerably less than that demonstrated to have no effect (48). For these reasons it is believed that addition of THF to fuel samples has no effect upon experimental results.

TABLE II: Organosulfur Spiking Compounds

Compound Name	Compound Formula	Boiling Point (760mm Hg)
n-Ethyl sulfide	$[CH_3CH_2]_2S$	90°C
n-Butyl sulfide	$[CH_3(CH_2)_3]_2S$	189°C
n-Pentyl sulfide	$[CH_3(CH_2)_4]_2S$	230°C
Tetrahydrothiophene		121°C
n-Butyl disulfide	$[CH_3(CH_2)_3]_2S_2$	227°C
n-Pentyl disulfide	$[CH_3(CH_2)_4]_2S_2$	141°C/17mm
Isopentyl disulfide	$[(CH_3)_2CHCH_2]_2S_2$	250°C
1-Propanethiol	$CH_3(CH_2)_2SH$	68°C
1-Butanethiol	$CH_3(CH_2)_3SH$	98°C
1-Pentanethiol	$CH_3(CH_2)_4SH$	137°C
Benzenethiol		169°C
p-Toluenethiol		195°C

TABLE II: Continued

1-Naphthalenethiol		145°C/10.3 mm
Toluene-3,4-dithiol		185°C
1-Benzothiophene		222°C
Dibenzothiophene		136°C/2 mm

Triplicate containers of each organosulfur spiked fuel sample were prepared in this manner. The Flint-glass containers were closed with Teflon-lined lids and placed in a thermostated oven at constant temperatures selected in the 121°-135° range. At twenty-four hour intervals, samples were removed from the oven; the coverslips were extracted with forceps and dried under a GE infrared lamp for 15 minutes to insure total liquid evaporation. The fuel samples were opened in this manner every twenty-four hours and exposed to air for an equal amount of time in order to replenish the oxygen available within the containers. The dried coverslips were then weighed on a Cahn Model 4700 electrobalance. This procedure was carried out with the final weighing being made at 168 hours (seven days).

Determination of Stabilizing/Destabilizing Effect of Sulfur-Containing Compounds

Individual organosulfur compounds including aliphatic sulfides, aliphatic disulfides, aliphatic and aromatic thiols, a dithiol, and thiophene derivatives, were added individually to 10 ml samples of Jet A fuel at a total sulfur concentration of 10 μg sulfur/ml Jet A Fuel. Solid sulfur-containing compounds were dissolved in THF. Liquid compounds were added neat, except in cases where spiking amounts were less than one microliter in which case a solution of the compound in the THF was prepared to increase spiking reproducibility. All samples were prepared in triplicate. The samples were incubated at 135°C. Coverslips were removed every 24 hours and weighed. The experiment was terminated at 168 hours.

Dependence of Deposit Formation upon Sulfur Concentration

Benzenethiol (thiophenol) and n-butyl sulfide were added to 10 mls of Jet A fuel. The sulfur concentrations of samples were set at 10, 100, 500, and 1000 μg sulfur/ml fuel. All samples were run in triplicate. Samples were incubated at 121°C with the experiment being terminated at 168 hours.

Dependence of Deposit Formation upon Temperature

Individual sulfur compounds were added to 10 mls of Jet A fuel at a concentration of 10 μg sulfur/ml fuel. Triplicate samples of each solution were incubated at 121°C, 130°C and 135°C. Coverslips were removed and weighed at 24 hour intervals and the experiment was terminated at 168 hours.

Dependence of Deposit Formation upon Base Strength

Results from accelerated storage tests as previously described at 121°C and 135°C, and 10 μg sulfur/ml Jet A fuel added were utilized to determine whether a dependence of deposit formation upon base strength existed.

In spite of the previously identified obstacles to determining absolute values of basicity, a relative order of basicity was developed for selected organosulfur spiking compounds. Neat samples of liquid aliphatic sulfides, disulfides and thiols/mercaptans were analyzed on a Varian EM 360 (60 Mhz) proton NMR utilizing a 10% internal tetramethylsilane (TMS) reference. Neat liquid samples of these compounds were then complexed with excess iodine, and again run under the same conditions on the proton NMR. The TMS reference peak was superimposed with the TMS peak of the neat uncomplexed plot, and the resulting difference in proton resonance chemical shift was measured. The single methylene group measured furthest downfield (greatest deshielding) was selected for standard shift measurement of each compound tested.

RESULTS AND DISCUSSION

Determination of Stabilizing/Destabilizing Effect of Sulfur-Containing Compounds

The slip technique was found to be a feasible method for measuring insoluble deposit weight because the insoluble deposit that is produced adheres to the glass coverslips at the temperatures and sulfur concentrations tested.

Results of accelerated storage tests run on all organosulfur compounds (10 μg sulfur/ml fuel) demonstrated that all sulfides and disulfides inhibited the rate of deposit formation and that all thiols/mercaptans and thiophene derivatives increased the deposit rate. Table III and Figure III show that deposition rate appears to depend upon the class of sulfur compounds. Values of triplicate sample deposit weights are shown in Appendix A.

Dependence of Deposit Formation upon Sulfur Concentration

The dependence of deposit formation upon concentration of sulfur added to Jet A fuel is reflected in Table IV and Figures IV and V. Values of triplicate sample deposit weight are shown in Appendix B. Assuming that the amount of deposit is directly related to the specific rate constant for the rate determining step, the slopes of the lines on a

TABLE III: Deposition from Jet A Spiked with Selected Organosulfur Compounds (135°C, 168 hrs, 10 μg Sulfur/ml Jet A Fuel)

Compound	μg Deposit
n-Butyl sulfide	294±36
n-Pentyl sulfide	280±29
n-Butyl disulfide	270±26
n-Pentyl disulfide	248±13
iso-Pentyl disulfide	232±23
1-Butanethiol	428±22
1-Pentanethiol	393±33
Benzenethiol	361±46
p-Toluenethiol	372±39
1-Naphthalenethiol	343±29
Toluene-3,4 dithiol	414±42
Dibenzothiophene	404±52
Control	322±33

FIGURE III

Effect of Added Sulfur-Containing Compounds on Deposition Rate

(135° C, 168 hrs, 10 μg Sulfur/ml Jet A Fuel)

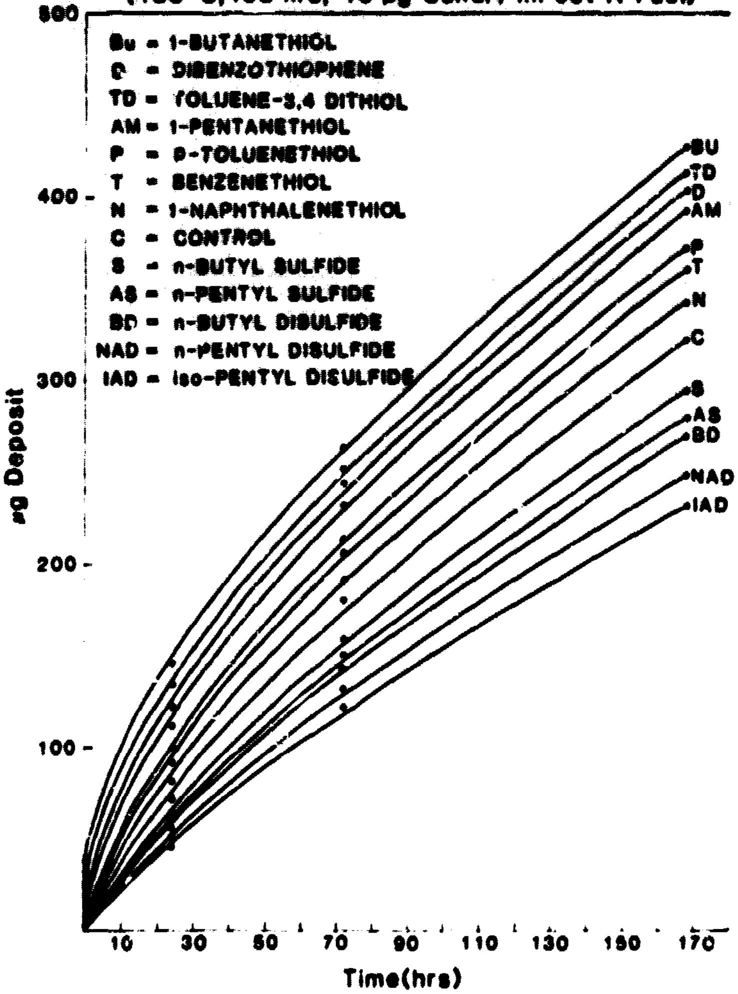


TABLE IV: Dependence of Deposit Formation upon Sulfur Concentration (121°C, 168 hrs)

Compound	Concentration (µg sulfur/ml fuel)	µg Deposit
Benzenethiol	10	84±19
Benzenethiol	100	104±11
Benzenethiol	500	172±15
Benzenethiol	1000	294±21
n-Butyl sulfide	10	68±3
n-Butyl sulfide	100	62±9
n-Butyl sulfide	500	48±5
n-Butyl sulfide	1000	41±6
Control	--	71±10

FIGURE IV

EFFECT of ADDED SULFUR CONCENTRATION on DEPOSITION RATE(BENZENETHIOL, 121°C)

