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

Abstract:
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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.

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by

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Stephen John Jette

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Date Chairperson, Graduate Committee

Approved for the Major Department

Dec. 23, 1985 John T. Sears
Date Head, Major Department

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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.

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.

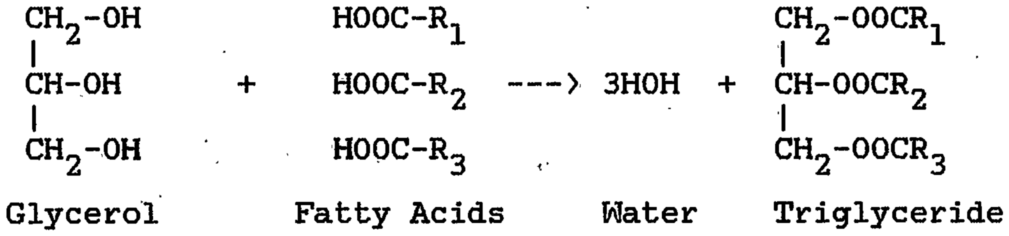
The interaction of the active copper forms with other system variables was also an object of this work. These variables included time of exposure, contact gas composition, and the presence and level of vegetable oil contamination.

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

THEORY

Oxidative Polymerization

Vegetable oils are predominantly composed of triglycerides. Triglycerides are the common reference for glyceral 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].



$$\begin{array}{lclclcl} CH_2\text{-}OH & & HOOC\text{-}R_1 & & & & CH_2\text{-}OOCR_1 \\ | & & & & & & | \\ CH\text{-}OH & + & HOOC\text{-}R_2 & \text{--->} & 3HOH & + & CH\text{-}OOCR_2 \\ | & & & & & & | \\ CH_2\text{-}OH & & HOOC\text{-}R_3 & & & & CH_2\text{-}OOCR_3 \\ \text{Glycerol} & & \text{Fatty Acids} & & \text{Water} & & \text{Triglyceride} \end{array}$$

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.

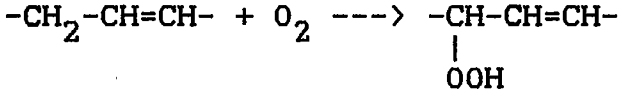
The unsaturated elements of sunflower oil can undergo autoxidation, the direct chemical attack by oxygen. Autoxidation with polyunsaturated vegetable oils, such as sunflower oil, frequently results in addition polymerization [10].

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:

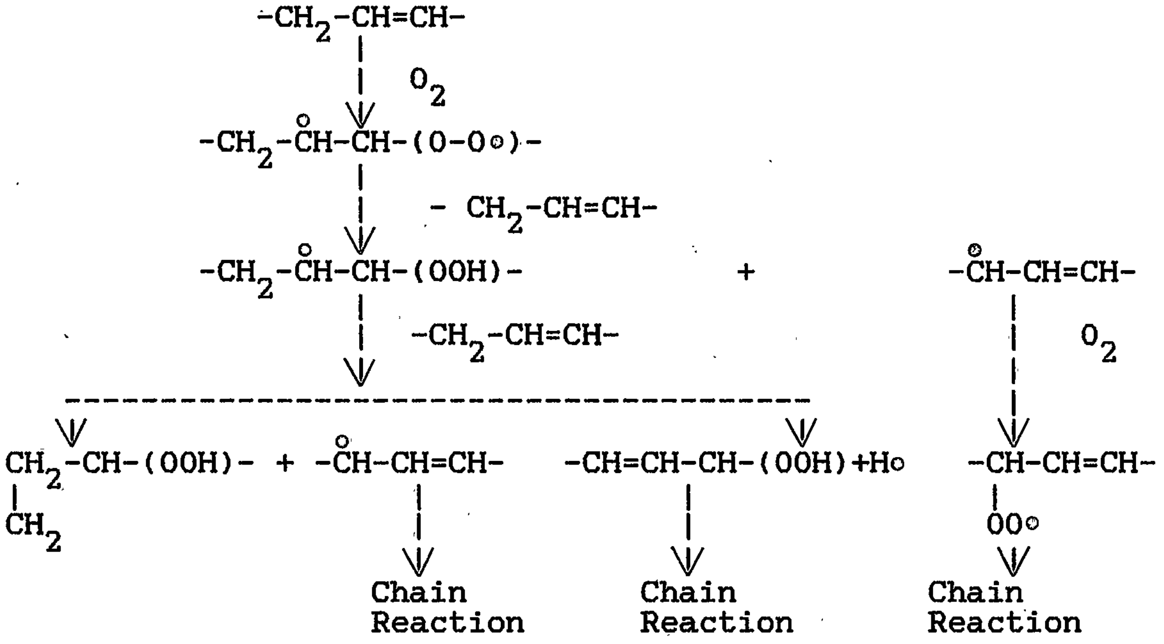


$$-CH_2-CH{=}CH- + O_2 \longrightarrow -\underset{\displaystyle OOH}{\underset{|}{CH}}-CH{=}CH-$$

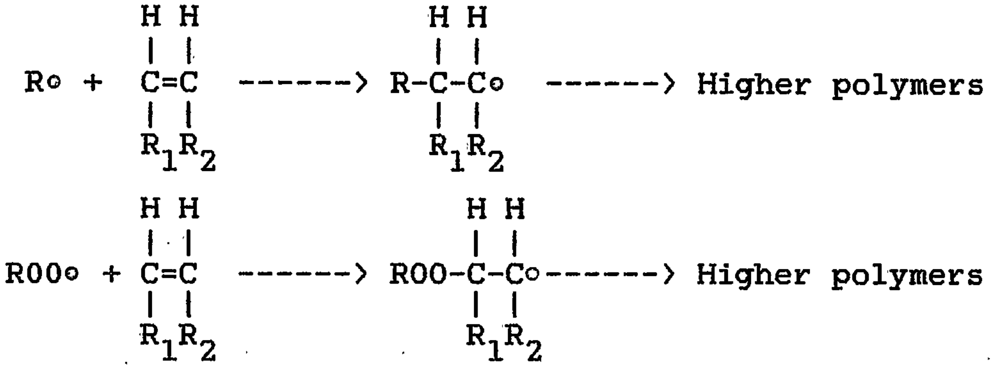
Bolland and Gee [13] established that substantial quantities of hydroperoxides were formed in the initial stages of autoxidation. The hydroperoxides were shown to be conjugated 90 percent of the time when linoleates were involved [14]. To produce the hydroperoxide by the above equation would require 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:



$$R\circ + \underset{R_1\,R_2}{\overset{H\ H}{C{=}C}} \longrightarrow R{-}\underset{R_1\,R_2}{\overset{H\ H}{C{-}C}}\circ \longrightarrow \text{Higher polymers}$$

$$ROO\circ + \underset{R_1\,R_2}{\overset{H\ H}{C{=}C}} \longrightarrow ROO{-}\underset{R_1\,R_2}{\overset{H\ H}{C{-}C}}\circ \longrightarrow \text{Higher polymers}$$

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.

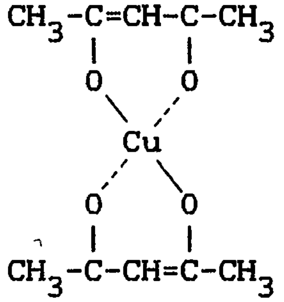
Most transition elements exhibit a number of oxidation states; copper is not an exception. Copper has three prevalent oxidation states Cu^{+1}, Cu^{+2}, and Cu^{+3}. A fourth state, Cu^{+4}, is known in Cs_2CuF_6 but is quite rare. Though Cu^{+2} is the most common oxidation state, it is usually difficult 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 O_2 at room temperature, if exposed to higher temperatures, it will react to form copper oxide (CuO).

The stereochemistry of copper compounds and its complexes can involve linear, planar, tetrahedral, square, diastereometric octahedral, octahedral, pentagonal bi-pyramidal, 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 dispersents. 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°, 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].

$RH + I^{\circ}$ -----> $R^{\circ} + IH$ Initiation

$R^{\circ} + O_2$ -----> RO_2° Propagation

$RO_2^{\circ} + RH$ -----> $ROOH + R^{\circ}$

$R^{\circ} + R'^{\circ}$ -----> RR' Termination

$R^{\circ} + R'O_2^{\circ}$ -----> RO_2R'

$RO_2^{\circ} + R'O_2^{\circ}$ -----> $RO_2R' + O_2$

Vinyl polymerization using the R° (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°, 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 valances and produce free radicals.

   $Cu^{+1} + ROOH \text{ -----> } Cu^{+2} + OH^{-1} + RO\circ$

2. The oxygen and metal ion may react directly. The resulting O_2^{-1} then readily reacts with a proton to form HO_2°.

   $Cu^{+1} + O_2 \text{ -----> } Cu^{+2} + O_2^{-1}$

   $O_2^{-1} + H^{+} \text{ -----> } HO_2^{\circ}$

3. A metal/oxygen complex may form which subsequently forms the HO_2° radical.

   $Cu^{+1} + O_2 \text{ -----> } Cu^{+1}\circ O_2$

   $Cu^{+1}\circ O_2 + XH \text{ -----> } Cu^{+2} + X^{-1} + HO_2^{\circ}$

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

   $Cu^{+2} + RH \text{ -----> } Cu^{+1} + H^{+1} + R\circ$

The radicals can initiate the chain reaction of autoxidation or the propagation step producing hydroperoxides. These hydroperoxides can rapidly decompose monomolecularly or bimolecularly, substantially increasing the number of free radicals for initiation [10].

$$ROOH \text{-----}\!> RO^{\circ} + HO^{\circ}$$

Monomolecular

$$\underset{\displaystyle H}{\underset{|}{ROO}} + HOOR \text{-----}\!> \underset{\displaystyle H}{\underset{|}{ROO}}...HOOR \text{-----}\!> HOH + RO^{\circ} + RO_2^{\circ}$$

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.

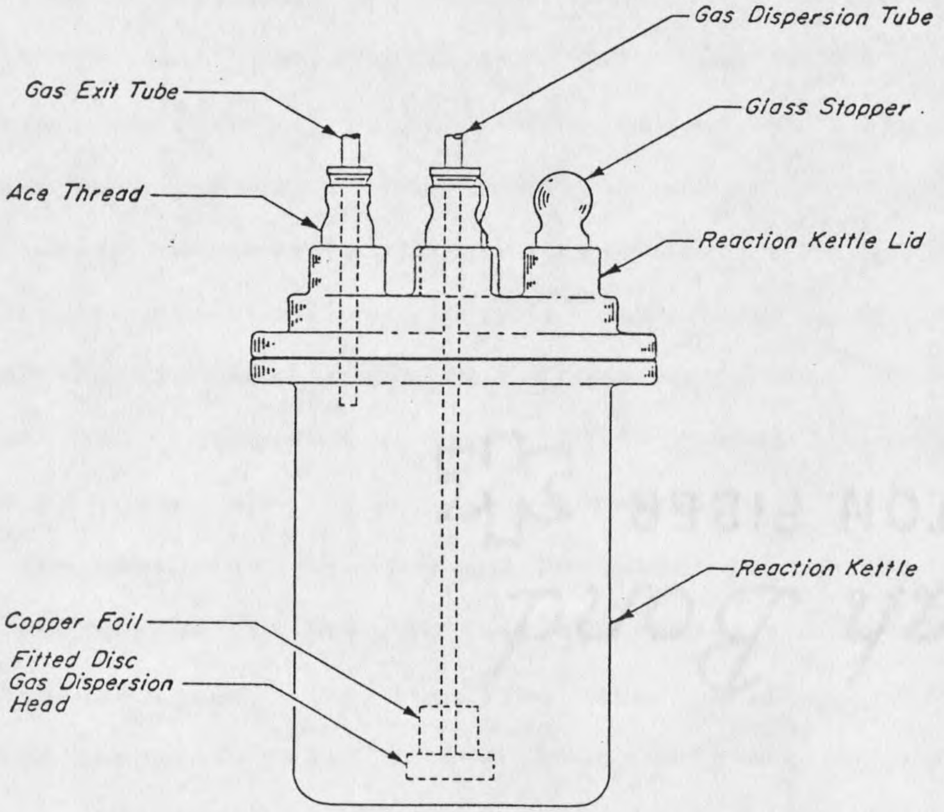


Figure 1. Single cell apparatus.

