Polymerization of sunflower oil diesel fuel
by Joan Patricia French Keller

Abstract:
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The research was conducted to understand and characterize the physical and chemical differences between polymer species contributing to viscosity and those contributing to insoluble gel. Addition polymerization was known to yield viscosity rise at conditions of this work. A theory was developed which hypothesized simultaneous oxidation of addition polymers in basestock oil to yield more polar compounds which formed the separate gel phase.

Experiments supported the polar gel theory. Attempts to homogenize or disperse the gel in basestock or commercial lube oils failed to show similarity to the physical behavior of non-gel addition polymers. Infrared spectroscopy also showed that gel contained more carbonyl groups than pure sunflower oil or addition polymerized sunflower oil.

Antioxidant and free radical initiator trials indicated gel was chemically different from addition polymerized sunflower oil, with the presence of oxygen being key to gel formation. A long chain amine was successful in preventing gel formation. When the acidic addition polymers were converted to less polar amides, the oil mixture remained a single phase. These results generally confirm that the polymers resulting from addition polymerization are polarized by oxidation to form the separate gel phase.

POLYMERIZATION
OF SUNFLOWER OIL DIESEL FUEL

by

Joan Patricia French Keller

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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APPROVAL

of a thesis submitted by

Joan French Keller

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

The mechanism of insoluble gel formation in hydrocarbon basestock lubricating oil contaminated with sunflower oil was studied in a laboratory apparatus simulating the conditions of a diesel engine crankcase. Two distinct and separate phases formed within the system when using basestock oil as the lubricating substrate - a solid insoluble gel phase and a supernatant liquid phase.

The research was conducted to understand and characterize the physical and chemical differences between polymer species contributing to viscosity and those contributing to insoluble gel. Addition polymerization was known to yield viscosity rise at conditions of this work. A theory was developed which hypothesized simultaneous oxidation of addition polymers in basestock oil to yield more polar compounds which formed the separate gel phase.

Experiments supported the polar gel theory. Attempts to homogenize or disperse the gel in basestock or commercial lube oils failed to show similarity to the physical behavior of non-gel addition polymers. Infrared spectroscopy also showed that gel contained more carbonyl groups than pure sunflower oil or addition polymerized sunflower oil.

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INTRODUCTION

Recently, fuel costs have declined, but an increased awareness that the supply of petroleum-based fuels is finite has sparked interest in finding new sources of motor fuels. Vegetable oils as alternate diesel engine fuels have received modest interest for several decades [1] . However, economic factors have favored the use of petroleum-based fuels [2] .

The use of vegetable oils as fuels for diesel engines is not a new concept. As far back as 1912, Rudolf Diesel, the inventor of the diesel engine, tried using vegetable oils as diesel fuels, but economics and design never favored their use [3] .

The development of the diesel engine has been based on the availability of petroleum-derived diesel fuel which in turn has been tailored to meet the needs of the current engines. During this period, a wealth of empirical knowledge has been developed that serves as the data base for the current diesel fuel specifications [4] .

Two principle problems have been identified with using vegetable oils directly as diesel fuels: 1) vegetable oils form carbon deposits inside the combustion chambers of direct injection engines and 2) vegetable oils carried into the crankcase polymerize in the lubricating oil. The thickened oil mixture plugs the oil filter, causes oil ring sticking and plugs orifices leading into and out of the crankcase. These problems can cause eventual engine failure. The above problems are related to the chemical structure differences between vegetable oils and diesel fuel [5] .

Positive aspects of vegetable oils as fuels are: 1) natural state is liquid and hence easily transported, 2) heat content is comparable to diesel fuel, 3) potential widespread availability and 4) renewability as resources [6] .

Studies have been performed on transesterification and decarboxylation of the vegetable oils for fuel purposes, either of which increases cost. Direct use of minimally processed vegetable oils should permit on-farm processing and minimize costs [5,7,8,9] .

This research is part of continuing work at this laboratory. Previous workers confirmed that lubrication oil thickens due to vegetable oil contamination. This thickening may cause an unacceptable viscosity rise [10,11,12] . These workers developed a set of standard conditions consisting of variables known to strongly influence the thickening of lubricating oil due to vegetable oil contamination.

The factors considered in developing the standard conditions were temperature, chemical environment and catalysts. Rewolinski [10] chose 150 C as the standard temperature because 150 C is a rough average temperature encountered by the oil as it travels through the crankcase and engine combustion areas. Rewolinski also showed viscosity rise due to vegetable oil polymerization was strongly influenced by the presence of oxygen. In a standard exposure oxygen was percolated through test oil mixtures. As oxygen flow rate increased, the rate of viscosity rise increased. The presence of nitrogen did not affect viscosity rise. Standard conditions include an oxygen flow rate of 2.0 ml/sec. Rewolinski also investigated the effects of varying vegetable oil concentration. As vegetable oil concentration increased, the rate of viscosity rise increased. To get a measurable viscosity rise in a reasonable period of time, standard conditions include 5.0 weight percent sunflower oil in the lubricating oil.

Jette's research [11] focussed on the role of copper catalyst in the system. Copper is a common engine wear metal, and Rewolinski had determined copper was a more important polymerization catalyst than iron. Jette went on to determine that soluble copper was the most important catalyst form. He used copper foil and observed that viscosity rise increased with increased copper foil area. As a result of this combined research, a 2 cm x 5 cm copper foil strip is present in the standard conditions. To control the amount of metal present in the system, all of the equipment in contact with the oil mixture is glass.

Lubrication oil thickening may be reduced by changing the engine design or perhaps by changing the chemical make-up of the lubricating oil. Engine design modifications are costly; therefore, alteration of the lubrication oil is more feasible [13] . Extensive work has been done on lubricating oils and conventional diesel fuel systems where system-specific antioxidants, dispersants and metal deactivators have been developed. There is a need to explore these areas with vegetable oil fuels.

The equipment used at this laboratory simulates the environment of a crankcase. Variables such as amount of copper, oxygen flow rate, amount of sunflower oil and temperature can be controlled to a greater degree than in an actual engine. Simulation also allows for repeated tests in the same apparatus as well as avoiding the recurring costs of replacing expensive engines upon their failure.

The use of hydrocarbon basestock as the lubricating oil substrate is desirable if a complete understanding of the contaminated system chemistry is sought. This is due to the unknown chemical nature of the additive package in the commercial lube oil.

Dutta [12] attempted to use hydrocarbon basestock contaminated with 5.0 weight percent sunflower oil and encountered the formation of two distinct phases. A gel formed as the sunflower oil polymerized, and this gel precipitated out as a separate phase. Viscosity measurements to quantify polymerization became meaningless for this two-phase system. Measuring viscosity was not the only problem Dutta encountered. He also discovered the amount of gel formed was difficult to quantify because the gel was swollen with lubricating oil. Until the mechanism(s) of gel formation in the current lubricating oil system is understood, viscosity measurements as a method to quantify polymerization of sunflower oil in basestock oil are meaningless.

RESEARCH OBJECTIVES

This research was conducted to understand the mechanism(s) of contaminant vegetable oil polymerization in a lubrication oil system. A primary goal was to understand the chemical nature of gel precipitation versus viscosity formation as vegetable oil polymerization occurs in the given system.

A further objective was to be able to utilize the hydrocarbon basestock lubricating oil in future studies so the impact of unknown chemical additives is eliminated. To accomplish this objective, the formation of insoluble gel must be sharply minimized. As the chemistry of the system is understood, gel formation and viscosity rise may be eliminated by future research findings.

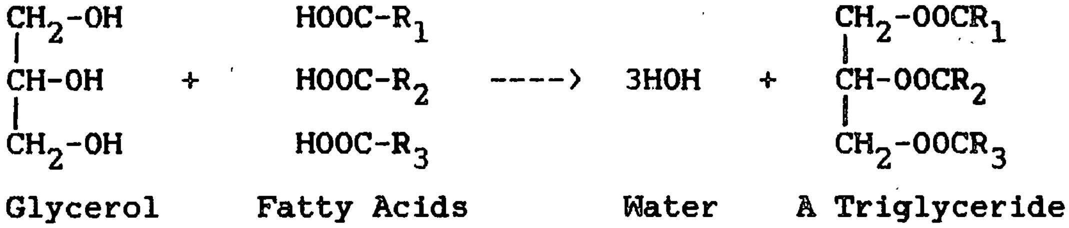
THEORY

The presence of oxygen in a diesel lubrication system contaminated with vegetable oil may produce a variety of chemical reactions. One of these reactions is oxidative polymerization where oxygen interacts with the double bonds of vegetable oils to initiate the formation of addition polymers. Other oxidation reactions may occur when oxygen cleaves a vegetable oil double bond to form aldehydes or acids. Ketones can also be formed without double bond cleavage. The possible reactions of vegetable oils and oxygen will be discussed in the following sections.

Oxidative Polymerization

Current diesel fuels are petroleum-derived and are chemically different from vegetable oils. Diesel fuel contains hydrocarbons which are arranged in straight or branched chains. It is usually paraffinic in nature, but may contain some aromatics. Vegetable oils, on the other hand, are water-insoluble, hydrophobic triglycerides (glycerol esters of fatty acids). A vegetable oil triglyceride is approximately three times larger than a typical diesel fuel component [14] .

Vegetable oil can be thought of as a reaction product of glycerol and fatty acids.



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

In the above reaction scheme, R_1, R_2 and R_3 symbolize the even numbered hydrocarbon chains of fatty acids that are usually 16 to 22 carbons in length. The size of R_1, R_2 and R_3 may vary depending upon the particular vegetable oil. They are typically different in chain length and number of double bonds. The degree of unsaturation of one triglyceride molecule can vary from zero to nine double bonds. The molecular weight of a typical triglyceride molecule is 750 to 1000. The fatty acids contribute roughly 95% of the total weight of the molecule and influence both the physical and chemical properties of the vegetable oils [14] .

The current research is using sunflower oil as the contaminant vegetable oil in the simulated lubricating system. Sunflower oil's primary unsaturated fatty acid constituents are oleic, linoleic and linolenic. An oleic fatty acid is an eighteen-carbon fatty acid with one double bond while linoleic has two double bonds and linolenic has three double bonds [14] . Compositions of typical sunflower molecules are shown in the following table.

Table 1: Fatty Acid Distribution in Sunflower Oil

Fatty Acid	Sunflower 1*	Sunflower 2**
Palmitic	6.0	6.4
Stearic	4.2	4.2
Oleic	18.7	23.9
Linoleic	69.3	61.4
Linolenic	0.3	3.0
Eicosenoic	0.1	---

*Kaufman and Ziejewski [15]
**Peterson, Wagner and Auld [13]

The double bonds in the sunflower oil may be attacked by oxygen. This process is sometimes referred to as autoxidation because the oxidation mechanism is autocatalytic. When vegetable oils are autoxidized, the result is addition polymerization which occurs by a free radical, hydroperoxide mechanism [14] .

Oxidative polymerization of vegetable oil occurs as described below [16] .

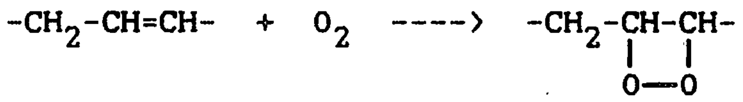
1. The initiation of the oxidative chain reaction is preceded by an induction period which has been attributed to the presence of natural antioxidants. There are no detectable changes in the vegetable oil physical or chemical properties. The induction period may be eliminated by adding a small quantity of a hydroperoxide.

2. The double bonds are directly attacked by oxygen, and hydroperoxides are formed. As oxygen is consumed, the polymerization reaction may be detected.

3. The hydroperoxides decompose to free radicals. The decomposition of these hydroperoxides causes the reaction to become autocatalytic.

4. High molecular weight, cross-linked polymers are formed by polymerization, and scission reactions yield low molecular weight compounds such as carbonyls and hydroxys.

The initiation of the radical chain reaction is a controversial topic. The autoxidation of vegetable oils was first thought to consist of an initial attack on the double bonds of the unsaturated fatty acids to form cyclic peroxides [17] . This reaction is depicted below.