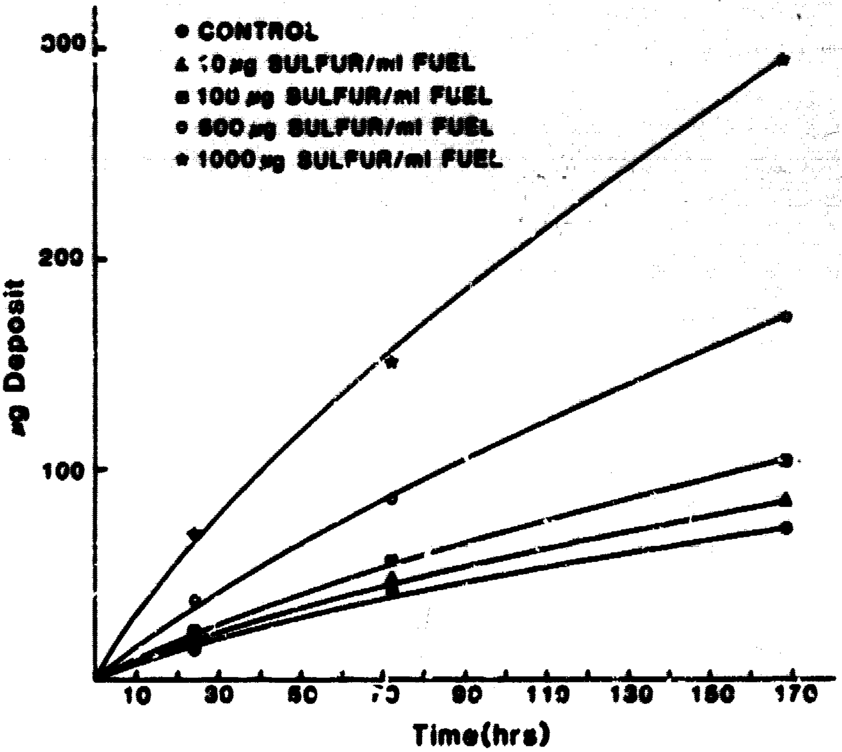
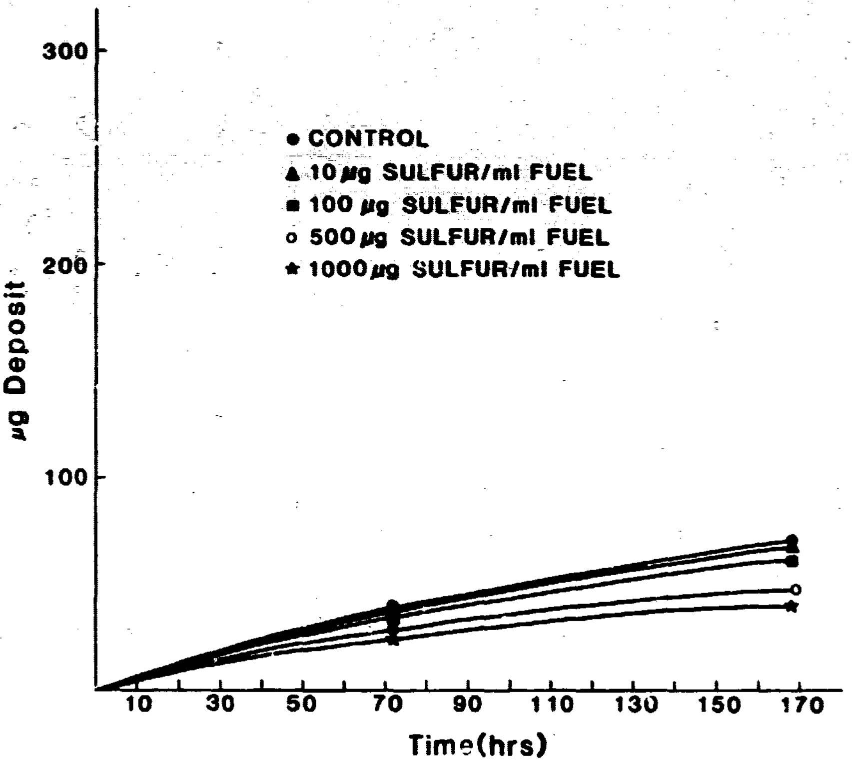


FIGURE V

Effect of Added Sulfur Concentration
on Deposition Rate
(n-Butyl Sulfide, 121°C)



deposit versus sulfur concentration plot should reflect the order of the reactions with respect to the sulfur compound. Figure VI illustrates this concept utilizing data obtained for benzenethiol, a compound that has been shown to increase deposition rate and n-butyl sulfide, a compound that has been shown to be a deposit inhibitor. The slopes for benzenethiol and n-butyl sulfide are 1.06 and -0.16 respectively. Benzenethiol appears to have a reaction order of one, within the error of the experiment.

An effort to describe the inhibitive effect of the alkyl sulfides as demonstrated by n-butyl sulfide's negative slope (-0.16) on the deposit vs. sulfur concentration plot (Figure VI) is offered. One possibility is that the sulfide inhibitor reacts with available oxygen in direct competition with the fuel/oxygen reaction to form a deposit precursor:

$$\text{Jet A Fuel} + O_2 \xrightarrow{k_1} B$$

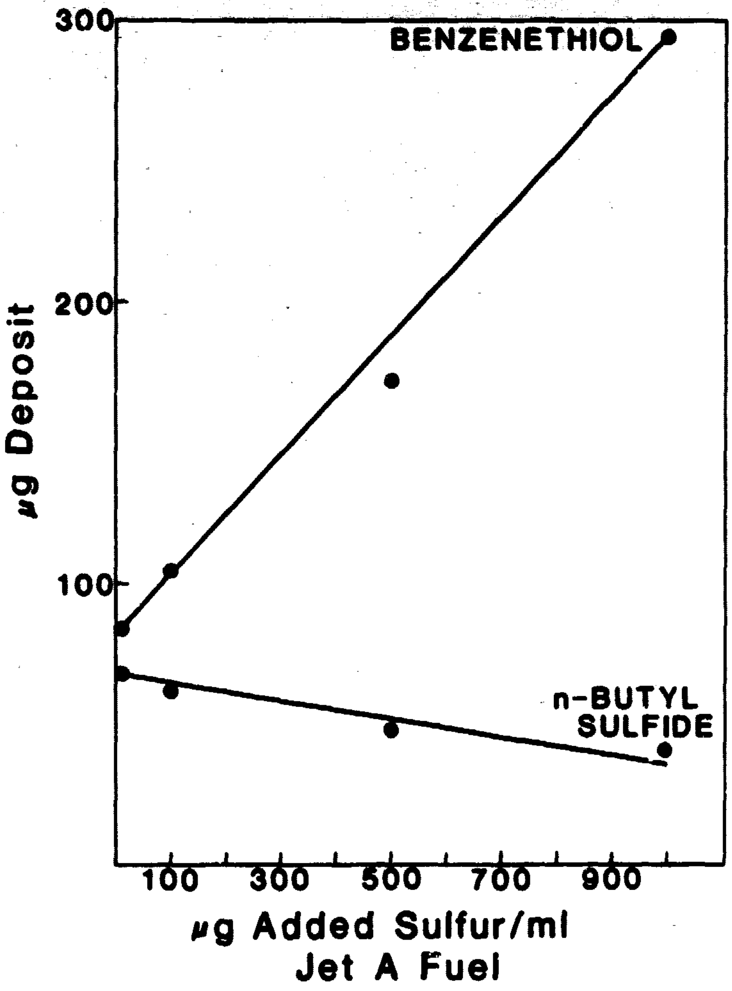
$$I + O_2 \longrightarrow C$$

$$B \xrightarrow{k_2} \text{deposit}$$

where B represents an intermediate or deposit precursor and I the inhibitor. A second possibility is that the inhibitor acts upon the deposit as a solvent reducing the amount of final insoluble product. Another possibility could be that

FIGURE VI

Deposit Versus
Added Sulfur Concentration



the inhibitor reacts immediately upon mixing with the fuel (i.e., a simple complexation reaction) and retards its ability to react with oxygen and form the precursor leading to insoluble fuel deposit. A final possibility is that the sulfide inhibitor reacts in a reversible reaction with the precursor (formed by oxidation of the fuel) to form a different soluble product, thus reducing available precursor for deposit formation.

In order to determine whether mechanism of inhibitor depletion of available oxygen is probable, the number of moles of O_2 and sulfur available in a closed storage test container were calculated. During testing the sealed 147 ml glass container had 10 ml of Jet A fuel and 137 ml of air in it. Calculations were made for 100 μg sulfur/ml fuel, 25°C, and 620 mm Hg pressure.

Number of moles O_2 in 137 ml of air:

$$137 \text{ l air} \times \underset{\substack{\text{(molar vol. of}\\ \text{ideal gas at}\\ \text{room temp.)}}}{\frac{1 \text{ mole gas}}{24.45 \text{ l}}} \times \frac{0.20 \text{ mole } O_2}{1.00 \text{ mole air}} \times \frac{620 \text{ mm Hg}}{760 \text{ mm Hg}} = 9.14 \times 10^{-4} \text{ mole } O_2$$

Number of moles sulfur in container at 100 μg S/ml Jet A fuel:

$$\frac{100\ \mu g\ \text{sulfur}}{1\ \text{ml fuel}} \times 10\ \text{ml fuel} \times \frac{1\ g\ \text{sulfur}}{10^{6}\ \mu g\ \text{sulfur}} \times \frac{1\ \text{mole sulfur}}{32.06\ g} = 3.12 \times 10^{-5}\ \text{moles S}$$

The molecular ratio of sulfur to O_2 available in the container is approximately .0341. Thus, at a concentration of 10 μg sulfur/ml fuel (the concentration at which most experimental accelerated storage tests were completed), the sulfur would consume approximately 0.341% of the O_2 available in the container if a reaction mole ratio of 1:1 moles sulfur to moles oxygen was assumed. Unless one were to assume an extremely high oxygen to sulfur reaction mole ratio, there is insufficient inhibitor to effectively decrease O_2 availability. This strongly suggests that deposit inhibition by direct competition with the fuel for oxygen is not likely.

The inhibitor reacting directly upon the fuel to retard its ability to react with oxygen is also unlikely, because it does not appear that the amount of sulfur should be sufficient to significantly affect the fuel/oxygen reaction. The lack of any apparent induction period for deposit formation with any of the sulfur-containing spiking compounds tends to support the concept that the inhibitor does not solubilize the deposit once it has been formed. An induction period should appear prior to the inhibitor being consumed and insoluble deposit appearing.

The remaining possibility is a reaction mechanism in which the inhibitor reacts with the deposit precursor. A kinetic description of the deposition rate of this reaction mechanism is shown below with A representing Jet A fuel, B an intermediate deposit precursor, and I being the inhibitor:

1. $A + O_2 \xrightarrow{k_1} B$
2. $B \xrightarrow{k_2} \text{deposit}$
3. $B + I \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} C$

To define a kinetic equation for this mechanism, with step 1 as the rate determining step, assume a steady state for B:

$$\frac{d[B]}{dt} = 0 = k_1[A][O_2] - k_2[B] - k_3[B][I] + k_{-3}[C]$$

$$[B] = \frac{k_1[A][O_2] + k_{-3}[C]}{k_2 + k_3[I]}$$

and $$\frac{d[\text{deposit}]}{dt} = \frac{k_2(k_1[A][O_2] + k_{-3}[C])}{k_2 + k_3[I]}$$

Note that within this equation for the rate of deposition, increasing [I] decreases $\frac{d[\text{deposit}]}{dt}$. This agrees with the results for n-butyl sulfide which shows a negative slope on the deposit vs. sulfur concentration plot (Figure VI).

Dependence of Deposit Formation upon Temperature

The Arrhenius equation is utilized to express the dependence of reaction rate upon temperature. It is

$$k = A\exp(-Ea/RT)$$

The specific rate constant is represented by k, and A is a preexponential or frequency factor, and Ea is the activation energy for the reaction (49,50,51). By plotting the logarithm of k versus the reciprocal of temperature (1/T), the slope of the resulting graph is $-Ea/R$ (enthalpy related) and the intercept is lnA (entropy related).

