



Copper catalysis of polymerization of sunflower oil diesel fuel  
by Stephen John Jette

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
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Abstract:

The role of copper catalyst in the oxidative polymerization of contaminant sunflower oil fuel in commercial lubrication oil was investigated in laboratory apparatus simulating engine crankcase conditions.

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Copper dissolves and becomes catalytically active in oil mixtures in both the presence and absence of oxygen. Oxygen does seem to accelerate copper dissolution but may somewhat deactivate dissolved copper. Sunflower oil appears to have little effect on copper dissolution phenomena.

A theory of dissolved copper and oxygen combining to yield free radicals which initiate triglyceride polymerization is supported by experimental results. Copper does not appear to catalyze the propagation phase of polymerization, as copper has little impact on a reaction system supplied with excess initiation free radicals.

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MONTANA STATE UNIVERSITY  
Bozeman, Montana

December 1985

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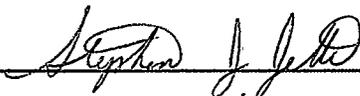
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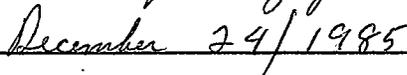
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## TABLE OF CONTENTS

	Page
APPROVAL.....	ii
STATEMENT OF PERMISSION TO USE.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	vii
INTRODUCTION.....	1
RESEARCH OBJECTIVES.....	5
THEORY.....	6
Oxidative Polymerization.....	6
Copper Metal.....	11
Copper Catalysis.....	14
EXPERIMENTAL.....	17
Equipment.....	17
Materials.....	21
Experimental Procedures.....	23
RESULTS AND DISCUSSION.....	27
SUMMARY.....	59
CONCLUSIONS.....	63
SUGGESTIONS FOR FUTURE RESEARCH.....	65
BIBLIOGRAPHY.....	67
APPENDIX.....	70

## LIST OF TABLES

Tables	Page
I. Atomic emission results for Run 6.....	34
II. Atomic emission results for..... Runs 10 and 11.	47
III. Total Base Number for Runs 10 and 11.....	48
IV. Total Base Number for Runs 17 and 18.....	56
V. Successive spectrographic analysis of used.... oil from a diesel locomotive crankcase.	70
VI. Atomic emission data for copper and..... common additive metals for selected runs.	71
VII. Operation parameters for oil bath runs.....	72
VIII. Total Base Number in mg KOH/g Oil..... for several runs.	73
IX. Limits for trace metal concentrations..... in used crankcase oils.	74

## LIST OF FIGURES

Figures	Page
1. Single cell apparatus.....	18
2. Oil bath.....	20
3. Operating diagram.....	22
4. Viscosity versus exposure time for standard..... conditions of Rewolinski [4] and the current work.	28
5. Viscosity versus exposure time for varying..... copper surface and sunflower oil concentration.	30
6. Viscosity versus exposure time with copper..... foil removal at 18 hours.	32
7. Viscosity versus exposure time for two..... samples of Phillips 66 HD SAE 30 at standard conditions.	36
8. Viscosity versus exposure time with copper..... foil removal and nitrogen gas changed to oxygen at 24 hours.	38
9. Viscosity versus exposure time with oxygen..... and copper foil for initial 48.5 hours. Copper foil removed and 5.0 percent sunflower oil addition at 48.5 hours.	42
10. Viscosity versus exposure time with oxygen..... and copper foil for initial 48.5 hours. Copper foil removed and 5.0 percent sunflower oil addition at 48.5 hours. Time zero at the point of sunflower oil addition.	43
11. Viscosity versus exposure time with nitrogen..... and copper foil for initial 48.5 hours. Copper foil removed, nitrogen changed to oxygen, and 5.0 percent sunflower oil addition at 48.5 hours.	45

Figures	Page
12. Viscosity versus exposure time with nitrogen..... and copper foil for initial 48.5 hours. Copper foil removed, nitrogen changed to oxygen, and 5.0 percent sunflower oil addition at 48.5 hours. Time zero at the point of sunflower oil addition.	46
13. Viscosity versus exposure time with cupric..... and cuprous oxides at standard conditions.	50
14. Viscosity versus exposure time for varying..... levels of cupric acetylacetonate at standard conditions.	52
15. Viscosity versus exposure time with nitrogen.... or oxygen and cupric acetylacetonate for initial 48.5 hours and 5.0 percent sunflower oil addition at 48.5 hours. Nitrogen changed to oxygen at 48.5 hours for Run 18.	54
16. Viscosity versus exposure time with nitrogen.... or oxygen and cupric acetylacetonate for initial 48.5 hours and 5.0 percent sunflower oil addition at 48.5 hours. Nitrogen changed to oxygen at 48.5 hours for Run 18. Time zero at the point of sunflower oil addition.	55
17. Viscosity versus exposure time using Lupersol... 130 as a free radical initiator.	58

ABSTRACT

The role of copper catalyst in the oxidative polymerization of contaminant sunflower oil fuel in commercial lubrication oil was investigated in laboratory apparatus simulating engine crankcase conditions.

Sunflower oil mixed at 5.0 percent in Phillips HD II SAE 30 lube oil was exposed to various forms of copper in catalytic quantities at 150 C for periods of 15 to 72 hours. Oil mixtures were contacted by percolation with both nitrogen and oxygen to provide agitation and/or an oxidizing environment. Polymerization was monitored by oil mixture viscosity, and both mixture acidity and dissolved copper concentrations were measured in selected experiments.

