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THE EFFECTS OF COPPER  
AND IRON ON THE STORAGE STABILITY  
OF JET A TURBINE FUEL

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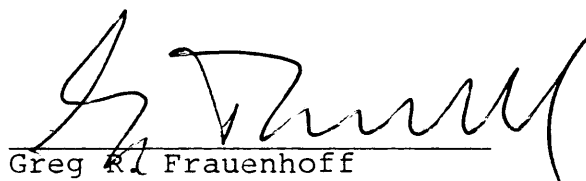
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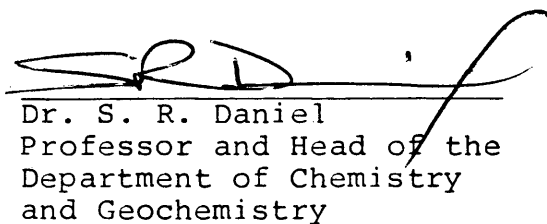
  
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## ABSTRACT

This study examined the effects of copper and iron on deposit formation in Jet A turbine fuel, in a 10/1 (vol./vol.) n-dodecane/tetralin model fuel, and on possible deposit precursors in the model fuel. Soluble copper, soluble iron, and copper metal greatly increased deposit formation in both Jet A and the model fuel. Iron metal had no effect in either fuel. In the case of copper metal the effect is not considered to be due to heterogeneous catalysis. The catalytic effect of the metals on deposit formation in the model fuel does not appear to be due to an increase in rate of the oxidation of tetralin or of the decomposition of  $\alpha$ -tetralin hydroperoxide. This suggests that the catalytic role of the metals involves processes other than redox reactions initiating free radical auto-oxidation mechanisms.

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## INTRODUCTION

Today's increasing demand for hydrocarbon-based fuels coupled with the decreasing supplies of petroleum sources for their manufacture has resulted in the petroleum industry examining alternative materials from which to produce hydrocarbon-based fuels. Among these alternatives is, of course, oil shale. It is possible to produce from oil shale gasolines, jet fuels, etc. with physical properties (volatility, heat capacity, etc.) similar to those of fuels produced from petroleum. However, the chemical composition, especially of minor constituents such as nitrogen or sulfur compounds, can differ greatly from that of petroleum-derived fuels (1). These minor constituents can enhance undesirable chemical properties of the fuel, such as their corrosive effect on metal surfaces and their susceptibility to degradation during storage (2).

Although, in most current fuels, these undesirable properties have been either eliminated or controlled, fuels produced from new sources still can present problems. In the past, controlling fuel degradation or corrosive properties was more by the trial-and-error addition of additives than as a result of any basic research into fuel chemistry.

It was, therefore, the objective of this research to examine one aspect of fuel chemistry, namely, the effect of

metals on jet fuel stability. Using a model system, the cause of this effect was also studied.

#### Deposit Formation

Most hydrocarbon-based fuels and oils undergo degradation reactions on storage or upon thermal stress in operating engines which can result in the formation of fuel-insoluble deposits. Such deposits can often cause engine failure due to, for example, plugged fuel nozzles or filters and decrease efficiency of fuel/lubricant heat exchangers (2). Hence, understanding the phenomena which produce and the materials which catalyze the formation of such deposits is a necessary step in the development of strategies to prevent deposit formation.

It is generally believed that the insoluble deposits formed under both storage and thermal conditions result from the reaction of certain fuel auto-oxidation products with each other (2). Which products are involved in deposition, however, is not yet known. Figure I summarizes some auto-oxidation reactions of a hydrocarbon.

Metals, both in metallic and ionic forms, have long been known to catalyze the formation of insoluble deposits resulting from the oxidation of hydrocarbon-based fuels and oils (2).

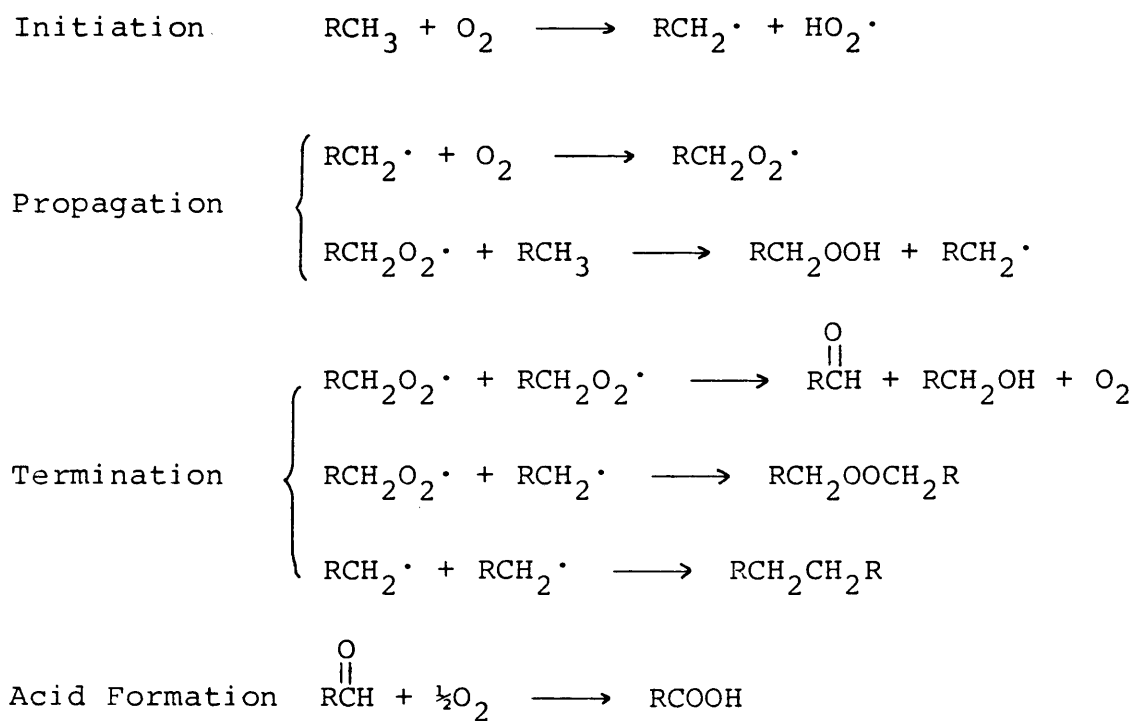


Figure I. Auto-oxidation reactions.

### Lubricating Oils

I would like to preface this next section with a quote by Matthijsen (3) which will illustrate the state of affairs regarding hydrocarbon oxidation studies in the years before ca. 1950.

"During the examination at regular intervals of the used lubricating oils...the question was raised as to whether the small metal splinters present in the used oil...might be able to increase or reduce the content of oxidation- or aging products.

Many references to the effects of metals, etc., on aging are to be found in the literature, but on the whole they are so vague that we have found it necessary to test this point ourselves.

We have learned from an elaborate study of the relevant literature of recent years on the aging of lubricating oil that twenty-three different laboratory oxidation methods have been worked out."

Matthijsen (3), in 1940, added .3 wt% metal turnings to lubricating oils and then heated the oils at 230°C for 85 minutes with constant mixing. After this treatment, he measured the sludge content (benzene soluble material obtained by repeated centrifugation of the oil with petroleum ether), viscosities at 100°C, acid numbers (number of mg KOH required to neutralize the free fatty acids), saponification numbers (mg KOH required for the complete saponification of 1 gram of oil) and Conradson residues (carbon residue after evaporation of the oil using strong heat) of the oils. All chromium, nickel and tungsten steels tested

and also cast iron increased the viscosities, acid numbers and sludge over the uncatalyzed oils, but the copper and brass materials tested reduced them. Further experiments with copper showed that it had a weakly positive catalytic effect on acid numbers, saponification numbers and Conradson residues in a paraffin-based oil up to 180°C, but strongly repressed the aging above 180°C. In a naphthene-based oil copper had only a slight catalytic effect over the entire temperature range. Naphthenes are saturated cyclic hydrocarbons.

In 1941, Davis, et al. (4) studied the catalytic effect of iron, lead, cadmium, copper and silver naphthenates on the oxidation of lubricating oils. Naphthenates are metal salts of naphthenic acid, a mixture of carboxylic acids found in petroleum. They found that, in the case of iron naphthenate for example, metal concentrations as low as 3 ppm significantly reduced the induction period for an oil. The induction period is the time required for the oil to absorb a given quantity of oxygen at 175°C (4). Fuels with short induction periods are more rapidly oxidized than fuels with long induction periods and, hence, were considered less stable. As will be shown later, however, the correlation between rapid oxidation of the fuel and fuel instability with respect to deposit formation may not be as

good as was once thought.

Larsen and Armfield (5) also studied catalysis of the oxidation of lubricating oils by iron, copper and lead naphthenates using the oxygen absorption technique. Below a metal concentration of 5 ppm they found copper more catalytically active than iron, but above 5 ppm the reverse was true. Lead was less active than either copper or iron.

In 1952, Diamond, et al. (6) found that copper concentrations as low as .1 ppm (metal added as the naphthenate) perceptibly increased the rate of oxygen absorption by aircraft oil at 250°C. Copper naphthenate was more catalytically active than iron naphthenate below 300 ppm (based on the metal) with maximum catalytic activity at 100 ppm. However, iron was more active above 300 ppm and its activity increased over the entire concentration range studied (10,000 ppm). Lead naphthenate's catalytic activity was appreciable at 600 ppm with its maximum at 2000 ppm, but declined sharply above 2000 ppm. Similar catalytic activity was found for the metals themselves whether in sheet form or fine dust (added at .5 weight %). Copper metal was found to be the most effective catalyst followed by iron and lead. Diamond ascribed the influence of the metals to homogeneous rather than heterogeneous catalysis. He based his contention on the fact that the uppermost layer of oil

where oxygen is absorbed through auto-oxidation reactions is not in contact with the metal surface. Most probably, he said, the solid surface acts merely as a source of catalytically active material (soluble metal soaps) which is the immediately active pro-oxidant.