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

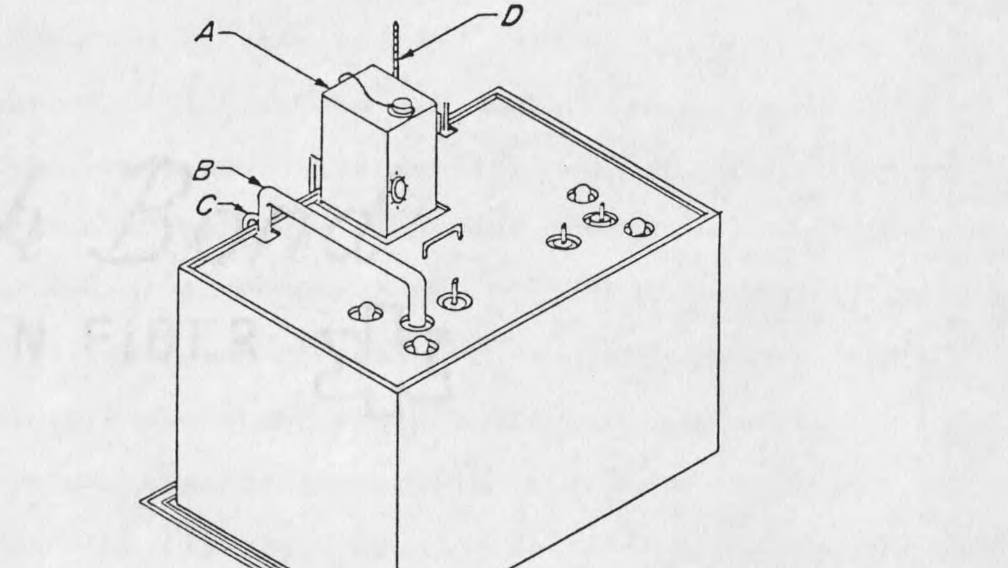


Figure 2. Oil bath.

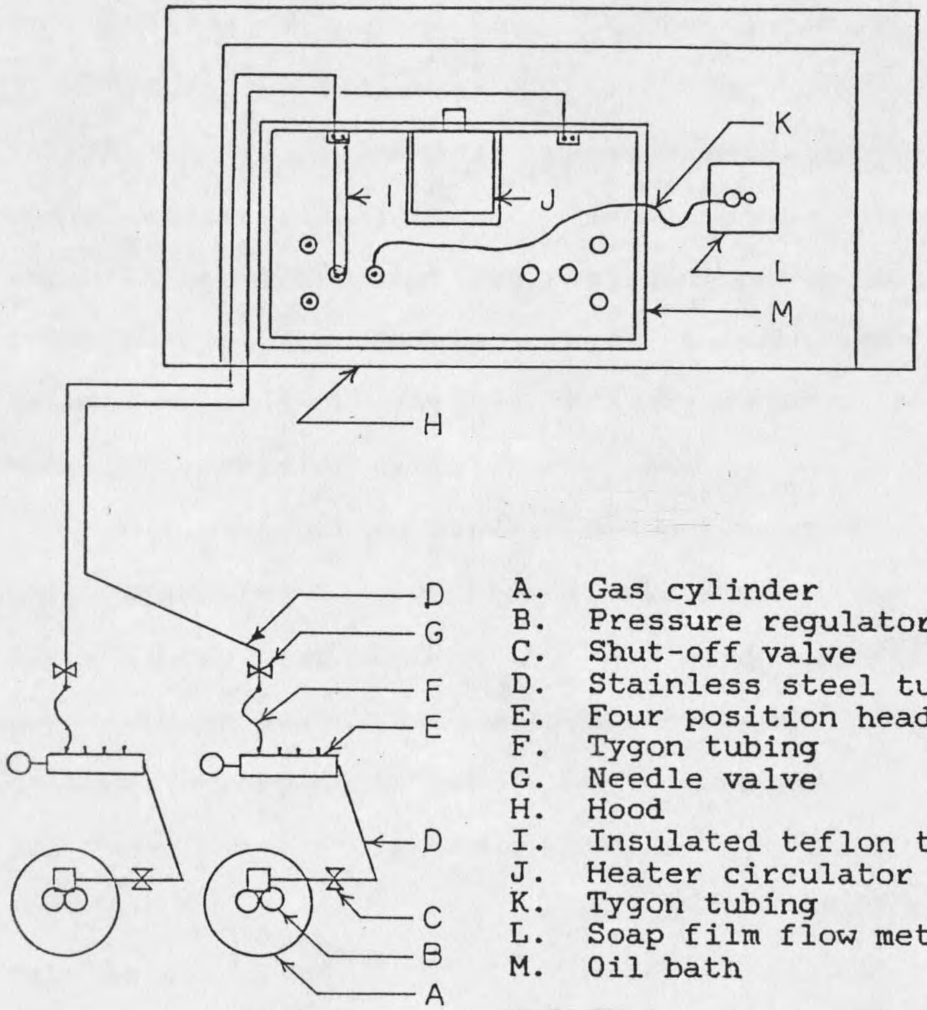
preheating coil and the glass tubing of the fritted disc. An overall diagram of the tubing and control valves is illustrated in Figure 3.

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



A. Gas cylinder
B. Pressure regulator
C. Shut-off valve
D. Stainless steel tubing
E. Four position header
F. Tygon tubing
G. Needle valve
H. Hood
I. Insulated teflon tubing
J. Heater circulator
K. Tygon tubing
L. Soap film flow meter
M. Oil bath

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 Cu_2O, 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^3/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 $HClO_4$ 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

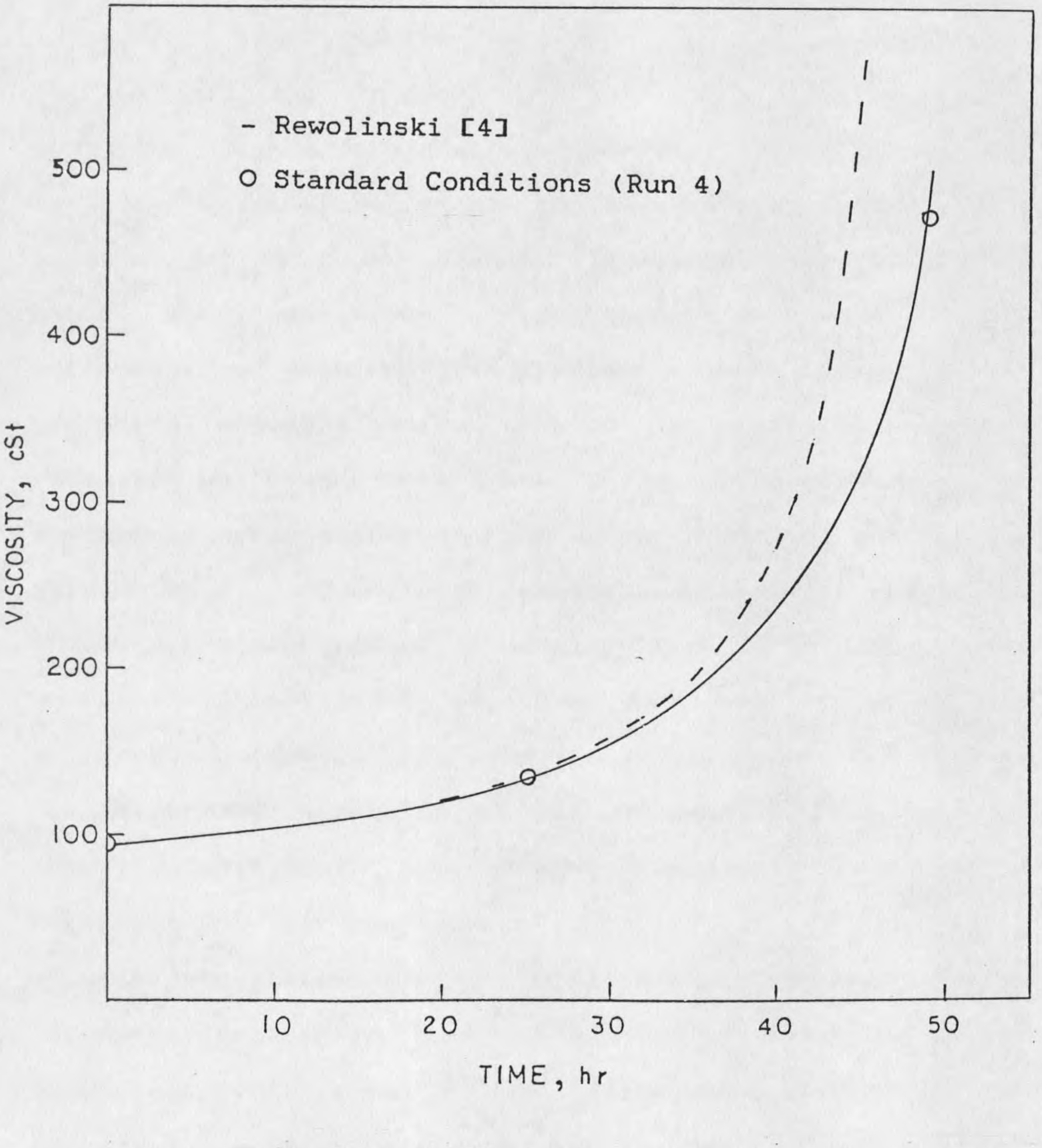


Figure 4. Viscosity versus exposure time for standard conditions of Rewolinski [4] and the current work.

comparable rate to Rewolinski's standard conditions though it was performed in the new single cell apparatus. The conditions of Run 4 were therefore selected for standard conditions in the single cell apparatus. These conditions were 500 ml sample, 5.0 percent sunflower oil, 120 cc/min oxygen flow, 150 C, and 2 cm x 5 cm of copper foil using Phillips HD II SAE 30.

Previous research demonstrated that an increase in copper surface area would increase the rate of viscosity rise. It was also established that an increase in vegetable oil concentration would yield an increase in the rate of rise. These results were also verified in early runs in the single cell apparatus.

Results of Runs 1, 2, 3 and standard conditions (Run 4) are given in Figure 5. Run 1 had no copper, Run 2 had 1 cm x 5 cm copper foil and Run 3 had 2 cm x 5 cm copper foil. Runs 2 and 3 had 4.7 percent sunflower oil instead of the target level of 5.0 percent. This was due to a calculational error which was eliminated in subsequent runs. All four runs used oxygen at 120 cc/min. Standard conditions are shown as a dashed line and will be presented as such in future figures when referenced.

Two trends are evident in Figure 5. The runs containing the same copper levels, 3 and 4, confirm that an

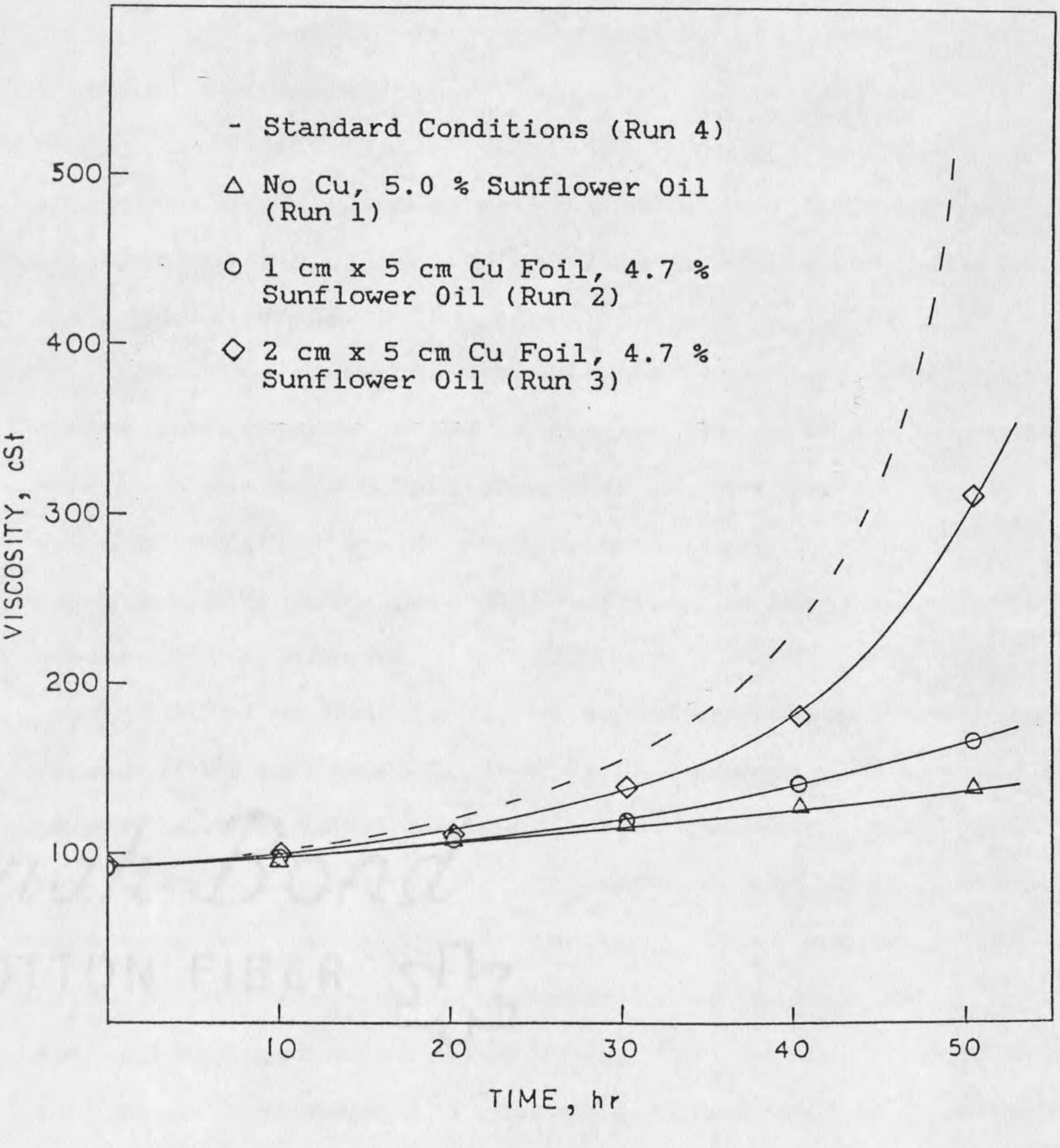


Figure 5. Viscosity versus exposure time for varying copper surface and sunflower oil concentration.

increase in vegetable oil increases rate of polymerization. Run 4 contained 5.0 percent sunflower oil while Run 3 contained 4.7 percent. This is consistent with earlier research by Rewolinski.