Dissolved copper species as opposed to metallic surface appear to be of primary importance in catalysis of the triglyceride addition polymerization. The impact of varying metallic copper surface seems to be largely due to effects on rate of copper solubilization.

Copper dissolves and becomes catalytically active in oil mixtures in both the presence and absence of oxygen. Oxygen does seem to accelerate copper dissolution but may somewhat deactivate dissolved copper. Sunflower oil appears to have little effect on copper dissolution phenomena.

A theory of dissolved copper and oxygen combining to yield free radicals which initiate triglyceride polymerization is supported by experimental results. Copper does not appear to catalyze the propagation phase of polymerization, as copper has little impact on a reaction system supplied with excess initiation free radicals.

## INTRODUCTION

Petroleum fuel stocks are among the most important energy sources available to modern society. The oil embargo of the early 1970s emphasized the United States' dependence on worldwide petroleum production. As a result, the search for suitable alternative fuels has intensified. An alternative fuel with a chemical structure and combustion properties similar to petroleum could logically substitute for petroleum products. A further advantage to a chemically similar alternative fuel would be the minimal modification of existing power-producing systems.

One of the key fuels in both agriculture and transportation is diesel oil. Rudolf Diesel, in the search for suitable fuels for his invention, successfully used vegetable oils as fuels in short-term evaluations. Diesel chose not to promote vegetable oils as diesel fuels because of economics and engine design considerations [1]. The drastic increase in the cost of petroleum has begun to remove the economic prohibition. However, the engine design problems remain as important considerations in current research.

Factors favoring vegetable oils as diesel fuels include heats of combustion similar to standard diesel oils, potential widespread availability, portability as liquids, and the fact that they are renewable. However, vegetable oils present several major difficulties when actually introduced as fuel. When used under normal operating conditions for diesel engines, vegetable oil fuels tend to cause coking of fuel injectors, varnish build-up on pistons and rings, and thickening of lubrication oil [2]. Blends of vegetable oils and conventional diesel fuel have been found to cause lesser problems, but engine manufacturers may still void warranties without further research on fuel mixtures [3].

Prior research at this laboratory has focussed on the thickening of lubrication oil due to vegetable oil contamination [4,5]. If the vegetable oil is present as a contaminant in a lubricating system, an excessive rise in viscosity may occur. A 375 percent increase in viscosity is considered a failure in lubrication oil tests [6].

The lubrication oil of an engine can become contaminated by incompletely combusted fuel passing from the combustion chamber to the crankcase. This dilution of the lubricating oil is more pronounced under loaded operating conditions when unburned fuel residue is most likely present

in the combustion chamber. Dilution takes place when either diesel oil or vegetable oils are used as fuels. Under normal oil change intervals thickening of the lubrication oil can be severe with vegetable oil fuels but not with diesel oils [7].

Lubrication oil thickening could be reduced by eliminating fuel dilution or possibly by modifying the lubrication oil. Changes in engine design to eliminate dilution would be costly, even if possible. Changing the chemical makeup of the lubrication oil may, therefore, be more feasible.

If the thickening is eliminated by the alteration of the lubrication oil, the vegetable oils become more viable fuel stocks for current engines (and hence a suitable alternative fuel) without costly design modifications.

The thickening is a result of oxidative polymerization of the unsaturated vegetable oil triglycerides. The polymerization is known to be catalyzed by transition metals [8], some of which are present as wear metals in diesel lubrication oil (Table V in the Appendix) [6]. Copper and iron are found to be common wear metal contaminants. Bauer et.al [9] found that a copper and iron mixed catalyst produced the thickening effect when used in a system designed to simulate the crankcase environment. Rewolinski

[4] has demonstrated in a similar manner that copper alone can catalyze the thickening polymerization reactions. Copper, therefore, was selected as the catalyst for continued experiments in this laboratory.

This particular investigation was designed to reveal the form(s) of copper, dissolved or solid surface, contributing to the catalysis of the polymerization reaction. As the form(s) and role of copper are clarified, future research will be aimed at modifying the lubrication oil to eliminate the catalytic affect.

### RESEARCH OBJECTIVES

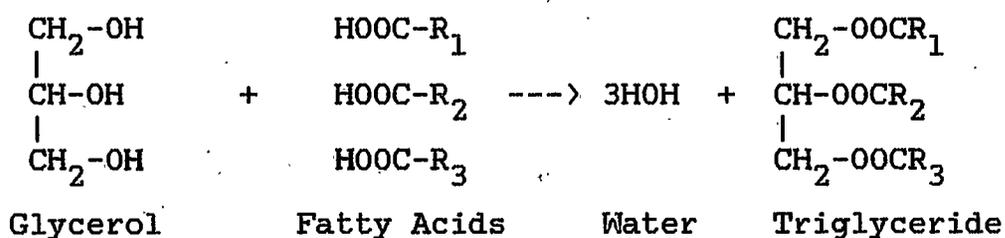
This research was conducted to characterize the role of copper catalyst in the polymerization of vegetable oil in a lubrication oil system. Specifically, the research sought to determine the dominant active form(s) of copper and clarify their function in the polymerization mechanism.

The interaction of the active copper forms with other system variables was also an object of this work. These variables included time of exposure, contact gas composition, and the presence and level of vegetable oil contamination.

A further goal was the identification of a suitable course for future research aimed at eliminating the catalytic effect of copper.