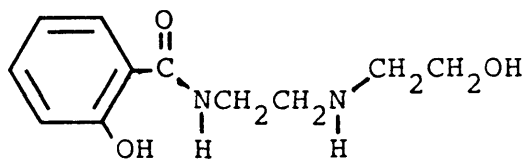
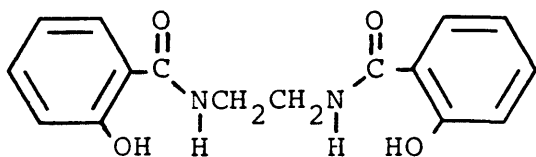
Irving and Thompson (7) investigated the effects of copper and iron naphthenates on the oxidation of transformer oils open to air at 120°C for 24 days. Soluble copper, between concentrations of zero and 50 ppm, greatly increased the rate of sludge formation but above 50 ppm little additional increase occurred. Also, induction periods for the oils decreased steadily (indicating increased oxidation) over copper concentrations from zero to near 100 ppm while leveling off thereafter. Copper was found to increase the acid numbers of some oils while decreasing those of others. In oils which had low acid numbers after uncatalyzed aging, copper had an accelerating effect on the acid numbers. But for oils with high acid numbers after uncatalyzed aging, the reverse was true. Iron was found to influence sludge formation to a lesser extent than copper, but its effect on acid numbers was similar.

#### Gasolines

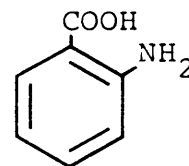
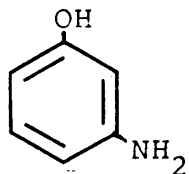
Walters, et al, (8,9,10) found that various metal naphthenates, including lead, iron, cobalt and most markedly

copper, catalyzed the formation of gum in cracked gasolines during both aging at 100°C and storage at 42°C. Gum is the heptane-insoluble residuum after evaporation of the gasoline. The addition of a metal deactivator, such as N-salicylal-N'-( $\beta$ -hydroxyethyl)ethylenediamine; N,N'-disalicylal-ethylenediamine or anthranilic acid (see Figure II), reduced the rate of gum formation in a gasoline spiked with a particular metal but not necessarily the rates for the gasoline spiked with other metals. The stabilizing effect of the deactivators is presumably due to their chelation of the metal ions in a less catalytically active complex. Induction periods for the gasolines were also lessened by the dissolved metals. When anti-oxidants, such as cresylic acid, aminophenol and catechol (see Figure II), were added, the original induction periods for the uncatalyzed gasolines were obtained.

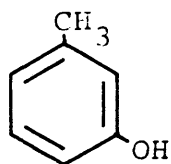
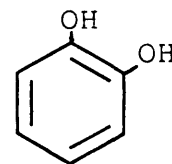
Pedersen (11), studied how metal oleates affected the induction period of cracked gasoline at 100°C. At 1 ppm metal concentration, copper was most detrimental followed by cobalt, manganese, iron, nickel and chromium. Copper oleate reduced the induction period by as much as 95%. He also studied the effect of 10 ppm copper on a gasoline from which all acidic compounds had been extracted with aqueous potassium hydroxide and potassium isobutyrate. The ex-

N-Salicylal-N'-( $\beta$ -hydroxyethyl) ethylenediamine

N,N'-Disalicylal ethylenediamine

Anthranilic acid  
(o-Aminobenzoic acid)

m-Aminophenol

Cresylic acid  
(mixture of cresols with  
meta isomer predominate)

Catechol

Figure II. Some metal deactivators and anti-oxidants (10).

tracted gasoline formed gum faster without copper present than with it when stored at room temperature. In the unextracted gasoline, however, the reverse was true. This led Pedersen to hypothesize that the catalytic role of copper involved reactions with either naturally-occurring or added anti-oxidants in the gasolines (which could be removed by the extraction) rather than the principal gasoline constituents. He cited the work of DuPont (12) to explain the stabilizing effect of copper on the extracted gasoline. DuPont found that copper and its compounds were anti-oxidants for certain terpenes. Terpenes are not, however, principal gasoline constituents (13).

Roels (14) has investigated the use of cupric acetate, oleate and stearate as accelerating agents in the aging of motor fuel for stability tests. Both the oleate and the stearate when added at concentrations of 4 ppm (based on copper) gave comparable results. They reduced the induction periods of some gasolines by over 90%. The acetate had less of an effect than either the oleate or stearate.

Gureyev and Sablina investigated the effects of metals on the stability of gasolines using the oxygen absorption technique (15). They found copper to have the greatest catalytic activity as it reduced the induction period by 70-80%. Brass, iron, lead, zinc, aluminum and tin were also

found harmful. In experiments using cyclohexene as a test fuel they found that neither copper nor iron decreased the induction period. However, in samples of cyclohexene containing a wood resin anti-oxidant, the metals reduced the induction periods. They concluded that the oxidation of fuels by metals is due to their reaction with added or naturally occurring anti-oxidants rather than with the hydrocarbon part of the fuel. Metal deactivators were found useful in controlling the deleterious effects of the metals.

#### Jet Fuels

More recent work has been devoted to establishing so-called threshold limits for metals in thermal oxidation studies on jet fuels. The threshold limit is the concentration of metal at which a fuel fails a particular thermal oxidation test (2). Copper naphthenate, at a concentration of 300 ppb, had a deleterious effect on the thermal stability of an isoparaffinic fluid (a mixture of branched, saturated hydrocarbons) when tested in a CFR coker (16). Threshold limits for soluble metals in JP-7 have been determined, using the Jet Fuel Thermal Oxidation Tester (JFTOT) (17), to be 15 ppb copper, 25 ppb iron, 100 ppb zinc and 100 to 250 ppb lead (note: a range was given for lead owing to difficulties in maintaining lead in

solution) (18). Limits for tetraethyl lead and lead naphthenate in JP-7 were determined to be 2000 and 500 ppb respectively (19). Cadmium was found to thermally degrade JP-5 at 180 ppb (20), and threshold concentrations for copper, iron and zinc in six JP-5 fuels have been determined to be 50-105 ppb copper, 136-165 ppb iron and 200-420 ppb zinc using the JFTOT test (21).

The effects of various metals and alloys on the thermal stability of Avtur 50, an aviation turbine fuel, have been studied (22). Copper was found to have the greatest detrimental effect on the stability of Avtur 50. Other harmful metals were beryllium, lead and tungsten.

Taylor (23) has studied the effects of copper, iron, nickel and cobalt acetylacetonates on the rate of formation of deposit in Jet A at 149°C in the presence of a constant air stream. At a metal concentration of 50 ppm the rate of deposit formation increased by a factor of from 40-120. Copper was found to be the most deleterious. Similar results were also obtained with the free metals.

Johnson, et al, (24) reported that deposit formation in JP-3 at 110°F increased when copper wire was added. Steel wire was found to have no effect.

#### Marine Diesel Fuels

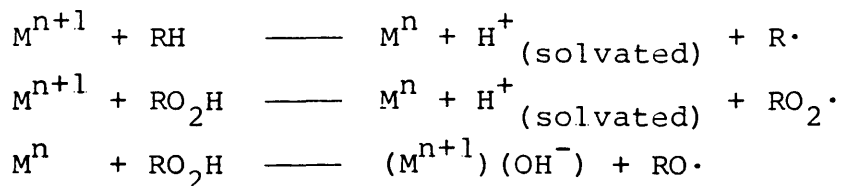
White (25) has conducted studies on the long range stor-

age stability of distillate fuels for ships and found that the fuels stored in tin cans developed deposits at a faster rate than those stored in soft glass and Pyrex bottles. However, little has been done on the effects of soluble metal compounds on the storage stability of marine diesel fuels. Although it is likely that if a given fuel is made thermally unstable by soluble metals its storage stability is also lessened, this has not been demonstrated.

#### Mechanism Studies

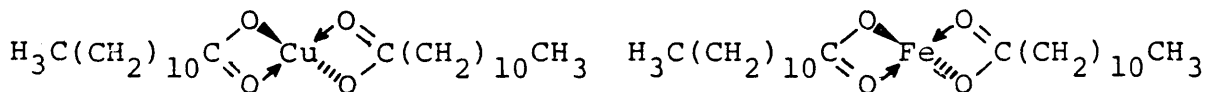
Although from the foregoing material one recognizes that much has been done regarding the effects of metals on fuel and oil oxidation stability, little work has been done on the cause of these effects. Taylor (26) has shown that metals catalyze the decomposition of organic hydroperoxides to alcohols, aldehydes and ketones, but Worstell (27) has determined that deposit formation in a model system is not kinetically controlled by the rate of hydroperoxide decomposition.

Most studies have suggested that the principal cause of metal catalysis in deposit formation involves free-radical initiation reactions of the following general types:



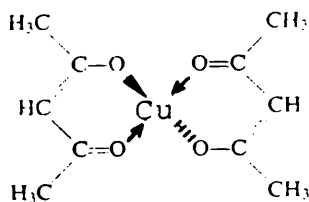
These reactions have been demonstrated to be important in the formation of, for example, cyclohexene hydroperoxide (28), and the decomposition of cumene hydroperoxide (29). But neither hydroperoxide formation nor decomposition has been demonstrated to be the rate controlling reaction in deposit formation, thus the role of metals is not yet understood.