The second trend is of greater relative importance to the object of this research. Runs 1, 2, and 3 demonstrate that increased copper surface results in a rise in polymerization rate. The copper surface could be serving as a site for the actual reaction, or the surface could be a source of catalytic metal species migrating into the bulk oil mixture. If the former is true, then the reduction of polymerization might begin with reducing active surface area or permanently coating such surfaces. This appears to be infeasible based on current engine designs. However, if the surface is acting as a source of soluble metal species, another preventive measure may be available. Soluble metal species may be rendered inactive by an oil additive selective for these species. The presence of the copper surface is important. However, the exact role of the surface needs clarifying.

Run 6 was conducted to see if it was necessary to have copper surface present following the onset of viscosity rise. At eighteen hours, the viscosity had increased approximately 30 percent at the standard conditions. At

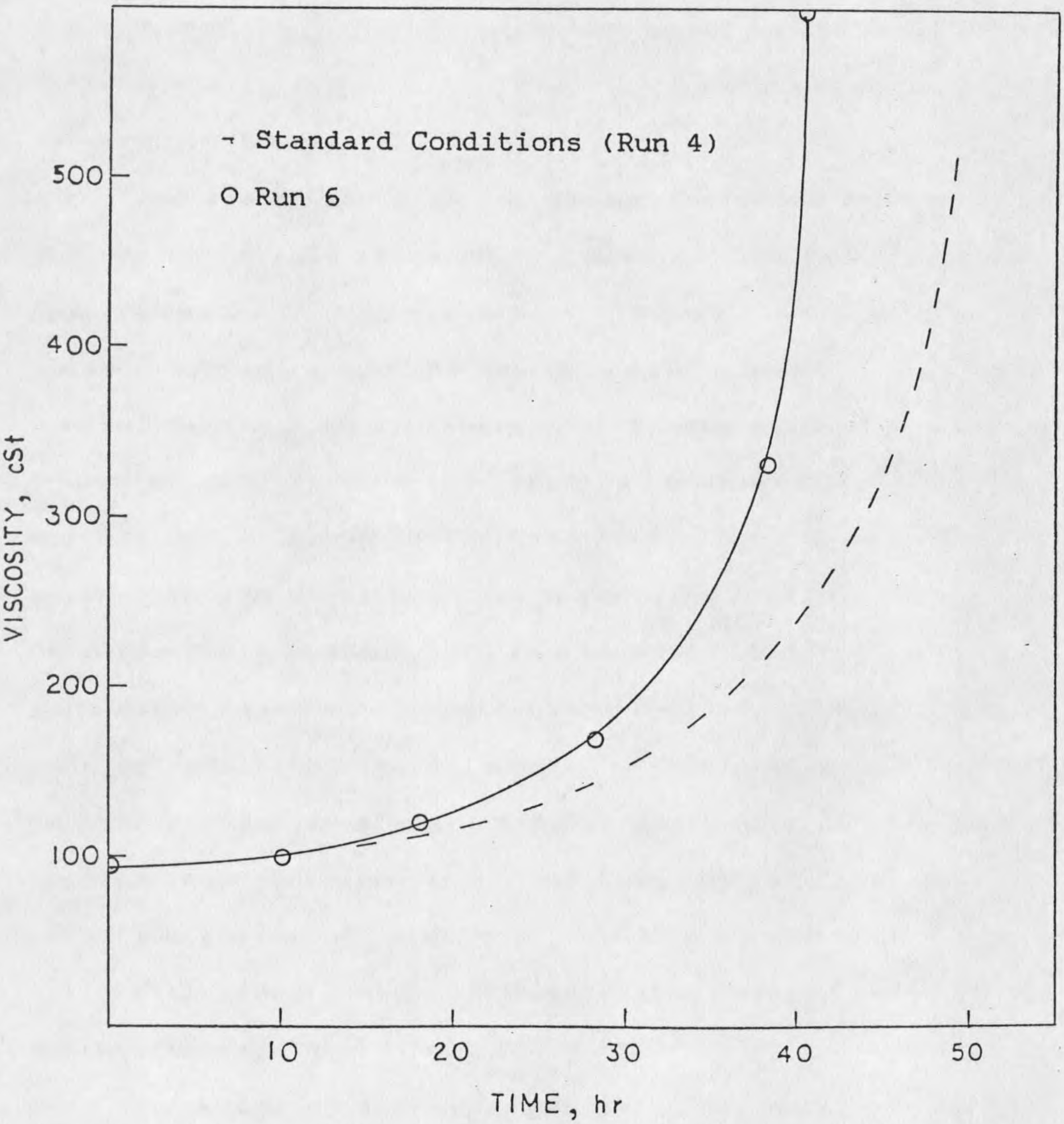


Figure 6. Viscosity versus exposure time with copper foil removal at 18 hours.

this point, the copper foil was removed. Figure 6 shows Run 6 in comparison to the standard conditions. The important feature is the fact that viscosity increase continued even after the removal of copper foil. This indicates that copper surface may be necessary for initiating the polymerization, or the surface may have released sufficient copper species to catalyze the reaction. It was felt that these differing speculations might be resolved if a metal content analysis was performed on the oil mixture.

Oil samples at the beginning and completion for Run 6 were analyzed by atomic emission (AE). Atomic emission tests were conducted by Case Lubricant Analysis Service in Indianapolis, Indiana. This service uses a non-flame atomization technique where the sample is volatilized by means of two electrically heated graphite plates. Accuracy of the results is within about 20 percent. The results in Table I represent the oil mixture before the copper foil was added and at 48 hours,the completion of Run 6.

The rise in copper content in the oil mixture supports the speculation that copper is migrating from the surface into the mixture but does not prove that surface catalysis is not involved.

Run No.	Time of Sample	Copper Level
6	0.0 hour	0.0 ppm
6	48.0 hour	2.0 ppm

Table I. Atomic emission results for Run 6.

The viscosity rise in Run 6 was actually somewhat higher than standard conditions. The oil mixture used in Run 6 was taken from a larger batch mixed for two runs. It is conceivable that the mixing of vegetable oil in the lubrication oil was incomplete, resulting in a vegetable oil variation in the batch mixture. Hence, the resulting level of vegetable oil contamination may have been slightly greater than the desired 5.0 percent. Future runs were all conducted using single batch mixtures to avoid this potential problem.

Having established that the copper foil need not be present to sustain the viscosity rise, it was necessary to begin using a second sample of Phillips 66 HD II SAE 30, referred to as new Phillips 66. The original, or first sample, was exhausted in Runs 1 through 6 and earlier scouting trials.

Atomic emission data indicated the additive metals differed substantially between the two samples of Phillips 66 (Table VI in Appendix). This difference was confirmed by contacting the technical representative for Amoco who had supplied the two samples.

The samples had been shipped from two separate sources. One was from a Wyoming refinery, the other from an Oklahoma refinery. Each of these refineries used a different additive package based on its source of crude oil. Though the packages were different, the oils met the same engine specifications for operation. Based on these findings, the standard conditions were repeated using the second sample of Phillips 66.

Figure 7 shows that viscosity rise in Run 7, standard conditions and new Phillips 66, varied significantly from standard conditions using the original Phillips 66 (Run 4). The viscosity rise in Run 7 occurred much more quickly than expected. Identical conditions were repeated in Run 8 to obtain more data points and confirm the results of Run 7. A comparison of Runs 7 and 8 shows there is some inherent variability in viscosity rise, but the disparities between Runs 4 and 7 and Runs 4 and 8 are well beyond this range of variability. It was concluded that the additive packages themselves were the primary contributing factors in the

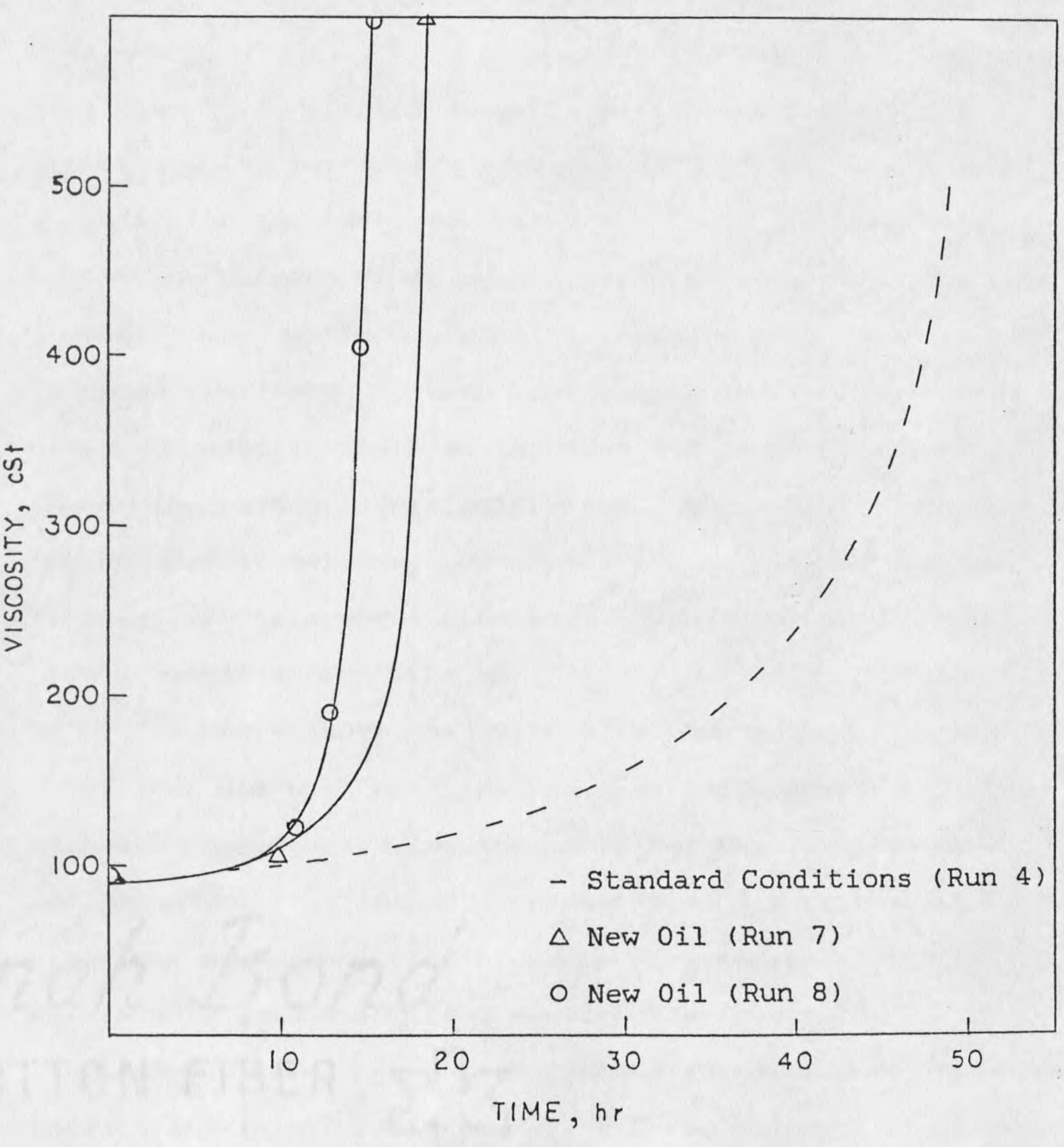


Figure 7. Viscosity versus exposure time for two samples of Phillips 66 HD SAE 30 at standard conditions.

differences between new and original standard condition results.

The fact that atomic emission spectra revealed different quantities of additive metals may tempt the reader to draw conclusions concerning the efficacy of individual additive metal compounds on copper activity. However, as pointed out by the Amoco technical representative and various literature references [32,33], the coordinated complex forms as well as other organometallics (unidentifiable by our means) can act differently under different circumstances. The additive metals may be present in more than one complex form. Also, the additive metal that is varying may not be the actual causal factor. A metal that appears to be constant in amount may vary greatly in activity based on a difference in complex form. The Amoco representative would not specify the metal forms present nor indicate the intended action of each. Speculation concerning lube oil additive metal activity was therefore left for future research efforts.

Experiments were continued using the new Phillips 66. A new standard as determined by Runs 7 and 8 was thus used for comparison in further experiments.