THEORYOxidative Polymerization

Vegetable oils are predominantly composed of triglycerides. Triglycerides are the common reference for glycerol esters of fatty acids. A vegetable oil triglyceride is approximately three times larger than a typical diesel fuel component with each constituent fatty acid roughly the same molecular weight as a typical diesel fuel molecule. While a diesel fuel is largely composed of straight and branched chain paraffins with some aromatics, vegetable oil is best described as a reaction product of glycerol and fatty acids [10].



Sunflower oil, the vegetable oil used in this investigation, characteristically has oleic, linoleic, and linolenic fatty acid structural components. These are 18 carbon fatty acids with one, two and three double bonds,

respectively. The actual ratio and composition of fatty acids in a particular oil can vary with climatic conditions, soil conditions, geographical location, plant maturity, and even location of the seed within the flower itself. Though genetics may be used to modify the extent of unsaturation, many factors that are not readily controllable affect fatty acid content.

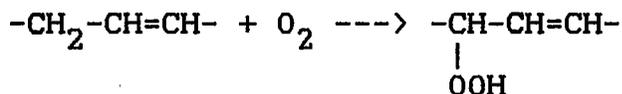
The unsaturated elements of sunflower oil can undergo autoxidation, the direct chemical attack by oxygen. Autoxidation with polyunsaturated vegetable oils, such as sunflower oil, frequently results in addition polymerization [10].

Rheimich and Austin [11] have given the major stages that occur during oxidative polymerization.

1. An induction period, preceeding the initiation of the oxidative chain reaction, during which no visible physical or chemical properties are changed. It is assumed that natural antioxidants are consumed during this induction period.
2. The interaction of oxygen with double bonds to form hydroperoxides. A considerable uptake of oxygen coincides with the beginning of a perceptible polymerization reaction.

3. A stage where polyunsaturates undergo conjugation of double bonds and isomerization of cis to trans forms.
4. Decomposition of hydroperoxides resulting in free radicals which in turn contribute to auto-catalysis.
5. Production of high molecular weight cross-linked polymers and low molecular weight carbonyl and hydroxyl compounds via polymerization and scission reactions.

The work of Rheimich and Austin was substantiated by Farmer and Sutton [12] who also demonstrated through product identification that an intact double bond exists alpha to the oxidation site. The reaction was proposed to be:

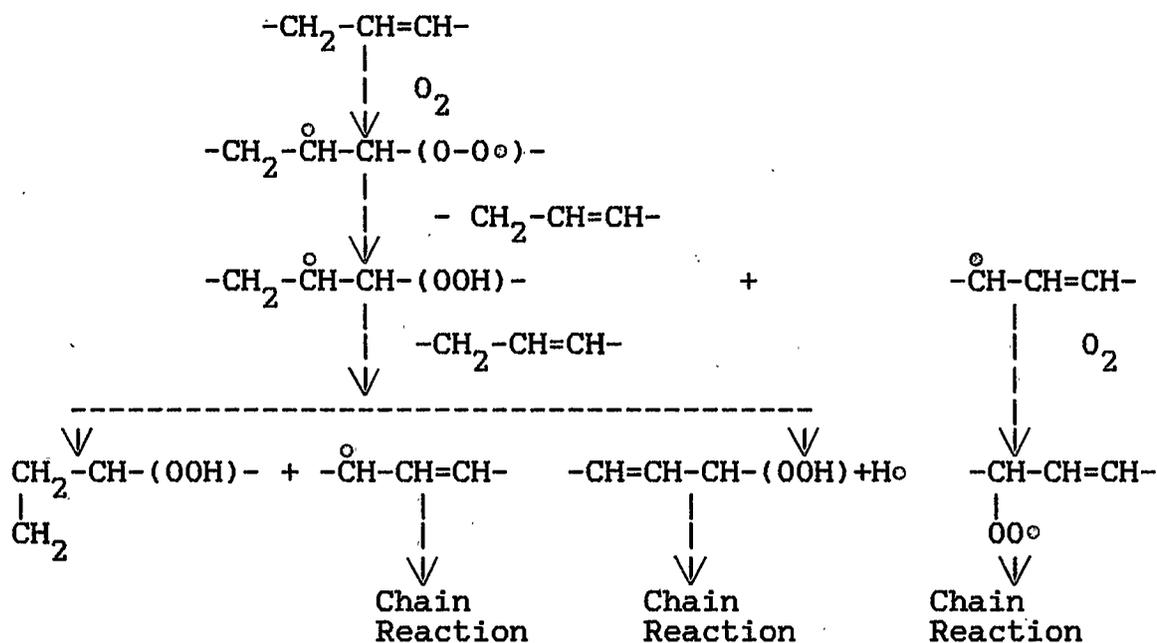


Bolland and Gee [13] established that substantial quantities of hydroperoxides were formed in the initial stages of autoxidation. The hydroperoxides were shown to be conjugated 90 percent of the time when linoleates were involved [14]. To produce the hydroperoxide by the above equation would require a source of energy to rupture the alpha-methylenic carbon-hydrogen bond. This bond, which has a strength of approximately 80 kcal/mole, can conceivably be