The amount of insoluble deposit formed in 168 hours was measured by the "slip" technique at three temperatures - 121°C, 130°C and 135°C. The same relative order of resulting deposit weight was found at all three temperatures (see Table III and Figure III). The narrow range of temperatures selected was due to restrictions resulting from the amount of insoluble deposit formed. At temperatures much below

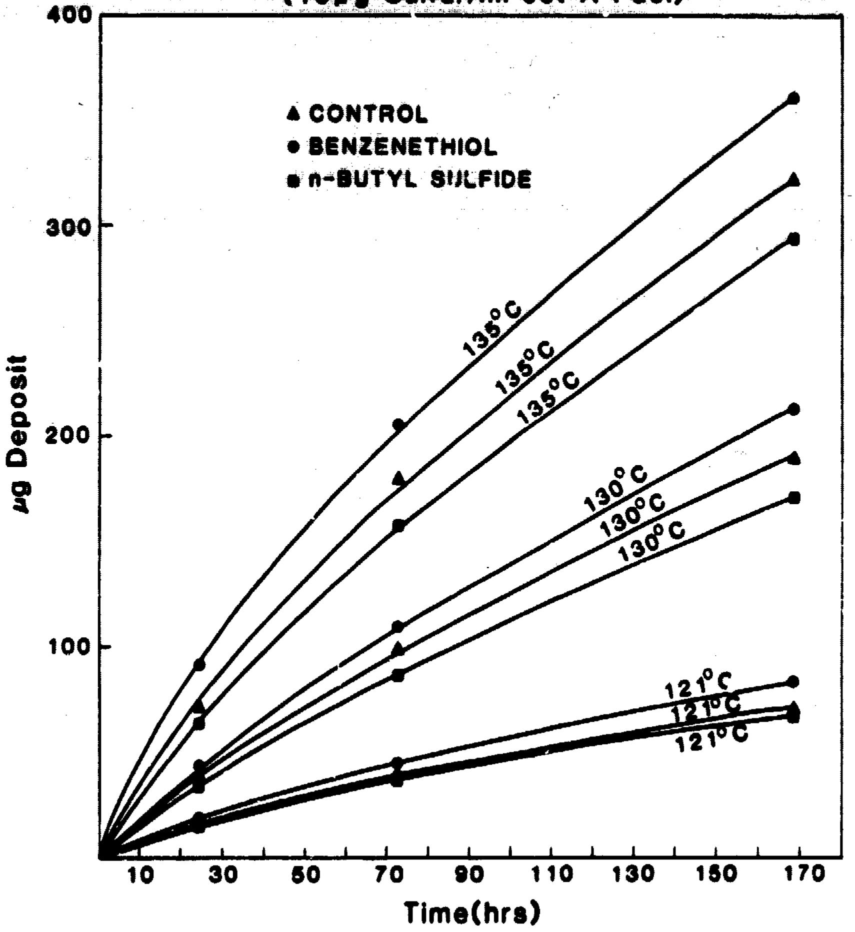
121°C, the formation of deposit was so slow that it would have been necessary to considerably extend the experimental time period. At temperatures much above 135°C the validity of the "slip" technique is placed in jeopardy because such a great amount of deposit is formed that it becomes suspended in the body of the liquid as well as deposited on the "slip". Figure VII shows the effects of temperature on the deposit weight in benzenethiol and n-butyl sulfide spiked fuel at 121°C, 130°C and 135°C for 168 hours. Triplicate values of sample deposit weight at all three temperatures are shown in Appendices A, B and C.

Measurable deposit was formed by the time that the first deposit measurement was taken (at 24 hours). No "induction periods" (initial periods during which deposit formation is delayed) were observed with any compound tested at any temperature. Such an induction period would be anticipated if the reaction of the sulfur compounds with oxygen was more rapid than the rate of deposition. The lack of an induction period was considered to be surprising particularly with sulfides, since certain sulfides are often used as antioxidant additives in fuels (52).

Bol'shakov et al. tested the additive effects of longer chain alkyl sulfides such as octyl sulfide at weight percents of sulfur from 0.05 to 0.2 in jet fuels. As tempera-

FIGURE VII

Effect of Temperature upon Deposit Weight
(10µg Sulfur/ml Jet A Fuel)



tures increased from 150°F-300°F deposit weight was found to decrease (52).

Table V lists resultant amounts of deposit at the three chosen accelerated storage temperatures for a number of other sulfur compounds. Two important assumptions are necessary before conclusions can be drawn from these Arrhenius plots. First, it must be assumed that the deposit weight is related to the specific rate of deposition. Secondly, it must be assumed that the rate of deposition reflects the rate of the controlling step of the overall reaction mechanism.

Arrhenius plots for fuel samples spiked with selected sulfur compounds and a control fuel sample are shown in Figure VIII. The slopes and intercepts for all of compounds tested are tabulated in Table VI by a least squares computation. The slope (-Ea/R) for a reaction with a "promoter" present should be smaller than the slope for a control reaction. Table VI shows that the thiols and thiophenes tested have smaller slope values than the control while sulfides and disulfides have a greater slope. It can be seen that the slope of the Arrhenius plot for each sulfur-spiked fuel sample increases as efficiency for promoting deposit formation decreases. Although there appears to be a significant difference in rate of deposition between sulfur compound

TABLE V: Effects of Sulfur Compounds on Deposition from Jet A (10 μg sulfur/ml fuel added, aged 168 hours at indicated temperature)

Compound Added		μg deposit	
	394°K	403°K	408°K
Control (No spike)	71±10	191±23	322±33
Toluene-3,4 Dithiol	110±10	249±29	414±42
Dibenzothiophene	104±13	243±23	404±52
1-Pentanethiol	94±7	233±29	393±33
p-Toluenethiol	87±13	--	372±39
Benzenethiol	84±19	214±26	361±46
1-Naphthalenethiol	78±7	--	343±29
n-Butyl sulfide	68±3	172±26	294±36
n-Pentyl sulfide	62±13	159±16	280±29
n-Butyl disulfide	55±6	156±13	270±26
n-Pentyl disulfide	49±3	133±26	248±13
i-Pentyl disulfide	42±10	123±16	232±23

FIGURE VIII

Temperature Dependence
of Sulfur Compound Effects
(Arrhenius Plot)

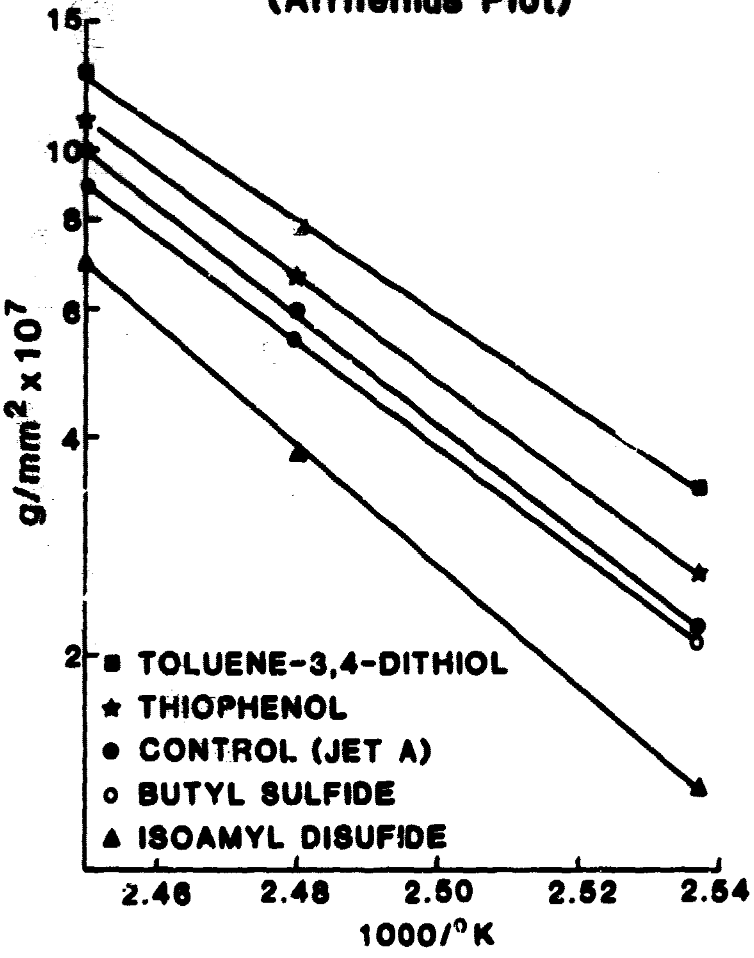


TABLE VI

Data from Arrhenius Plots (Least Squares Computation)

COMPOUND	SLOPE	INTERCEPT	REGRESSION COEFFICIENT
TOLUENE-3,4-DITHIOL	15.25	23.78	-.9993
DIBENZOTHIOPHENE	15.72	24.92	-.9995
AMYLMERCAPTAN	16.49	26.78	-.9997
p-TOLUENETHIOL	16.67	27.18	-.9999
BENZENETHIOL	16.85	27.60	-.9999
1-NAPHTHALENETHIOL	17.15	28.28	-1.000
CONTROL	17.30	28.77	-.9999
n-BUTYL SULFIDE	16.93	27.56	-.9998
n-AMYL SULFIDE	17.25	28.30	-.9995
n-BUTYL DISULFIDE	18.02	30.14	-.9999
n-AMYL DISULFIDE	18.52	31.27	-.9992
i-AMYL DISULFIDE	19.48	33.57	-.9993

classes, the differences as illustrated by Arrhenius plots are considerably less pronounced than those of analogous experiments with nitrogen heterocyclic compounds completed by Worstell. Furthermore, in contrast to results obtained with organosulfur compounds, Worstell found that the slope for each nitrogen spiked sample increased as the efficiency for promoting deposit formation increased (53).

It is advantageous to investigate whether the appearance of the deposit changes with respect to the temperature at which the experiments were conducted. Linearity of Arrhenius plottings within the temperature range selected suggests that there is no significant change in the reaction mechanism. Photomicrographs (45:1) were taken of insoluble deposit formed on glass coverslips in several sulfur-spiked Jet A fuel samples tested at 121°C and 135°C for 168 hours.

The appearance of the deposit does not appear to change significantly with the different temperature test conditions. In Figure IX and Figure XV the deposit from a control sample run at 121°C and 135°C respectively reveal small, black dentritic (thread-like) particles. Figure X shows the deposit formed in a fuel sample spiked with n-butyl sulfide at 121°C. The particle formation is very similar - only slightly lighter in texture. n-Pentyl sulfide spiked fuel at 121°C (Figure XI) apears virtually the