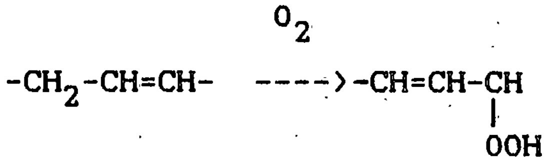


$$\mathrm{-CH_2-CH{=}CH-} \;+\; \mathrm{O_2} \;\text{----}\!> \;\mathrm{-CH_2-}\underset{\mathrm{O-O}}{\underset{|\quad\;|}{\mathrm{CH-CH}}}\mathrm{-}$$

Later work showed the initial products to contain noncyclic, alpha-methylenic hydroperoxides with the double bonds still intact [18] . If the double bond were still intact, this would imply the alpha-methylenic carbon-hydrogen bond was broken. This bond has a strength of 80 kcal/mole. Since there is little available energy to break this relatively strong bond, investigators have concluded the oxygen directly attacks the carbon-carbon double bond [19,20,21,22] .

Only a few of the carbon-carbon double bonds need be attacked to produce hydroperoxides. Once formed, even in trace amounts, hydroperoxides can act as catalysts. At this point, it should be mentioned that the initiation of autoxidation may be due to metal catalysts since most fatty esters contain metal [23,24] .

Hydroperoxides are formed by oxidative attack at the carbon-carbon double bond. As the oxygen attacks the double bond, the electrons rearrange in such a manner that the double bond is shifted. This shifting is often referred to as conjugation [20,21] .



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

Hydroperoxides may decompose by several mechanisms. When hydroperoxides decompose, the following groups can be produced: tertiary radicals, hydroxyl radicals, carbonyls and a carbon-carbon cleavage. The hydroperoxides may decompose to form free radicals in the following manner [19] .

$$\mathrm{ROOH} \dashrightarrow \mathrm{RO}\circ + \mathrm{HO}\circ$$

$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{ROO}} + \mathrm{HOOR} \dashrightarrow \underset{\substack{|\\ \mathrm{H}}}{\mathrm{ROO}}\ldots\mathrm{HOOR} \dashrightarrow \mathrm{HOH} + \mathrm{RO}\circ + \mathrm{ROO}\circ$$

The mechanism of chain propagation is agreed upon among investigators [25] . The initiation products may be oxidized or may combine with another hydrocarbon to produce the following reactions.

$$\mathrm{R}\circ + \mathrm{O}_2 \dashrightarrow \mathrm{ROO}\circ$$

$$\mathrm{ROO}\circ + \mathrm{RH} \dashrightarrow \mathrm{ROOH} + \mathrm{R}\circ$$

Termination reactions generally consume free radicals and often yield polymers. Some of these reactions are shown below [19,25] .

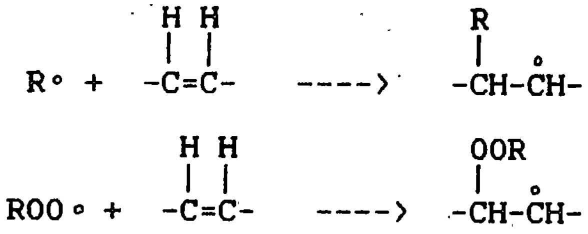
$$\mathrm{ROO}\circ + \mathrm{ROO}\circ \dashrightarrow \mathrm{ROOR} + \mathrm{O}_2$$

$$\mathrm{ROO}\circ + \circ\mathrm{OH} \dashrightarrow \mathrm{ROH} + \mathrm{O}_2$$

$$\mathrm{R}\circ + \mathrm{R}\circ \dashrightarrow \mathrm{R{-}R}$$

$$\mathrm{ROO}\circ + \mathrm{R}\circ \dashrightarrow \mathrm{ROOR}$$

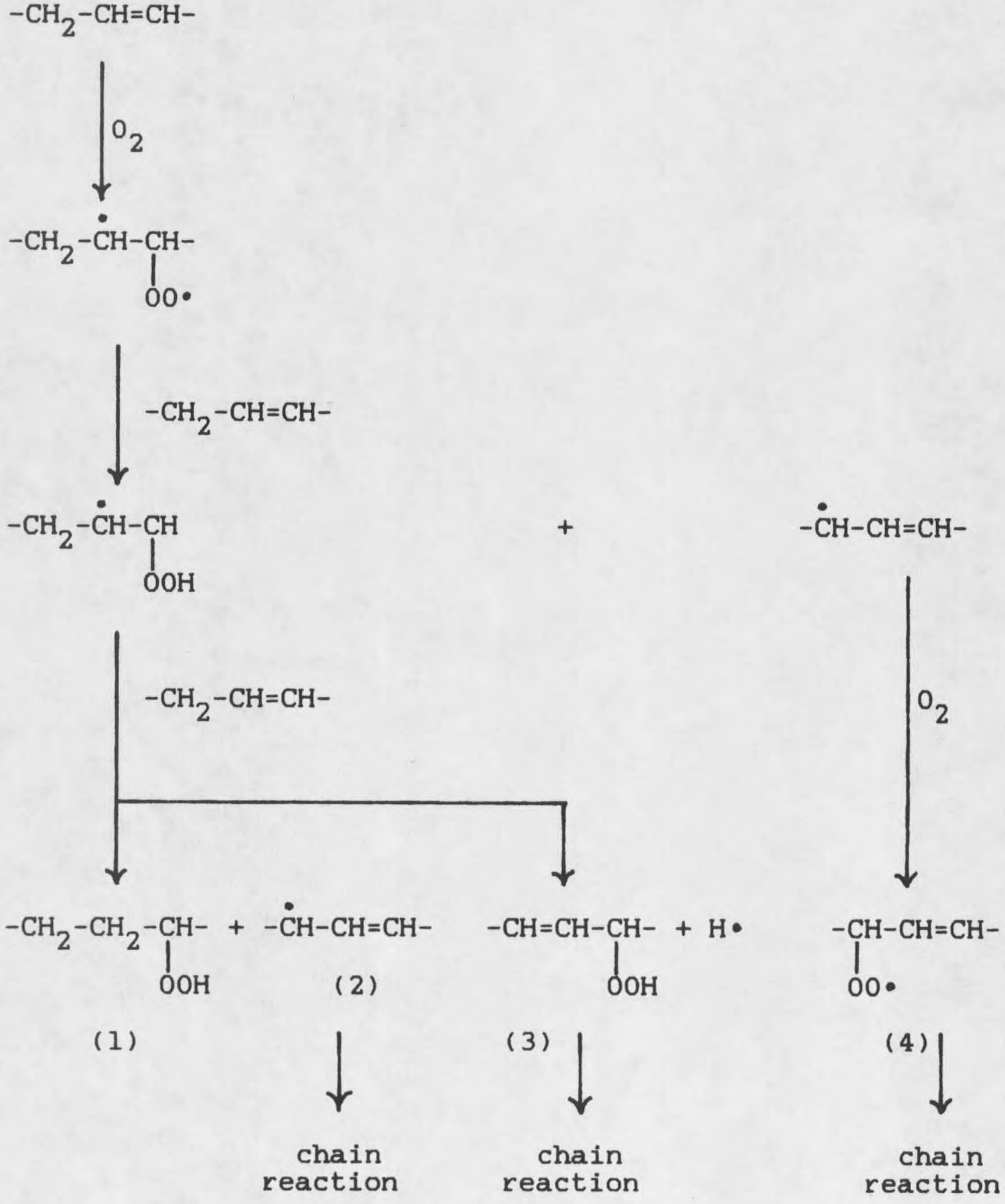
Free radicals may also attack carbon-carbon double bonds and produce larger hydrocarbon free radicals [19,25] .



$$\mathrm{R}\circ + -\overset{\substack{\mathrm{H}\\|}}{\mathrm{C}}=\overset{\substack{\mathrm{H}\\|}}{\mathrm{C}}- \dashrightarrow -\overset{\substack{\mathrm{R}\\|}}{\mathrm{C}}\mathrm{H}-\overset{\circ}{\mathrm{C}}\mathrm{H}-$$

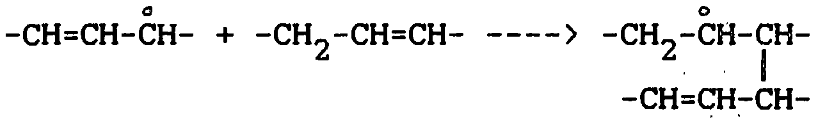
$$\mathrm{ROO}\circ + -\overset{\substack{\mathrm{H}\\|}}{\mathrm{C}}=\overset{\substack{\mathrm{H}\\|}}{\mathrm{C}}- \dashrightarrow -\overset{\substack{\mathrm{OOR}\\|}}{\mathrm{C}}\mathrm{H}-\overset{\circ}{\mathrm{C}}\mathrm{H}-$$

The following general scheme describes oxidative attack of the double bond, formation of hydroperoxides, hydroperoxide decomposition, chain reactions and termination reactions [19,24] .



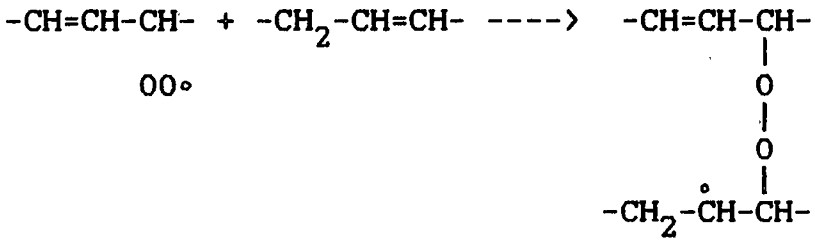
Each of the radicals may react with a variety compounds [19,25] . These are detailed below.

Radical (2) may react with a carbon-carbon double bond and polymerize to form another radical. This is the primary polymerization pathway.



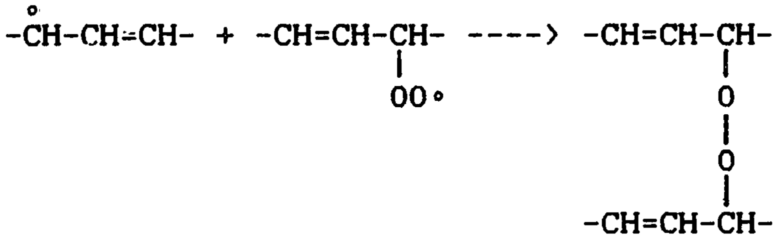
$$-CH{=}CH-\overset{\circ}{C}H- \; + \; -CH_2-CH{=}CH- \; \text{---->} \; \begin{array}{c} -CH_2-\overset{\circ}{C}H-CH- \\ | \\ -CH{=}CH-CH- \end{array}$$

Radical (4) has the capability to attack a carbon-carbon double bond to produce polymer products and continue the chain reaction.



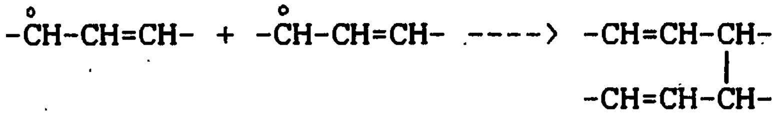
$$\begin{array}{c} -CH{=}CH-CH- \\ OO^{\circ} \end{array} \; + \; -CH_2-CH{=}CH- \; \text{---->} \; \begin{array}{c} -CH{=}CH-CH- \\ | \\ O \\ | \\ O \\ | \\ -CH_2-\overset{\circ}{C}H-CH- \end{array}$$

Radical (2) may also combine with Radical (4) and polymerize to a nonradical polymer.