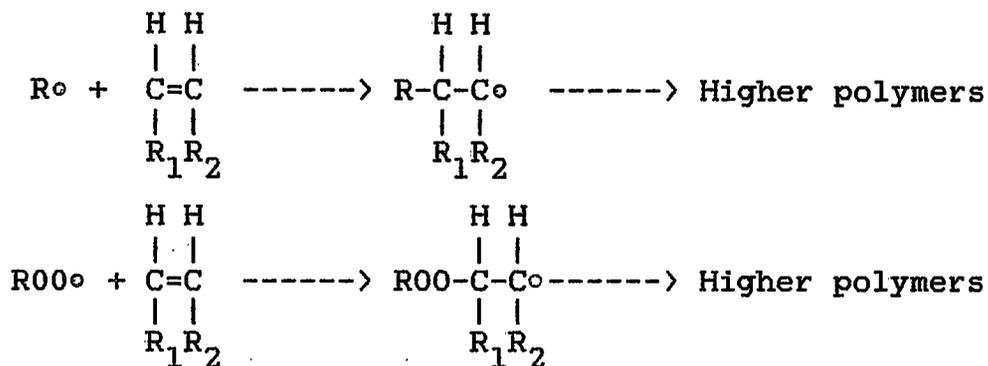
broken when hydrogen abstraction is performed via a free radical [15]. The high energy requirements would seem to indicate that free radical formation must precede hydroperoxide formation.

The purported formation of free radicals prior to the hydroperoxides prompted several investigators [16,17,18], almost simultaneously, to postulate that the initial oxidative attack occurred at the double bond and not alpha to the double bond. Bolland and Gee [16] proposed that a small quantity of diradical, formed by oxygen attack on the double bond, would be sufficient to initiate the chain reaction.

The reaction mechanism would then be described as follows [19].



As free radicals are formed, high molecular weight polymers may also be produced by an additional mechanism, vinyl polymerization:



Hydroperoxides, the main initial product generated by autoxidation, can react by other pathways when present as conjugated hydroperoxides of linoleate. Oxygenated products are saturated and unsaturated aldehydes, ketones, acids and other bifunctional oxygenated compounds. Though oleic constituents are less reactive, readily formed hydroperoxides of linolenic and linoleic constituents can catalyze the oxidation of oleic species. After the initial induction period, a considerable amount of polymerization can occur [10].

The initial attack at the double bond has low thermodynamic probability as argued by Uri [8]. However, trace metal contaminants such as copper may produce free radicals by electron transfer and thereby initiate

autoxidation. Thus, trace metal contaminants (or additives) and their radical-producing ability may become important factors in the mechanism of oxidative polymerization as discussed later in this review.

### Copper Metal

Copper is a transition metal and is the completing element in the first transition series of the periodic table. The first transition series contains elements that are progressively filling their third energy levels with electrons. Copper has a completely filled 3d shell and one 4s electron when in a neutral state. The ready availability of d electrons is responsible for the transition character of copper.

Transition metals, and hence copper, have three characteristic properties [20].

1. Unpaired electrons are readily elevated from d energy levels to higher energy levels by visible light. The unabsorbed light results in a characteristic color.
2. The high catalytic activity of transition metals is thought to be related to the ease by which electrons are gained, lost, or moved between shells.

3. Transition metals participate in the formation of coordination compounds. Coordination compounds are neutral compounds formed between a complex ion (transition metal here) and other ions or molecules.

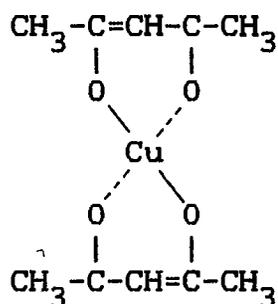
Most transition elements exhibit a number of oxidation states; copper is not an exception. Copper has three prevalent oxidation states  $\text{Cu}^{+1}$ ,  $\text{Cu}^{+2}$ , and  $\text{Cu}^{+3}$ . A fourth state,  $\text{Cu}^{+4}$ , is known in  $\text{Cs}_2\text{CuF}_6$  but is quite rare. Though  $\text{Cu}^{+2}$  is the most common oxidation state, it is usually difficult to predict from the electronic configuration of a transition element which is the most stable state [20,21].

The copper cation will readily form a complex ion with groups containing nitrogen and sulfur as donor atoms. Though copper does not react appreciably with  $\text{O}_2$  at room temperature, if exposed to higher temperatures, it will react to form copper oxide ( $\text{CuO}$ ).

The stereochemistry of copper compounds and its complexes can involve linear, planar, tetrahedral, square, diastereometric octahedral, octahedral, pentagonal bipyramidal, and diastereometric dodecahedron geometries. Brief descriptions of various geometries are given in inorganic texts by authors such as Cotton and Wilkinson [21,22]. These diverse geometries may be modified by the environment in which they are present [20-24].

The lubrication oil used in this research, Phillips HD II SAE 30, contains an additive package composed of detergents, antioxidants, surfactants and dispersants. The specific additive contents and their chemical nature are trade secrets and thus are unknown factors in this work. Chemical analyses revealed boron, magnesium, calcium, phosphorus and zinc present as additives in the lubrication oil. These metals are in complexes specific for their role in the lubrication oil. Copper introduced into the lubrication oil may be complexed by existing additives, the extent of which is unknown.