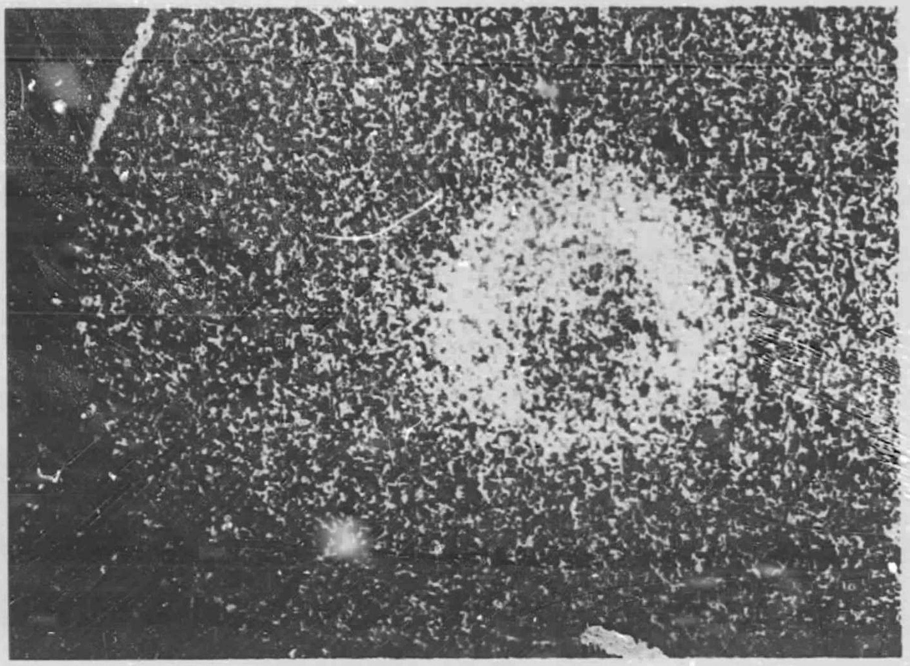


FIGURE IX: Jet A Fuel Stored at 121°C, 168 hours

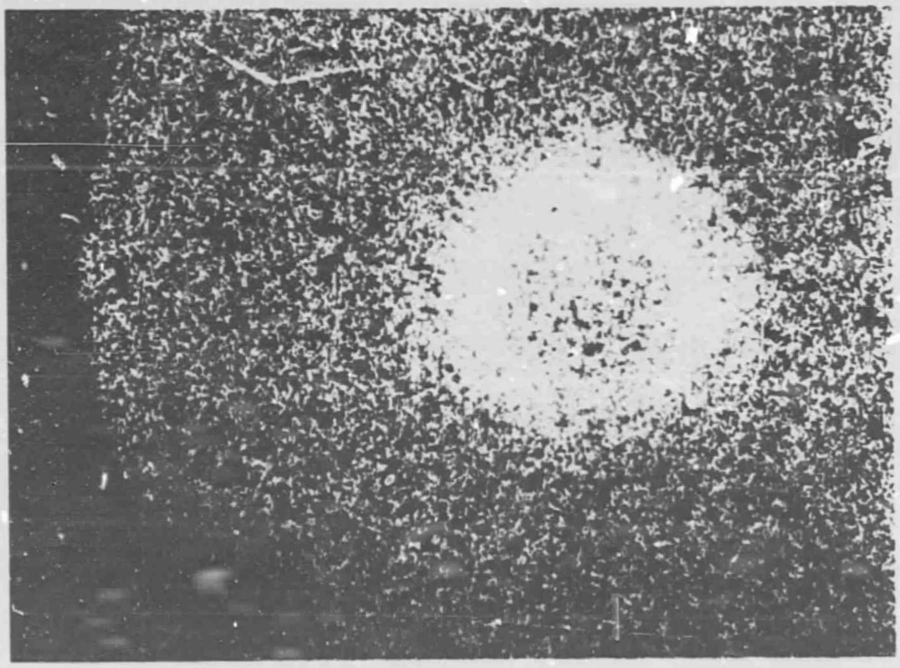


FIGURE X: Jet A Fuel Spiked with n-Butyl sulfide and Stored at 121°C, 168 hours

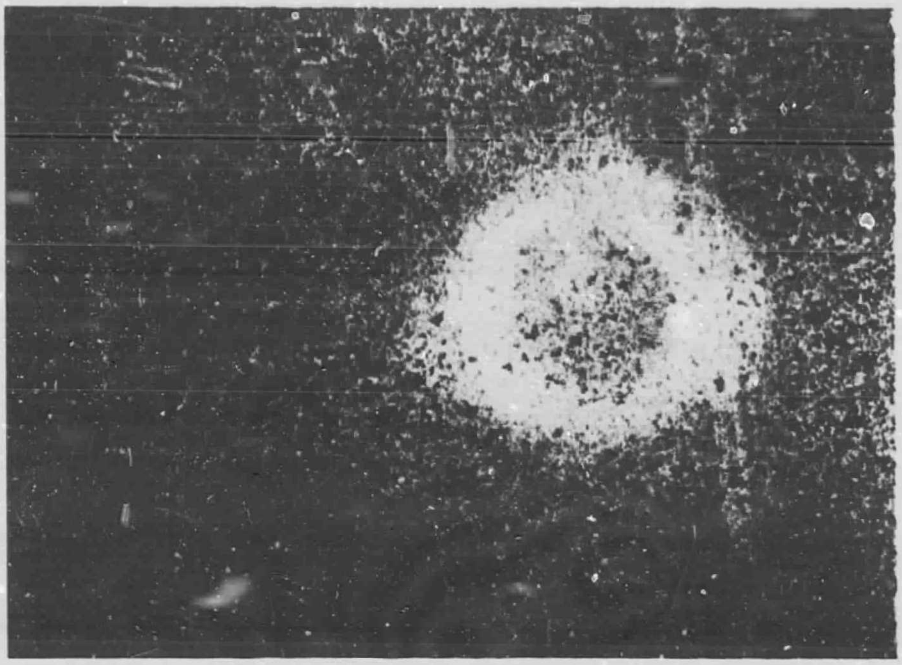


FIGURE XI: Jet A Fuel Spiked with n-Pentyl Sulfide and Stored at 121°C, 168 hours.

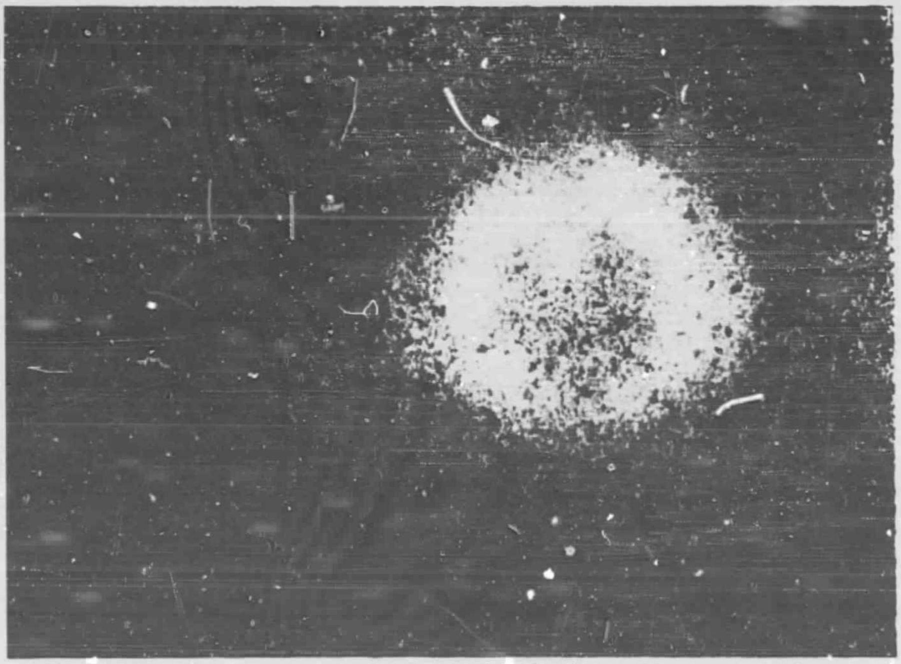


FIGURE XII: Jet A Fuel Spiked with iso-Pentyl Disulfide and Stored at 121°C, 168 hours

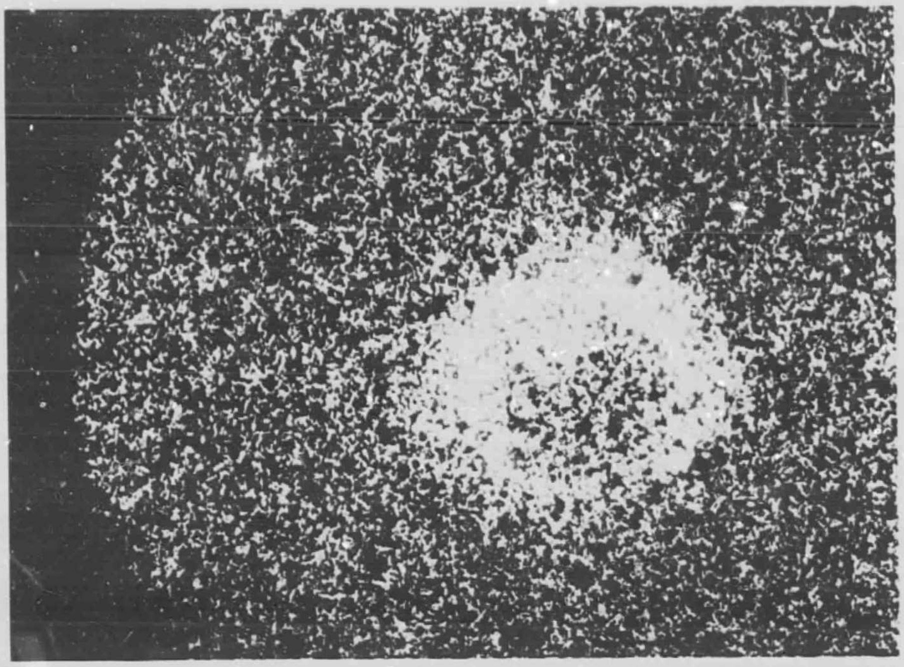


FIGURE XIII: Jet A Fuel Spiked with Toluene-3,4 dithiol and Stored at 121°C, 168 hours

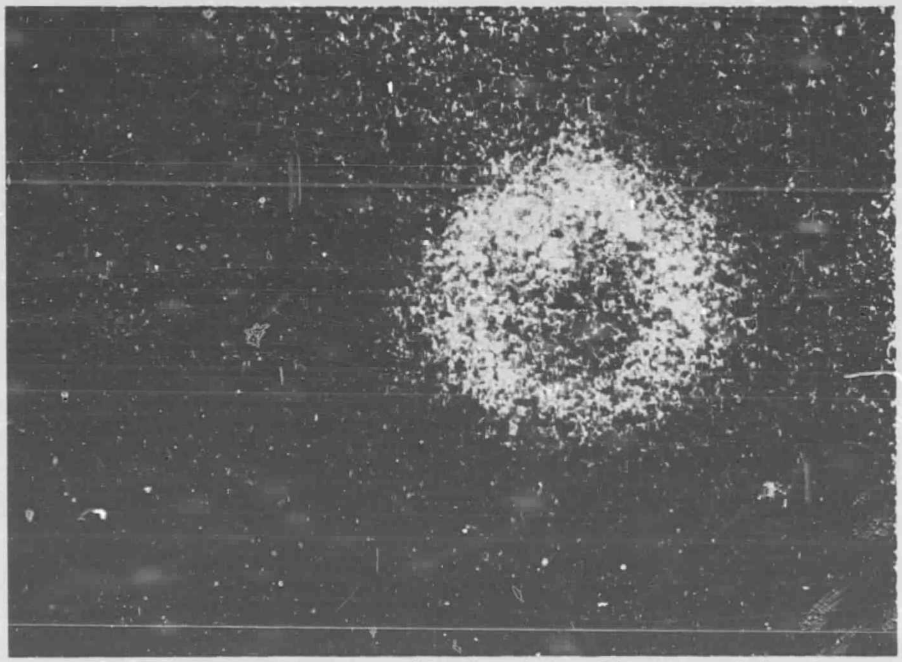


FIGURE XIV: Jet A Fuel Spiked with Dibenzothiophene and Stored at 121°C, 168 hours