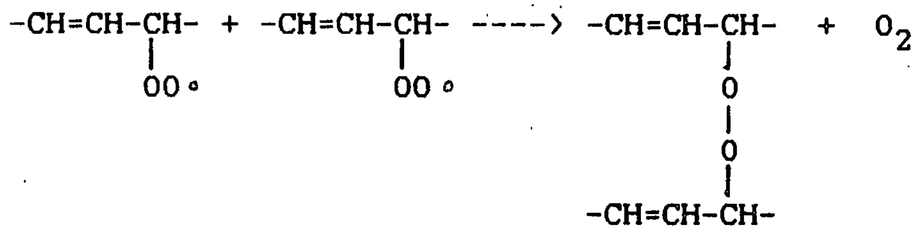
$$-\overset{\circ}{C}H-CH{=}CH- \; + \; \begin{array}{c} -CH{=}CH-CH- \\ | \\ OO^{\circ} \end{array} \; \text{---->} \; \begin{array}{c} -CH{=}CH-CH- \\ | \\ O \\ | \\ O \\ | \\ -CH{=}CH-CH- \end{array}$$

Two Radical (2)'s may polymerize to a nonradical polymer.



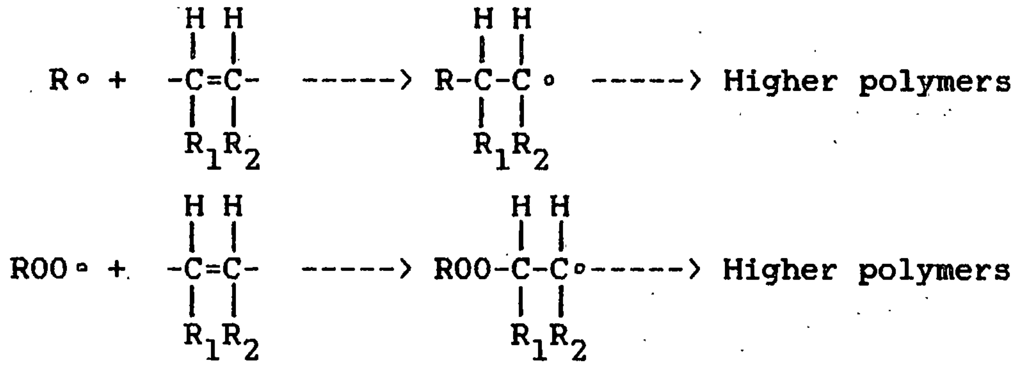
$$-\overset{\circ}{C}H-CH{=}CH- \; + \; -\overset{\circ}{C}H-CH{=}CH- \; \text{---->} \; \begin{array}{c} -CH{=}CH-CH- \\ | \\ -CH{=}CH-CH- \end{array}$$

Two Radical (4)'s may polymerize.



$$\text{-CH=CH-}\underset{\text{OO}\circ}{\text{CH}}\text{-} + \text{-CH=CH-}\underset{\text{OO}\circ}{\text{CH}}\text{-} \longrightarrow \begin{array}{c}\text{-CH=CH-CH-}\\ |\\ \text{O}\\ |\\ \text{O}\\ |\\ \text{-CH=CH-CH-}\end{array} + O_2$$

Another way to visualize Radical (2) or (4) attacking a carbon-carbon double bond is shown below [25] .



$$\text{R}\circ + \text{-}\overset{\text{H}}{\underset{\text{R}_1}{\text{C}}}\text{=}\overset{\text{H}}{\underset{\text{R}_2}{\text{C}}}\text{-} \longrightarrow \text{R-}\overset{\text{H}}{\underset{\text{R}_1}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{R}_2}{\text{C}}}\circ \longrightarrow \text{Higher polymers}$$

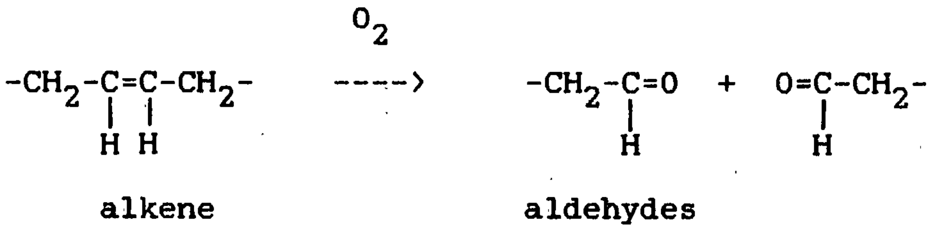
$$\text{ROO}\circ + \text{-}\overset{\text{H}}{\underset{\text{R}_1}{\text{C}}}\text{=}\overset{\text{H}}{\underset{\text{R}_2}{\text{C}}}\text{-} \longrightarrow \text{ROO-}\overset{\text{H}}{\underset{\text{R}_1}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{R}_2}{\text{C}}}\circ \longrightarrow \text{Higher polymers}$$

This predominant polymerization pathway to higher polymers is known as vinyl polymerization.

Other Oxidation Reactions

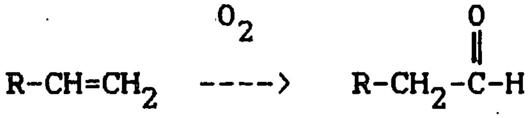
Besides oxidative polymerization, there exist other oxidation mechanisms. The double bonds in the sunflower oil can also be homolytically cleaved by oxygen. When oxygen cleaves the double bond, the alkene molecule is converted into two smaller molecules [26] .

The products of cleavage each contain a carbon-oxygen double bond with the oxygens attached to the carbons present in the original carbon-carbon double bond [27] .



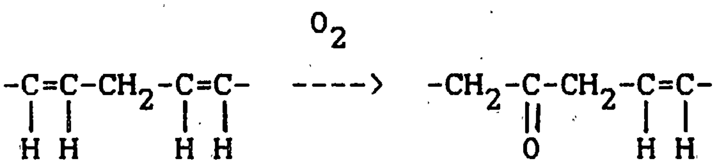
$$\mathrm{-CH_2-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_2-} \xrightarrow{O_2} \mathrm{-CH_2-\underset{H}{\underset{|}{C}}=O} + \mathrm{O=\underset{H}{\underset{|}{C}}-CH_2-}$$

Aldehydes may also be formed without cleavage of the carbon-carbon double bond. If a hydrocarbon molecule contains a terminal double bond, this bond may be attacked; and an aldehyde may be formed [26] .



$$\mathrm{R-CH=CH_2} \xrightarrow{O_2} \mathrm{R-CH_2-\overset{O}{\overset{\|}{C}}-H}$$

Oxygen may open the hydrocarbon chain (without cleavage of the double bond) in the following manner to form ketones [26,27] .



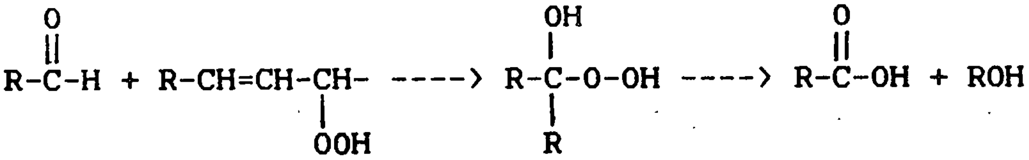
$$\mathrm{-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_2-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-} \xrightarrow{O_2} \mathrm{-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-}$$

Aldehydes can undergo further oxidation with extreme ease. They are readily converted to carboxylic acids by copper and heat [26] .

$$\mathrm{RCHO} \xrightarrow{O_2} \mathrm{RCOOH}$$

aldehyde carboxylic acid

Another mechanism by which aldehydes are converted to carboxylic acids and alcohols may be [26,27]



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + R\text{-}CH{=}CH\text{-}\underset{OOH}{\underset{|}{CH}}\text{-} \text{----}\rangle\ R\text{-}\overset{OH}{\overset{|}{\underset{R}{\underset{|}{C}}}}\text{-}O\text{-}OH \text{----}\rangle\ R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + ROH$$

Aldehydes may undergo autoxidation in a manner similar to that of hydrocarbons. Hydroperoxide radicals act as the chain carriers, and the products can be acids [28] .

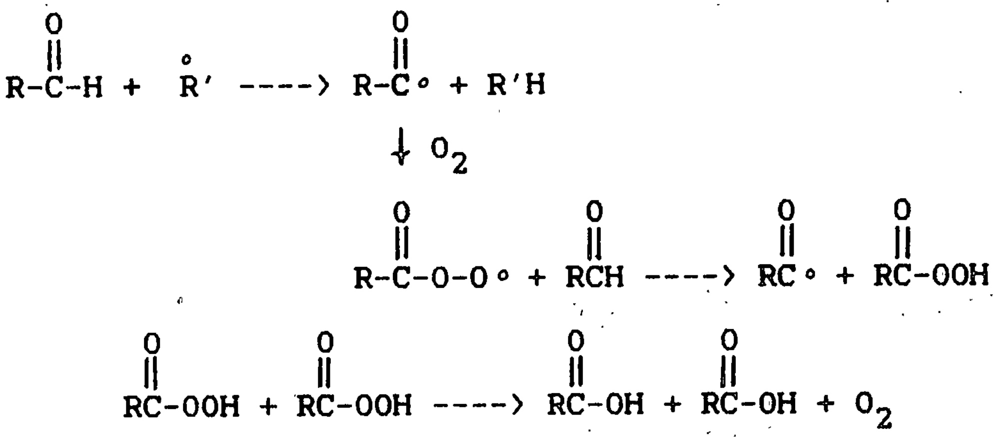
$$RCHO + \overset{\circ}{R}' \text{----}\rangle\ R\overset{\circ}{C}O + R'H$$

$$R\overset{\circ}{C}O + O_2 \text{----}\rangle\ RCO_3{}^\circ$$

$$RCO_3{}^\circ + RCHO \text{----}\rangle\ RCO_3H + R\overset{\circ}{C}O$$

$$RCO_3H + RCO_3H \text{----}\rangle\ RCO_2H + RCO_2H + O_2$$

The mechanism for these reactions may be as follows:



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + \overset{\circ}{R}' \text{----}\rangle\ R\text{-}\overset{O}{\overset{\|}{C}}{}^\circ + R'H$$

$$\downarrow O_2$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O^\circ + R\overset{O}{\overset{\|}{C}}H \text{----}\rangle\ R\overset{O}{\overset{\|}{C}}{}^\circ + R\overset{O}{\overset{\|}{C}}\text{-}OOH$$

$$R\overset{O}{\overset{\|}{C}}\text{-}OOH + R\overset{O}{\overset{\|}{C}}\text{-}OOH \text{----}\rangle\ R\overset{O}{\overset{\|}{C}}\text{-}OH + R\overset{O}{\overset{\|}{C}}\text{-}OH + O_2$$

A molecule of oxygen is regenerated, and two acids are produced. Acids are generally the terminal oxidation pathway products.

Oxidation of ketones requires breaking carbon-carbon bonds, and from a thermodynamic viewpoint takes place only under severe conditions. If conditions exist where cleavage can take place, ketones are cleaved on either side of the carbonyl group to yield a mixture of carboxylic acids [26] .

Both aldehydes and ketones contain the carbonyl group, C=O and are referred to as carbonyl compounds. The carbonyl group plays an important role in determining the chemistry of aldehydes and ketones.

The carbonyl group provides a site for nucleophilic addition and increases the acidity of the hydrogen atoms attached to the alpha carbon. Both these effects are consistent with the structure of the carbonyl group [26,27].

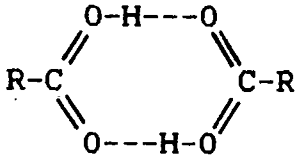
The carbonyl group contains a carbon-oxygen double bond. The pi electrons pull strongly toward oxygen and make carbonyl carbon electron-deficient and carbonyl oxygen electron-rich. Because the carbonyl group is flat, it is susceptible to unhindered approach from above or below. Approach is perpendicular to the plane of the group. Since the polarized carbonyl group is accessible, it is highly reactive [26,27] .

Because aldehydes and ketones both contain the carbonyl group, they resemble each other closely in most of their properties. An aldehyde has a carbon and a hydrogen atom attached to the carbonyl group while there are two carbons attached to the carbonyl group of ketones. This difference in structure affects their properties in two ways: (a) aldehydes are easily oxidized, whereas ketones are oxidized only with difficulty; (b) aldehydes are usually more reactive than ketones toward nucleophilic addition.