A well-known copper complex, cupric acetylacetonate, can be used to introduce a soluble copper form into a lubrication oil system. The general formula follows [23]:

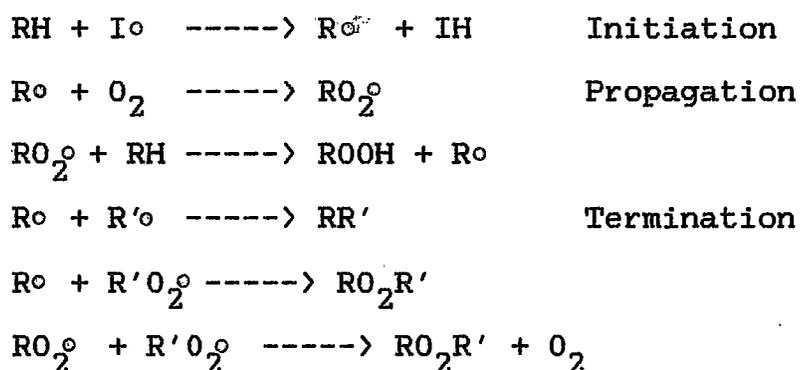


Acetylacetonates are relatively non-volatile and are soluble in most organic solvents. Cupric acetylacetonate also has the ability to complex additional molecules, simultaneously altering its coordination number [23]. The coordination number is the number of non-metal atoms surrounding the central metal ion or atom [20].

The coordination number modification allows the complexed copper to participate in the catalysis similar to metallic copper, as described in the following section.

### Copper Catalysis

Autoxidation addition polymerization is believed to occur via a free radical mechanism, as discussed earlier. A radical, represented by  $I^\circ$ , removes a hydrogen atom from a hydrocarbon producing a new radical which may undergo propagation or termination reactions. These polymerization steps are outlined below [8].

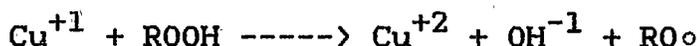


Vinyl polymerization using the  $R^\circ$  (triglyceride radical) may continue in the formation of higher polymers.

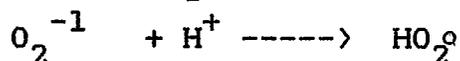
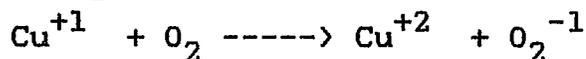
There is considerable agreement concerning the propagation and termination sequences; however, there is uncertainty as to the formation of the original free radical,  $I^\circ$ , necessary for the initiation [16].

The catalytic activity of copper, which can readily shift valence states in oxidation-reduction reactions, may involve several alternate pathways [8,10].

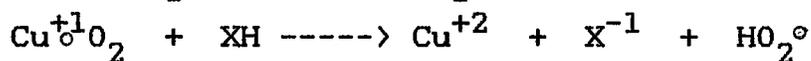
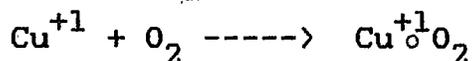
1. Trace hydroperoxides may shift the metal valences and produce free radicals.



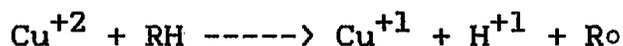
2. The oxygen and metal ion may react directly. The resulting  $\text{O}_2^{-1}$  then readily reacts with a proton to form  $\text{HO}_2^{\circ}$ .



3. A metal/oxygen complex may form which subsequently forms the  $\text{HO}_2^{\circ}$  radical.



4. Electron transfer to the metal ion may result in the oxidation of the alpha methylenic group.

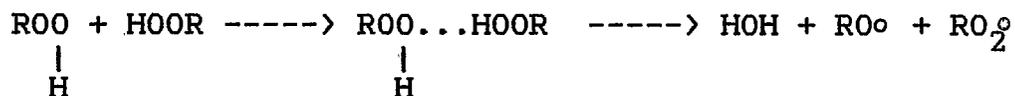


The radicals can initiate the chain reaction of auto-oxidation or the propagation step producing hydroperoxides. These hydroperoxides can rapidly decompose monomolecularly

or bimolecularly, substantially increasing the number of free radicals for initiation [10].



Monomolecular



Bimolecular

The copper is shown in ionic form. It may actually be a complexed ion at that respective oxidation state within the complex.

According to Uri, "the kinetic and thermodynamic probabilities for formation of free radicals by metal-catalyzed initiation reactions are considerably more favorable than the Bolland and Gee proposals of diradicals by direct oxidation of a double bond" [10].

## EXPERIMENTAL

### Equipment

The primary experiments in this research were conducted in a single cell reactor apparatus designed to minimize the impact of multiple sample removals and other inherent experimental error. It is referred to as a single cell because each run was completed using the contents of one cell, where in previous research [4] two to four cells of 50 ml samples were required. The single cell consisted of a 500 ml reaction kettle fitted with a four post entrance lid (Figure 1). Each entrance was 24/40 standard taper ground glass to insure gas-tight seals when greased.

The center lid opening and one side opening were fitted with Ace threads to provide airtight seals for entering and exiting gas tubes. The entering tube terminated with a 30 mm diameter glass frit. The glass frit was positioned in the bottom and center of the kettle to provide maximum gas-to-liquid contact. The exiting tube remained well above the oil surface providing a gas flow escape. The gas flow was then passed (via tygon tubing) to a soap film flow meter.