This study, therefore, examined the following topics: the effect of 1) copper metal, iron metal and low concentrations (.1-10 ppm based on the metal) of cupric and ferrous laurate (see below) on the storage stability of Jet A fuel and 2) copper metal, iron metal and low concentrations of cupric and ferrous laurate (attempts at the synthesis of ferric laurate were unsuccessful) on deposit formation in a model system. Also, the effects of the metals on the

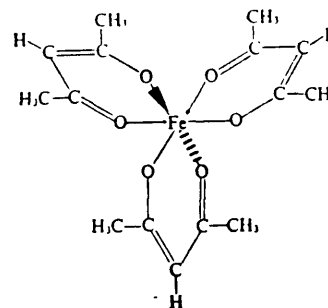


Cupric Laurate

Ferrous Laurate



Cupric Acetylacetonate



Ferric Acetylacetonate

concentration of tetralin,  $\alpha$ -tetralin hydroperoxide and  $\alpha$ -tetralin hydroperoxide's decomposition products  $\alpha$ -tetralone and  $\alpha$ -tetralol in this model system were studied. Jet A stability was determined using an accelerated storage test at 121°C. The model system used was composed of 10 parts by volume n-dodecane and one part by volume tetralin. Tetralin readily undergoes oxidation at the  $\alpha$ -position forming  $\alpha$ -tetralin hydroperoxide (30). Since most previous studies (10,21) suggest that either hydroperoxide formation or decomposition is important in deposit formation, this system lends itself nicely to determining whether or not the catalytic role of metals in deposit formation is due to their effect on hydroperoxide formation or decomposition. Although it has been found that pure n-dodecane auto-oxidizes at 130°C, this auto-oxidation does not result in deposit (31). Hence, only the products of the auto-oxidation of tetralin:  $\alpha$ -tetralin hydroperoxide,  $\alpha$ -tetralone and  $\alpha$ -tetralol were monitored by high performance liquid chromatography (HPLC) (32).

## EXPERIMENTAL

Experiments were performed to determine the effect of soluble metal compounds and bulk metals on deposit formation in Jet A fuel under accelerated storage conditions. Since copper metal is readily attacked and solubilized in many fuels (20,21,33,34,35,36,37,38) and is present in aircraft fuel systems, it was used in this study. Iron was also studied since ferroalloys are common storage materials. The metals were added to the fuel as either their laurates (dodecanoates) or acetylacetonates, both of which are readily soluble in non-polar media and can be prepared in pure form. Control experiments were also performed to assess the influence of lauric acid and acetylacetone on deposit formation.

### Preparation of Chemicals and Reagents

Jet A turbine fuel, a typical petroleum-derived commercial jet fuel, 13% aromatic, was acquired from the National Aeronautics and Space Administration Lewis Research Center in Cleveland, Ohio and stored in glass at 4°C. Prior to use it was filtered through a fine, sintered-glass funnel using an aspirator.

Practical grade n-dodecane and tetralin were obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J.. Prior to use, dodecane was washed with concentrated sulfuric acid until the acid layer was colorless. The n-dodecane layer was then neutralized with dilute aqueous sodium hy-

dioxide, washed with deionized water and distilled. Tetralin was distilled and then passed through 60-200 mesh silica gel (Eagle Chemical Co., Mobile, Ala.) which had been activated at 400°C for 24 hours. Purity of each was checked using a Varian model 3700 gas chromatograph fitted with a 6' x 1/8" 3% SE-30 (silicone) on Chromosorb W column.

Reagent grade iron wire (.009" diameter) and primary standard grade potassium dichromate were obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. and used without further purification.

Copper foil (.002" thick) was purchased from Sargent Welch Scientific Co., Skokie, Ill.. It was rinsed with acetone and air dried prior to use.

HPLC-grade iso-octane, HPLC-grade chloroform, reagent grade concentrated sulfuric acid and reagent grade concentrated nitric acid were purchased from Fisher Scientific Co., Fair Lawn, N. J.. Ethanol, present as a stabilizer in the chloroform, was removed by passage through activated silica gel.

Analytical reagent grade acetonitrile and U. S. P. granular grade ferrous sulfate heptahydrate were purchased from Mallinckrodt Chemical Works, St. Louis, Mo..

Reagent grade absolute ethanol was obtained from U. S.

Industrial Chemicals Co., New York, N. Y..

Lauric acid was purchased from Eastman Organic Chemicals, Rochester, N. Y..

Reagent grade hydrochloric acid was obtained from MCB Manufacturing Chemicals, Inc., Cincinnati, Ohio.

Cupric laurate was prepared by the method of Whitmore and Lauro (39) and purified by recrystallization from absolute ethanol. The observed melting point was 110-113°C (reported melting point 111-113°C (40)).

Cupric and ferric acetylacetonate were prepared by the method of Fernelius and Bryant (41). Cupric acetylacetonate was recrystallized from acetone. Ferric acetylacetonate was recrystallized from 44% aqueous ethanol. Its observed melting point was 183-184°C (reported melting point 184°C (40)).

Ferrous laurate was prepared under a nitrogen atmosphere in the setup shown in Figure III. Lauric acid (.0184 moles) was dissolved in 25 ml of ethanol and titrated with ~.2 N aqueous sodium hydroxide to the phenolphthalein end point. The solution was brought to ~150 ml with water, boiled for several minutes to remove most of the ethanol and then poured into a three-neck flask under nitrogen. Ferrous sulfate heptahydrate (.00957 moles, 4.3% theoretical excess) was dissolved in 50 ml of freshly-boiled

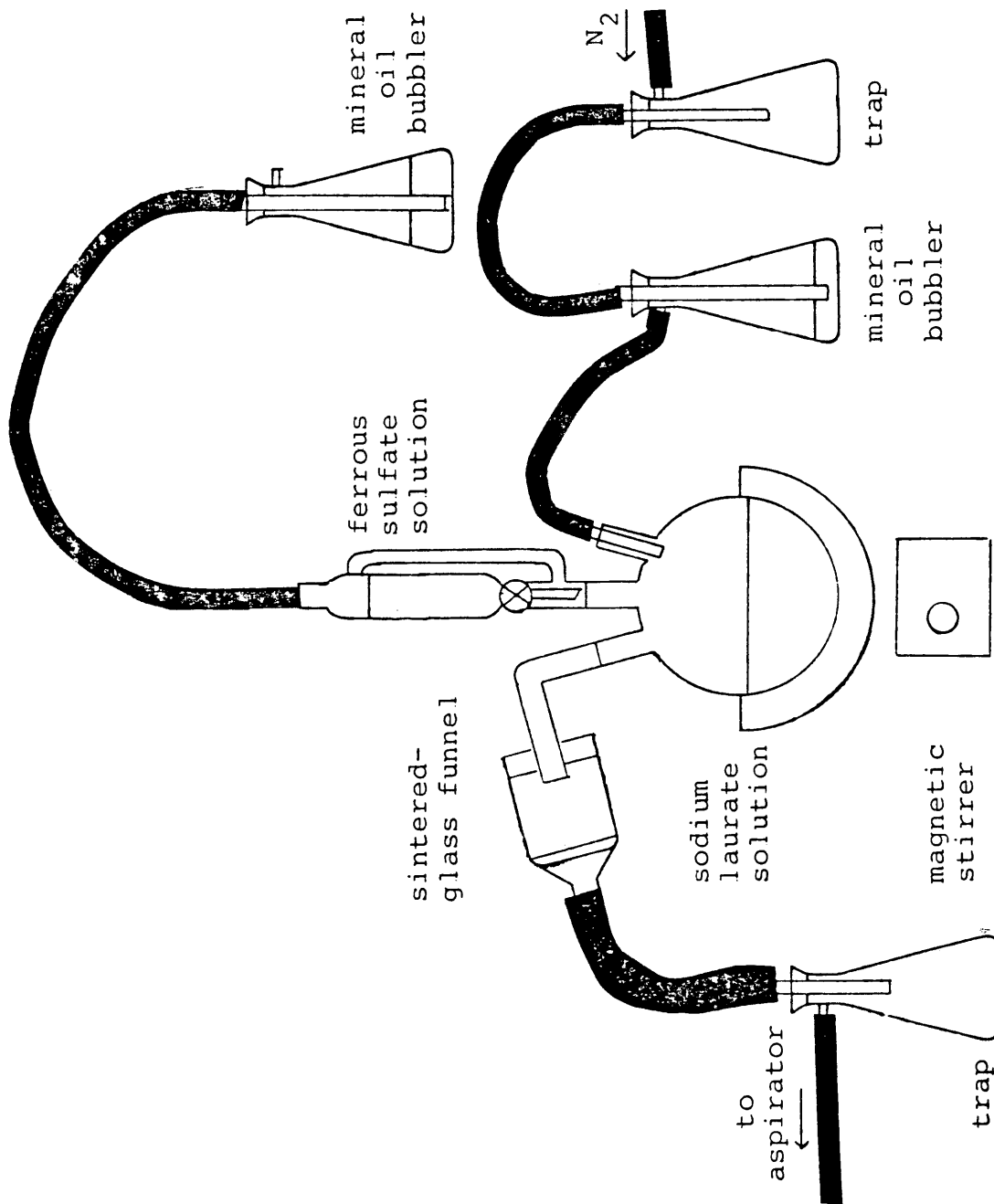


Figure III. Apparatus for the synthesis of ferrous laurate.

water. Small amounts of sodium hydrosulfite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) were added with stirring to the aqueous ferrous sulfate solution until any cloudiness or yellow color due to ferric ion was removed. The ferrous sulfate solution was then added dropwise with stirring to the aqueous sodium laurate solution maintained at a temperature between  $60^\circ\text{C}$  and  $80^\circ\text{C}$ . After the addition was completed, the solution, which now contained a snow white precipitate of ferrous laurate, was allowed to stand at  $60\text{--}80^\circ\text{C}$  for 2 hours. The solution was then filtered through a coarse, sintered-glass funnel and the precipitate was washed with several portions of freshly boiled water. It was then dried for several days under a constant stream of nitrogen. Weight percent iron of the dry precipitate was determined by dichromate titration to be 12.22 (theoretical 12.29).