The next objective was to confirm that copper was being solubilized, perhaps as catalytically active species. Run 9 was conducted by initially using nitrogen as the

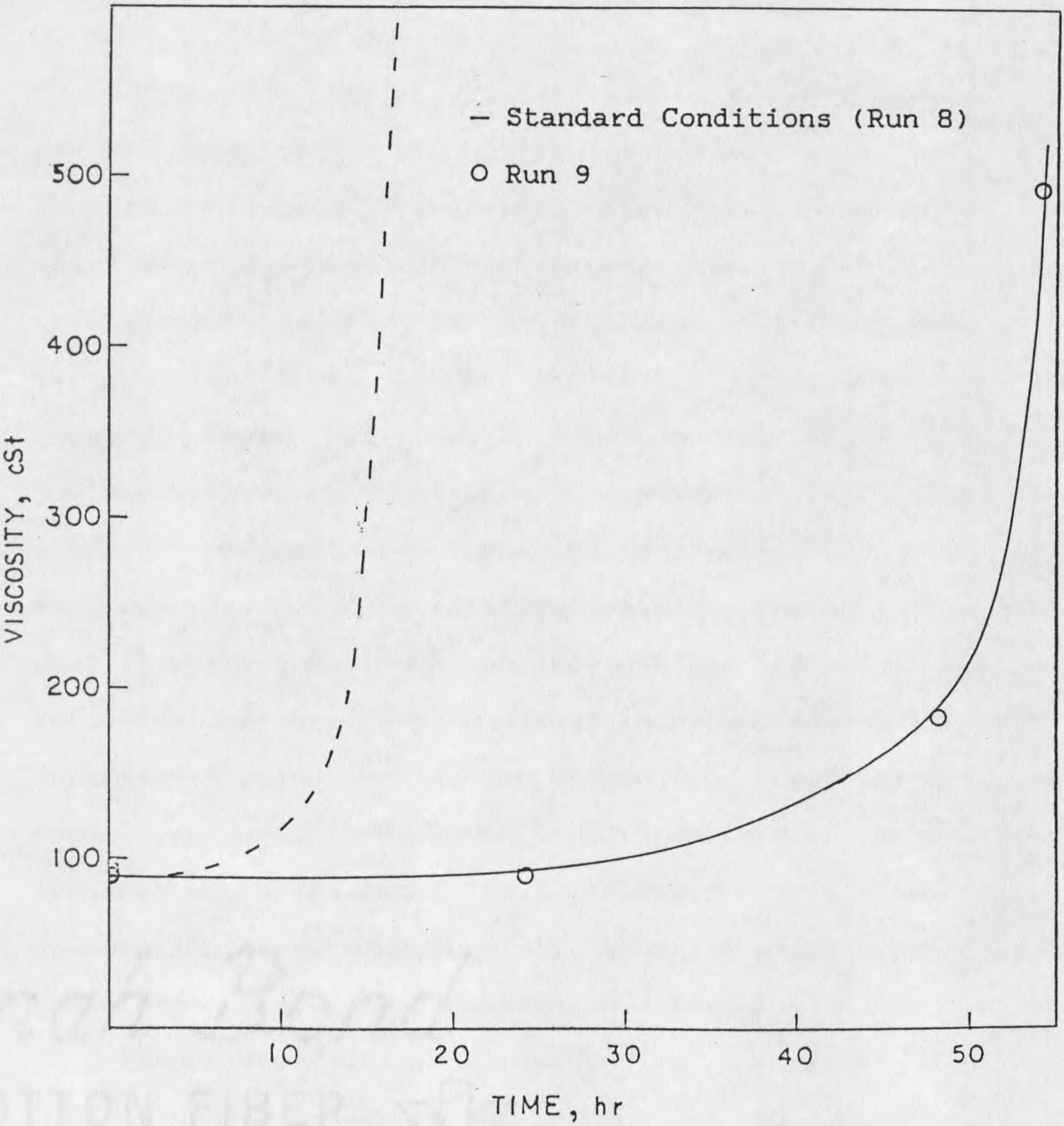


Figure 8. Viscosity versus exposure time with copper foil removal and nitrogen gas changed to oxygen at 24 hours.

agitating gas, otherwise using standard conditions of 5.0 percent sunflower oil and 2 cm x 5 cm copper foil. After running the experiment for 24 hours, the copper foil was removed and the nitrogen gas changed to oxygen. Figure 8 shows the resulting viscosity rise.

The results of Run 9 allow three important conclusions to be drawn. First oxygen is clearly necessary for any appreciable plant oil polymerization as demonstrated in earlier work [4]. If oxygen were unnecessary, polymerization would have occurred within 15 hours as with standard conditions. Secondly, copper surface (as foil) need not be present for polymerization initiation as long as the oil mixture has been exposed to copper foil. This would indicate that the copper is dissolving and is active in the dissolved form. The third point is that, if copper is dissolving, it will dissolve with or without oxygen present. The copper that is dissolved in the presence of nitrogen, however, may only become active upon exposure to oxygen. Thus oxygen may be necessary to convert dissolved copper into a catalytically active state.

As discussed previously oxygen and copper can react to form free radicals. Run 9 supports the idea that copper ion participates in an oxidation-reduction reaction involving oxygen as the electron acceptor. Atomic emission data indicated a rise in copper content from 0.0 ppm to 2.0 ppm at the point of copper foil removal. This shows copper is taken into solution but that oxygen is necessary to begin polymerization. This supports the assumption that copper and oxygen are primarily responsible for forming the original free radicals necessary for initiation.

At this point the possibility existed that the vegetable oil was a causal factor in the copper solubilization. A series of experiments was designed to help clarify the impact of vegetable oil presence on phenomena incidental to actual polymerization. These experiments were also used to further verify the catalytic form of the copper.

The experiments in the following series have in common the fact that sunflower oil was not introduced into the lubrication oil until 48.5 hours after the reactor cell containing the lube oil had been placed in the 150 C oil bath. This pretreatment time period was well beyond the time required for significant viscosity rise under standard conditions. Thermal exposure is eliminated as a contributing factor in any predisposition of vegetable oil to addition polymerization in these experiments. Also, the vegetable oil is not present to aid in the copper solubilization nor is the vegetable oil being exposed to the copper surface (foil).

Each run began with 500 ml of uncontaminated lubricating oil. The lubricating oil was placed in the test cell and the appropriate catalyst added. The gas flow was initially either nitrogen or oxygen. At the completion of 48.5 hours in the hot oil bath a 5.0 percent contamination of sunflower oil was added to the lubrication oil. This was accomplished without removing the cell from the oil bath. In certain experiments copper foil was removed just before the addition of the sunflower oil. The gas flow was never interrupted for longer than 5 minutes during these adjustments. If nitrogen was the initial gas, this was changed to oxygen immediately following the vegetable oil addition.

The first run in this series, Run 10, was performed using new Phillips 66, 2 cm x 5 cm copper foil, and the gas was oxygen for the entire run. The copper foil was removed at 48.5 hours and a 5.0 percent level of sunflower oil was added. The plot of Run 10 is given in Figure 9. The 48.5 hours without sunflower oil shows a slight increase in viscosity, 31 centistokes, which is negligible in comparison with the viscosity rise for contaminated oil. Several hours after the sunflower oil addition a significant rise begins, exceeding 375 percent within 18 hours.

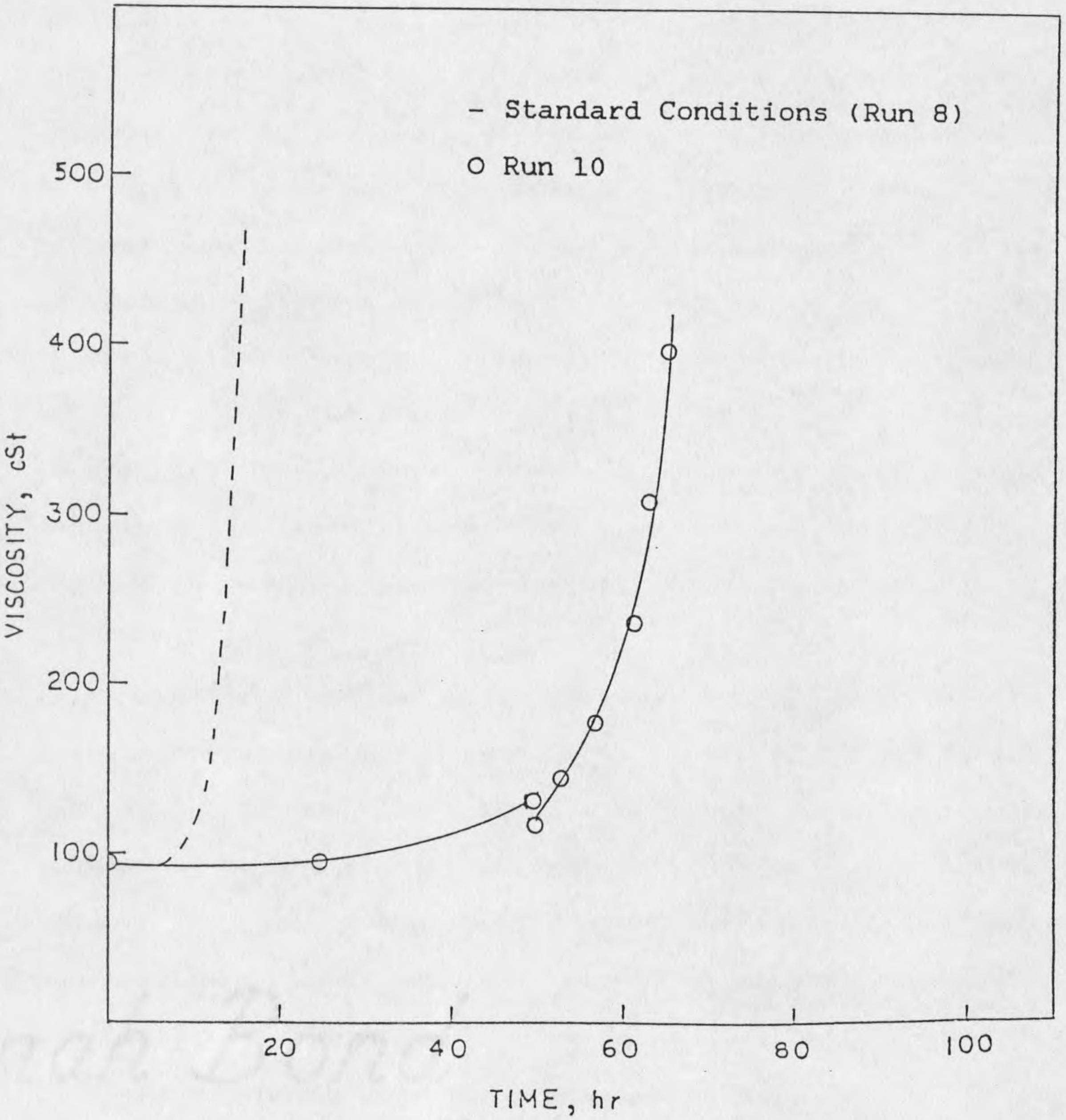


Figure 9. Viscosity versus exposure time with oxygen and copper foil for initial 48.5 hours. Copper foil removed and 5.0 percent sunflower oil addition at 48.5 hours.

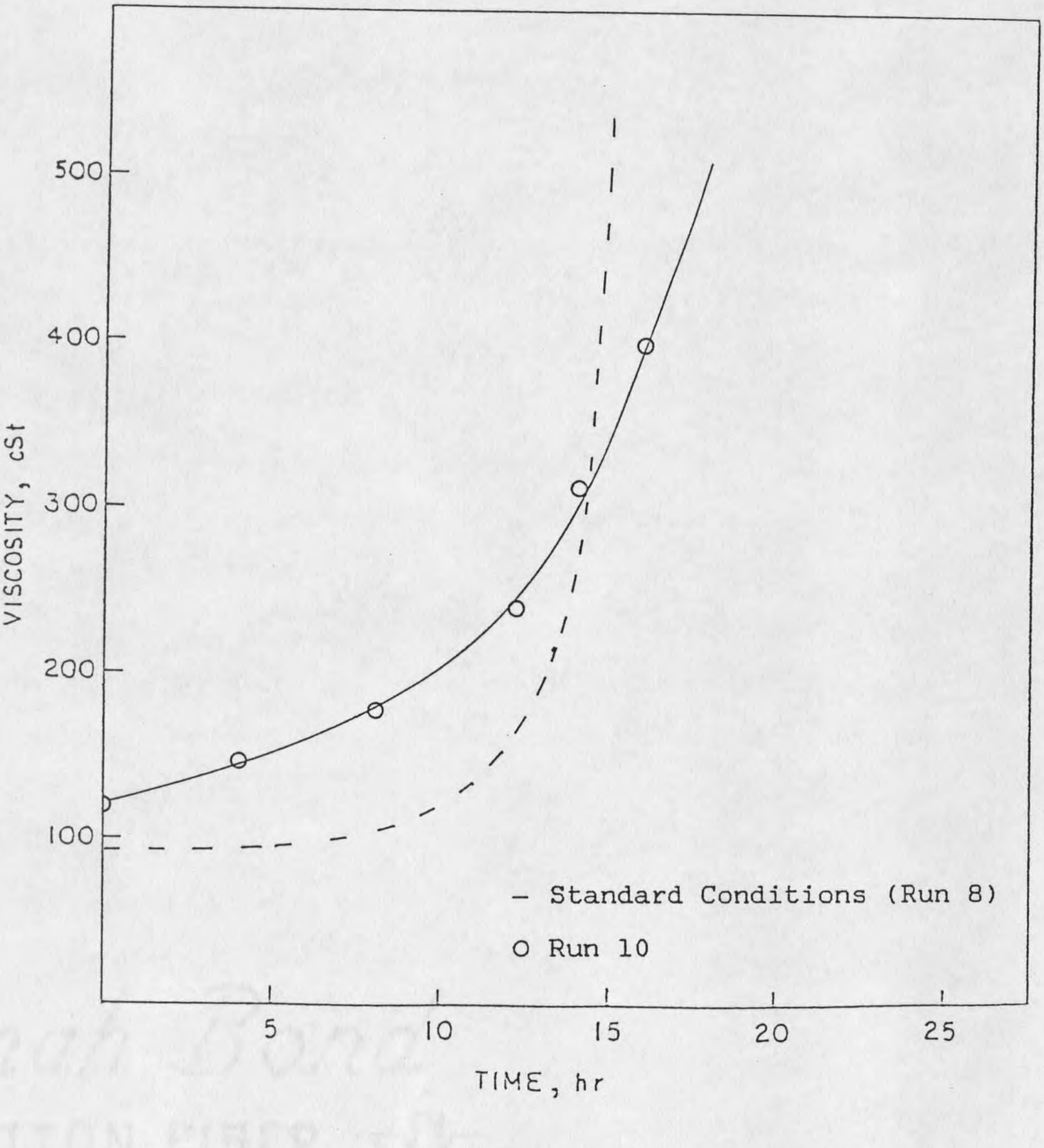


Figure 10. Viscosity versus exposure time with oxygen and copper foil for initial 48.5 hours. Copper foil removed and 5.0 percent sunflower oil addition at 48.5 hours. Time zero at the point of sunflower oil addition.