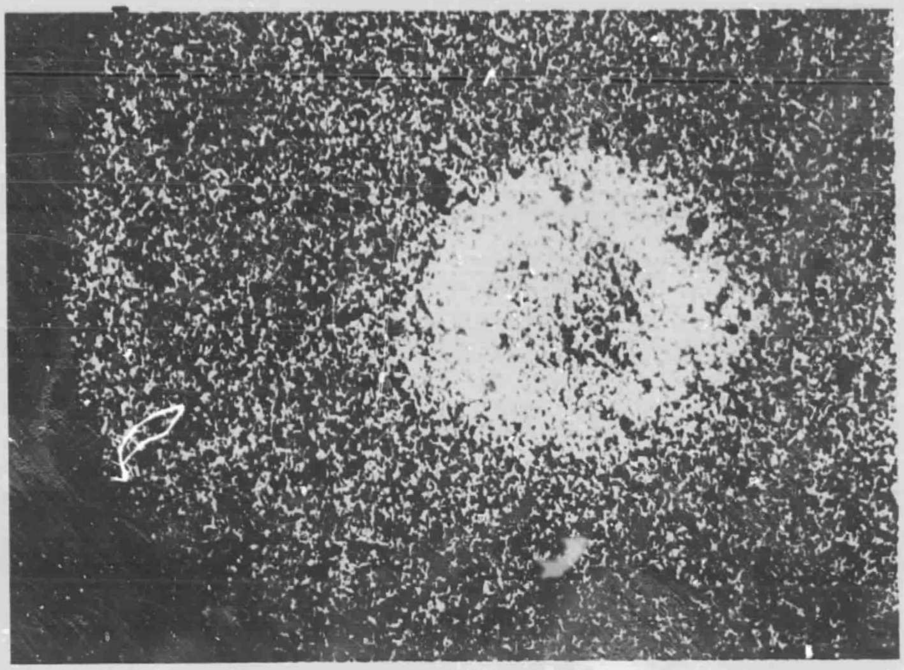


FIGURE XV: Jet A Fuel Stored at 135°C, 168 hours

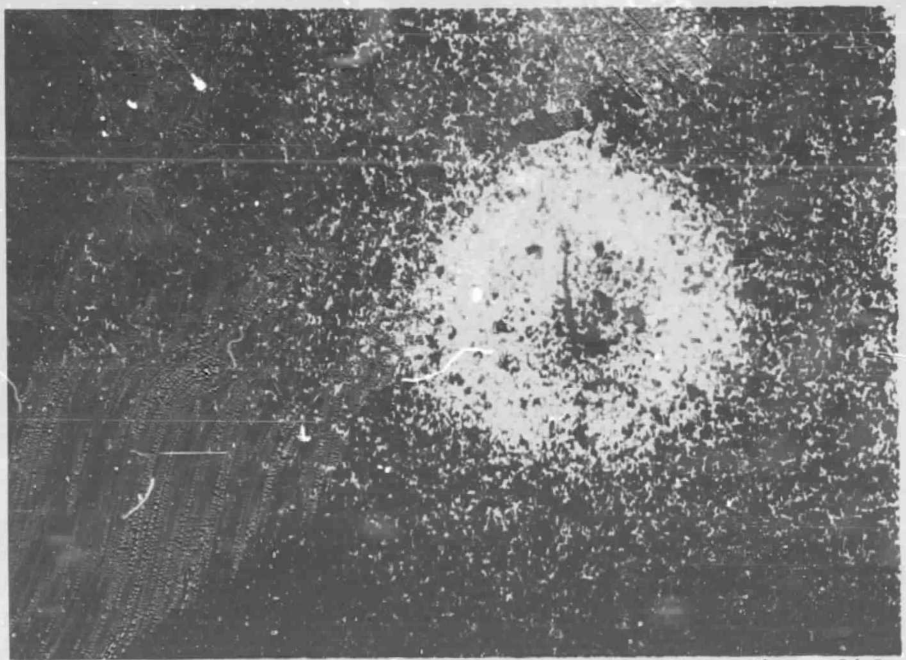


FIGURE XVI: Jet A Fuel Spiked with n-Pentyl disulfide and Stored at 135°C, 168 hours

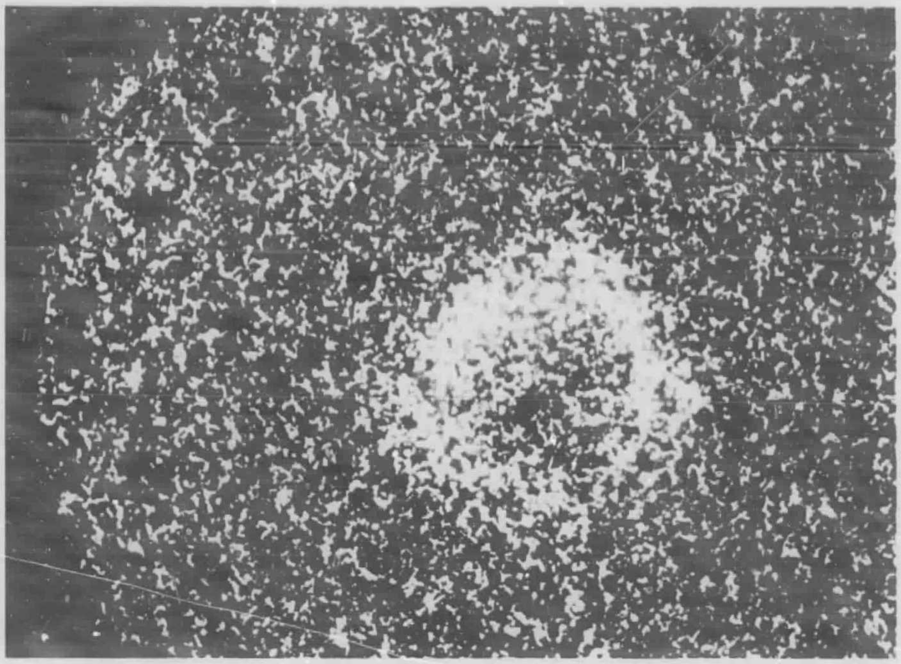


FIGURE XVII: Jet A Fuel Spiked with Benzenethiol and Stored at 135°C, 168 hours

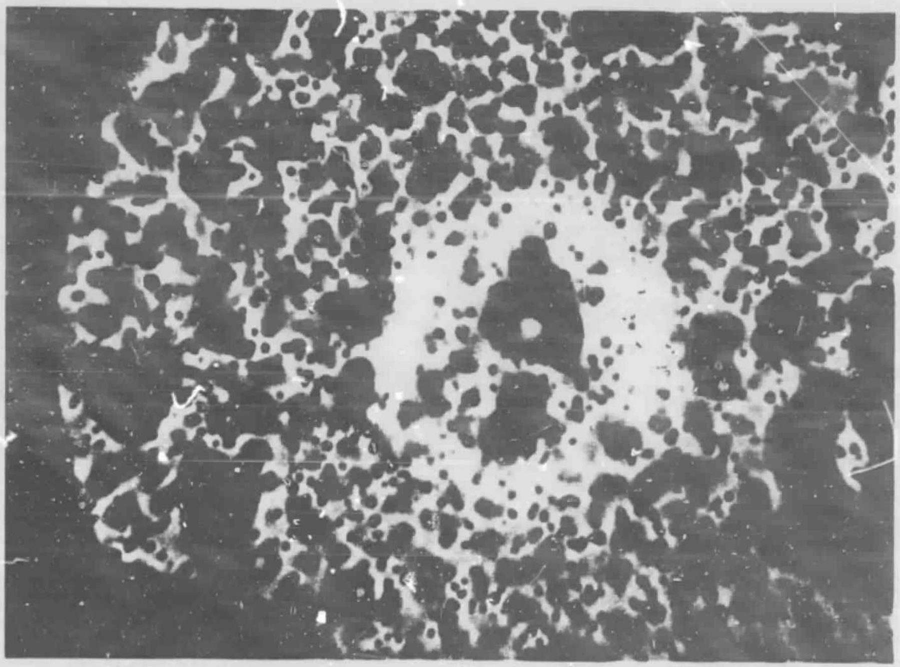


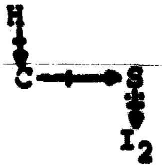
FIGURE XVIII: Jet A Fuel Spiked with Quinoline and Stored at 135°C, 168 hours same as n-butyl sulfide, as does the iso-pentyl disulfide spiked sample at 121°C (Figure XII). Indeed all three appear much like the control with deposit forming somewhat less densely. Samples spiked with toluene-3,4 dithiol (Figure XIII) and dibenzothiophene (Figure XIV) at 121°C also have a similar appearance (fine black particles), though deposit formed more densely than the control. At 135°C deposit formed by n-pentyl disulfide spiked fuel sample (Figure XVI) is less dense and the benzenethiol spiked sample (Figure XVII) more dense than the control sample at 135°C. And yet all photographed samples remain very similar in appearance. This is in contrast to the deposit formed in the heterocyclic nitrogen spiked samples observed by Worstell. Some nitrogen samples appeared similar to those spiked with sulfur compounds and others had an amber liquid-like appearance within the same temperature range (54). Results obtained from sulfur-spiked samples would tend to support the hypothesis that the deposit does not change in appearance within the selected temperature range and probably there is no change in the reaction mechanism as well.

Dependence of Deposit Formation upon Base Strength

Proton NMR resonance chemical shift change resulting from complexation of n-butyl sulfide and n-pentyl sulfide with I_2 are illustrated in Figures XIX through XXII.

The apparent downfield change of shift reflects the effect of reduced electron density (deshielding) around the hydrogen nucleus. In this case, the specific methylene peak being looked at results from the electron density around the hydrogen bonded to the carbon immediately adjacent to the sulfur atoms in each compound.

Inductive effects result from the donation of the non-bonding electron pair from the sulfur atoms of individual sulfur spiking compounds. This electron pair donation occurs as sulfur complexes with more acidic I_2. As sulfur donates electrons to I_2, its electron density decreases - increasing its electronegativity. Sulfur's increased electronegativity results in it "pulling" electrons towards itself from the carbon bonded to it, causing the carbon to become more electronegative. In turn, increased electronegativity of the carbon atom pulls electrons from the hydrogen bonded to it - reducing electron density around the hydrogen nucleus (see diagram below).



The fact that all sulfur compounds were tested neat on the PNMR may be considered a most significant factor to the resulting chemical shift data. Results may have been altered to some degree had a standard solvent been utilized in which all sulfur samples were soluble.