Since it is more convenient to measure small volumes of liquid than small weights of solid, a solution of cupric laurate in tetrahydrofuran (THF) was prepared. THF was distilled from lithium aluminum hydride prior to use. Small concentrations of THF have been shown to have no significant effect on the results of deposit formation at  $121^\circ\text{C}$  (42).

#### Analytical Methods

The amount of deposit formed in Jet A was measured using

a method developed by Worstell (27). A preweighed, soft-glass microscope coverslip of  $3.24 \text{ cm}^2$  area was placed in a soft glass jar of 147 ml capacity. Both coverslips and jars were purchased from VWR Scientific, Inc., San Francisco, Calif.. Ten milliliters of Jet A fuel were then added and spiked with a THF solution containing the metal complex under study or with the metal compound itself. The jar was then sealed with a PTFE-lined lid and placed in an oven at  $121^\circ\text{C}$ . Every 24 hours the amount of deposit on the coverslip was measured. The jar was removed from the oven; allowed to cool to room temperature and opened. The coverslip was removed with forceps, dried under an infrared heat lamp and then weighed. The amount of deposit on the coverslip was expressed in milligrams.

Prior to use, all jars were cleaned in a chromic acid bath for 48 hours. They were then rinsed with deionized water and placed in an aqueous sodium bisulfite solution for 24 hours. This treatment reduces any Cr(VI) adhering to the walls of the jar to Cr(III) facilitating its removal. Finally, the jars were rinsed several times with deionized water and air dried. This procedure has been shown not to influence deposition rate (27).

The model system deposit most often consists of a gummy residue and, hence, measurement of its weight is not

amenable to the above technique for Jet A deposit. The amount of deposit was, therefore, determined as follows. Ten milliliters of the dodecane/tetralin mixture were added to a tared soft-glass jar of 147 ml capacity and spiked with a THF solution of the metal complex of interest or a carefully weighed quantity of the metal compound itself. The jar was then sealed with a PTFE-lined lid and placed in an oven at 121°C. Every two days the jar was removed from the oven and opened in order to replenish the air supply. After a suitable aging period (10-14 days), the jar was removed from the oven; the remaining liquid, which contains no suspended solids, was discarded; and the residue adhering to the jar was washed twice with petroleum ether. The jar and contents were then dried at 121°C for 10 hours and weighed. The amount of deposit was expressed in grams.

Soluble components of the model system were analyzed using a Waters Associates high performance liquid chromatograph (HPLC). A method developed by Worstell (32) for the determination of tetralin hydroperoxide and its decomposition products by HPLC was used. A solvent of approximate composition 65% (by volume) iso-octane, 34% chloroform and 1% acetonitrile was used to elute 1  $\mu$ l samples of model fuel through a  $\mu$ -Porasil column at a flow rate of 2 ml per minute. The solvent was redistilled after use to remove

analyte material. Iso-octane or acetonitrile was added as needed to bring the retention times of the four species of interest, namely tetralin, tetralone, tetralin hydroperoxide and tetralol, to ~2 minutes, ~4 minutes, ~11 minutes and ~20 minutes respectively. The UV absorbance at 254 nm of the eluent, measured using a Waters Associates model 440 absorbance detector, was recorded and peak areas integrated with a Hewlett Packard model 3390A integrator. A Waters Associates model R 401 differential refractometer was used to detect changes in the refractive index of the eluent and these changes were recorded and peak heights measured with another Hewlett Packard 3390A integrator.

The total amount of deposit formed in Jet A was determined by a two step technique. Deposit which adhered to the container walls was determined in a manner similar to that used for model fuel deposit but with the samples being aged for only 7 days. Deposit which did not adhere to the vessel walls was collected by filtering the aged Jet A through a tared, fine sintered-glass filtering crucible. The deposit was then washed with several portions of petroleum ether, dried at 121°C for 10 hours and weighed. Total deposit was the sum of the values for adhering and non-adhering deposit.

Spectral work was done using a Varian Cary 219 spectro-

photometer with 1-cm-path-length quartz cuvettes.

Analysis of Jet A fuel for copper was done by Geolabs of Lakewood, Colo. using graphite furnace atomic absorption spectroscopy.

## RESULTS AND DISCUSSION

Jet A StudiesSoluble Copper

As most previous studies have shown that soluble copper has an adverse effect on the thermal stability of jet fuels, it was not surprising to find that it increased the rate of deposit formation in Jet A. In Table I are the results for cupric acetylacetonate in Jet A and they show the increase in deposit for copper-catalyzed samples. Use of the word catalysis may be misleading (though it will be used in the text for convenience) as a Jet A sample originally containing  $1.4 \times 10^{-4}$  M cupric laurate had only  $1 \times 10^{-6}$  M copper after 7 days aging. When and how the copper is removed (e.g., adsorbed on the organic deposit or as an insoluble oxide) is not known. Even so, at a copper concentration of  $.76 \times 10^{-5}$  M the deposition rate is doubled, and, since total deposit weights for control samples are on the order of .6 mg and  $.76 \times 10^{-5}$  M cupric acetylacetonate represents only .020 mg of added solid, the increased deposition is not due to precipitation of the copper species. Acetylacetonate, at a concentration of  $4.9 \times 10^{-4}$  M, had no effect on deposit (.103 mg vs. .110 mg for control samples). Additional data on copper was obtained with cupric laurate (Table II).

The laurates of both copper (II) and iron (II) were

Table I. The effects of cupric acetylacetonate on deposit formation in Jet A aged for 7 days at 121°C.

| <u>Copper concentration<br/>(moles/liter)</u> | <u>Deposit weight<br/>on plate after<br/>7 days (mg)</u> | <u>Number of<br/>samples</u> | <u>Average<br/>deviation<br/>(mg)</u> |
|---|--|------------------------------|---------------------------------------|
| Control                                       | .110   | 7                            | .014                                  |
| $.16 \times 10^{-5}$                          | .119   | 3                            | .011                                  |
| $.31 \times 10^{-5}$                          | .133   | 3                            | .026                                  |
| $.76 \times 10^{-5}$                          | .225   | 3                            | .021                                  |
| $1.4 \times 10^{-5}$                          | .195   | 3                            | .013                                  |
| $7.7 \times 10^{-5}$                          | .181   | 2                            | .004                                  |
| $12.0 \times 10^{-5}$                         | .304   | 3                            | .014                                  |
| $16.0 \times 10^{-5}$                         | .325   | 1                            | -                                     |

Table II. The effects of lauric acid, cupric laurate and ferrous laurate on deposit formation in Jet A aged for 7 days at 121°C.

| <u>Spiking compound</u> | <u>Concentration (moles/liter)</u> | <u>Deposit weight on plate after 7 days (mg)</u> | <u>Number of samples</u> | <u>Average deviation (mg)</u> |
|-------------------------|------------------------------------|--|--------------------------|-------------------------------|
| Control                 | -                                  | .134   | 3                        | .021                          |
| Lauric Acid             | $9.78 \times 10^{-5}$              | .110   | 3                        | .032                          |
| Cupric Laurate          | $5.0 \times 10^{-5}$               | .327   | 3                        | .020                          |
| Ferrous Laurate         | $13.5 \times 10^{-5}$              | .126   | 3                        | .013                          |

prepared when it was found that ferric acetylacetonate was thermally unstable under the aging conditions. With  $5.0 \times 10^{-5}$  M cupric laurate the amount of deposit formed after aging was nearly the same as that formed with  $16.0 \times 10^{-5}$  M cupric acetylacetonate (.327 mg and .325 mg respectively). The seemingly lower catalytic activity of the acetylacetonate is probably not significant as experiments with cupric acetylacetonate were performed on a different batch of Jet A than was used for all other Jet A experiments.

Lauric acid, when added in an amount roughly equivalent to that of laurate in  $5 \times 10^{-5}$  M cupric laurate, showed a slight inhibition of deposit formation but the difference (.110 mg vs. .134 mg) is not considered significant. Therefore, it is reasonable to assume that the catalysis in samples containing either cupric or ferrous laurates is due to the cupric or ferrous complexes and not laurate ion.

#### Soluble Iron

As stated earlier, it was found that ferric acetylacetonate (the soluble iron compound which was originally to have been studied) was not stable under the aging conditions. This was evidenced when, during experiments involving the model fuel, a light red precipitate formed at the bottom of samples containing the acetylacetonate after having been aged for less than three hours at  $121^{\circ}\text{C}$ . Also,

the absorbance at 440 nm (the wavelength for maximum absorbance of ferric acetylacetonate in this solvent system) for model fuel samples spiked with ferric acetylacetonate and aged at 121°C for just a few hours dropped to the baseline value. The detection limit for ferric acetylacetonate in the model system was determined to be  $.2 \times 10^{-5}$  M. And so, ferrous laurate was prepared as an alternative spiking compound.