Figure 10 is a plot of the standard conditions and Run 10 using 48.5 hours as time zero for Run 10. The viscosity rise in Run 10 begins quickly after the addition of sunflower oil. At 4.0 hours following the addition, viscosity has increased over 20 centistokes while at standard conditions it has increased less than 5 centistokes.

The next experiment in this series, Run 11, was performed using nitrogen gas flow prior to the vegetable oil addition, with all other factors the same as in Run 10. Run 11 shows a viscosity rise result similar to that of Run 10, as seen in Figure 11. When zero time is taken as the time of vegetable oil addition and plotted with the standard case (Figure 12) it is seen that the curve for Run 11 approximates the standard even more closely than Run 10.

The atomic emission (Table II) reveals a copper content of 28 ppm at 48.5 hours for Run 10, well above the 2 ppm measured at 24 hours in Run 9. Recall that in Run 9 vegetable oil was present from the beginning of the run. This demonstrates that vegetable oil is not the causal factor in copper solubilization. It also shows that the soluble copper level at 48.5 hours may be greater than that throughout a standard condition run.

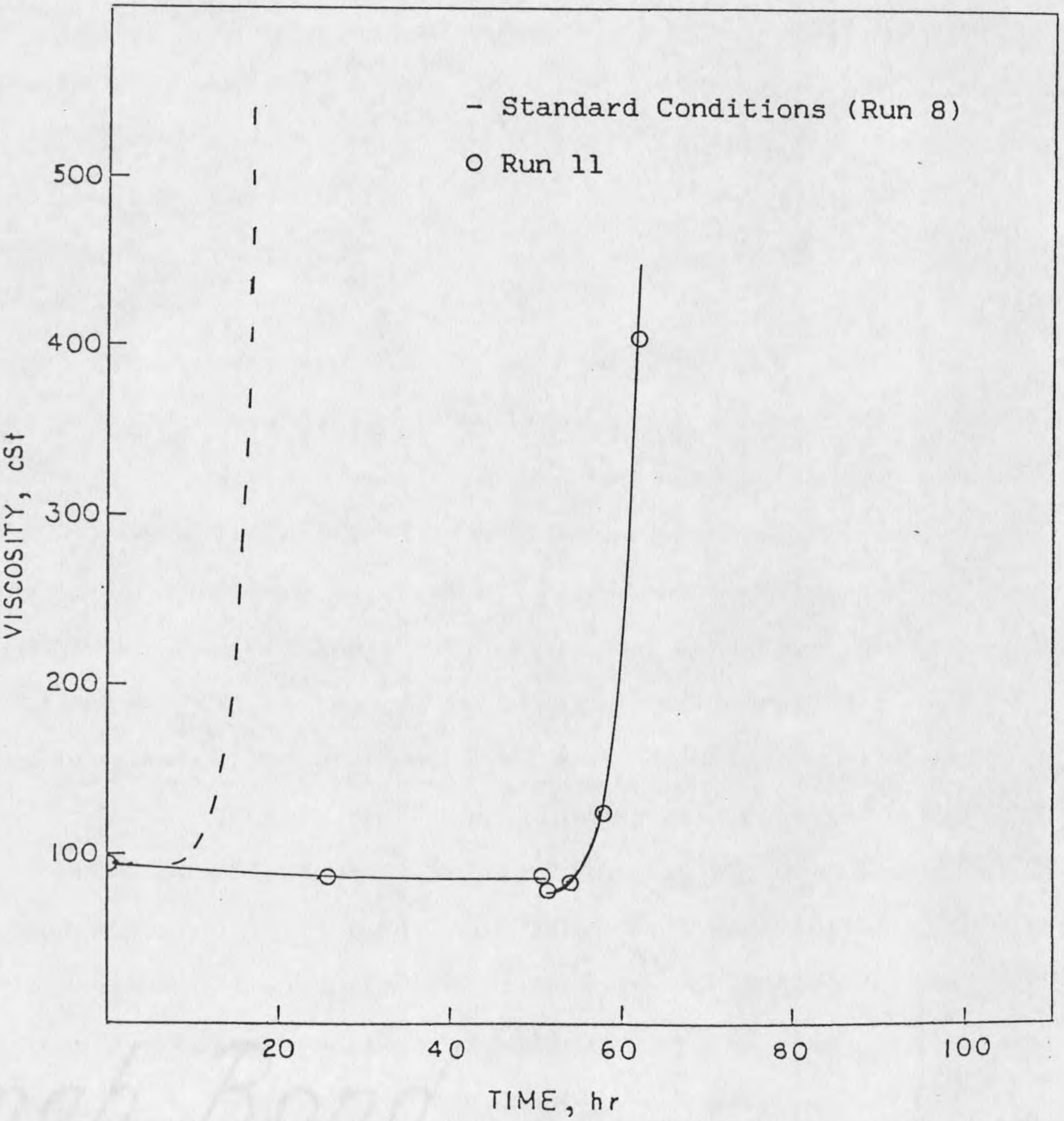


Figure 11. Viscosity versus exposure time with nitrogen and copper foil for initial 48.5 hours. Copper foil removed, nitrogen changed to oxygen, and 5.0 percent sunflower oil addition at 48.5 hours.

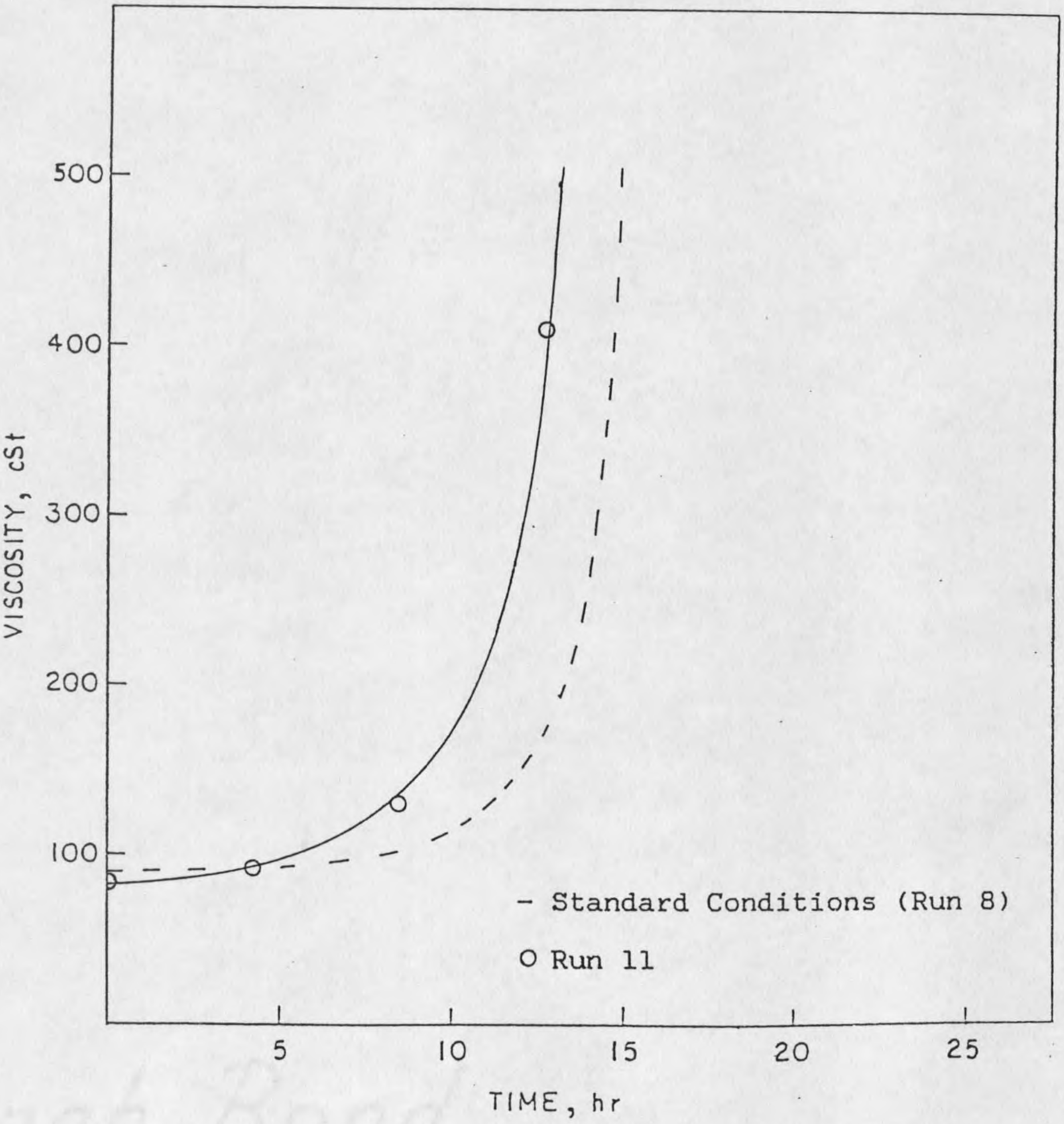


Figure 12. Viscosity versus exposure time with nitrogen and copper foil for initial 48.5 hours. Copper foil removed, nitrogen changed to oxygen, and 5.0 percent sunflower oil addition at 48.5 hours. Time zero at the point of sunflower oil addition.

Run No.	Time of Sample	Copper Level
10	48.5 hours	28 ppm
11	48.5 hours	14 ppm

Table II. Atomic emission results for Runs 10 and 11.

The differences between Runs 10 and 11 emphasize the complexity of the present system. It appears that exposure of the lubrication oil to oxygen and heat is leading to slight oxidative polymerization of the lubricating oil. This is based on the small rise in viscosity over the initial 48.5 hours in the absence of the vegetable oil. This rise does not occur with nitrogen. Total Base Number data also shows that oxidation of the lube oil is taking place in Run 10, probably at points of unsaturation. Table III shows that the TBN (at 48.5 hours) for Run 10 with oxygen flow throughout is far less than TBN for Run 11 using nitrogen.

Run No.	Initial TBN	TBN at 48.5 hrs
10	7.0	2.6
11	7.7	6.0

Table III. Total Base Number for Runs 10 and 11.

Oxidative degradation may be directly affecting the lubrication oil and its additives. The chemistry involved makes it very difficult to speculate as to the actual components being oxidized. It is conceivable that oxygen may be oxidizing the copper, thereby increasing the copper availability for complexing in the system. This might explain the higher copper content of Run 10. Also the lubrication oil additives may react with oxygen in such a way that the soluble copper activity is altered, resulting in a change in viscosity rise.

The important results from Run 10 and 11 are that copper dissolves in lube oil with either nitrogen or oxygen present and that vegetable oil is not necessary to dissolve the copper. These runs also lead to the conclusion that soluble copper is probably the active catalytic form(s), requiring only an initial exposure of lubrication oil to copper surface. It is also noted that although oxygen is not necessary for dissolving copper, oxygen may enhance the rate of dissolution.

Having tentatively concluded that the active form(s) of copper catalyst was dissolved species, it was felt this could be verified if a known soluble form of copper would yield similar results. This soluble form could then be used in later research to minimize polymerization rate by limiting soluble copper levels.

Cupric and cuprous oxides were tested at approximately 20 ppm copper by weight as substitutes for copper foil in Runs 12 and 13. The other operating parameters for these runs were at standard conditions. The oxides were tested as fine powders, making it possible for the viscosity and mixing action of the oil to maintain the oxide particles in suspension. However, it is possible that some of the particles agglomerated and settled. Figure 13 is a plot of Runs 12 and 13 using the two copper oxides and standard conditions.