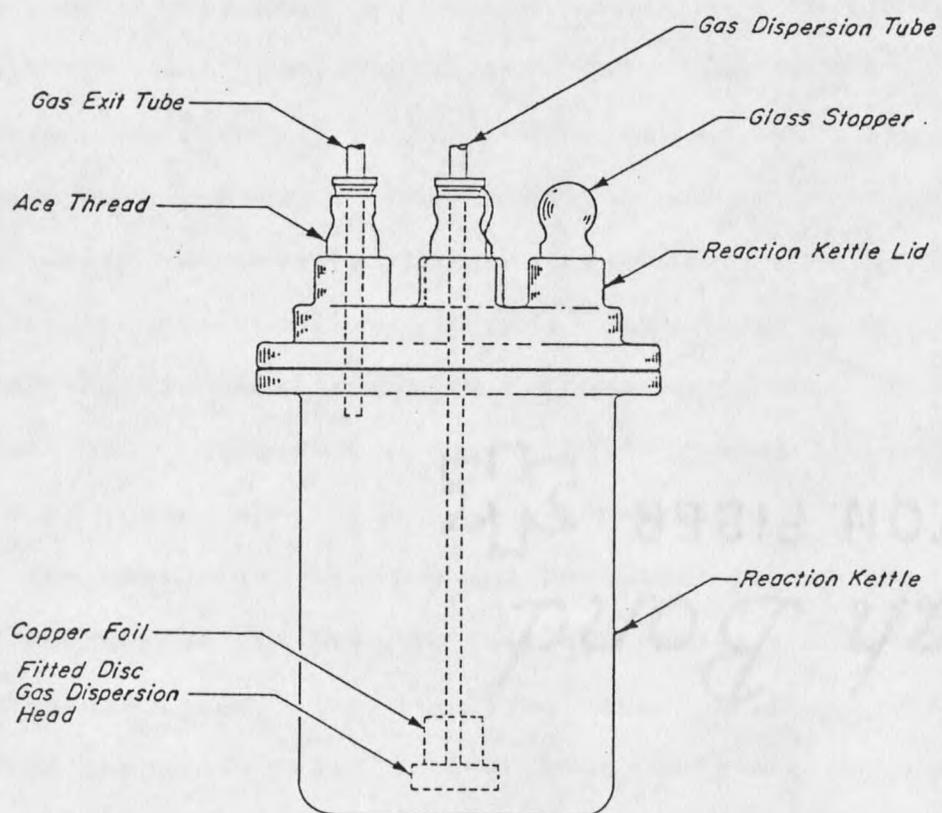


Figure 1. Single cell apparatus.

Thin copper foil, 0.125 mm thick, used as catalyst was cut in 5.0 cm lengths and rolled end-to-end. The resulting cylinder of copper was placed over the gas dispersion tube and supported by the fritted glass surface. This provided intimate gas, metal, and oil contact (Figure 1).

The reaction kettle was placed in an oil bath (Figure 2) capable of holding two test cells. The oil bath was maintained at a temperature of 150 C using a Polyscience Model 73 immersion circulator. The Polyscience Model 73 has automatic temperature control with a precision of 0.2 C and circulates approximately 13 liters of heating oil per minute. The oil bath was also fitted with a sheet metal cover and side panel insulation to minimize heat losses. The oil bath was situated in a venting hood to remove any noxious vapors.

Gas was provided via pressurized cylinders secured outside the hood. Nominal 1/4 inch stainless steel tubing was plumbed from the tank regulator to a four-position header equipped with a 0-30 psi pressure gauge. Two permanent headers were employed, one for nitrogen and one for oxygen. Tygon tubing was used to link a header position to a precision needle valve. The valve was connected by stainless steel tubing to a preheating coil submerged in the oil bath. Insulated teflon tubing was employed between the