The results for ferrous laurate in Jet A are summarized in Table II. As can be clearly seen, it had little, if any, effect on the measured deposit weights. In fact, samples aged with ferrous laurate showed a slight reduction in deposit. However, after seven days aging there was present in the iron-catalyzed samples noticeable amounts of solid material which did not adhere to the vessel walls and its weight was not, therefore, measurable using the slip technique. Large amounts of suspended solids had not been previously observed in any experiments as the deposit normally adheres to the surface. Presumably this unattached material was the same as deposit on the vessel walls but with the distinction of being either formed in solution rather than at an active surface site on the glass or dislodged from the glass surface after having formed. And so, an experiment was performed to determine the total amount of

deposit, both deposit adhering to the glass surface and non-adhering deposit, formed in Jet A spiked with ferrous laurate. The results for this experiment are summarized in Table III (note: this table gives total deposit weights not the weight of deposit on a glass microscope coverslip). These data clearly show the catalytic effect of soluble iron on deposit formation in Jet A.

#### Copper Metal

Copper metal was found to catalyze deposit formation as shown by the data in Table IV. Plotted in Figure IV are deposit weights versus total surface area of copper added to the fuel samples. This figure shows a rough correlation between surface area and deposit weight possibly suggesting heterogeneous catalysis. However, it did not appear that deposit formed preferentially on the metal surface. The surface of the copper was greatly tarnished indicating possible corrosion of it, but attempts to determine the true weight loss in the copper were unsuccessful as the deposit on it could not be satisfactorily removed. Nevertheless some copper specimens lost at least .2 mg even without the complete removal of deposit from them (most specimens, however, showed a net "increase" in weight). A .2 mg addition of copper to a 10 ml Jet A sample is equivalent to a copper concentration of about  $3 \times 10^{-4}$  M. Soluble copper, when

Table III. The effect of ferrous laurate on deposit formation in Jet A aged for 7 days at 121°C.

| <u>Iron concentration<br/>(moles/liter)</u> | <u>Total deposit<br/>after 7 days<br/>(mg)</u> | <u>Number<br/>of<br/>samples</u> | <u>Average<br/>deviation<br/>(mg)</u> |
|---|--|----------------------------------|---------------------------------------|
| Control                                     | .6   | 3                                | .2                                    |
| $15.5 \times 10^{-5}$                       | 4.0  | 3                                | 1.0                                   |

Table IV. The effects of copper and iron on deposit formation in Jet A aged for 7 days at 121°C.

| <u>Metal</u> | <u>Surface area<br/>of metal<br/>(cm<sup>2</sup>)</u> | <u>Deposit weight<br/>on plate after<br/>7 days (mg)</u> | <u>Number<br/>of<br/>samples</u> | <u>Average<br/>deviation<br/>(mg)</u> |
|--------------|---|--|----------------------------------|---------------------------------------|
| Control      | -   | .134   | 3                                | .021                                  |
| Iron         | 3.0   | .137   | 3                                | .031                                  |
| Copper       | 1.6   | .186   | 3                                | .015                                  |
| Copper       | 3.2   | .233   | 2                                | .019                                  |
| Copper       | 6.5   | .246   | 2                                | .052                                  |

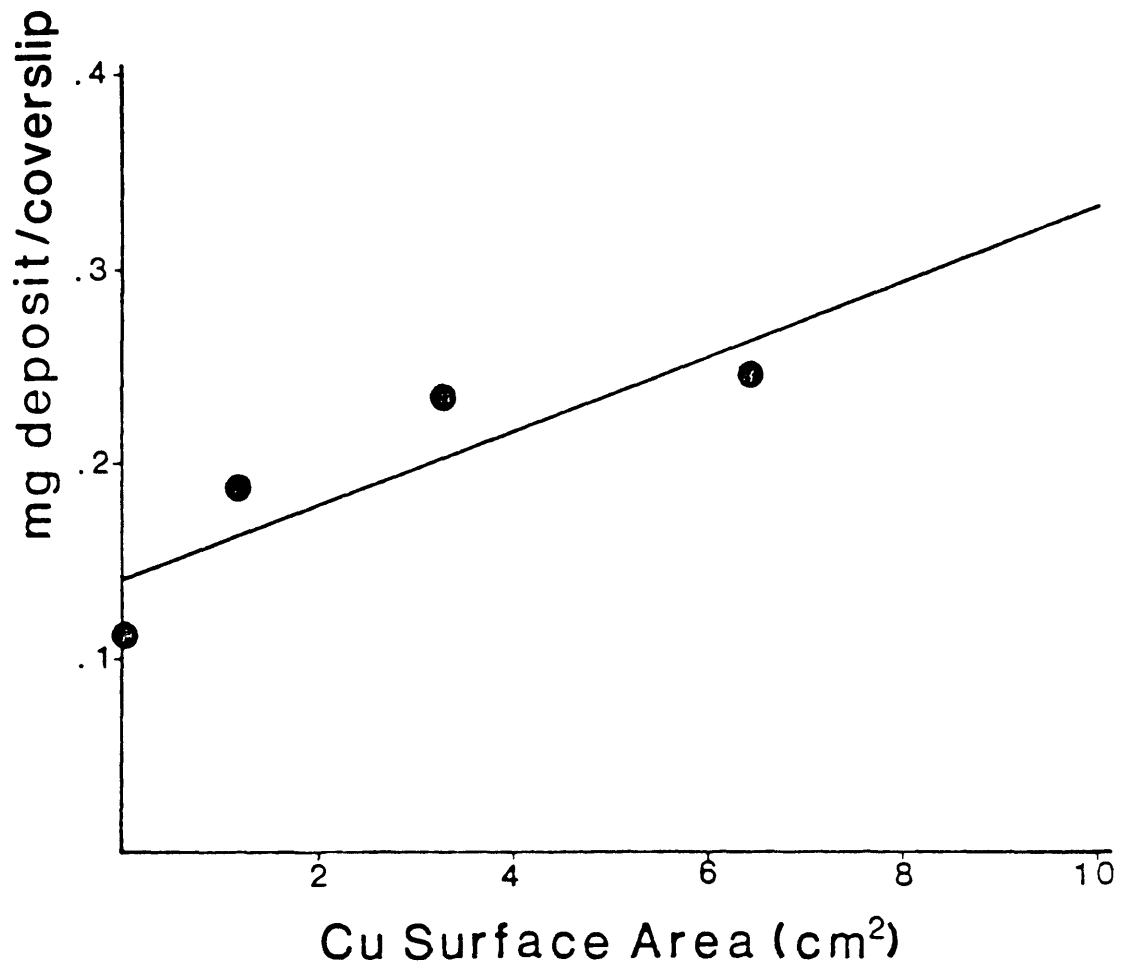


Figure IV. The effect of copper metal on deposit formation in Jet A aged for 7 days at 121°C.

added as the acetylacetonate, at only half this concentration almost tripled the amount of deposit formed in Jet A.

During the experiments involving copper metal an occasional sample (about one in five) developed a tremendous amount of deposit (around 2-4 mg). These striking amounts could not be accounted for by any external contamination of the samples and their comparative frequency was above that expected as a result of incompletely cleaned sample jars. The deposit weights for these samples were excluded from the calculations of the numbers shown in Table IV and Figure IV. Justification for their exclusion was based on the t test at the 90% confidence level. But because of their relative frequency and because no obvious contamination was present, these large deposit weights can possibly be explained as the result of homogeneous rather than heterogeneous catalysis. Since copper is known to dissolve in many fuels (20,21,33,34,35,36,37,38), it is conceivable that large amounts of copper were dissolved by the fuel thereby drastically increasing the deposition rate as a result of homogeneous catalysis. Since not all samples containing copper were affected, it may be that rapid copper dissolution can occur only at very active regions in the copper metal, regions where impurities might prevent the formation of a comparatively unreactive surface. These

active regions may be rare, i.e. completely absent from one half inch square of metal and present in another. Once dissolution has begun at an active site, more fresh copper is open to attack by the fuel and so the process continues. The concept of active surface sites could also be used in an argument for heterogeneous catalysis. Indeed, in Jet A aged for 7 days at 121°C in contact with copper metal (6 cm<sup>2</sup>), little dissolved copper was found ( $1.3 \times 10^{-6}$  M vs.  $.9 \times 10^{-6}$  M in Jet A itself). However, the possibility of copper being dissolved and then later removed from the solution phase cannot be eliminated.

#### Iron Metal

Iron metal had no significant effect on the fuel with regard to deposit formation. Samples containing iron developed only .137 mg deposit on the slip after 7 days compared with .134 mg for the control samples.

The iron metal did not appear to become corroded as the experiment progressed and after seven days its surface remained shiny and free of deposit. Also, the weight of iron after aging did not change significantly, it being .17017 g before and .17021 g after. Although previous experimenters have also observed no tendency for iron to be attacked by JP-5 (20) or JP-7 (36) fuels, it is, nonetheless, intriguing that copper is dissolved but iron is not. One might

expect the reverse to be true as copper is generally considered more "noble" than iron. It may be that, in reverse of aqueous media, iron is passivated in hydrocarbon media and copper is not. Alternatively, ligands which form sufficiently stable iron complexes may not be present in the fuels to make the oxidation of iron thermodynamically possible.

#### Model System Studies

Since, as discussed earlier, fuel auto-oxidation is an important first step towards deposit formation, the next set of experiments deals with the oxidation of tetralin in n-dodecane. The immediate product of the oxidation of tetralin is  $\alpha$ -tetralin hydroperoxide. Subsequently, as a result of hydroperoxide decomposition,  $\alpha$ -tetralone and  $\alpha$ -tetralol are produced. Further oxidation products have not yet been isolated and identified in this study, nor has the final insoluble compound (or compounds) resulting from the oxidation of tetralin in n-dodecane been identified. As a result, the above mentioned tetralin oxidation products were the only ones whose concentrations were monitored during the model system experiments.