The copper oxides show catalytic activity less than that of the standard conditions using copper foil. This may indicate poor solubility. It might also indicate that the copper oxides are less active forms. These unknowns

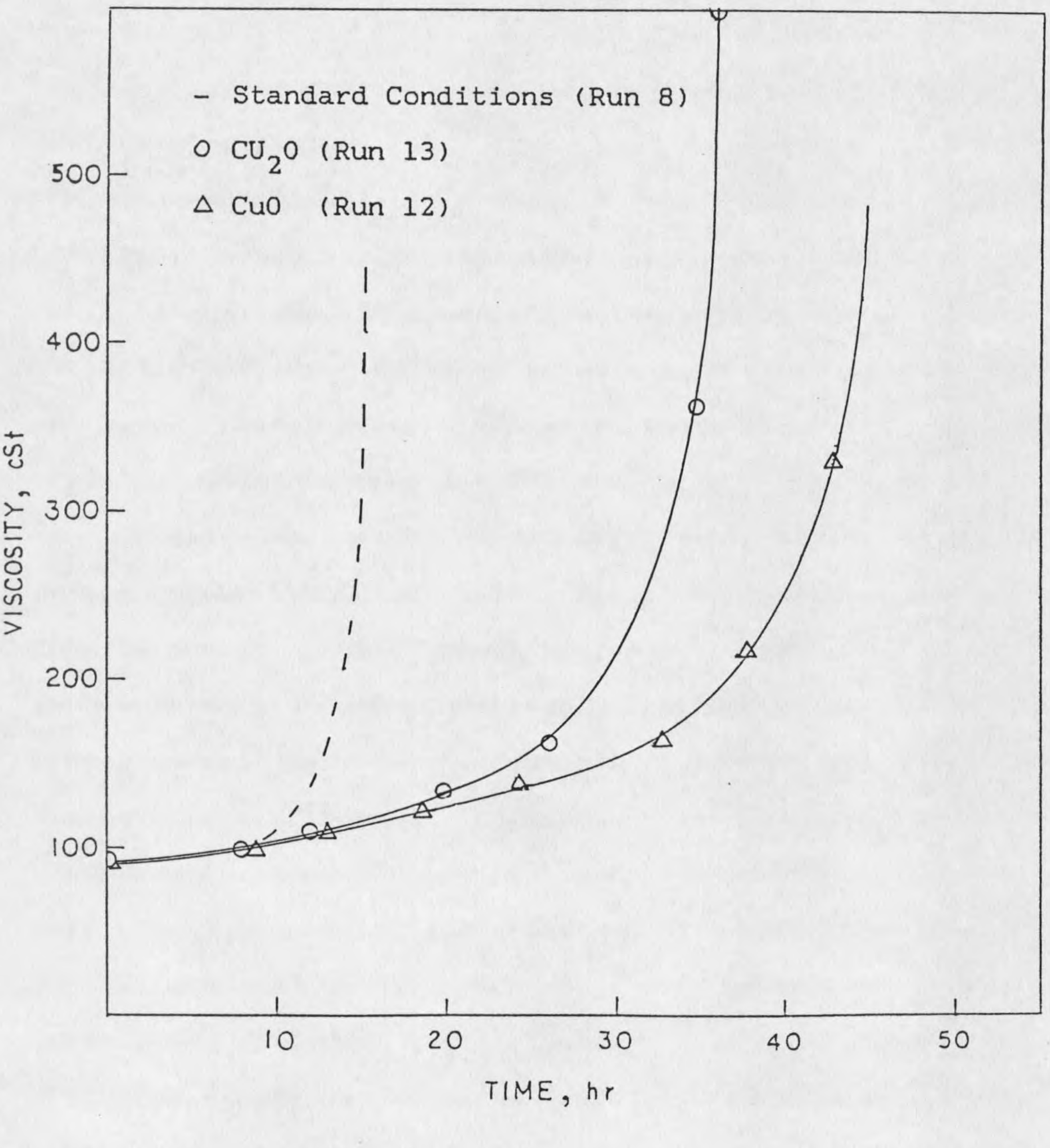


Figure 13. Viscosity versus exposure time with cupric and cuprous oxides at standard conditions.

prevented the use of these oxides as a copper source for future experiments.

Another copper source was chosen from a group of coordination complexes. The complex selected was cupric acetylacetonate. As discussed earlier, metal acetylacetonates are generally very soluble in organic systems. An additional advantage is that, should the copper be released by decomposition of the complex, the acetylacetonate fragments will evaporate [30].

Run 14 was conducted using 5.0 ppm copper by weight with cupric acetylacetonate as the source. The value of 5.0 ppm was chosen based on atomic emission results in standard condition runs. The viscosity rise as seen in Figure 14 appears to be a close replication of standard conditions. The experiment was repeated using 1.0 and 10.0 ppm copper as cupric acetylacetonate. These were Runs 15 and 16, respectively, also plotted in Figure 14. Results at 5.0 and 10.0 ppm are quite similar and easily within the inherent variability of this system as determined by repeated experiments at standard conditions (Figure 7). There is a definite trend that as the amount of dissolved copper decreases the rate of viscosity rise also decreases. However, the similarity of results at 5.0 and 10.0 ppm indicates that the dissolved copper may be reaching a point

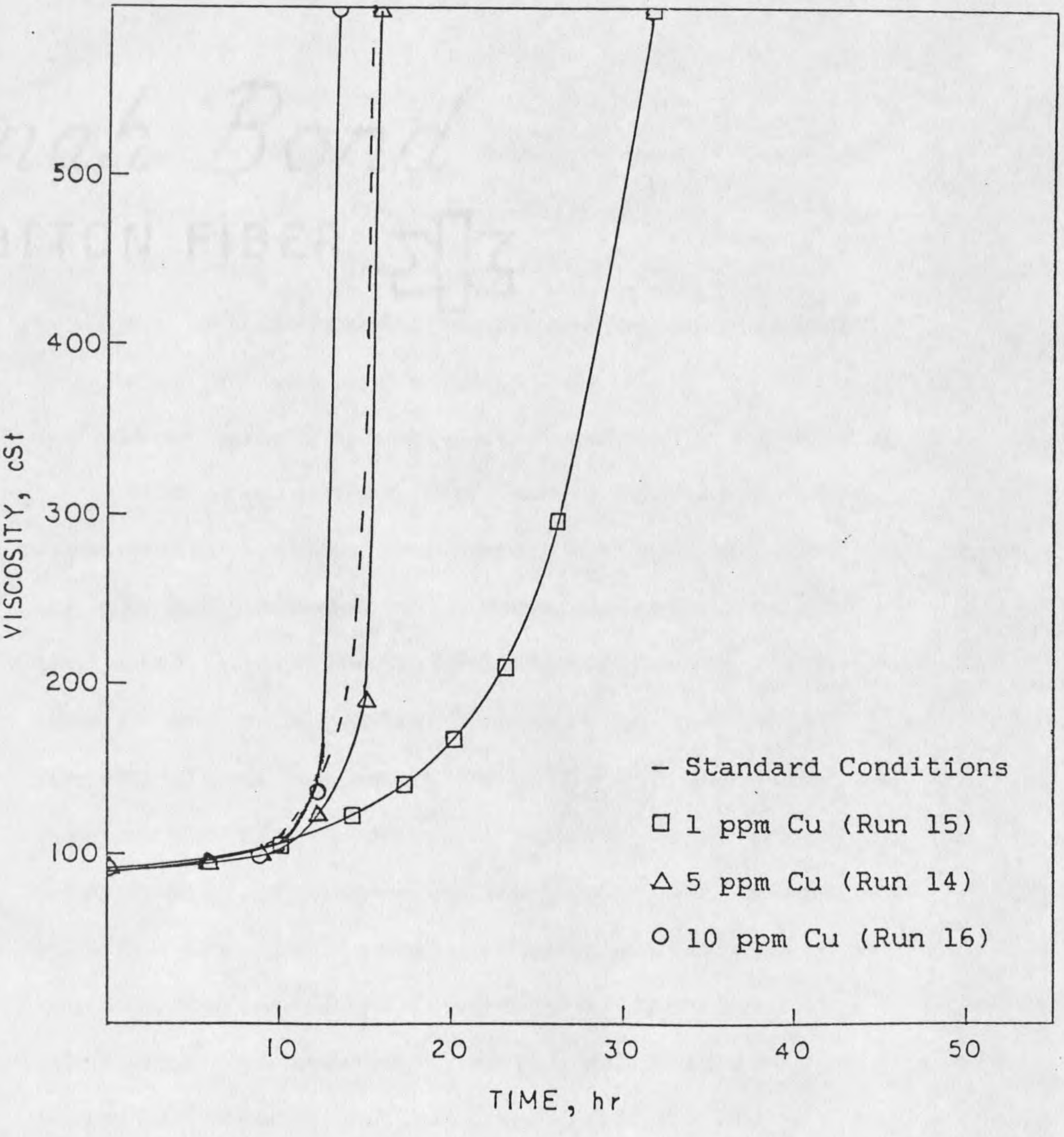


Figure 14. Viscosity versus exposure time for varying levels of cupric acetylacetonate at standard conditions.

where its concentration is no longer the rate limiting factor.

The cupric acetylacetonate at 10.0 ppm copper was next used in 48.5 hour pretreatment experiments. Run 17 used oxygen flow throughout while Run 18 initially used nitrogen. The overall results, as shown in Figure 15, parallel the results for previous pretreatment experiments with copper foil.

The confirmation of cupric acetylacetonate as a soluble copper catalyst is a significant finding. However, these pretreatment experiments again revealed a difference between runs exposed to oxygen or nitrogen for the initial 48.5 hours. Figure 16 plots standard conditions (Run 8) and Runs 17 and 18 where time zero is the point of vegetable oil addition (48.5 hours). As before, it appears the lubrication oil is being slightly degraded during the 48.5 hour period. However, due to control of the copper addition, equal amounts of copper were present in both runs and did not depend on rate of copper dissolution. The curve for the oxygen run has a profile similar to that for a lower copper catalyst level, while the curve for the nitrogen run is similar to a copper level of 10.0 ppm and standard run conditions. This indicates that the oxygen may deactivate the catalytic activity of the dissolved copper species.

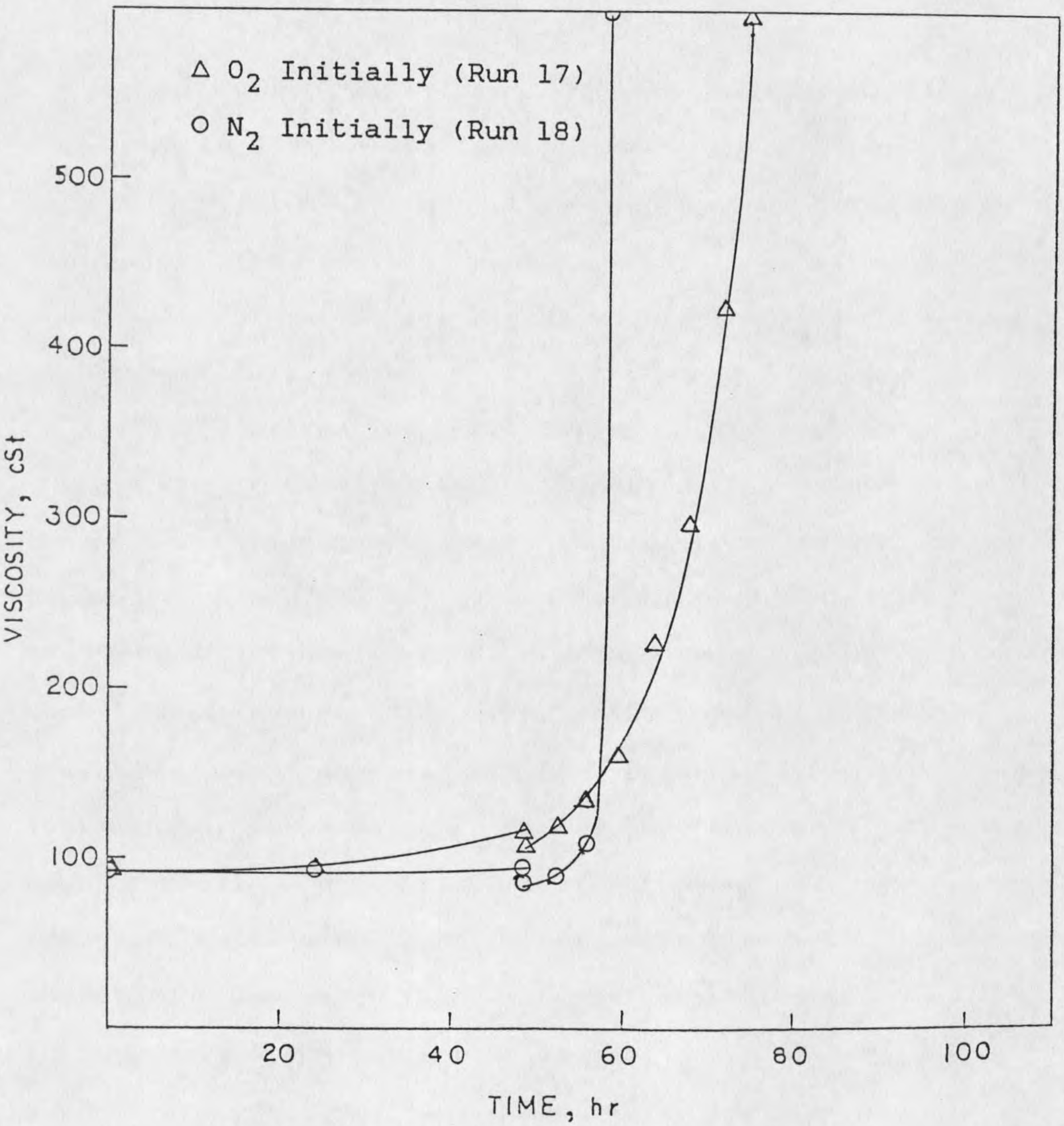


Figure 15. Viscosity versus exposure time with nitrogen or oxygen and cupric acetylacetonate for initial 48.5 hours and 5.0 percent sunflower oil addition at 48.5 hours. Nitrogen changed to oxygen at 48.5 hours for Run 18.