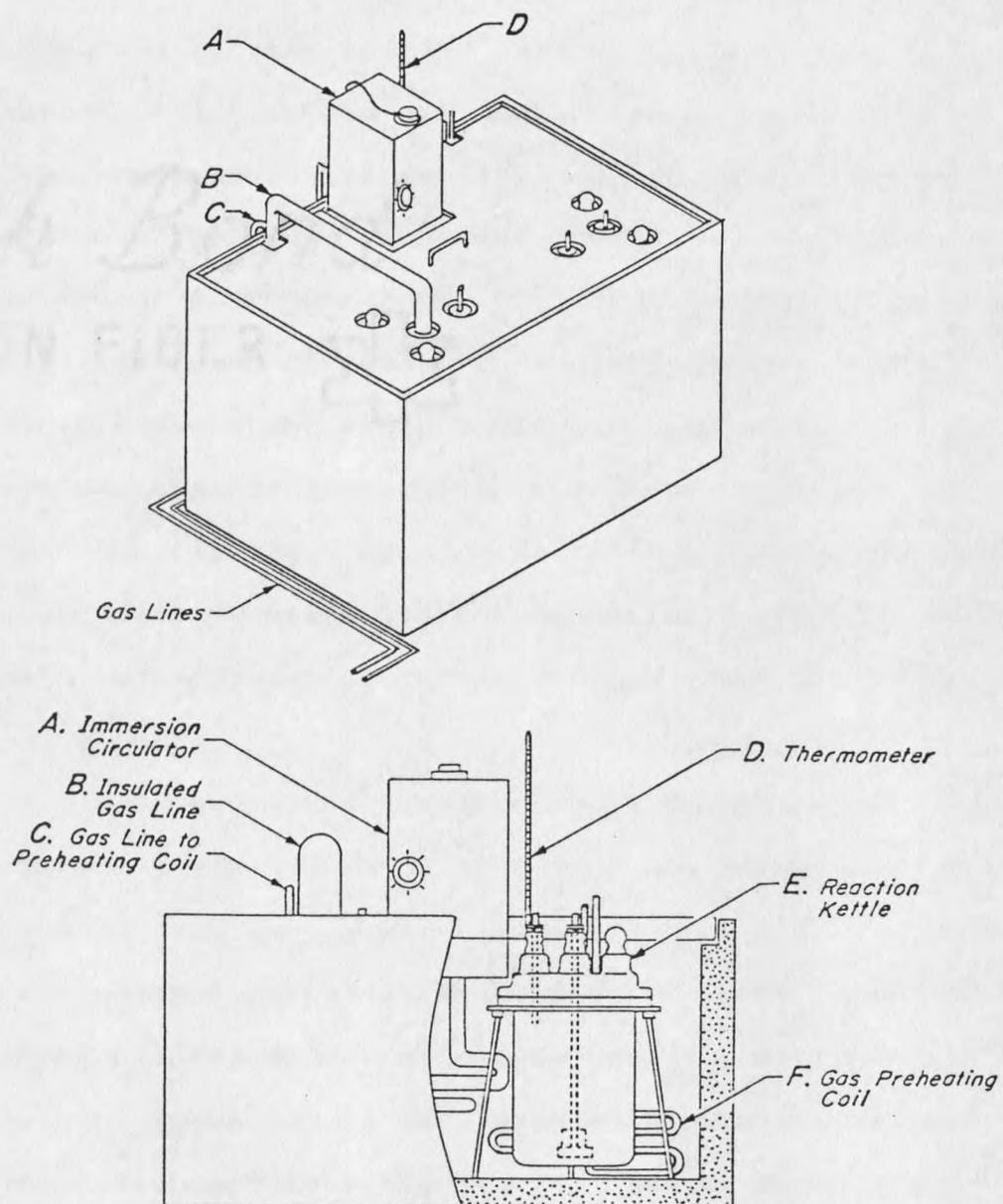


Figure 2. Oil bath.

preheating coil and the glass tubing of the fritted disc. An overall diagram of the tubing and control valves is illustrated in Figure 3.

Viscosity of lubrication oil samples was measured using calibrated serial 350 and 400 Cannon-Fenske viscometers capable of measuring 120-500 and 500-1200 centistokes, respectively. Viscometers were mounted in a water bath maintained at 40 C (within 0.2 C) by another Polyscience Model 73 immersion circulator.

Initial scouting experiments were conducted in a multi-cell apparatus as described by Chance Rewolisnki [4]. Samples were exposed as 50 ml aliquouts to 150 degree temperatures and 2,000 ml/hr gas flow. Procedures were followed according to Rewolsinki's work.

### Materials

The vegetable oil used throughout the research was sunflower mill oil from Continental Grain Company of Culbertson, Montana. It had an iodine value of 140. The sunflower oil was centrifuged, when necessary, at 5000 rpm for 20 minutes to remove visible solids left from mill processes. Lubrication oil was provided by Phillips under

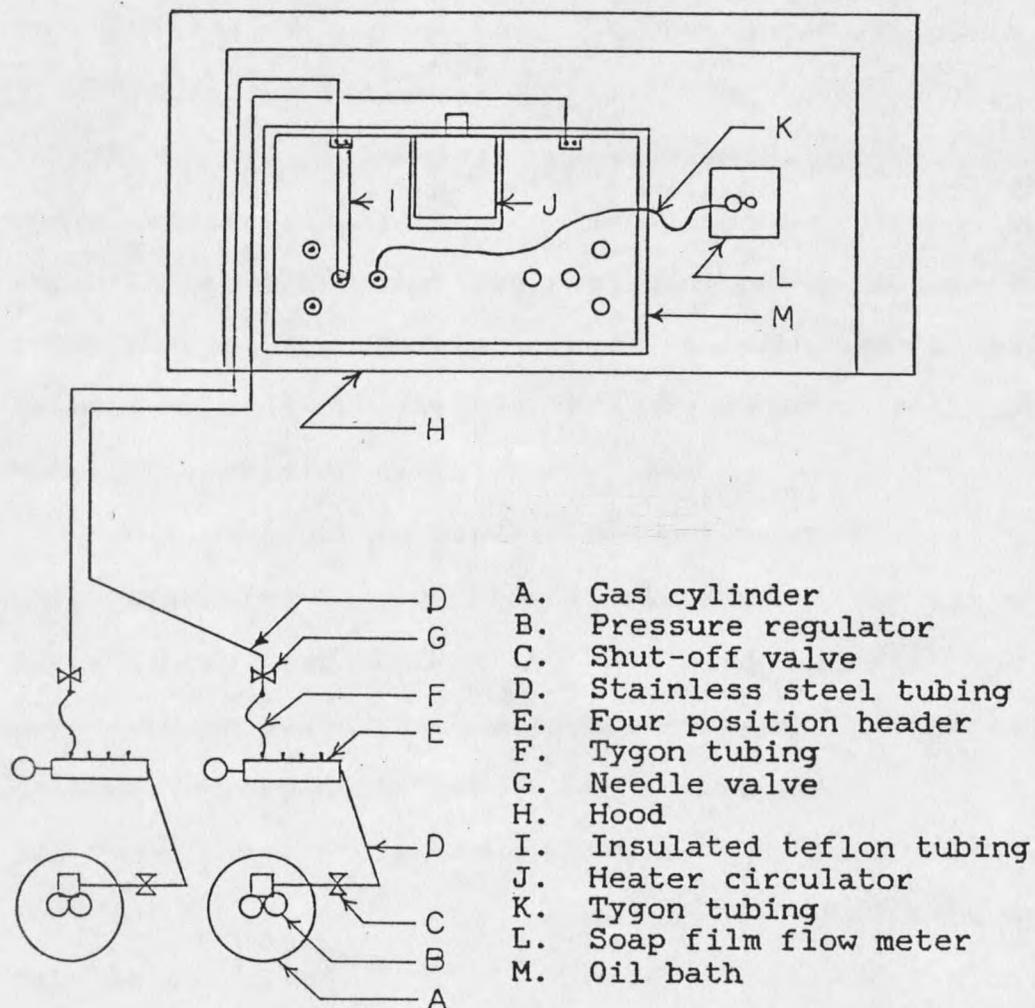


Figure 3. Operating diagram.