Before examining the data, it should be stated that due to their comparatively small molar absorptivities (see Table V) the detection and area measurement of both the

Table V. Response factors and regression coefficients for tetralin,  $\alpha$ -tetralone,  $\alpha$ -tetralin hydroperoxide and  $\alpha$ -tetralol in model fuel.

| <u>Compound</u>                     | <u>Response factor<br/>(moles/liter/<br/>normalized area)</u> | <u>Number<br/>of<br/>samples</u> | <u>r*</u> |
|-------------------------------------|---|----------------------------------|-----------|
| Tetralin                            | .417  | 4                                | .9990     |
| $\alpha$ -Tetralone                 | .0114   | 4                                | .9996     |
| $\alpha$ -Tetralin<br>Hydroperoxide | .418  | 4                                | .9961     |
| $\alpha$ -Tetralol                  | .517  | 4                                | .9950     |

\*Linear regression coefficient from concentration versus normalized area.

$\alpha$ -tetralin hydroperoxide and  $\alpha$ -tetralol HPLC peaks presented problems. As the chromatogram in Figure V shows, it was not unusual for interfering peaks to make identification and quantization of the  $\alpha$ -tetralin hydroperoxide and  $\alpha$ -tetralol peaks difficult. Compounding this problem was the small height to width ratio of these peaks, especially in the case of  $\alpha$ -tetralol. This greatly enhanced the difficulty of determining the beginning and end points for the low broad peaks and thereby introduced significant uncertainty in their measurement. Therefore, where values in the following tables are followed by a "?" it indicates that the author is not confident in the identification or quantization of a peak and a duplicate run of the sample did not resolve the problem.

#### Copper Metal

Copper metal was found to greatly increase the total amount of deposit in the model system as Table VI clearly shows. However, a correlation between deposit weight and surface area of added copper does not appear. In addition, the average deviation among samples is quite large. This great variability between samples may be a result of the same type of phenomena which caused the occasionally large deposit weights in Jet A to which copper metal was added. The copper metal became tarnished, but deposit did

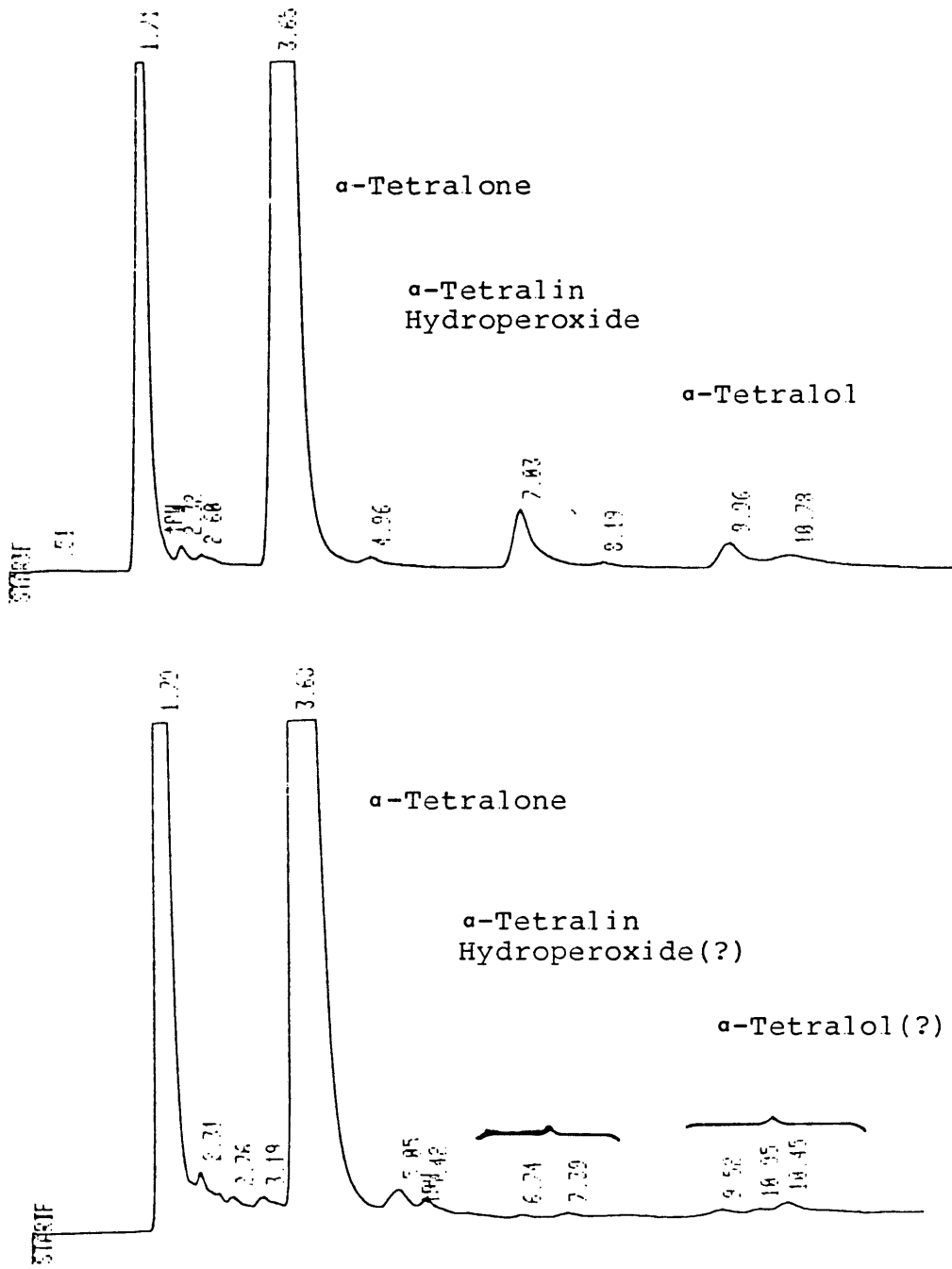


Figure V. Comparison of HPLC chromatograms for model fuel control sample and  $1.51 \times 10^{-4}$  M ferrous laurate sample after 72 hours at  $121^{\circ}\text{C}$ .

Table VI. The effect of copper metal on deposit formation in model fuel aged for 260 hours at 121°C.

| <u>Area Cu<br/>metal (cm<sup>2</sup>)</u> | <u>Deposit weight<br/>after 260 hrs.<br/>(gms.)</u> | <u>Average<br/>deviation (gms.)</u> | <u>Number of<br/>samples</u> |
|---|---|-------------------------------------|------------------------------|
| Control                                   | .1053   | .0257                               | 3                            |
| 3.2                                       | .1550   | .0956                               | 3                            |
| 6.5                                       | .1909   | .0613                               | 3                            |
| 9.7                                       | .1430   | .0116                               | 3                            |

not preferentially form on it nor was significant copper found in the solution phase.

The HPLC data for these experiments are summarized in Table VII. Samples containing copper metal formed  $\alpha$ -tetralone more rapidly than did control samples. There does not, however, appear to be a correlation between the rate of formation of  $\alpha$ -tetralone and surface area of copper added. At 48 hours all the copper samples had nearly equivalent amounts of  $\alpha$ -tetralone. Sometime around 92 hours the concentration of  $\alpha$ -tetralone reached a maximum and began rapidly declining thereafter. Visible amounts of deposit were generally observed in the samples after 4 or 5 days aging and this is roughly when the  $\alpha$ -tetralone concentration began to fall. Although it is not completely understood if  $\alpha$ -tetralone itself or a further oxidized species derived from  $\alpha$ -tetralone is a deposit precursor, recent experiments have demonstrated that large amounts of deposit can be formed from the reaction of  $\alpha$ -tetralone with  $\alpha$ -tetralin hydroperoxide under air but not under  $\text{CO}_2$  (43). In the control experiments,  $\alpha$ -tetralone reached a maximum concentration near the end of the experiment.

The levels for  $\alpha$ -tetralin hydroperoxide in the copper samples were considerably lower than those for control samples. At 48 hours, control samples had already reached

Table VII. The effects of copper metal on the oxidation products of tetralin in model fuel aged for 260 hours at 121°C.

$\alpha$ -Tetralone concentration (moles/liter)

| <u>Area Cu metal (cm<sup>2</sup>)</u> | <u>48 hrs.</u> | <u>92 hrs.</u> | <u>212 hrs.</u> | <u>260 hrs.</u> |
|---------------------------------------|----------------|----------------|-----------------|-----------------|
| Control                               | .071           | .100           | .157            | .136            |
| 3.2                                   | .103           | .148           | .104            | .097            |
| 6.5                                   | .108           | .128           | .081            | .067            |
| 9.7                                   | .105           | .165           | .063            | .062            |

$\alpha$ -Tetralin hydroperoxide concentration (moles/liter)

| <u>Area Cu metal (cm<sup>2</sup>)</u> | <u>48 hrs.</u> | <u>92 hrs.</u> | <u>212 hrs.</u> | <u>260 hrs.</u> |
|---------------------------------------|----------------|----------------|-----------------|-----------------|
| Control                               | .198           | .105           | .014            | .009            |
| 3.2                                   | -              | -              | .007            | .003            |
| 6.5                                   | -              | .044           | .005            | -               |
| 9.7                                   | -              | .004           | .006            | .012            |

$\alpha$ -Tetralol concentration (moles/liter)

| <u>Area Cu metal (cm<sup>2</sup>)</u> | <u>48 hrs.</u> | <u>92 hrs.</u> | <u>212 hrs.</u> | <u>260 hrs.</u> |
|---------------------------------------|----------------|----------------|-----------------|-----------------|
| Control                               | .043           | .043           | .017            | .010            |
| 3.2                                   | -              | .121(?)        | .022            | -               |
| 6.5                                   | -              | .043           | -               | -               |
| 9.7                                   | -              | .055           | .017            | .025            |

their maximum concentration of hydroperoxide while no hydroperoxide at all could be detected in the copper containing samples. After reaching a maximum, the hydroperoxide concentration in the control samples gradually declined.