The deshielding effect of the reduced electron density around the hydrogen nucleus registers as a downfield shift change on the PNMR plot. Thus, Lewis basicity is reflected on the PNMR plot as a downfield shift change when comparing the neat sulfur compound and the compound complexed with I_2 (55). Expanded sweep width (1 ppm) measurements of the single methylene peak are illustrated in Figures XX and XXII. Such expanded sweep width facilitated shift change measurement and interpretation.

n-Butyl sulfide has a change in shift of 10 cps and n-pentyl sulfide shift change is 4 cps. Identical tests were successfully completed for all aliphatic sulfides, disulfides and thiols available. Shift measurement for all aromatics, though attempted, were negligible even with an expanded sweep width of 1 ppm. It is suspected that this is a

FIGURE XIX
PNMR Plot of n-Butyl Sulfide Shift Change
(5 ppm Sweep Width)

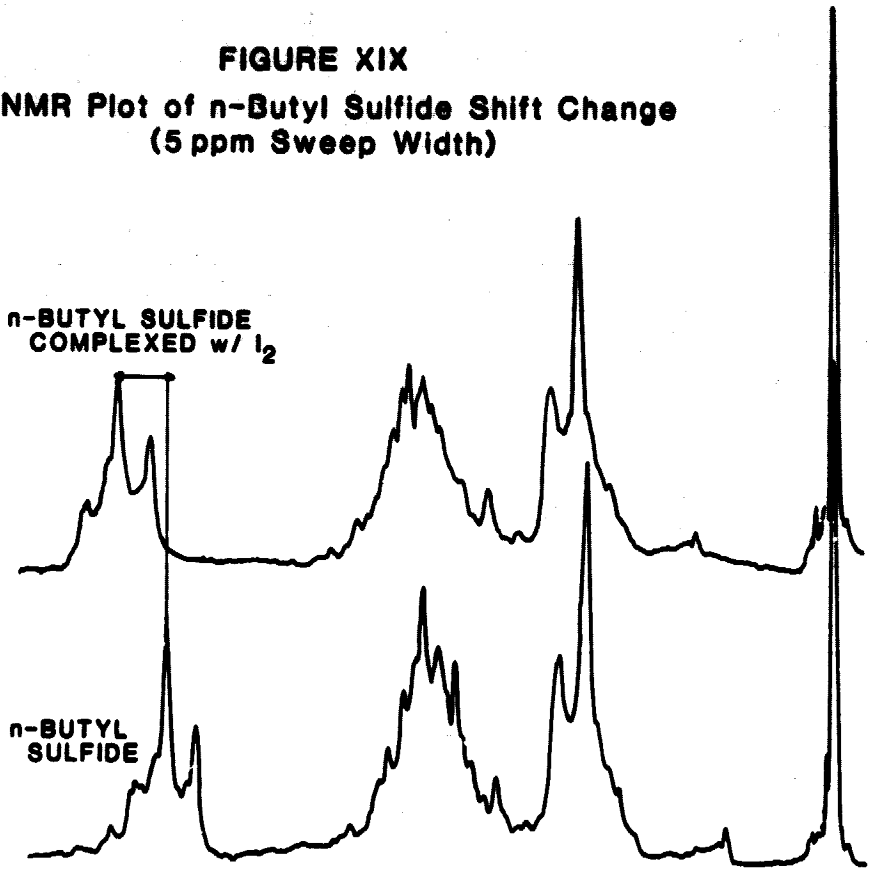


FIGURE XX

PNMR Plot of n-Butyl Sulfide Methylene Peak Shift Change (1 ppm Sweep Width)

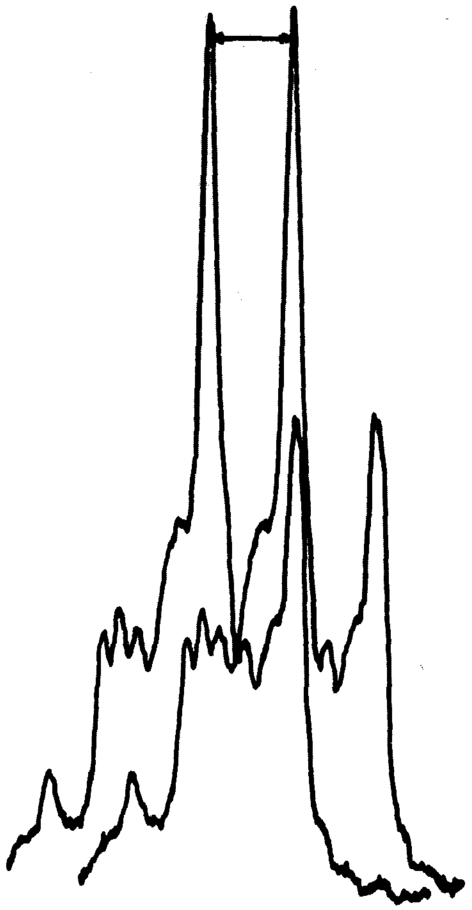


FIGURE XXI
PNMR Plot of n-Pentyl Sulfide
Shift Change
(5 ppm Sweep Width)

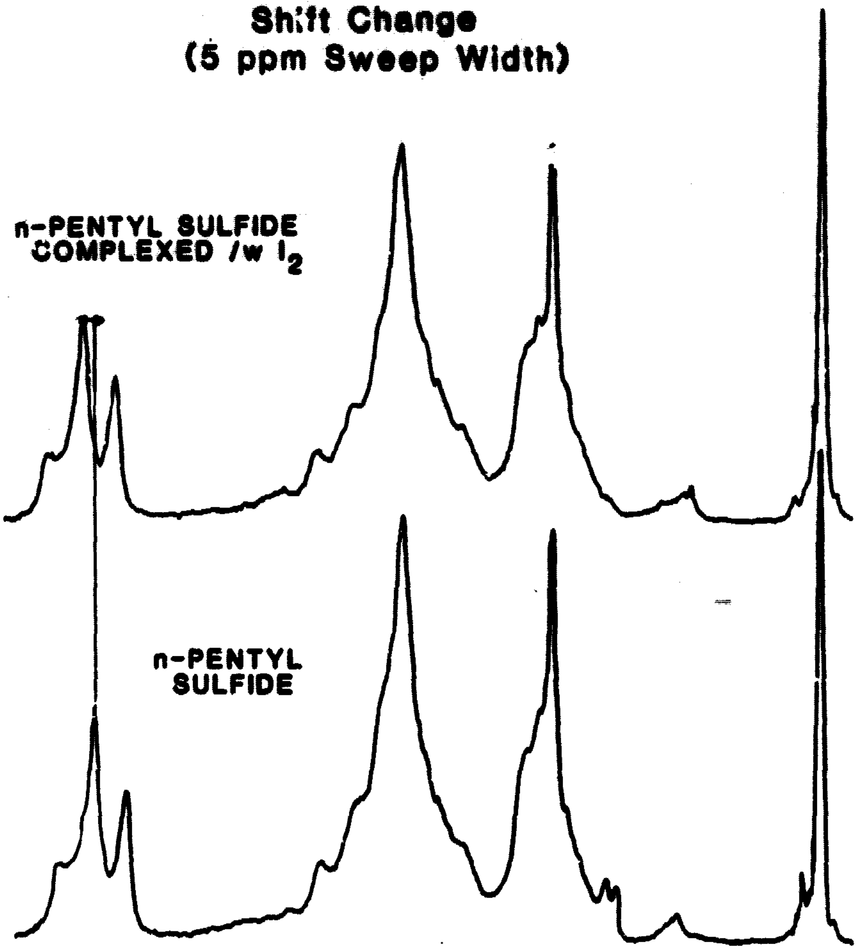
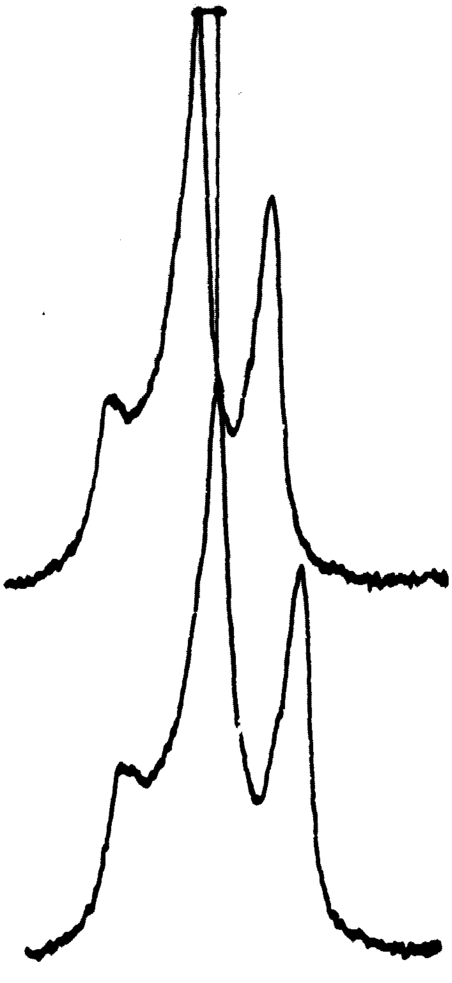


FIGURE XXII
PNMR Plot of n-Pentyl Sulfide Methylene
Peak Shift Change
(1 ppm Sweep Width)



result of the additional effects of "ring currents". Such a phenomenon is due to the circulation of π electrons around the orbitals of an aromatic ring induced by the externally applied magnetic field (56). The aromatic sulfur molecules therefore possess an excess magnetic susceptibility in the direction perpendicular to the plane of the ring over that parallel to the plane (57). The secondary magnetic field due to a ring current is opposed to the externally applied field such that protons located inside the ring are shielded while protons outside the ring are deshielded. The degree of shielding is dependent upon the density of π electrons in the ring (56). Ring current effects offset the smaller inductive effect which may account for reduced shift change.

Equal concentrations of sulfur (10 µg/ml Jet A fuel) were utilized for accelerated storage tests. Therefore differences in rate of deposit formation were suspected to be a result of chemical differences at the sulfur atom.

With the exception of the aliphatic disulfides, the measured relative order of chemical shift reflects little disparity when compared to a suggested ranking order of pKa's (Lewis basicity) provided by D.D. Perrin. These pKa values are based on analogous compounds of oxygen and nitrogen, and shown in Table VII (58). The pKa of tetrahydrothiophene is given by Arnett et al. via solvent extraction

Table VII: Suggested Basicity Order and Chemical Shift Change Measurements (58).

Suggested pKa Order (decreasing basicity)

Tetrahydrothiophene (-5.0,-7.0)
n-Butyl sulfide
n-Hexyl sulfide
1-Butanethiol
1-Dodecanethiol
n-Ethyl disulfide
n-Propyl disulfide
Benzenethiol

Chemical Shift Order
(decreasing basicity/decreasing CPS shift)

Tetrahydrothiophene (16)
n-Ethyl sulfide (14)
n-Butyl sulfide (10)
n-Pentyl sulfide (4)
n-Pentyl disulfide (4)
1-Propanethiol (3)
n-Butyl disulfide (3)
1-Butanethiol (2)
iso-Pentyl disulfide (2)
1-Pentanethiol (1)
Benzenethiol (0)

methods as being approximately -5.0 (59). Using this value as standard, absolute values of pKa could possibly be assigned to all shift measurements determined. However, this could easily prove inaccurate. First because another absolute pKa value needed to standardize shift measurements is not available. Secondly, more recent pKa value estimates for tetrahydrothiophene (-7.0) by Scorrano conflict with Arnett's mesurements (40,44). Furthermore, there is no immediate need to establish actual pKa values, as shift measurements can reveal whether a basicity-deposit formation relationship exists.