Nucleophilic addition is the characteristic reaction of carbonyl compounds [26,27] .

Aldehydes, ketones and carboxylic acids are polar in nature. Once formed, they may not be soluble in nonpolar solvents because polar groups tend to associate with themselves more readily than with the solvent. These groups hydrogen bond, and precipitation or phase separation may occur as they form in a system.

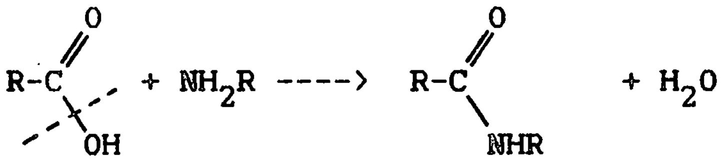
For example, carboxylic acid molecules are polar and can form hydrogen bonds with each other. Two carboxylic acids can strongly hydrogen bond in the following manner: [26]



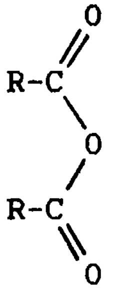
In this case, the carboxylic acid molecules are held together by two hydrogen bonds. Carboxylic acids readily hydrogen bond in hydrocarbon solvents. Once hydrogen bonded, they are less likely to react with other chemical species in the system.

Carboxylic acids were given their name because their most characteristic property is <u>acidity</u>. The hydroxyl group of an acid can be replaced by NHR to yield amides. Amides are functional derivatives of acids and contain the carbonyl group. Amides undergo hydrolysis to revert to acids and amines [26,27] .

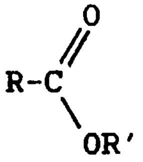
Formation of amides involves cleavage of the C-OH bond of the acid: [26]



Anhydrides and esters are also functional derivatives of carboxylic acids. The hydroxyl group is replaced by OOCR or OR′ respectively [26,27] .



anhydride

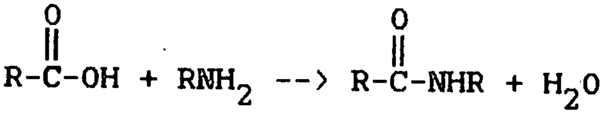


ester

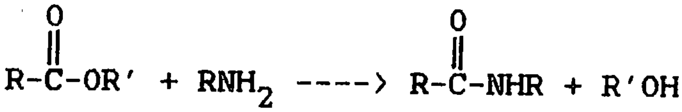
The presence of the carbonyl group makes these latter groups polar [27] .

As the number of carbonyl species in a nonpolar system increases, they may precipitate or form a separate liquid phase. If the acidic species could be reacted with a long chain amine, the resulting amide should be less polar and remain soluble in a nonpolar system. If enough of the acids became long chain amides, oxidized triglycerides might remain in solution in a nonpolar oil solvent.

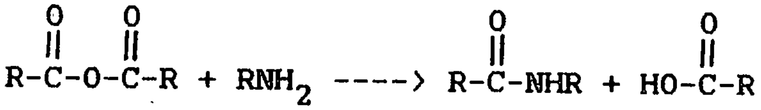
Amides can be derived from acids, esters and anhydrides. Some examples are shown on the following page [27] .



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH + RNH_2 \dashrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}NHR + H_2O}$$



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OR' + RNH_2 \dashrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}NHR + R'OH}$$



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R + RNH_2 \dashrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}NHR + HO{-}\overset{O}{\overset{\|}{C}}{-}R}$$

Sunflower oil consists of a variety of molecular weights. Making one portion of an extremely large molecule polar may not make the entire molecule polar enough to form a separate phase in a nonpolar oil solvent. Each molecule might have to contain a number of polar groups before it separates. The resulting phase may be a solid (or gel) with entrapment of other molecules such as a nonpolar oil solvent.

EXPERIMENTAL

Equipment

The environment of the crankcase of a diesel engine was simulated in the laboratory in the form of a reaction kettle placed in an oil bath heater. All the experiments were conducted in a pair of 500 ml reaction kettles fitted with four post entrance lids (Figure 1).

Two of the openings (the center and one side) on each kettle lid were fitted with Ace threads to provide airtight seals for entering and exiting gas tubes, respectively. Air tight seals were necessary to provide a controllable environment as well as to measure the gas flow rate. Silicon grease insured gas-tight seals between each entrance and its ground glass stopper. As shown in Figure 1, the entering gas tube was connected to a 30 mm glass frit that provided gas percolation through the oil mixture. The glass frit was accurately positioned in a fixed location with consistent positioning from experiment to experiment. Gas percolation could be observed by removing a glass stopper. The exiting tube was connected to tygon tubing leading to a soap film flow meter which measured the gas flow. Flow was normally adjusted to 2.0 ml/sec.

Copper was used as a catalyst in all experiments. Copper foil with an area of 20 cm^2 was rolled into a cylinder and placed over the gas dispersion tube. The copper foil was 5 cm long, 2 cm wide and 0.125 mm thick. When forming the cylinder, the ends were touching, not overlapping. When resting on the fritted glass surface, the copper was in intimate contact with both the gas and oil (Figure 1).

The reaction kettle(s) was placed in the oil bath (Figure 2). The oil bath contained paraffin oil which reached a higher level on the reaction kettle than the level of the oil mixture within the kettle. A Polyscience Model 73 immersion circulator was utilized to maintain an oil bath temperature of slightly above 150 C. 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 automatic temperature control was adjusted to a setting where the oil mixture within the kettle (not in the bath) was maintained at 150 C. The temperature within the reaction kettle was checked periodically with a thermometer. The oil bath was well insulated with approximately 2 inches of vermiculite insulation between steel plates that formed the sides and bottom of the bath. A tight fitting steel lid covered the vapor space above the kettle(s) and bath oil. The oil bath was placed under a venting hood.

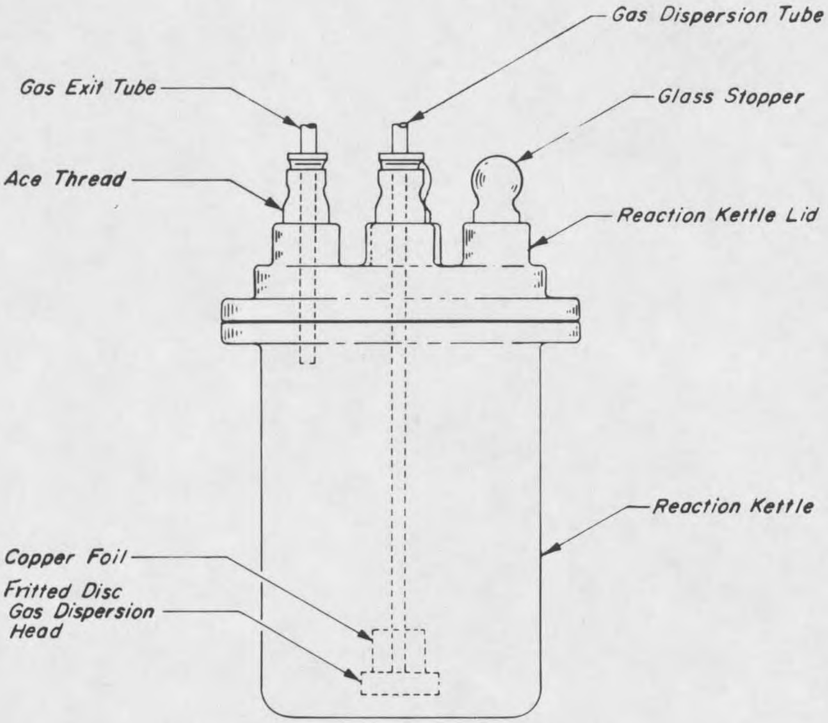


Figure 1. Reaction Kettle

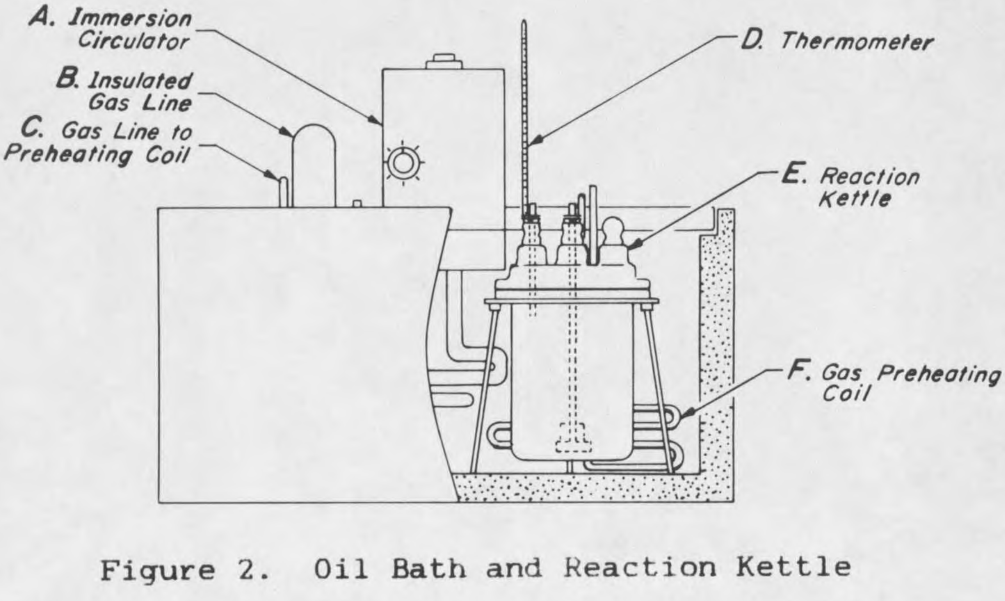


Figure 2. Oil Bath and Reaction Kettle

High pressure cylinders supplied the gas (oxygen or nitrogen) to the reaction kettle. Stainless steel tubing exited from the gas cylinder regulator to enter a four-position gas header mounted on a steel frame placed beside the oil bath. Two precision needle valves were connected to the headers via tygon tubing to control gas flow to the reaction kettles. Gas was preheated by passing it through a one-quarter inch coil of stainless steel tubing that was immersed in the oil bath. Insulated teflon tubing connected the preheating coil to the glass stem of the frit. Gas flow was adjusted to 2.0 ml/ sec. An operating diagram is shown in Figure 3.