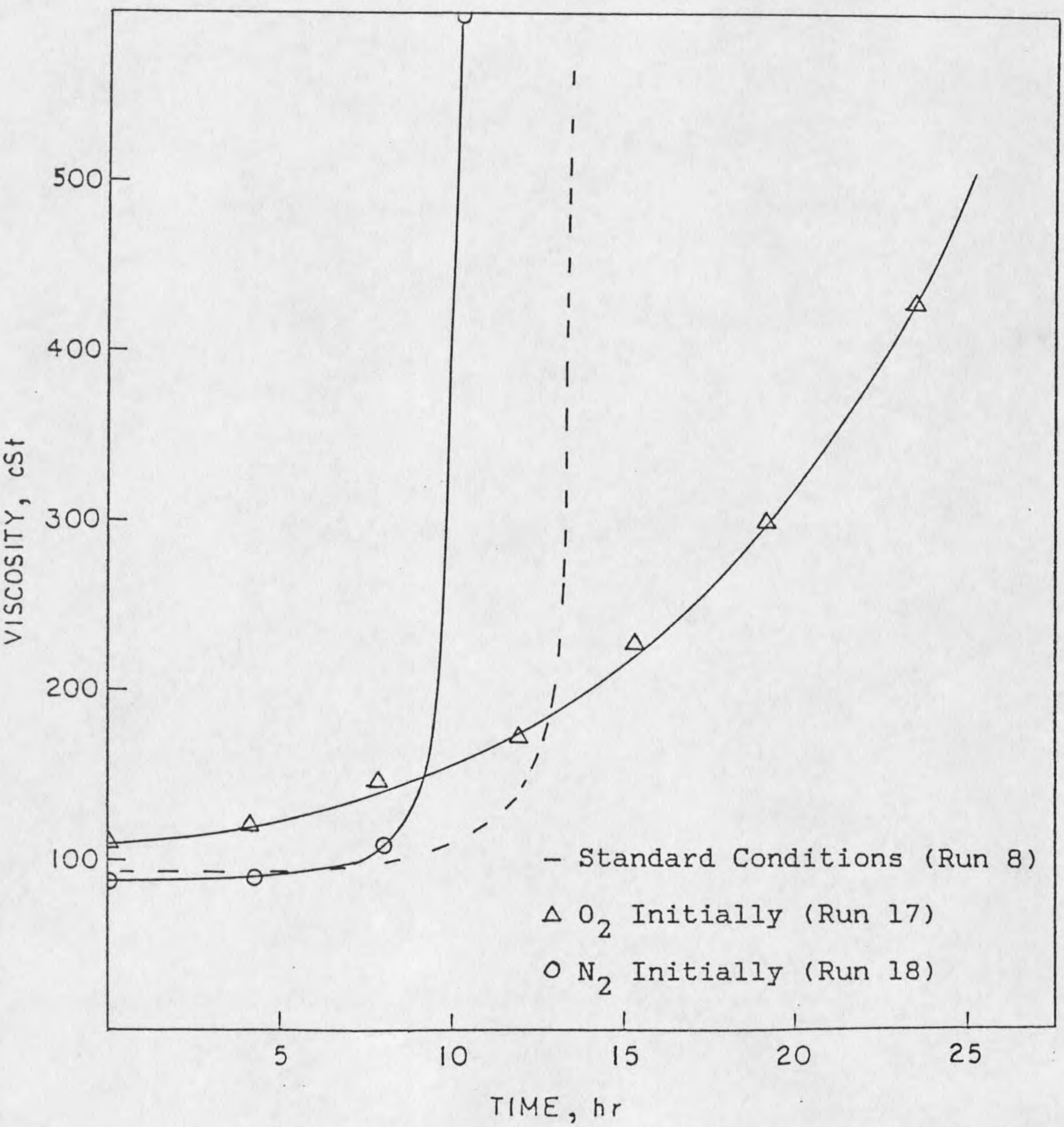


Figure 16. Viscosity versus exposure time with nitrogen or oxygen and cupric acetylacetonate for initial 48.5 hours and 5.0 percent sunflower oil addition at 48.5 hours. Nitrogen changed to oxygen at 48.5 hours for Run 18. Time zero at the point of sunflower oil addition.

This deactivation is not as evident when vegetable oil is available for oxidative polymerization.

Total Base Number data in Table IV indicate results similar to those of Runs 10 and 11 with copper foil. At 48.5 hours the oxygen run had a significantly reduced TBN value when compared to nitrogen at 48.5 hours. Again, oxidation of the lube oil to acidic species probably accounts for the difference in TBN.

Run No.	Initial TBN	TBN at 48.5 hrs
17	7.0	1.54
18	7.0	6.47

Table IV. Total Base Number for Runs 17 and 18.

It was speculated earlier in this thesis that the copper catalyst might be primarily involved in initiation of the polymerization reaction. Scouting experiments with a confirmed free radical initiator tend to support this speculation. Lupersol 130, a commercial hydroperoxide, is known to initiate addition polymerization by spontaneously decomposing into free radicals. Lupersol 130 was added in periodic additions of 0.48 ml Lupersol at 1.5 hour intervals. Two runs (19 and 20) were conducted with the original lubrication oil with and without copper foil catalyst, respectively. Nitrogen flow was used throughout the run. The results are given in Figure 17 and are compared with the standard condition case for the original oil. The curves for Runs 19 and 20 are similar. If copper were important in the propagation phase, Run 20 containing copper should have an accelerated viscosity rise. However, the lack of an increased rate indicates copper is not involved in propagation but initiation. This reinforces the theoretical concept that the copper catalyst is a key in providing the initial free radicals. These free radicals are then capable of abstracting a hydrogen alpha to the double bond and hence initiating the free radical polymerization reaction.

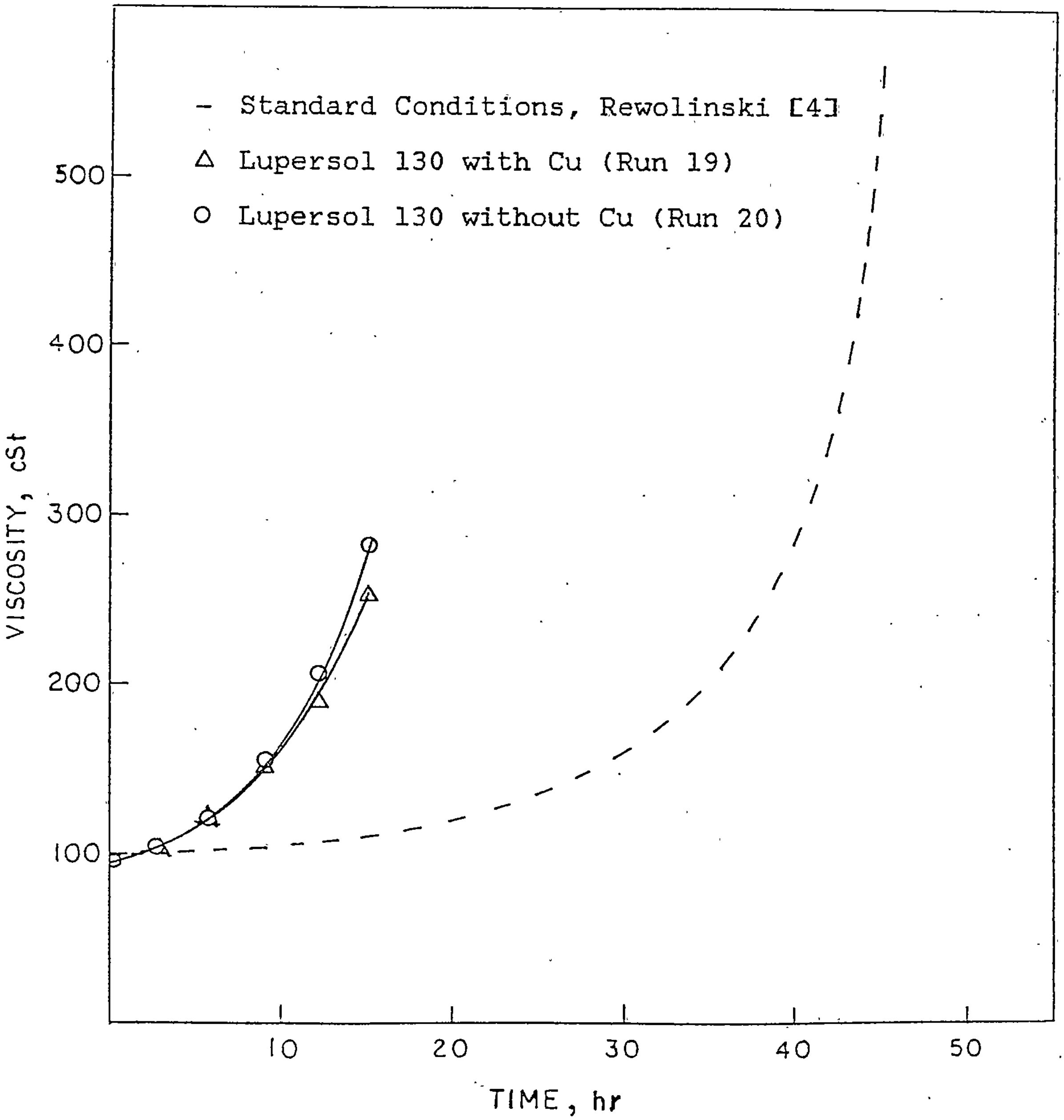


Figure 17. Viscosity versus exposure time using Lupersol 130 as a free radical initiator.

SUMMARY

This research demonstrated that catalysis of sunflower oil polymerization in commercial lubrication oil containing unknown additives creates a highly complex chemical system. Any review of the results of this work must be mindful of the multiple possible interactions among system components and, therefore, the care with which conclusions must be drawn. It is evident that any additive developed to mitigate the activity of copper (or other) catalyst must be tested widely. New additives must be fully compatible with other additive formulations present for other reasons.

Copper foil was found to contribute soluble forms of copper catalytically active in the polymerization of vegetable oil. The amount of metallic copper surface exposed to oil mixture was important in the rate of polymerization, but it appears to have been primarily related to the rate of copper solubilization. An increase in surface area would logically increase the rate at which copper is dissolved. The increased rate of copper solubilization would then give an increase in polymerization.

A series of pretreatment experiments was designed to demonstrate that the copper was indeed dissolving and that contaminant vegetable oil was not responsible for that solvation. These experiments verified that copper slowly dissolved in oil mixtures at simulated crankcase conditions. They also revealed that oxygen appears to accelerate the rate at which copper dissolves, but that oxygen may be deactivating the copper as well, especially when vegetable oil is not present. Vegetable oil contamination seems to have little if any effect on the rate of copper dissolution.

Though metallic copper foil had been determined as a source of dissolved copper species, control of the amount dissolved was difficult. It was felt that future research in the areas of poisoning or sequestering additives would benefit if the amount of copper could be quantified at the point of catalyst addition. Experiments were therefore conducted with materials that would be sources of readily dissolved copper.

Cuprous and cupric oxides were tested as copper sources but gave polymerization rates far below those expected for the levels of copper chosen. These compounds apparently had only minimal solubility in test oil mixtures. A third copper compound, cupric acetylacetonate, demonstrated high levels of catalytic activity at standard conditions.

Results parallel those achieved with metallic copper foil exposure. Based on the chemistry of the acetylacetonate and the polymerization results achieved, cupric acetylacetonate was identified as a source for soluble active copper. Precise amounts of copper can therefore be added to an oil mixture, providing control of this system variable in subsequent research.

Experiments in a multi-cell apparatus indicated soluble copper species were of primary importance in initiation of the triglyceride polymerization reaction. These experiments were conducted using Lupersol 130 to provide excess free radical initiators with and without copper present. No enhancement of polymerization rate was given by the presence of copper as would be expected if copper catalyzed the propagation phase of reaction. Theory for copper catalysis suggests that copper and oxygen can function together in the production of free radicals. These free radicals in turn initiate addition polymerization. Without the initial free radicals provided by the combined presence of copper and oxygen, energy constraints associated with other mechanisms of forming free radicals might limit the overall polymerization.

The results of viscosity rise experiments were supported using atomic emission spectroscopy and alkaline reserve experiments. Both tests were helpful in developing valid conclusions. Viscosity rise experiments had provided initial indications often without being conclusive. When used as a whole the atomic emission, Total Base Number, and viscosity data reinforced each other and helped clarify experimental results.