Thus, the basicity order of aliphatic sulfides and thiols correspond to the sequence suggested by Perrin. The disulfides, however, do not. If basicity is key to the mechanism of organosulfur compounds in jet fuel, then the reaction of disulfides in fuel appears to occur by a totally different mechanism. Although the basicity of the sulfides and thiols appear to decrease with increasing aliphatic carbon chain length, the reverse appears to occur with the disulfides. Without testing additional aliphatic disulfides it is impossible to confirm an order of basicity.

Table VIII provides a list of aliphatic sulfides, disulfides and thiols with values of measured chemical shift and deposit formation in Jet A fuel at a storage temperature of 121°C for 168 hours. The dependence of deposit formation upon basicity (chemical shift measurement) at 121°C is illustrated in Figure XXIII.

For the entire selection of sulfur bases, no correlation is found. However, within the sulfide compound class excluding tetrahydrothiophene a correlation coefficient of .9944 was calculated, and the correlation coefficient for the aliphatic thiols was .9643. Table IX lists the least squares computation of slope, intercept and regression coefficient for each compound class as well as overall computations.

Insoluble deposit versus chemical shift change plots of sulfides excluding tetrahydrothiophene and of thiols are consistent with base catalysis as expressed by the Bronsted equations if µg deposit is taken as a measurement of specific rate. Due to its molecular structure, the reduced steric hindrance at the sulfur atom of tetrahydrothiophene compared to alkyl sulfides may cut down the amount of entropy loss in forming a complex with I_2. Such an effect would have resulted in an increased shift change evaluation though not necessarily increased relative basicity. This occurrance is offered as a possible explanation for an absence of correlation with tetrahydrothiophene on the sulfide log deposit versus change in chemical shift plot.

TABLE VIII: Chemical Shift Change and Jet A Fuel Storage Test Deposit Weight Values (121°C, 168 hrs, 10 μg sulfur/ml fuel)

Compound	Deposit (μg)	Chemical Shift Change
Tetrahydrothiophene	65±10	16
n-Ethyl sulfide	70±6	14
n-Butyl sulfide	68±3	10
n-Pentyl sulfide	62±13	4
n-Butyl disulfide	55±6	3
n-Pentyl disulfide	49±3	4
iso-Pentyl disulfide	42±10	2
1-Propanethiol	100±23	3
1-Butanethiol	97±16	2
1-Pentanethiol	94±7	1
Benzenethiol	84±19	0
Control	71±10	--

FIGURE XXIII

Jet A Deposit Weight (121°C) and PNMR Chemical Shift Change

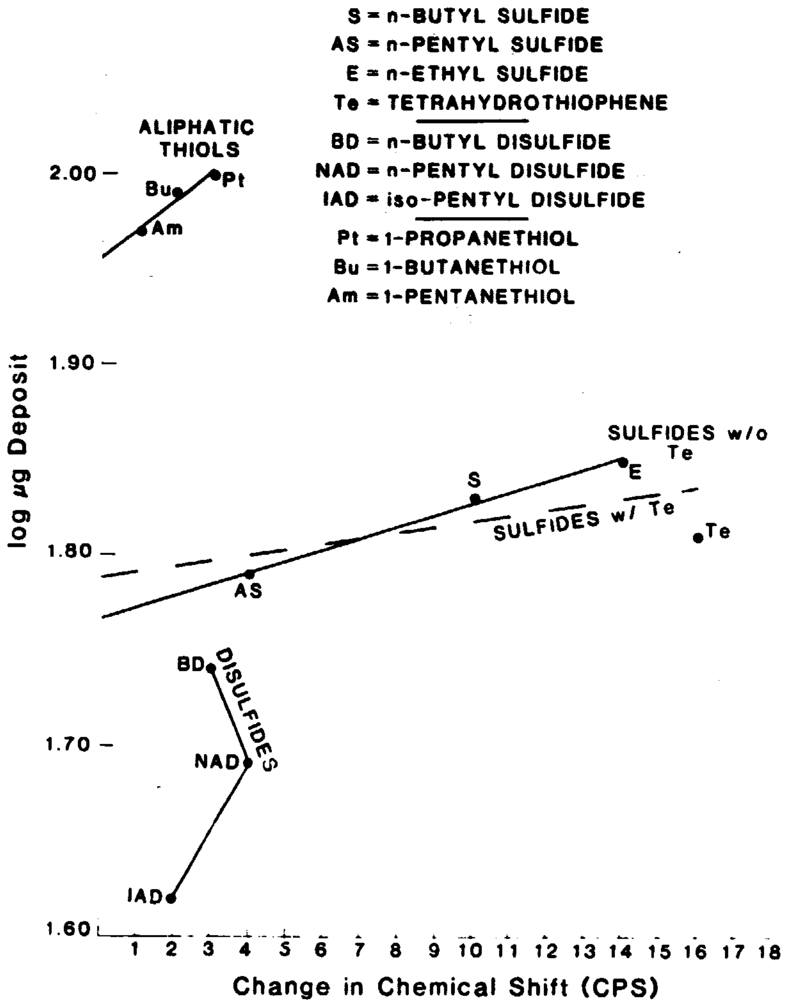


TABLE IX: Data from Deposit Weight and Chemical Shift Change Plots (Least Squares Computation)

Compound Class	Slope	Intercept	Regression Coefficient
Aliphatic Thiols	.0150	1.957	.9643
Aliphatic Sulfides (w/ Tetrahydrothiophene)	.0029	1.789	.3429
Aliphatic Sulfides (w/o Tetrahydrothiophene)	.0061	1.767	.9944
Aliphatic Disulfides	.0350	1.578	.3372
All classes (combined)	-.0016	1.838	.0045

Published results of relative deposition rate in fuel oils and jet fuel spiked with sulfur-containing compounds are shown in Table X. These results are compared to deposition results in Jet A fuel at 121°C-135°C and 10 μg sulfur/ml fuel. It is important to realize that though many contradictions appear the test conditions vary widely. The experiments with Jet A are the only tests known, other than Worstell's, to have been completed with less than 100 μg sulfur/ml fuel (8). An accurate comparison of data under widely varied sets of test conditions is most difficult.

TABLE X: Comparative Results of Deposition Rate with Sulfur Spiking Compound Classes

	Experimental results 121-135°C, 10 μg sulfur/ml Jet A fuel	Thompson fuel oil 100°F, 100-1000 μg sulfur/ml fuel	Taylor's Jet Fuel results ~540°C, 3000 μg sulfur/ml fuel, 1 ppm O_2	Taylor's & Wallace's Jet fuel results 200-450°F, 1000 μg sulfur/ml fuel
Sulfides	Alkyl sulfides-deposit inhibitors	Alkyl sulfides-little effect	Alkyl/Aromatic sulfides-deposition rate increase	Aromatic sulfides-deposition rate increase except diphenyl sulfide (no effect)
Disulfides	Alkyl disulfides-deposit inhibitors	Promotes sludge formation	Alkyl/Aromatic disulfides-deposition rate increase	Aromatic disulfides-deposition rate increase
Thiols	Aromatic/Aliphatic Thiols- increases rate of deposition	Alkyl thiols-little effect Thiophenol- promotes sludge formation	1-decanethiol- deposition rate increases	Alkyl thiols- deposition rate increase
Thiophenes	Increases rate of deposition	Little effect	Condensed thiophenes-no effect	Condensed thiophenes-deposition rate increase Dibenzothiophene- no effect

CONCLUSIONS

In brief review of results obtained, the following observations were made:

1. There exists a significant difference in effect on deposition rate between sulfur compound classes.

2. Alkyl sulfides and disulfides inhibited deposition rate in Jet A fuel during accelerated storage stability tests.

3. All thiols and thiophene derivatives tested increased deposition rate in Jet A fuel.

4. Effects were less pronounced with organosulfur spiked samples than with analagous experiments with nitrogen compounds.

5. No induction period was observed in deposit formation for any sulfur-spiked samples at 121°C, 130°C, or 135°C.

6. The slope of increased concentration of an inhibiting alkyl sulfide versus deposition rate is negative.

7. Arrhenius plots appeared linear within the 121°C-135°C temperature range.

8. Slope of the Arrhenius plots for each sulfur-spiked sample increases as efficiency for promoting deposit formation decreases.

9. Deposit appeared as small dentritic particles for all samples tested at 121°C, 130°C and 135°C.

The following conclusions are made from the acquired experimental results:

1. The concept that the mechanism of deposit formation involves autoxidation of sulfur reagents is not supported.

2. Rate of deposition is a function of the concentration of individual sulfur compounds.

3. Rate of deposit formation for organosulfur spiked Jet A fuel samples decreases with increased activation energy as related to the slope of Arrhenius plots.

4. Alkyl sulfides and alkyl thiols influence the formation of insoluble deposit through base catalysis.

5. The inhibiting mechanism of alkyl sulfides is a result of sulfur's reactivity with intermediate soluble precursors to deposit in Jet A fuel.

A great deal remains unresolved concerning the actual mechanism by which sulfur compounds influence insoluble deposit formation in Jet A fuel. Determination of absolute basicity measurements of many of the weak organosulfur bases might provide the opportunity for greater understanding of the character of the mechanism's transition state.

Further experimentation with additional alkyl disulfides analogous to those completed may provide more information about the apparent mechanistic differences with which they influence insoluble deposit in Jet A fuel.

Accelerated storage tests utilizing deposit inhibiting and deposit promoting sulfur compounds previously tested could be completed in the model system of dodecane and tetralin developed by Worstell (8). A test of this nature should provide further insight into the mechanism by which the sulfide inhibitors retard deposit formation.

REFERENCES CITED

1. Mills, G.A., "Advances in Fuel Chemistry 1961-1974," 168th National Meeting, American Chemical Society, Fuel Division, Sept. 1974, p. 178.

2. Tissot, B.P. and D.H. Welte, Petroleum Formation and Occurance, Springer-Verlag, 234, 356(1978).

3. Robinson, W.E. and G.U. Dinneen, "Constitutional Aspects of Oil Shale Kerogen," Proc. 7th World Petro. Congr. 3, 669(1967).

4. Sturm, G.P., Jr., P.W. Woodward, J.W. Vogh and J.E. Dooley, "Analyzing Syncrude from Western Kentucky Coal," BERC/RI-75/12, 3(1975).

5. Dooley, J.E., G.P. Sturm, Jr., P.W. Woodward, J.W. Vogh and C.J. Thompson, "Analyzing Syncrude from Utah Coal," BERC/RI-75/7, p. 6(1975).

6. Orr, W.L., "Sulfur in Heavy Oils, Oil Sands and Oil Shales," Reprint from: Oil Sand and Oil Shale Chemistry, Verlag Chemie, NY, p. 224(1978).

7. Smith, H.M., "Qualitative and Quantitative Aspects of Crude Oil Composition," U.S. Bureau of Mines Bull., 642(1968).

8. Worstell, J.H., S.R. Daniel, and G. Frauenhoff, "Deposit Formation in Liquid Fuels 3. The Effect of Selected Nitrogen Compounds on Diesel Fuel," Fuel, Vol. 60, #6, 485, June 1981.