Viscosity of the oil mixture was periodically measured using calibrated Cannon-Fenske viscometers. Specific viscometers were used for specific viscosity ranges. Viscometers were placed in a constant temperature water bath that was maintained at 40 C by a Polyscience Model 73 immersion circulator. The Polyscience Model 73 has automatic temperature control with a precision of 0.2 C. To take a sample, one of the kettle lid glass stoppers was removed and 8 ml of the oil mixture was pipetted from the reactor. The 8 ml sample was then transferred to the viscometer. In an attempt to standardize the pipetting procedure, the pipet was placed 8 inches below the surface of the steel lid on the oil bath. Two viscosity

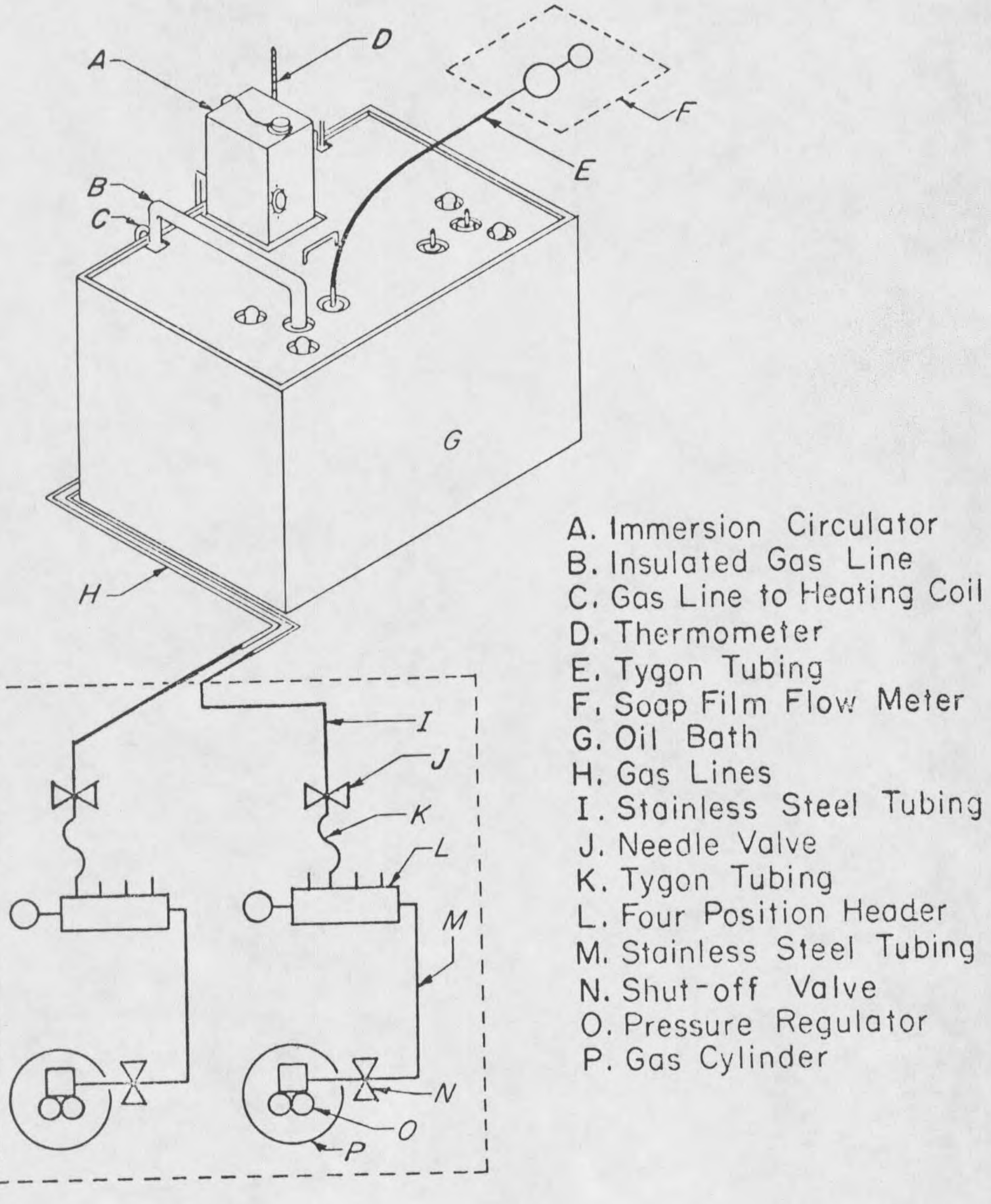


Figure 3. Oil Bath and Operating Diagram

measurements were taken on each sample, and the average value was used as the data point. If necessary, the sample was then saved for a Total Base Number (TBN) titration. If not, it was returned to the reaction kettle.

In an attempt to quantify the rate of gel formation, care was taken to note when gel was first observed as particles in the viscometer when taking a viscosity measurement. Once gel was observed in the viscometer, the frit and copper foil were checked for gel formation. When the copper surface and dispersing area of the frit were covered with gel, the experiment was stopped. At the end of each experiment, the gel was allowed to drain on paper towels in an attempt to remove as much of the supernatant as possible. The gel was then weighed. This allowed approximate comparison of gel formation from experiment to experiment.

Total Base Number (TBN) indicates the alkalinity of the oil mixture. TBN values were determined according to ASTM D 2896, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration". This standard method suggested using the back titration method to get sharp end points when working with used oils. Excess standard $HClO_4$ solution was added to a prepared sample. The excess was then back titrated with standard sodium acetate solution. An Orion Research Model 901 Microprocessor

Ionalyzer fitted with a Corning sleeve-type saturated glass electrode was used to detect the endpoints [29] .

The iodine value of the sunflower oil was determined to provide a relative indication of the amount of unsaturation present. This value was determined according to ASTM Standard 1959-69 which is applicable to vegetable oils and their fatty acids [30] .

Fourier transform infrared spectroscopy (FTIR) was used to determine relative amounts of carbonyl groups in selected samples. FTIR is a low-cost, computer-controlled digitization of spectra which enables the user to extract information in a matter of seconds. With older infrared spectroscopic instruments, shelves of spectra were recorded on chart paper. FTIR spectra is stored in the computer [31] . A Nicolet 5DX computer system with a helium-neon laser and a sodium chloride sample chamber was employed.

Materials

The vegetable oil used at the beginning of the research was sunflower mill oil from Continental Grain Company of Culbertson, Montana. It had an iodine value of 140. Early in the research, the Culbertson oil supply became depleted. New sunflower mill oil was obtained from Cargill Incorporated in Fargo, North Dakota. It had an iodine value of 144. Hydrocarbon basestock lubricating oil was provided by Phillips Petroleum in Bartlesville, Oklahoma. Two different batches of basestock oil were obtained.

Lupersol 130 was provided by Lucidol Pennwalt Corporation of Buffalo, New York. Zinc dialkyl dithiocarbamate (ZDTC) was supplied under the tradename, Vanlube AZ, by R. T. Vanderbilt Company, Inc. of Norwalk, Connecticut. Octadecylamine (ODA) was obtained from Aldrich Chemical Co. Zinc dialkyl dithiophosphate (ZDTP) was supplied under the tradename, Lubrizol 1395, by Phillips Petroleum Company of Bartlesville, Oklahoma. Paranox 107 was obtained from Exxon Chemicals of Houston, Texas. Tertiary butylhydroquinone (TBHQ) was received from Eastman Chemical Products, Inc. of Kingsport, Tennessee under the name Tenox TBHQ Food-Grade Antioxidant. Sattva Chemical Company of Stamford, Connecticut provided the copper stearate. All other chemicals were reagent grade.

From the standpoint of safety, inherent problems arise when working with hot oils. The experimental apparatus was placed under a venting hood to remove noxious vapors. Care was taken when working with the high pressure gas cylinders. All waste oils and cleaning agents were treated as hazardous wastes and disposed of through Montana State University's Chemical and Hazardous Waste Department. Gloves, safety glasses and aprons were worn when handling hot oils.

RESULTS AND DISCUSSION

Any given commercial lubricating oil contains an additive package that is specifically designed for that particular oil. The oil additive package contains chemicals that maximize engine performance. Some of these chemicals are dispersants, detergents, rust inhibitors, oxidation inhibitors, viscosity modifiers and friction reducers. With the presence of such a wide variety of chemicals, the additive package chemistry is extremely complex. Each of these additives are chemicals and may react with one another to form new compounds when placed in the lubricating oil.

The previous workers [10,11,12] in this laboratory showed commercial lubricating oil contaminated with 5.0 weight percent sunflower oil degraded rapidly. Degradation was quantified by viscosity measurements, with polymerization of the oil mixture measured by viscosity rise.

To begin the current research, a standard run was made with Super HD II low ash MIL-L-2104C API CD SAE 30 commercial lubricating oil contaminated with 5.0 weight percent sunflower oil. Standard conditions consisted of the oil mixture being exposed to 20 cm^2 copper foil, 150 C and 2 ml/sec oxygen percolation. Figure 4 presents the viscosity rise for this case. Sunflower oil polymerization was rapid, and simulated engine failure occurred within 20 hours. In a commercial lubricating oil experiment, failure takes place when the viscosity of the oil mixture reaches or exceeds 500 centistokes. This result was consistent with previous work.

Due to the unknown chemical nature of the additive package in commercial oil, Dutta [12] attempted to use SAE 30 hydrocarbon basestock oil in his research. When using basestock oil as the lubricating substrate, new problems were encountered. Dutta contaminated basestock oil with 5.0 weight percent sunflower oil and exposed the mixture to standard oxygen flow, copper foil and 150 C. He observed severe degradation of the oil mixture within twenty hours and noted formation of insolubles which he referred to as a heavy sludge. The viscosity data of Dutta, shown as a dotted line in Figure 5, are viscosities taken of the clear liquid above the sludge. This clear liquid will be referred to as the supernatant phase.

To familiarize the current researcher with the use of basestock oil, Dutta's standard conditions experiment was verified. Hydrocarbon basestock contaminated with 5.0 weight percent sunflower oil was exposed to copper foil, oxygen percolation and 150 C. Viscosity data of the supernatant can be seen in Figure 5. Formation of

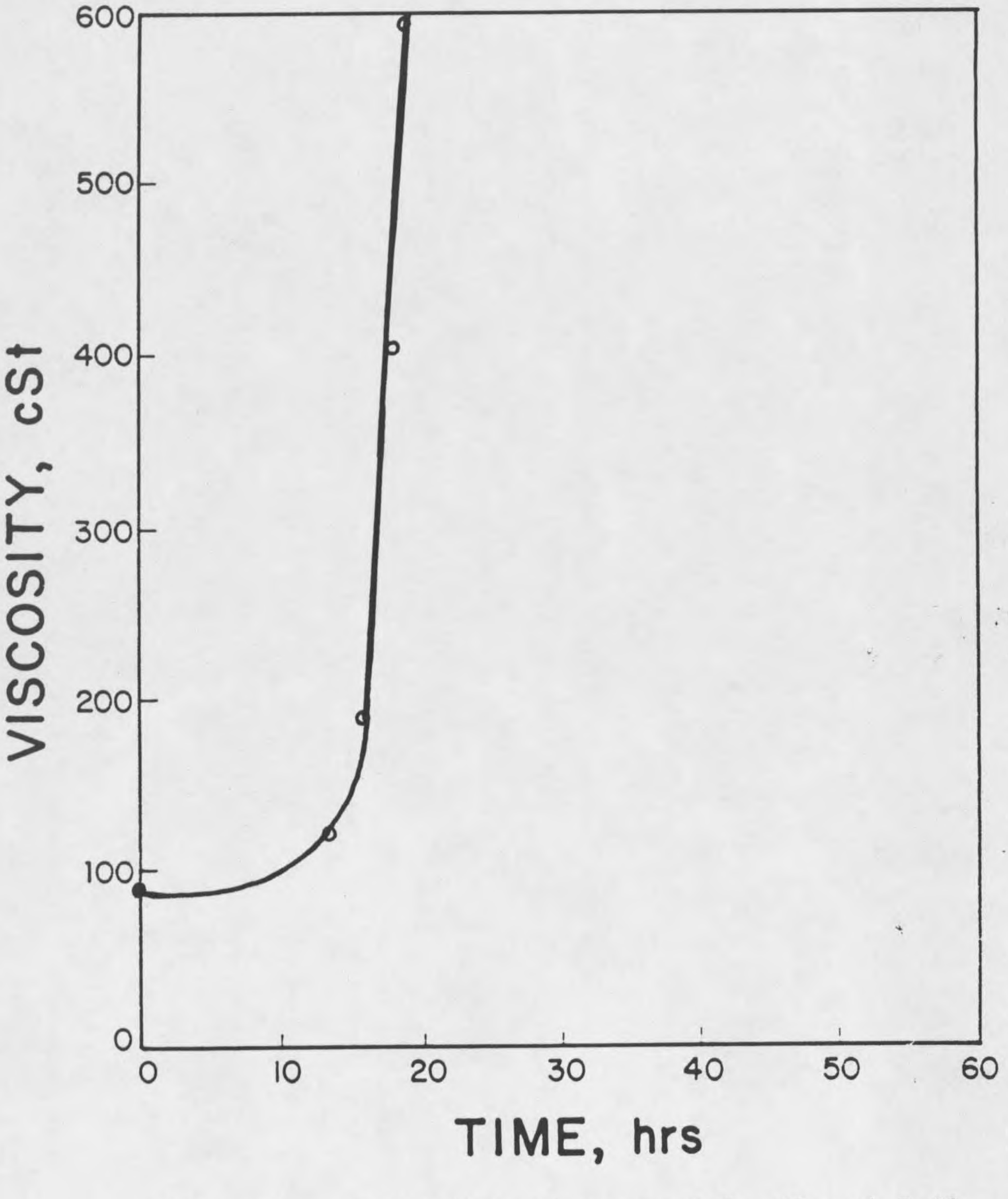


Figure 4. Viscosity of commercial oil and 5.0% sunflower oil vs. time for standard conditions.