CONCLUSIONS

1. Soluble copper species appear to be of primary catalytic importance in the free radical polymerization of sunflower oil in lubrication oil at simulated engine crankcase conditions.

2. It appears that copper and oxygen act in combination to form the initial free radicals necessary for the oxidative polymerization of contaminant sunflower oil. Copper does not seem to catalyze the propagation phase of the polymerization mechanism.

3. Oxygen is not required to dissolve copper in a lubrication oil system. Preliminary evidence suggests however that oxygen does enhance the rate of dissolving of copper.

4. The presence of sunflower oil is not a governing factor in the rate of solubilization of copper at the conditions of this research.

5. Oxygen may deactivate dissolved copper over long exposure times, especially where vegetable oil is not initially present. When vegetable oil is present the polymerization reaction may proceed too rapidly for the copper to be deactivated.

6. Cupric acetylacetonate provides a source of soluble, catalytically active copper which parallels results given by metallic copper foil. The compound provides a means to control concentrations of soluble copper in subsequent experiments.

SUGGESTIONS FOR FUTURE RESEARCH

1. One of the key approaches to seeking an additive to limit copper catalytic activity may be the comparison of the two additive packages used in the two different Phillips 66 batches of lubrication oil. It is obvious that the additive package in the lubrication oil from the Wyoming refinery more readily inhibits the rise in viscosity. A detailed examination of these additive packages may reveal specific additives effective in limiting polymerization.

2. Additional research should include the screening of other engine oil wear metal contaminants. If these other metals, which are known to include iron, chromium, lead, and silver, produce catalytic effects on triglyceride polymerization, it may be necessary to develop more general additives or mixtures of additives.

3. The research in this thesis indicates that the presence of oxygen may be influencing the solubilization of copper. It also indicates that in some instances oxygen may actually be reducing the activity of the dissolved copper. These two phenomena should be reviewed in greater detail as there are

other possible mechanisms which could yield the observed results. There may be the possibility of using the deactivation effect to an advantage or of using it in conjunction with a particular additive chemistry.

4. There are prescribed acceptable limits for trace metal concentrations in used crankcase oils. It would be advantageous to work at these contamination levels. Table IX in the Appendix lists trace metal contaminants at maximun recommended limits in parts per million. Used lubrication oils would normally be discarded if metal levels exceed those listed. If the additives are effective at these maximum metal levels, the additives will probably be effective at lower metal contamination levels.

BIBLIOGRAPHY

1. Nitske, W.R., and Wilson, C.M., Rudolf Diesel, Pioneer of the Age of Power, 1st ed., University of Oklahoma Press, Norman, (1965).

2. Pryde, E.H., "Vegetable OIls as Diesel Fuels: Overview," J. Am. Oil Chem. Soc. 60(8):1557-1558 (1983).

3. Peterson, C.L., Wagner, G.L., and Auld, D.L., "Vegetable Oil Substitutes Diesel Fuels," Power and Machinery Division, ASME, Paper 81-3578 (Oct.,1982).

4. Rewolinski, C., "Vegetable Oil Dilution of Diesel Engine Lubricating Oil," Thesis, Montana State University, Bozeman, MT (1984).

5. Dutta, A., "Polymerization of Lubrication Oil Base Stock Contaminated With Sunflower Oil," Thesis, Montana State University, Bozeman, MT (1985).

6. CRC Handbook of Lubrication, Vol.1, The Chemical Rubber Co., Cleveland (1983).

7. Bruwer, J.J., Boshoff, B.V.D., Hugo, F.J.C., Fuls, J., Hawkins, A.N., Van der Walt, Engelbrecht, A., and Duplessis, A.,"The Utilization of Sunflower Seed Oil as a Renewable Fuel for Diesel Engines," Agricultural Energy, Vol 2, ASAE (1980).

8. Uri, N., Autoxidation and Antioxidants, Lundberg, W. O., Ed., Vol. 1, Ch. 2, Wiley-Interscience, New York (1961).

9. Bauer, D. J., Marks, J. S., and Liljedahl, J. B., "A Method for Evaluating the Thickening of Lubricating Oil When Vegetable Oil is Used as a fuel in Diesel Engines," ASAE Paper presented at the International Conference on Plant and Vegetable Oils as Fuels, Fargo (Aug. 12-4, 1982).

10. Sonntag, N. O. V., Bailey's Industrial Oil and Fat Products, 4th ed., Vol. 1, Svern D, Ed., pp. 1-45, 135-159, Wiley - Interscience, New York (1979).

11. Rheineck, A. E., and Austin, R. O., "Treatise on Coatings," Myers, R. R., and Long, J. S., Eds. Vol. 1, Part 2, Ch. 4, Marcel Dekker, New York (1968).

12. Farmer, E. H., and Sutton, D. A., J. Chem. Soc. 119 (1943).

13. Bolland, J. L., and Gee, G., Trans. Faraday Soc., 42:236-243 (1946).

14. Privett, O. S., Lundberg, W. O., Khan, N. A., Tolberg, W. E., and Wheeler, D. H., J. Am. Oil Chem. Soc., 30:61 (1953).

15. Formo, M. W., Bailey's Industrial Oil and Fat Products, 4th Ed., Vol. 1, Swern, D., Ed., pp. 678-816, John Wiley & Sons, New York (1979).

16. Bolland, J. L., and Gee, G., Trans. Faraday Soc. 42:244 (1946).

17. Farmer, E. H., Trans. Faraday Soc., 42:228 (1946).

18. Gunstone, F. D., and Hilditch, T. P., J. Chem. Soc. 1022 (1946).

19. Swern, D., Fatty Acids, 2nd ed., Part 2, Markley, K. S. Ed., pp. 1387-1436, Interscience Publishers, INc. New York (1961).

20. Bailar, J. C., Moeller, T., Kleinberg, J., Guss, C. O., Castellion, M. E., Metz, C., Chemistry, Academic Press, Inc., New York, pp. 804-836, (1978).

21. Cotton, F. A., and Wilkinson, G., Basic Inorganic Chemistry, John Wiley & Sons, Inc., New York, pp. 379-416, (1976).

22. Cotton, F. A., and Wilkinson, G., Advanced Inorganic Chemistry, 4th ed., John Wiley & Sons, New York, pp 798-821 (1980).

23. Huckel, W., Structural Chemistry of Inorganic Compounds, Volume I, Elsevier Publishing Co., INc., New York, pp. 47-148 (1950).

24. Collman, J. P., Hegedus, L. S., Principles and Applications of Organotransition Metal Chemistry, University Science Books, California: (1980).

25. "Total Base Number of Petroleum Products by Potentiometirc Percholoric Acid Titration," ASTM D 2896, 1974 Annual Book of ASTM Standards, part 24, ASTM, pp. 870-875 (1974).

26. "Iodine Value of Drying Oils and Fatty Acids," ASTM D 1959-69, Annual Book of ASTM Standards, part 29, ASTM, pp. 283-286 (1979).

27. Jennings, P. W., Personal Communication, Montana State University, Bozeman, MT (1985).

28. Wexler, H., "Polymerization of Drying Oil," Chem. Reviews 64(6):591 (1964).

Sample No.	1	2	3	4	5	6	7
Engine miles	501,000	509,000	516,000	533,000	538,000	547,000	554,000
(km)	(806,281)	(819,156)	(830,422)	(857,780)	(865,827)	(880,311)	(891,577)
Miles since last sample	4,000	8,000	7,000	17,000	4,000	9,000	7,000
(km)	(6,437)	(12,875)	(11,265)	(27,359)	(6,437)	(14,484)	(11,265)
Miles since last oil change	4,000	12,000	19,000	36,000	4,000	13,000	20,000
(km)	(6,437)	(19,312)	(30,577)	(57,936)	(6,437)	(20,922)	(32,187)
Iron (ppm)	17	18	20	39	12	19	23
Lead (ppm)	21	24	31	59	11	17	24
Copper (ppm)	14	16	17	36	12	16	21
Chromium (ppm)	1.0	1.8	2.0	51	4.3	2.9	1.4
Silver (ppm)	0.3	0.4	0.5	2.1	0.3	0.4	0.5

Note: Oil changed at 534,000 mi (859,390 km).

Table V. Successive spectrographic analyses of used oil from a diesel locomotive crankcase. (CRC Handbook of Lubrication [6])

RUN NO	TIME HOURS	COPPER	MAGNESIUM	CALCIUM	BARIUM	PHOSPHORUS	ZINC	NEW 66 OIL	ORIGINAL 66
4	0.0	0	576	1539	0	1039	1227		X
4	72.0	5	148	507	0	682	410		X
6	0.0	0	550	890	0	1210	1230		X
6	48.0	2	162	530	0	871	517		X
7	24.2	2	1280	7	0	1157	1118	X	
10	48.5	28	990	5	0	986	1212	X	
11	48.5	14	1172	4	0	890	1078	X	
13	38.0	1	485	4	0	882	960	X	
14	.5	5	1490	0	0	1270	1280	X	
17	.5	9	1058	6	0	1088	1208	X	

Table VI. Atomic emission data for copper and common additive metals for selected runs.

Run No	Nitrogen Time Exposure	Oxygen Time Exposure	Copper Added	Copper Foil Time Exposure	Time of Sun Oil Addition	% Sun. Oil Added
1	None	0.0-90.0	None	None	0.0 hr	5.0
2	None	0.0-70.0	1cmx5cm	0.0-70.0 hr	0.0 hr	4.7
3	None	0.0-60.0	2cmx5cm	0.0-60.0 hr	0.0 hr	4.7
4	None	0.0-60.0	2cmx5cm	0.0-60.0 hr	0.0 hr	5.0
6	None	0.0-48.0	2cmx5cm	0.0-18.0 hr	0.0 hr	5.0
7	None	0.0-24.0	2cmx5cm	0.0-24.0 hr	0.0 hr	5.0
8	None	0.0-17.0	2cmx5cm	0.0-17.0 hr	0.0 hr	5.0
9	0.0-24.0	24.0-64.0	2cmx5cm	0.0-24.0 hr	0.0 hr	5.0
10	None	0.0-70.5	2cmx5cm	0.0-48.5 hr	48.5 hr	5.0
11	0.0-48.5	48.5-64.5	2cmx5cm	0.0-48.5 hr	48.5 hr	5.0
12	None	0.0-48.0	CuO	None	0.0 hr	5.0
13	None	0.0-48.0	Cu_2O	None	0.0 hr	5.0
14	None	0.0-18.0	Cu AcAc	None	0.0 hr	5.0
15	None	0.0-30.0	Cu AcAc	None	0.0 hr	5.0
16	None	0.0-15.0	Cu AcAc	None	0.0 hr	5.0
17	None	0.0-78.0	Cu AcAc	None	48.5 hr	5.0
18	0.0-48.5	48.5-60.5	Cu AcAc	None	48.5 hr	5.0

Table VII. Operation parameters for oil bath runs.

Run No									
1	Time hr	0.0	11.0	20.0	30.0	40.0			
1	TBN	---	8.7	7.6	1.6	0.6			
2	Time hr	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0
2	TBN	5.6	4.5	3.3	2.1	1.0	1.0	0.0	0.4
3	Time hr	0.0	10.0	20.0	30.0	40.0	50.0		
3	TBN	---	6.7	3.4	2.2	1.0	0.4		
6	Time hr	0.0	10.0	18.0	28.0	38.0	48.0		
6	TBN	---	5.2	3.7	2.2	0.9	1.1		
7	Time hr	0.0	10.0	20.7					
7	TBN	6.5	5.5	2.8					
10	Time hr	0.0	24.0	48.5	48.6	52.5	56.5	66.5	
10	TBN	---	6.1	2.6	1.5	1.1	0.9	0.3	
11	Time hr	0.0	24.0	48.5	48.6	52.5	56.5	60.5	64.5
11	TBN	7.7	6.2	6.0	6.0	6.4	3.4	0.9	1.5
14	Time hr	0.0	6.0	9.0	12.0	15.0	18.0		
14	TBN	7.2	5.8	4.6	2.8	2.0	2.2		
15	Time hr	0.0	10.0	14.0	17.0	20.0			
15	TBN	6.8	---	3.4	---	2.8			
16	Time hr	0.0	6.0	9.0	12.0	15.0			
16	TBN	6.2	4.0	4.3	4.0	1.9			
17	Time hr	0.0	48.5	48.6	60.3				
17	TBN	---	1.5	1.5	0.8	-			
18	Time hr	0.0	48.5	48.6	56.5	60.5			
18	TBN	---	6.5	6.5	3.4	2.2			
*	Time hr	0.0	10.0	20.0	30.0				
*	TBN	6.7	5.9	3.7	1.5				

Table VIII. Total Base Number in mg KOH/g oil for several runs .

* This run had no copper, 5.0 percent Sunflower Oil, and was performed in new Phillips 66 lube oil.

Metal	Diesel, dual-fuel, and gas engines Max conc (ppm)
Aluminum	40
Boron	20
Chromium	40
Copper	40
Iron	100
Lead	100
Potassium	50
Silicon	20
Silver	6

Table IX. Limits for trace metal concentrations in used crankcase oils.
(CRC Handbook of Lubrication [6])

Jette, Stephen John
Copper catalysis of
polymerization of...

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