9. Hartough, H.D., "Chemistry of the Sulfur Compounds in Petroleum." Advances in Petroleum Chemistry and Refining, Vol. III, 420(1960).

10. Nixon, A., Autoxidation and Autoxidants, Vol II, Ed. by W.O. Lundberg, Interscience Publishers, New York, p. 697(1962).

11. Williams, A.L. and R.D. Offenhauer, Ind. Eng. Chem., 49, No. 8, 1259(1957).

12. Denison, G.H., Jr., *Ind. Eng. Chem.*, *36*, *No. 5*, 477(1944).

13. Kirchner, J.P., D.P. Osterhout, and W.R. Schwindeman, *Petroleum Processing*, 67(1956)

14. Kascorla, A.R., J.H. Cromwell, and D. Milson, *Analytical Chemistry*, *24*, *No. 12*, 1959(1952).

15. Offenhauer, R.D., J.A. Brenner, and R.C. Miller, *Ind. Eng. Chem.*, *49*, *No. 8*, 1265(1957).

16. Sachanen, A.N., *The Chemical Constituents of Petroleum*, Reinhold Publishing, 111(1945).

17. Orr, W.L., "Sulfur in Heavy Oils, Oil Sand and Oil Shales," Reprint from: *Oil Sand and Shale Chemistry*, Verlag Chemie, NY, p. 225(1978).

18. Wallace, J.J., "Chemistry of Fuel Instability," *Advances in Petroleum Chemistry and Refining*, *9*, 378-382(1964).

19. Thompson, R.B., L.W. Drudge, and J.A. Chenicek, *Ind. Eng. Chem.*, *41*, *No. 12*, 2715(1949).

20. Oswald, A.A. and C.D. Ruper, "Cooxidation of Mercaptans and Olefins," Presented before the Divsion of Petroleum Chemistry, American Chemical Society, Boston Meeting, April 5-10, 1959.

21. Kharasch, M.S., W. Nudenberg and G.H. Mantell, *J. Org. Chem.*, *16*, 524(1951).

22. Ford, J.F., R.C. Pitkethly, and V.O. Young, *Tetrahedron*, *4*, 325(1958).

23. Oswald, A.A., and J.J. Wallace, "Anionic Oxidation of Thiols and the Co-oxidation of Thiols with Olefins," N. Kharasch, ed., *Organic Sulfur Compounds*, *Vol. II*, Pergamon, New York, 1966.

24. Pallen, R.H., and C. Sievertz, *Can. J. Chem.*, *35*, 723(1957).

25. Elmquist, E., *Symposium on Stability of Distillate Fuel Oils, ASTM STP #244*, Philadelphia, PA, 26(1959).

26. Clinkenbeard, W., Symposium on Stability of Distillate Fuel Oils, ASTM STP #244, Philadelphia, PA, 23(1959).

27. Schwartz, F., M. Whisman, C. Allbright, and C. Ward, Bu. Mines Bull. 660, pp. 1-58(1972).

28. Schwartz, F., M. Whisman, C. Allbright, and C. Ward, Bu. Mines Bull. 626, pp. 1-46(1964).

29. Taylor, W., and T. Wallace, Ind. Eng. Chem., Prod. Res. Devel., 6, 258-262(1967).

30. Thompson, R., L. Drudge, and J. Chenicek, Ind. Eng. Chem., 41, 2715(1949).

31. Thompson, R., J. Chenicek, L. Drudge, and T. Symon, Ind. Eng. Chem., 43, 925(1951).

32. Johnson, C., D. Fink, and A. Nixon, Ind. Eng. Chem., 46, 2166(1954).

33. Nixon A., Autoxidation and Autoxidants, Vol. II, Ed. by W.O. Lundberg, Interscience Publishers, New York, p. 743(1962).

34. Taylor, W., and T. Wallace, Ind. Eng. Chem., Prod. Res. Devel., 7, 198(1968).

35. Taylor, W., Ind. Eng. Chem., Prod. Res. Devel., 13, 133(1974).

36. Taylor, W., Ind. Eng. Chem., Prod. Res. Devel., 15, 64(1976).

37. Worstell, J.H., "The Efect of Nitrogen Compounds on Jet A and Diesel Fuels," (Doctoral Thesis, Colorado School of Mines), p. 123, 1980.

38. Arnett, E.M., C.Y. Wu., J.N. Anderson, and R.D. Bushick, J. Am. Chem. Soc., 84, 1674(1962).

39. Scorrano, G., P. Bonvicini, A. Levi, V. Luchini, J. Chem. Soc. Perkin Trans. II, 2267(1972).

40. Scorrano, G., Professor of Chemistry, Institute di Chimica Organica Dell 'Universita, Padova, Italiy, personal communication, 30 September, 1980.

41. Capozzi, G., V. Lucchini, G. Modena, and F. Rivetti, *J. Chem. Soc. Perin Trans. II*, 900(1975).

42. Scorrano, G., G. Modena, V. Lucchini, A. Levi, and P. Bonvicini, *J. Am. Chem. Soc.*, *95*, 5960(1973).

43. Lucchini, V., G. Scorrano, A. Levi, F. DiFuria, and R. Curci, *J. Chem. Soc. Perkin Trans. II*, 1975(1974).

44. Arnett, E.M., E.J. Mitchell, and T.S.S.R. Murtz, *J. Am. Chem. Soc.*, *96*, 3875(1974).

45. Arnett, E.M., R.J. Reynolds, Professor of Chemistry, Duke University, personal communication, August 29, 1980.

46. Worstell, J.H., "The Effect of Nitrogen Compounds on Jet A and Diesel Fuels," (Doctoral Thesis, Colorado School of Mines), pp. 43-44, 52, 1980.

47. Chritian, J.G., A.J. Chiantella, J.E. Johnson, and H.W. Carhart, *Ind. Eng. Chem.*, *50*, *No. 8*, 1153(1958).

48. Dahlin, K.E., "The Effects of Coal Syncrude Derived Nitrogen Compounds on Jet Fuel Stability." (Masters Thesis, Colorado School of Mines), p. 22, 1979.

49. Laidler, K., *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, p. 4, 1939.

50. Arrhenius, S., *Z. Physik Chem.*, *4*, 226(1889).

51. Hinshelwood, C., K. Laidler, and E. Timm, *J. Chem. Soc.*, 848(1938).

52. Bol'shakov, G., E. Glebovskaya, and Z. Kaplan, *Khim. Seraorgan. Soedin., Soderzhashch Neftyakh. Neftprod.*, *8*, 406(1968).

53. Worstell, J.H., "The Effect of Nitrogen Compounds on Jet A and Diesel Fuels," (Doctoral Thesis, Colorado School of Mines), pp. 74-77, 1980.

54. Worstell, J.H., "The Effect of Nitrogen Compounds on Jet A and Diesel Fuels," (Doctoral Thesis, Colorado School of Mines), pp. 78-83, 1980.

55. Karchner, J.H., "Divalent Sulfur-Based Functions," Treatise on Analytical Chemistry, Part II, Vol. 13, 469(1966).

56. Leyden, D.E., and R.H. Cox, "Analytical Applications of NMR," John Wiley and Sons, Inc., p. 32, 1977.

57. Leader, G.R., Anal. Chem., 42, 16(1970).

58. Perrin, D.D., Medical Chemistry Group, The John Curtin School of Medical Research, Australian National University, personal communication, July 31, 1980.

59. Arnett, E.M., W.Y. Wu., J.H. Anderson, and R.D. Bushick, J. Am. Chem. Soc., 84, 1675(1962).

APPENDICES

A. Triplicate Sample Deposit Weight Values (μg deposit) at 135°C and 10 μg sulfur/ml Jet A Fuel

Spiking Compound	24 hrs	72 hrs	168 hrs
n-Butyl sulfide	57	140	241
	60	165	310
	75	169	331
n-Pentyl sulfide	52	129	253
	63	158	263
	65	163	324
n-Butyl disulfide	49	125	231
	51	135	281
	68	166	298
n-Pentyl disulfide	41	109	229
	57	140	257
	58	147	258
Isopentyl disulfide	40	102	198
	44	128	240
	54	136	258
1-Butanethiol	137	245	404
	141	250	419
	160	297	461
1-Pentanethiol	92	203	368
	120	243	370
	124	250	441
Benzenethiol	82	174	293
	85	216	393
	109	228	397
p-Toluenethiol	88	197	314
	104	200	401
	108	239	401
1-Naphthalenethiol	76	164	318
	79	201	324
	91	295	387
Toluene-3,4-dithiol	119	230	351
	140	239	438
	143	287	453
Dibenzothiophene	110	214	361
	114	255	369
	142	263	482
Control	65	163	295
	84	171	299
	88	206	372

B. Triplicate Sample Deposit Weight Values (μg deposit) at 121°C and 10 μg sulfur/ml Jet A Fuel

Spiking Compound	24 hrs	72 hrs	168 hrs
Tetrahydrothiophene	13	29	53
	14	39	62
	18	43	80
n-Ethyl sulfide	15	34	61
	15	38	74
	18	45	75
n-Butyl sulfide	13	32	73
	17	41	65
	18	41	66
n-Pentyl sulfide	12	32	42
	13	36	68
	20	37	76
n-Butyl disulfide	10	27	49
	14	34	51
	15	35	65
n-Pentyl disulfide	10	23	46
	13	29	47
	13	35	54
Isopentyl disulfide	9	23	32
	10	24	37
	14	31	57
1-Propanethiol	17	47	76
	23	53	90
	26	59	134
1-Butanethiol	17	48	73
	19	48	106
	27	60	112
1-Pentanethiol	14	39	84
	22	54	97
	24	57	101
Benzenethiol	16	37	60
	17	50	79
	21	51	113
Toluene-3,4-dithiol	15	50	95
	23	58	116
	31	66	119
Dibenzothiophene	19	48	91
	23	56	97
	24	58	124
p-Toluenethiol	15	40	67
	18	45	87
	24	56	107

Appendix B: Continued

1-Naphthalenethiol	17	37	67
	17	42	82
	20	47	85
Control	14	35	60
	17	37	67
	20	48	86

C. Triplicate Sample Deposit Weight Values (μg deposit) at 130°C and 10 μg sulfur/ml Jet A Fuel

Spiking Compound	24 hrs	72 hrs	168 hrs
n-Butyl sulfide	29	81	151
	35	84	154
	41	99	211
n-Pentyl sulfide	27	68	135
	34	82	166
	35	96	176
n-Butyl disulfide	24	62	142
	34	84	150
	38	91	176
n-Pentyl disulfide	24	64	94
	27	65	145
	30	78	160
Isopentyl disulfide	25	53	99
	25	64	131
	28	75	139
Benzenethiol	38	90	188
	45	117	201
	49	123	253
1-Pentanethiol	39	105	189
	48	125	251
	57	130	259
Dibenzothiophene	41	105	219
	52	126	233
	57	147	277
Toluene-3,4-dithiol	47	112	205
	49	132	265
	60	143	277
Control	31	86	171
	39	103	177
	47	105	225