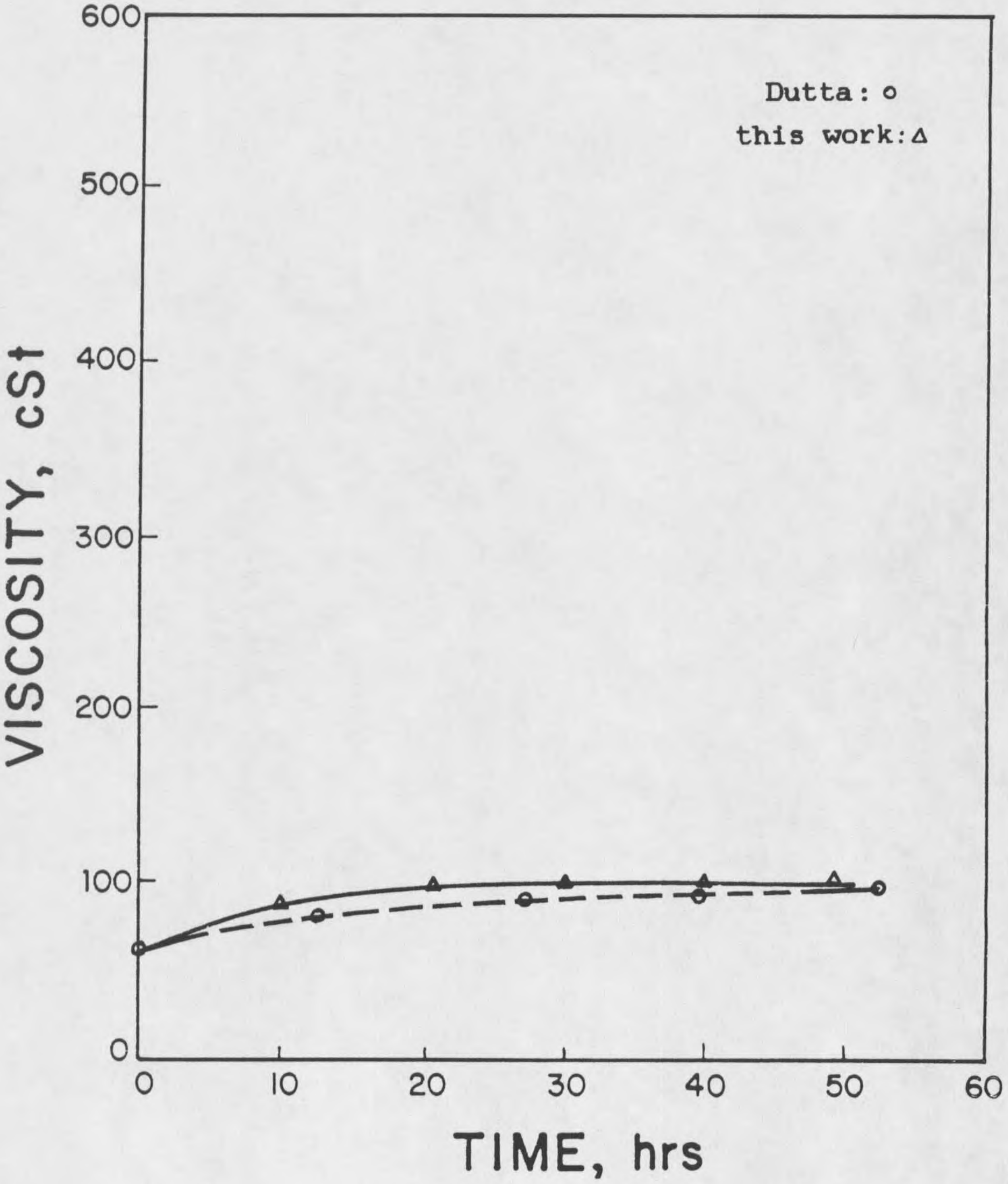


Figure 5. Viscosity of basestock oil and 5.0% sunflower oil vs. time for standard conditions.

appreciable insolubles (referred to as gel or sludge) occurred within 8 to 10 hours. Both gel and viscosity results are consistent with Dutta's work. The gel blanketed the copper foil and was 1/8 to 1/4 inch thick on the sides and bottom of the reaction vessel. The gel was sticky with an irregular surface structure with nipples of gel protruding into the supernatant.

The proportion of supernatant to gel was approximately nine to one. This result was not unexpected because the current researcher felt that polymerized sunflower oil was contributing to gel formation. The original concentration of sunflower oil in the latter experiment was nine and one-half to one. The gel is highly swollen with supernatant. This may account for the small difference in the above proportions.

The gel was difficult to quantify. Initial attempts were made to gravimetrically measure the gel, but these methods of quantification were not reliable because the gel phase was swollen with lubricating oil. Since two phases are formed when using hydrocarbon basestock oil, the current researcher felt the viscosity measurements alone meant little regarding degradation. It was also difficult to avoid gel particles when pipetting the supernatant, and even fine gel particles lodged in the viscometer and distorted viscosity measurements.

When using the commercial lube oil, sunflower oil polymerization resulted in viscosity rise with only a slight amount of gel at the end of a run [10,11] . Dutta's [12] research in the basestock oil indicated sunflower oil polymerization contributed to gel formation. The gel phase must be eliminated from the system if oil degradation is going to be measured by viscosity rise. Gel is largely unquantifiable and adds another complication to the research.

Preliminary experiments (Runs 1 and 2) were done in an attempt to find milder conditions where the sunflower oil polymers might contribute to viscosity rise rather than gel formation. Since the addition polymerization reaction may have a lower activation energy than the other oxidation reactions that form aldehydes, ketones and acids, decreasing the temperature might produce increased viscosity rise and reduced gel [27] . From Dutta's [12] results, standard conditions of 5.0 weight percent sunflower oil, 150 C, 2.0 ml/sec oxygen flow and presence of copper foil produced gel within 10 hours; and supernatant viscosity rose only slightly within 60 hours. In order to avoid gel at a lower temperature and get measurable viscosity rise in a reasonable time frame, more sunflower oil may be necessary. A control of standard conditions (basestock oil, oxygen percolation, copper foil and 150 C) with 25.0 weight percent sunflower oil (Run 1) was run to establish a baseline for an increased sunflower oil trial at reduced temperature.

Viscosity measurements of the supernatant in Run 1 showed little viscosity rise (similar to standard conditions) as shown in Figure 6. Gel formation was first observed at 8 hours. Upon completion of the experiment at 55 hours, the mixture was removed from the oil bath and allowed to cool. Twenty to thirty hours later, uneven gel formation with ridges protruding above the surface was observed. As anticipated, more gel was observed in this experiment with 25.0 weight percent sunflower oil than in a standard conditions experiment with 5.0 weight percent sunflower oil. This was consistent with prevailing thinking that sunflower oil polymerizes and forms gel simultaneously. Increasing the amount of sunflower oil in the system resulted in an increase in the amount of gel formed.

Lowering the temperature from 150 C to 135 C might not allow oxidation to the species contributing to gel to proceed as rapidly as those contributing to addition polymerization. This might limit gel formation. This experiment (Run 2) was conducted at 135 C with 25.0 weight percent sunflower oil, basestock oil, copper foil and oxygen percolation and gave viscosity rise similar to Run 1 where the higher temperature was used. This result is also shown in Figure 6. Significant gel formation was observed in the

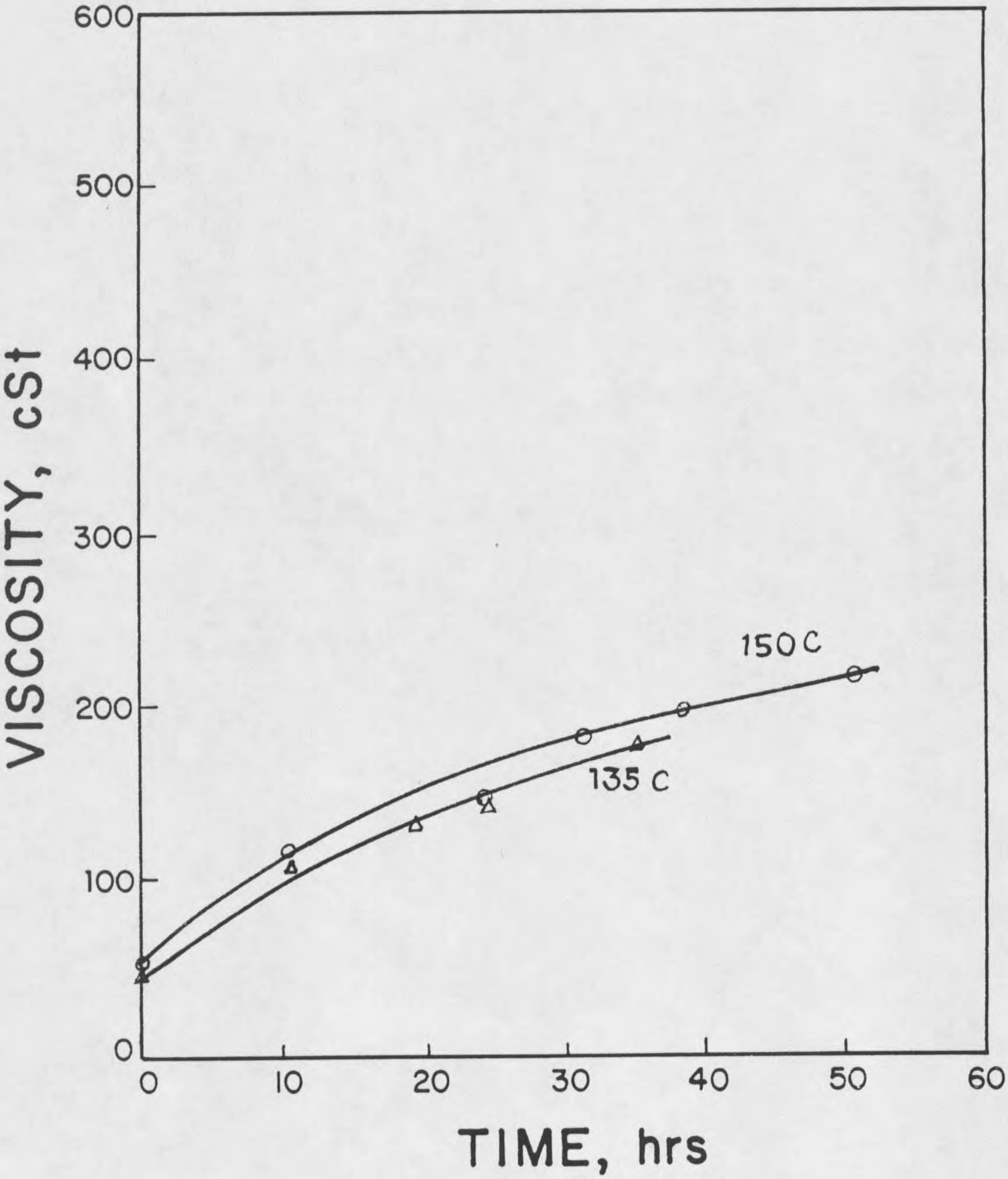


Figure 6. Viscosity of basestock oil and 25.0% sunflower oil vs. time for standard conditions at 150 C and 135 C.

same time frame as Run 1 (8 to 10 hours). Unexpectedly, slightly more gel seemed to be present in Run 2 at 135 C than in Run 1 at 150 C.

It was concluded that lower temperature did not alleviate the problems associated with gel formation. Future work would emphasize understanding the formation of the gel phase and its relation to viscosity rise.

When working with polymers, it is often difficult to distinguish and classify the differences between solids (especially gels) and liquids. The difference between the species that contribute to gel and the species contributing to viscosity might be slight, and vigorous homogenization might show them to be physically similar species. If the gel could be physically dispersed and made to contribute to viscosity rise, one might conclude the species contributing to gel and viscosity rise are physically and chemically similar.