$\alpha$ -Tetralol is the most difficult of the three oxidation products to successfully and reproducibly detect and quantify and so data for it may, at times, be confusing. Fortunately, however, it appears to be the least important of tetralin's oxidation products as regards deposit formation (27). In control samples, the general trend for  $\alpha$ -tetralol is similar to that for  $\alpha$ -tetralone and  $\alpha$ -tetralin hydroperoxide, that is, rising to a maximum, in the case of  $\alpha$ -tetralol sometime between 48 and 92 hours, and declining thereafter. Samples containing copper showed no  $\alpha$ -tetralol at 48 hours, but after this time they were reasonably close to those for the control samples, with one exception. A general problem, which is more prominent in the metal samples, is the greater number of compounds detected in the model system as it is aged (see Figure V). The appearance of neighboring peaks can greatly affect the measurement of low broad peaks such as that for  $\alpha$ -tetralol introducing even greater inaccuracies than are present under the best of conditions. These neighboring peaks may help explain the disparity between copper samples and control samples

at 48 hours with respect to the  $\alpha$ -tetralol concentration.

#### Iron Metal

As the data in Table VIII show, iron metal had no significant effect on deposit formation in the model fuel nor did it have any effect on the oxidation products of tetralin (see Table IX). This result is not surprising as iron metal did not have a catalytic effect on deposit formation in Jet A. No significant weight loss of iron occurred during the experiment, there being .17201 gm initially and .17192 gm after 360 hours. The iron also remained shiny and free of deposit. Experiments with iron metal were carried out for a longer period of time than those for copper (360 vs. 260 hours) in order to enhance any difference there might be between the iron and control samples.

#### Soluble Copper

Soluble copper, added as the laurate, was found to catalyze the formation of deposit in the model fuel at a concentration of  $1.71 \times 10^{-4}$  M, but had no effect or even a slight inhibition on deposit formation at concentrations of  $3.0 \times 10^{-5}$  M and below. These data are summarized in Tables X and XI. Lauric acid was found to have no effect on deposit formation and so it must be concluded that both the apparent inhibition and catalysis of deposit are due to copper complexes in the model fuel.

Table VIII. The effect of iron metal on deposit formation in model fuel aged for 360 hours at 121°C.

| <u>Area Fe<br/>metal (cm<sup>2</sup>)</u> | <u>Deposit weight<br/>after 360 hrs.<br/>(gms.)</u> | <u>Average<br/>deviation (gms.)</u> | <u>Number of<br/>samples</u> |
|---|---|-------------------------------------|------------------------------|
| Control                                   | .0777   | .0205                               | 3                            |
| 3.8                                       | .0712   | .0136                               | 3                            |

Table IX. The effects of iron metal on the oxidation products of tetralin in model fuel aged for 360 hours at 121°C.

$\alpha$ -Tetralone concentration (moles/liter)

| <u>Area Fe metal (cm<sup>2</sup>)</u> | <u>48 hours</u> | <u>141 hours</u> | <u>360 hours</u> |
|---------------------------------------|-----------------|------------------|------------------|
| Control                               | .064            | .132             | .148             |
| 3.8                                   | .046            | .139             | .150             |

$\alpha$ -Tetralin hydroperoxide concentration (moles/liter)

| <u>Area Fe metal (cm<sup>2</sup>)</u> | <u>48 hours</u> | <u>141 hours</u> | <u>360 hours</u> |
|---------------------------------------|-----------------|------------------|------------------|
| Control                               | .194            | .063             | .004             |
| 3.8                                   | .189            | .086             | .006             |

$\alpha$ -Tetralol concentration (moles/liter)

| <u>Area Fe metal (cm<sup>2</sup>)</u> | <u>48 hours</u> | <u>141 hours</u> | <u>360 hours</u> |
|---------------------------------------|-----------------|------------------|------------------|
| Control                               | .042            | .062             | .035             |
| 3.8                                   | .065            | .046             | .040             |

Table X. The effects of low concentrations of cupric laurate on deposit formation in model fuel aged for 260 hours at 121°C.

| <u>Copper concentration (moles/liter)</u> | <u>Deposit weight after 260 hrs. (gms.)</u> | <u>Average deviation (gms.)</u> | <u>Number of samples</u> |
|---|---|---------------------------------|--------------------------|
| Control                                   | .0632                                       | .0001                           | 2                        |
| $1.0 \times 10^{-5}$                      | .0364                                       | .0025                           | 3                        |
| $2.0 \times 10^{-5}$                      | .0521                                       | .0050                           | 2                        |
| $3.0 \times 10^{-5}$                      | .0404                                       | .0100                           | 3                        |

Table XI. The effects of high concentrations of cupric laurate and lauric acid on deposit formation in model fuel aged for 267 hours at 121°C.

| <u>Contents</u>                             | <u>Deposit weight<br/>after 267 hrs.<br/>(gms.)</u> | <u>Average<br/>deviation<br/>(gms.)</u> | <u>Number of<br/>samples</u> |
|---|---|---|------------------------------|
| Control                                     | .0540   | .0116                                   | 3                            |
| 3.24 x 10 <sup>-4</sup> M<br>Lauric Acid    | .0549   | .0157                                   | 3                            |
| 1.71 x 10 <sup>-4</sup> M<br>Cupric Laurate | .1514   | .0560                                   | 3                            |

Dissolved copper, whether in high or low concentrations, affected the oxidation products of tetralin in a manner similar to that found for copper metal (see Tables XII and XIII). Increased initial concentrations of tetralone were found along with significantly smaller amounts of  $\alpha$ -tetralin hydroperoxide. Also, the concentration of  $\alpha$ -tetralol, though lower than the concentration in control samples early in the experiment, was nearly the same as control samples after 92 hours.

#### Soluble Iron

Ferrous laurate at a concentration of  $1.51 \times 10^{-4}$  M greatly increased the amount of deposit in the model system (see Table XIV). It did not appear to have as great an effect on the concentration of  $\alpha$ -tetralone (see Table XV) as did soluble copper or copper metal in the early part of the experiment, but with the onset of visible amounts of deposit the  $\alpha$ -tetralone concentrations dropped drastically compared with control samples. Its effect on the hydroperoxide also followed the pattern set by copper, that is, significantly lesser amounts than control samples. Soluble iron did not appear to have any effect on the amount of  $\alpha$ -tetralol formed.

Based on the foregoing data, it can be said that copper, whether added as the metal or a fuel soluble compound,

Table XII. The effects of low concentrations of cupric laurate on the oxidation products of tetralin in model fuel aged for 260 hours at 121°C.

$\alpha$ -Tetralone concentration (moles/liter)

| Copper concentration (moles/liter) | 46 hrs. | 92 hrs. | 140 hrs. | 188 hrs. | 260 hrs. |
|------------------------------------|---------|---------|----------|----------|----------|
| Control                            | .020    | .048    | .083     | .100     | .108     |
| $1.0 \times 10^{-5}$               | .048    | .052    | .100     | .131     | .137     |
| $3.0 \times 10^{-5}$               | .045    | .068    | .086     | .121     | .116     |

$\alpha$ -Tetralin hydroperoxide concentration (moles/liter)

| Copper concentration (moles/liter) | 46 hrs. | 92 hrs. | 140 hrs. | 188 hrs. | 260 hrs. |
|------------------------------------|---------|---------|----------|----------|----------|
| Control                            | .025    | .013(?) | .015     | .006     | .008     |
| $1.0 \times 10^{-5}$               | .008(?) | -       | -        | .003     | .007     |
| $3.0 \times 10^{-5}$               | .007(?) | -       | .005     | .006     | .007     |

$\alpha$ -Tetralol concentration (moles/liter)

| Copper concentration (moles/liter) | 46 hrs. | 92 hrs. | 140 hrs. | 188 hrs. | 260 hrs. |
|------------------------------------|---------|---------|----------|----------|----------|
| Control                            | -       | .072    | .031     | .024     | .023     |
| $1.0 \times 10^{-5}$               | -       | .016    | .033     | .025     | .019     |
| $3.0 \times 10^{-5}$               | -       | .019    | .017     | .018     | .017     |

Table XIII. The effects of high concentrations of cupric laurate and lauric acid on the oxidation products of tetralin in model fuel aged for 267 hours at 121°C.