the label of Phillips Petroleum but was produced by Amoco Oil. The lubrication oil was produced at two separate refineries, but both met the requirements to be labeled as Phillips 66 HD II SAE 30. Copper catalyst was available as 0.125 mm thick foil or powdered forms of  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ , and cupric acetylacetonate. All powders were reagent grade. The free radical initiator, Lupersol 130, was provided by Lucidol Pennwalt Corporation of Buffalo, New York.

#### Experimental Procedures

Samples of lubrication oil contaminated with vegetable oil were placed in the 500 ml reaction kettle. The individual sample size was 500 ml of oil mixture. The reaction kettle was labeled as 500 ml but would actually accommodate 1,000 ml. This provided room for expansion and possible foaming of the mixture, thereby preventing overflow losses.

The 30 mm gas dispersion tube was centered in the bottom of the reaction kettle approximately 8.0 cm below the oil mixture surface. Copper foil was cut in 1 cm x 5 cm and 2 cm x 5 cm strips and formed into cylinders approximately 1.5 cm in diameter. The foil was then centered over the gas

entrance tube while supported by the fritted glass of the dispersion tube. When powdered copper compounds were used, the foil was not present. Powdered forms were thoroughly stirred into the oil mixture before sealing the reaction kettle.

The ground glass surfaces of the reaction kettle and lid flanges were then greased with Dow Corning high vacuum grease. The lid was placed over the reaction kettle with the stem of the gas dispersion tube protruding through the center opening. The lid was pressed and rotated to insure an air tight seal between reaction kettle and lid.

The four ground glass lid openings were also greased. Ace thread stoppers were used to provide an air tight seal around the stem of the gas dispersion tube and a 5.0 cm length of 1/4 inch stainless steel tubing was used as a gas exit. The remaining openings were sealed using ground glass stoppers.

The sealed reaction kettle containing the prepared sample was placed in an oil bath maintained at 150 C. The oil bath level was approximately one inch above the test mixture level to insure 150 C temperatures in the mixture.

The temperature of 150 C was chosen based on the assumption that a diesel engine crankcase operating temperature is approximately 150 C. This assumption is

supported by the Oldsmobile III D test [6]. This test evaluates an oil for its resistance to oxidative thickening at oil sump temperatures controlled at 150 C.

Immediately after immersion in the oil bath, the bath lid was positioned above the reaction kettle and the gas flow tube was attached to the stem of the gas dispersion tube. The gas flow was adjusted to 120 cm<sup>3</sup>/min as measured by a soap film flow meter adjacent to the oil bath. Gas percolation through the oil mixture sample was visually checked for problems of surging or excessive foaming.

Periodic samples were removed during each run. The time intervals between samples were dictated by the experiment being performed. One of the glass stopped ports was removed and 8 ml of the test mixture was pipetted from the test cell. The 8 ml sample was then transferred to a viscometer maintained at 40 C in the water bath. The 40 C temperature is used to evaluate excess viscosity rise in used motor oil as discussed in the Handbook of Lubrication [6]. Following the viscosity determination the sample was prepared for Total Base Number (TBN) titrations, returned to the reaction kettle, or discarded where appropriate.

TBN indicates the acid neutralization power of the lubrication oil. TBN values were determined potentiometricly using ASTM Standard D 2896-73 [6]. This is a back titration

method where excess standard  $\text{HClO}_4$  solution is added to a prepared sample. The excess is then back titrated with standard sodium acetate solution. This method is preferred for used motor oils because inflection points may be difficult to determine by other TBN procedures [25]. Iodine values are a relative indication of unsaturation present. These values were determined according to ASTM Standard 1959-69. This is the Wijs procedure for determination of unsaturation in drying oils. It is applicable to vegetable oils and their fatty acids [26].

## RESULTS AND DISCUSSION

The purpose of several initial experiments was to establish a set of baseline conditions which would yield at least a 375 percent increase in viscosity within sixty hours. These conditions would then be used as a standard for comparison when operating parameters were varied.

Preliminary studies related to this project were conducted by Chance Rewolinski [4]. The apparatus that Rewolinski used differed from that used in most of the current work. Rewolinski established standard conditions which gave a significant viscosity rise in less than sixty hours. A first goal of this work was to approximate Rewolinski's results, allowing for valid comparison between the differing apparatus. If comparable results were achieved, work could then continue from Rewolinski's base of experiments.

Figure 4 shows plots of oil mixture viscosity versus exposure time for Run 4 of the current work. The dashed line represents results at standard conditions for Rewolinski. These standard conditions were 150 C, 5.0 percent sunflower oil, 2000 ml/hr oxygen flow, and the presence of copper wire. Run 4 shows viscosity rising at a































































