A standard basestock oil/sunflower oil experiment was run for twenty hours. The viscosity was measured and found to be 103 centistokes. Gel from this experiment was swollen with the supernatant. Most of the supernatant was removed from the gel by draining and "patting" dry with an absorbent cloth. The "dried" gel was then weighed. The proportion of gel to supernatant was determined to be approximately ten to ninety. The gel, in proper proportions, was then homogenized at room temperature in the supernatant phase. Homogenization of the gel/supernatant mixture in a Waring high speed laboratory blender (Model 700B) at 20,000 rpm for five minutes produced a slight viscosity rise from 103 to 110 centistokes. At twenty minutes of homogenization, the viscosity was 124 centistokes. Further homogenization produced increased viscosity rise. At 75 minutes of homogenization, the viscosity appeared to decrease. These results can be seen in Figure 7.

The reliability of the viscosity measurements in Figure 7 was questionned. Upon closely examining the flow of the mixture through the viscometer, fine gel particles were detected. Once gel particles are detected, viscosity measurements may not be reliable. Upon ceasing homogenization, the mixture was inspected under bright lighting where a distinct two phase system was observed. The fine gel particles gradually settled from the supernatant phase. Homogenization had produced a finely dispersed two phase system where the above viscosities have little meaning. Fine gel particles probably distorted the viscosity measurements when passing through the viscometer. This led to the conclusion that physical agitation did not cause the gel to revert, even temporarily, to a single phase, viscous material.

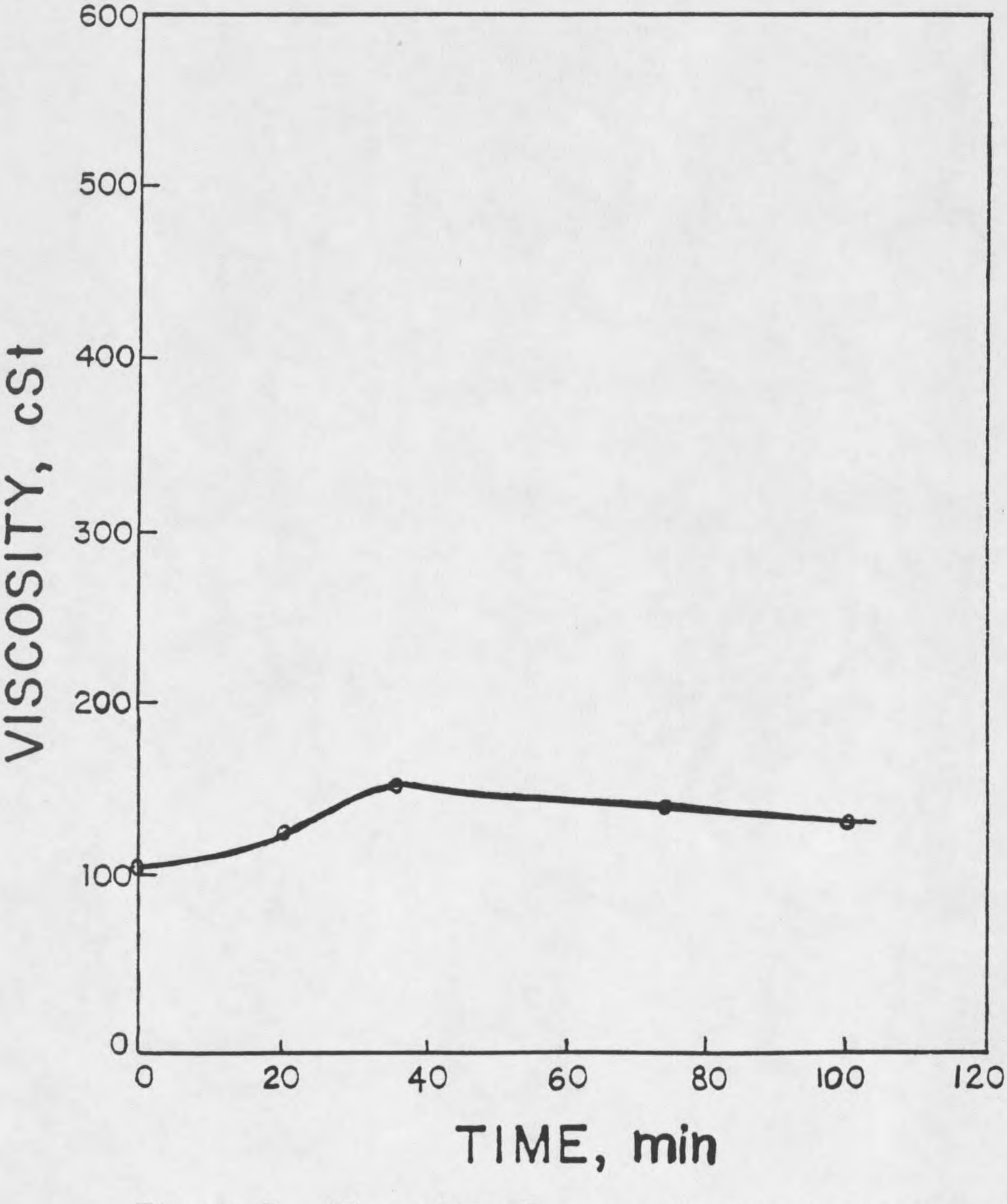


Figure 7. Viscosity of supernatant/gel mixture vs. time of homogenization.

Dispersants and surfactants in the commercial oil additive package are intended to disperse inorganic substances such as dirt/grime, but they may be a factor in preventing the gel phase from precipitating [32] . It was believed the commercial oil dispersant might be able to keep the gel in solution and thus yield a meaningful viscosity rise. Some of the "dried" gel from a basestock experiment was heated in the commercial lubricating oil at a ratio of ten to ninety for 24 hours at 150 C. The mixture was checked every four hours. No physical changes in the nature of the gel were observed. The additive package in the lube oil did not appear to change the physical or chemical nature of the gel. The amount of gel present did not appear to decrease, and the gel particles remained a separate phase from the commercial oil. This result was not surprising because the commercial oil dispersants are not designed to disperse organic species. This result indicated the gel-forming species were chemically different from the species contributing to viscosity.

A commercial organic dispersant, Paranox 107, was obtained from Exxon Chemicals of Houston, Texas. Paranox 107 is a succinamide-based, ashless dispersant. It was felt that this strong dispersant might be able to keep the gel-forming species dispersed as they are being formed. The dispersant in the commercial oil may not have been able to disperse the gel that was already highly associated in the homogenized gel/commercial oil experiment. The amide part of the dispersant is basic in nature and might interact with acidic species to keep them dispersed. Due to proprietary reasons, the exact chemical structure of Paranox 107 could not be obtained. A Phillips 66 representative speculated Paranox 107 may be capable of dispersing organic chemical species in the present system and recommended using 1.0 to 5.2 weight percent [32] .

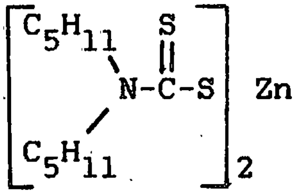
Paranox 107 was added at 3.0 weight percent to the basestock oil/sunflower oil mixture and exposed to oxygen percolation, copper foil and 150 C (Run 3). Gel formation was observed by 14 hours. Recall that gel appeared in a standard conditions experiment in 8 to 10 hours. Presence of the gel again made taking meaningful supernatant viscosity measurements difficult. The commercial dispersant may have worked for a short period of time, but gel formation still occurred. This again indicated the viscosity-forming species and the gel-forming species were chemically different.

The homogenization trials and the commercial dispersant experiment indicated formation of the gel phase was not simply a physical separation. It was felt the additives in the commercial oil might act in either of two ways: 1) chemically inhibit gel formation or 2) keep gel suspended.

If the gel were merely suspended, it might be chemically the same as viscosity-forming species.

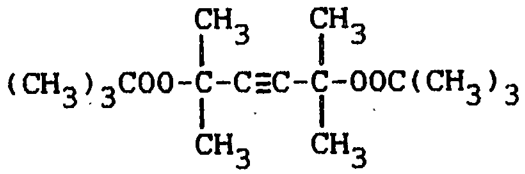
Dutta [12] found two experimental situations where little gel was produced in experiments using basestock oil. Both these experiments were reproduced and confirmed in the present work because they were pivotal to the direction of future research. These experiments are discussed in the following paragraphs.

An antioxidant, zinc dialkyl dithiocarbamate (ZDTC), is sometimes used in commercial oil as an oxidation inhibitor and an anti-wear agent. ZDTC is thought to inhibit corrosion by inhibiting oxidation of the lube oil to acidic species as well as by forming a protective film on metal surfaces. The mechanism by which ZDTC acts is not well understood, but ZDTC is believed to decompose hydroperoxides. The recommended usage level in a diesel oil lubricating system is 1.0 weight percent. The structure of ZDTC is given below.



In Run 4 where 1.0 weight percent ZDTC was added at time zero to the 5.0 weight percent sunflower oil and basestock oil and exposed to copper foil, standard oxygen percolation and 150 C, no viscosity rise and no gel formation of significance were observed (Figure 8). The ZDTC appeared to block polymerization and hence viscosity rise and gel formation. This work confirms the finding of Dutta [12] with ZDTC.

Rewolinski [10] showed oxidative polymerization of commercial oil proceeded by a free radical mechanism. In Rewolinski's work, a commercial peroxide (Lupersol 130) was periodically added to the commercial oil system under a nitrogen environment, and viscosity rise matching that produced with oxygen percolation was observed. The structure of Lupersol 130 is shown below.



$$(CH_3)_3COO-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-OOC(CH_3)_3$$

Lupersol 130 is known to homolytically cleave at 0-0 bonds to produce free radicals which catalyze the chain reaction of oxidative polymerization. It is widely used as a free radical initiator in vinyl polymerization.

Dutta [12] used Lupersol 130 with 5.0 percent sunflower oil in the basestock oil and subjected the mixture to a nitrogen environment, copper catalyst and 150 C. The Lupersol 130 was added at 0.5 weight percent every four hours. He observed significant viscosity rise with