$\alpha$ -Tetralone concentration (moles/liter)

| <u>Contents</u>                             | <u>51 hrs.</u> | <u>120 hrs.</u> | <u>. 267 hrs.</u> |
|---|----------------|-----------------|-------------------|
| Control                                     | .033           | .117            | .184              |
| 3.24 x 10 <sup>-4</sup> M<br>Lauric Acid    | .045           | .116            | .189              |
| 1.71 x 10 <sup>-4</sup> M<br>Cupric Laurate | .099           | .174            | .073              |

$\alpha$ -Tetralin hydroperoxide concentration (moles/liter)

| <u>Contents</u>                             | <u>51 hrs.</u> | <u>120 hrs.</u> | <u>267 hrs.</u> |
|---|----------------|-----------------|-----------------|
| Control                                     | .055           | .114            | -               |
| 3.24 x 10 <sup>-4</sup> M<br>Lauric Acid    | .024           | .052            | -               |
| 1.71 x 10 <sup>-4</sup> M<br>Cupric Laurate | -              | -               | -               |

$\alpha$ -Tetralol concentration (moles/liter)

| <u>Contents</u>                             | <u>51 hrs.</u> | <u>120 hrs.</u> | <u>267 hrs.</u> |
|---|----------------|-----------------|-----------------|
| Control                                     | .042           | .059            | .049            |
| 3.24 x 10 <sup>-4</sup> M<br>Lauric Acid    | .046           | .059            | .081            |
| 1.71 x 10 <sup>-4</sup> M<br>Cupric Laurate | .029           | .039            | .060            |

Table XIV. The effect of ferrous laurate on deposit formation in model fuel aged for 269 hours at 121°C.

| <u>Iron concentration<br/>(moles/liter)</u> | <u>Deposit weight<br/>after 269 hrs.<br/>(gms.)</u> | <u>Average<br/>deviation<br/>(gms.)</u> | <u>Number of<br/>samples</u> |
|---|---|---|------------------------------|
| Control                                     | .0621   | .0167                                   | 3                            |
| $1.51 \times 10^{-4}$                       | .1549   | .0115                                   | 3                            |

Table XV. The effects of ferrous laurate on the oxidation products of tetralin in model fuel aged for 269 hours at 121°C.

$\alpha$ -Tetralone concentration (moles/liter)

| <u>Iron concentration<br/>(moles/liter)</u> | <u>72 hrs.</u> | <u>145 hrs.</u> | <u>269 hrs.</u> |
|---|----------------|-----------------|-----------------|
| Control                                     | .088           | .143            | .188            |
| $1.51 \times 10^{-4}$                       | .099           | .068            | .043            |

$\alpha$ -Tetralin hydroperoxide concentration (moles/liter)

| <u>Iron concentration<br/>(moles/liter)</u> | <u>72 hrs.</u> | <u>145 hrs.</u> | <u>269 hrs.</u> |
|---|----------------|-----------------|-----------------|
| Control                                     | .084           | .035            | .011            |
| $1.51 \times 10^{-4}$                       | .032           | -               | .014            |

$\alpha$ -Tetralol concentration (moles/liter)

| <u>Iron concentration<br/>(moles/liter)</u> | <u>72 hrs.</u> | <u>145 hrs.</u> | <u>269 hrs.</u> |
|---|----------------|-----------------|-----------------|
| Control                                     | .045           | .063            | .043            |
| $1.51 \times 10^{-4}$                       | .043           | .055            | .039            |

greatly increased the rate of deposit formation in the model fuel provided, in the case of cupric laurate, that the concentration was high enough. It is also clear that copper had a significant catalytic effect on the formation of  $\alpha$ -tetralone at both high and low concentrations. This suggests that copper either accelerates the formation or decomposition of  $\alpha$ -tetralin hydroperoxide via a mechanism similar to the general case shown on page 13. Owing to the very low, in some cases undetectable, amount of  $\alpha$ -tetralin hydroperoxide in the copper samples early in the experiments (~48 hrs.) one might be lead to believe that copper is catalyzing only the decomposition of the hydroperoxide. However, experiments with cupric acetylacetonate have shown that, in the very early hours of aging, copper has a significant effect on the rate of formation of the hydroperoxide (see Table XVI).

Despite this catalytic effect of copper on hydroperoxide formation and decomposition it does not appear that this is the cause of the increased rate of deposit formation in some copper samples. First, Worstell (27) has shown that the rate of deposit formation in the model fuel is not controlled by hydroperoxide decomposition and, second, at low copper concentrations there is a catalytic effect on the formation of  $\alpha$ -tetralone but none on the rate of deposit

Table XVI. The effects of cupric acetylacetonate on the oxidation products of tetralin in model fuel (9 parts by volume n-dodecane to 1 part by volume tetralin) aged at 121°C.

| <u><math>\alpha</math>-Tetralone concentration (moles/liter)</u> |          |          |          |          |          |          |          |          |          |
|--|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Copper concentration (moles/liter)                               | 1.2 hrs. | 1.8 hrs. | 2.4 hrs. | 2.8 hrs. | 3.2 hrs. | 3.5 hrs. | 3.7 hrs. | 4.3 hrs. | 4.6 hrs. |
| Control  |          | .001     |          | .001     |          | .002     |          | .002     |          |
| $1.6 \times 10^{-5}$   | .002     |          | -        |          | -        |          | .025     |          | .013     |

| <u><math>\alpha</math>-Tetralin hydroperoxide concentration (moles/liter)</u> |          |          |          |          |          |          |          |          |          |
|---|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Copper concentration (moles/liter)  | 1.2 hrs. | 1.8 hrs. | 2.4 hrs. | 2.8 hrs. | 3.2 hrs. | 3.5 hrs. | 3.7 hrs. | 4.3 hrs. | 4.6 hrs. |
| Control   |          | .032     |          | .051     |          | .096     |          | .096     |          |
| $1.6 \times 10^{-5}$  | .015     |          | .088     |          | .134     |          | .131     |          | .134     |

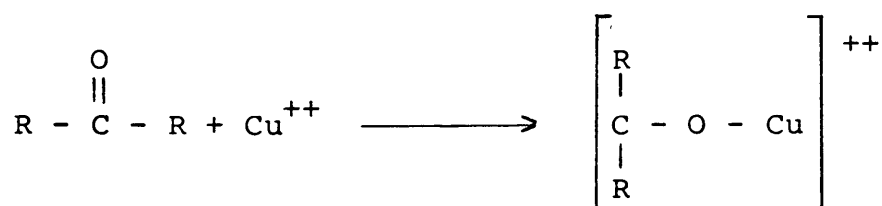
| <u><math>\alpha</math>-Tetralol concentration (moles/liter)</u> |          |          |          |          |          |          |          |          |          |
|---|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Copper concentration (moles/liter)                              | 1.2 hrs. | 1.8 hrs. | 2.4 hrs. | 2.8 hrs. | 3.2 hrs. | 3.5 hrs. | 3.7 hrs. | 4.3 hrs. | 4.6 hrs. |
| Control   |          | -        |          | -        |          | -        |          | -        |          |
| $1.6 \times 10^{-5}$  | -        |          | .013     |          | .011     |          | .025     |          | .028     |

formation.

Soluble iron produced amounts of deposit comparable to those for the highest concentration of soluble copper and copper metal. It did not appear, however, to have as great an effect on the concentration of  $\alpha$ -tetralone early on in the experiment but, similar to copper, very low concentrations of hydroperoxide were present.

The lack of correlation between increased tetralin oxidation and increased deposit formation suggests that the cause of metal catalysis lies elsewhere.

Possible alternative causes for the catalytic effect of the metals on deposit formation aside from initiating free radical oxidation reactions involve metal-precursor complexes. Coordination of two immediate deposit precursors to the same metal ion could enhance the likelihood of their reacting to form deposit as a result of either bringing the precursors into close proximity or improving geometric constraints on their reaction. Another possible mode of catalysis involving such complexes is the improvement of an important electrophilic site in a precursor molecule, thereby, lowering the activation energy for its reaction with another precursor. An example of this effect follows:



Through coordination of the ketone oxygen with a metal ion the partial positive charge on the ketone carbon is increased. The greater this partial positive charge is, the lower the activation energy required for the ketone carbon to react as an electrophile. As this model presumably requires displacement of a ligand from one of the coordination sites on the copper, one would expect different catalytic activity for different copper complexes. The reason for this is the ease of removal of given ligands. As the data show, a sizable difference in catalytic activity between cupric acetylacetonate and cupric laurate in Jet A was observed.

Attempts were made to develop a suitable method for noting changes in the coordination sphere around the metal ions during aging of the model system. These attempts were directed towards detecting changes in the wavelength of maximum absorbance in the visible range for the metal complexes. Unfortunately, this region was effectively swamped by a variety of oxidation products.

As regards the formation of model fuel deposit in general, the observation that a decrease in the  $\alpha$ -tetralone con-

centration accompanied the appearance of deposit suggests the importance of  $\alpha$ -tetralone in deposit formation. In samples where the largest amounts of deposit formed there were greater decreases in the  $\alpha$ -tetralone concentration. Control samples, which formed less deposit than metal catalyzed samples, tended to have a leveling off in the concentration of  $\alpha$ -tetralone rather than an actual decrease. Since there is no reason to suspect that  $\alpha$ -tetralone formation ceased (there was still significant tetralin present), this apparent leveling of the  $\alpha$ -tetralone concentration is most likely due to less deposit being formed, i.e. less  $\alpha$ -tetralone being consumed in forming deposit.

## CONCLUSIONS

Based on the foregoing data, the following conclusions have been reached:

- 1) Copper, whether added as the metal or a fuel soluble compound, increases deposit formation in Jet aged at 121°C. In the case of copper metal, the primary cause of this effect is probably not due to heterogeneous causes.
- 2) Iron metal has no effect on deposit formation in Jet A and is not attacked nor dissolved by the fuel. Soluble iron, however, does increase deposition, most notably, formation of deposit which does not adhere to the vessel walls.
- 3) High concentrations ( $1.71 \times 10^{-4}$  M) of cupric laurate and ferrous laurate increase deposition in the model fuel. They also accelerate the formation of  $\alpha$ -tetralone, reduce the level of  $\alpha$ -tetralin hydroperoxide present at any given time and have little effect on the concentration of  $\alpha$ -tetralol. Low concentrations of cupric laurate ( $3.0 \times 10^{-5}$  M) have a similar effect on the oxidation products of tetralin but do not increase deposit formation. Therefore, the catalytic effect of the metals in deposit formation in the model fuel is not considered to be due

to their increasing the rate of oxidation of tetralin nor the rate of decomposition of  $\alpha$ -tetralin hydroperoxide.

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