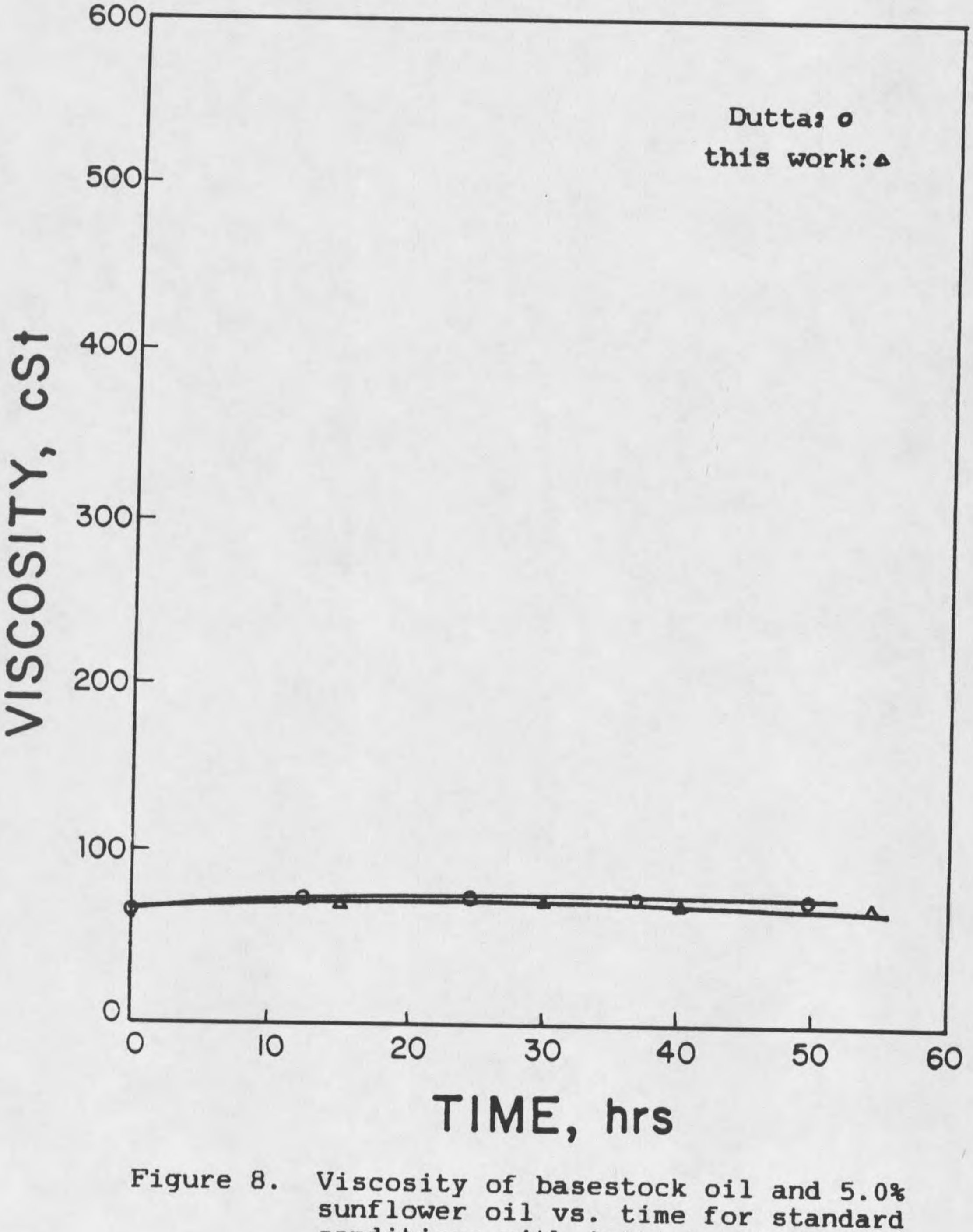


Figure 8. Viscosity of basestock oil and 5.0% sunflower oil vs. time for standard conditions with initial addition of 1.0% ZDTC.

negligible gel formation. Viscosity rise was not as rapid as that encountered when using commercial oil and oxygen, but still occurred.

In this work, the free radical initiator at 0.5 weight percent was added every four hours to the 5.0 weight percent sunflower oil/basestock oil mixture with exposure to nitrogen percolation, copper catalyst and 150 C (Run 5). This trial resulted in essentially no gel and gave the viscosity rise presented in Figure 9. Dutta's results are shown on Figure 9 as a dotted line.

Zinc dialkyl dithiocarbamate, ZDTC, blocked viscosity rise and gel formation in the basestock oil with oxygen while the Lupersol 130 experiment yielded viscosity rise without oxygen. No gel was formed in the absence of an oxygen atmosphere. These experiments seemed to indicate that gel is a separate chemical species produced by oxidation.

If oxygen produced gel and Lupersol 130 without oxygen yielded only viscosity rise, what would happen if they were used simultaneously? One might expect to get both viscosity rise and gel formation. Lupersol 130 free radicals might make species which could contribute to viscosity rise while simultaneous oxidation might result in gel formation.

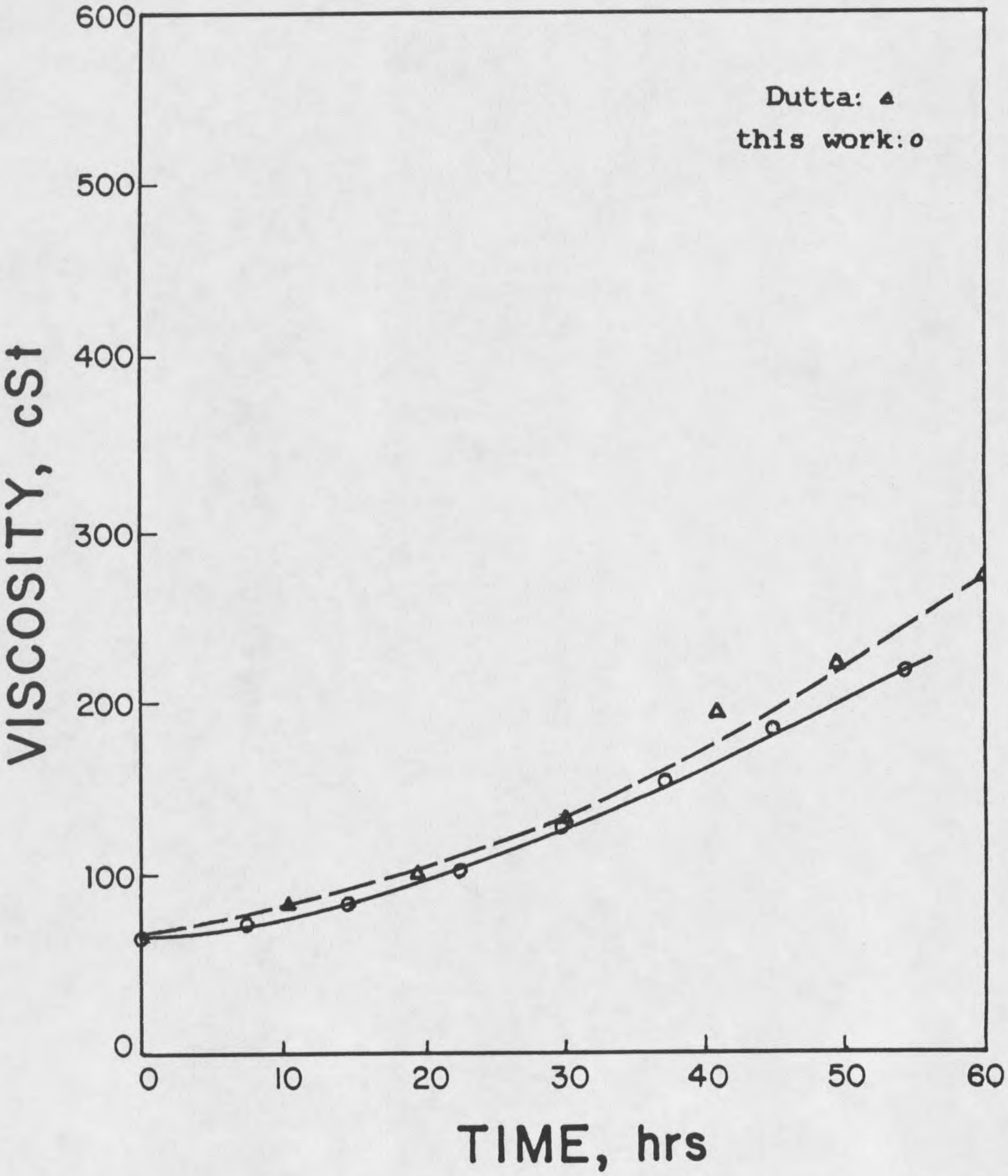


Figure 9. Viscosity of basestock oil and 5.0% sunflower oil vs. time for standard conditions with nitrogen and additions of 0.5% Lupersol 130 every 4 hours.

An experiment with 0.5 weight percent Lupersol 130 added every four hours at standard conditions with oxygen present (Run 6) produced significant gel in a time frame similar to standard conditions without Lupersol 130 (8 to 10 hours). Only one viscosity measurement was taken because the gel formation by 8 hours was so great that gel particles plugged the viscometer. It was speculated that this result occurred because the triglycerides simultaneously polymerized and oxidized with the resulting polymers perhaps precipitating due to their "carbonyl polarity."

Previous results indicated ZDTC was an antioxidant inhibiting polymerization that produced viscosity rise and gel formation. What if more free radicals as derivatives of Lupersol 130 were added to the earlier experiment using 1.0% ZDTC with oxygen in an exposure of 5.0% sunflower oil in basestock oil? Dutta [12] showed ZDTC does not prevent viscosity rise when used with a nitrogen atmosphere and Lupersol 130 present. Current and past research indicated ZDTC does not inhibit the initiator role of Lupersol 130 but does seem to work as an antioxidant. If ZDTC, oxygen and Lupersol 130 were all present in the sunflower/basestock system, the results might be no gel formation but significant viscosity rise because ZDTC may block the oxidation of polymers to gel and yet allow Lupersol 130 to produce viscosity rise.

An experiment using 1.0 weight percent ZDTC, basestock oil, 5.0 weight percent sunflower oil, 0.5 weight percent Lupersol 130 added every four hours, copper foil, oxygen and 150 C (Run 7) produced heavy gel. Viscosity results were again difficult to take because gel formation occurred in such large quantities by 8 hours that the gel particles plugged the viscometer.

The experiments with ZDTC and/or Lupersol 130 are summarized below.

Table 2: Summary of Experiments with Additives

ZDTC oxygen	ZDTC Lupersol 130 nitrogen	ZDTC Lupersol 130 oxygen	Lupersol 130 oxygen
no viscosity little gel	viscosity little gel	gel	gel

A strong hypothesis may be made regarding Table 2. Zinc dialkyl dithiocarbamate (ZDTC) appears to block oxidative polymerization, but not the oxidation reactions that cause polymerized material to become increasingly polar. The ZDTC may be blocking hydroperoxide formation, but not hydroperoxide decomposition. When Lupersol 130 is present, hydroperoxides are already present and decomposition of the hydroperoxides occurs. In the ZDTC, Lupersol 130 experiment with nitrogen present, the polymers contribute to viscosity rise. In the same experiment with oxygen present, the polymers may undergo oxidation and form gel. ZDTC cannot stop the oxidation reactions that cause polarity. When ZDTC is present, polymer is still being made. As oxidation occurs, the polymer becomes increasingly polar. The oxidation reactions appear to be fast enough to knock the polymer out of solution to form gel before it contributes to viscosity rise. When Lupersol 130 and oxygen are used simultaneously, oxidation of the polymers results in gel formation.

These foregoing results led to a re-evaluation of the research approach. It was decided that pursuing a system with two additives, Lupersol 130 and ZDTC, was not in the best interest of future research. Dealing with a simple chemical system might be the best approach.

At this point in the research, the original supply of hydrocarbon basestock oil was exhausted. The new basestock oil was obtained from Phillips 66 and is known as Baltic Oil ISO UG 68, Grade 315, 81550. Jette [11] found different supplies of commercial lubricating oil had different additive packages which were formulated for and based on their source of crude oil. These lubricating oils from different sources with their customized additive packages gave viscosity rise in different time frames.

Due to Jette's [11] findings, the new basestock oil was exposed to standard conditions with 5.0 weight percent sunflower oil, oxygen percolation, copper foil and 150 C (Run 8). Gel was still produced but at a later time. The old basestock oil and standard conditions produced gel in 8 to 10 hours, while the new basestock oil and standard conditions did not produce significant gel until 15 to 20 hours. Supernatant viscosity rise with the new basestock oil was similar to supernatant viscosity rise with the old basestock oil. This comparison is shown in Figure 10.

Why did the old basestock oil produce gel at ten hours and the new basestock oil at twenty hours? Perhaps atomic emission spectroscopy would identify a key difference between these oils. Samples of both basestock oils were sent to Lubricon Laboratory in Indianapolis, Indiana and analyzed for trace metal content.

Atomic emission data indicated differences in trace metals as shown in Table 3.

Table 3: Atomic Emission Data

	Old Basestock ppm	New Basestock ppm
Iron	1	1
Aluminum	1	1
Copper	1	2
Tin	3	0
Silicon	5	5
Sodium	2	8
Magnesium	3	6
Zinc	3	9
Barium	0	4

It is difficult to pinpoint any significant differences that may be causing the delay of gel formation in the new basestock oil. Some possibilities are tin may be acting as a catalyst while other metals such as sodium, zinc, magnesium and barium may be acting as deactivators. These tests from Lubricon are not extremely accurate below ten parts per million; therefore, the small parts per million numbers shown in Table 3 may not really indicate significant differences between the two basestock oils.

On visual inspection, the new basestock oil appeared to be more iridescent than the old basestock oil. It was speculated aromatics were involved and might somehow

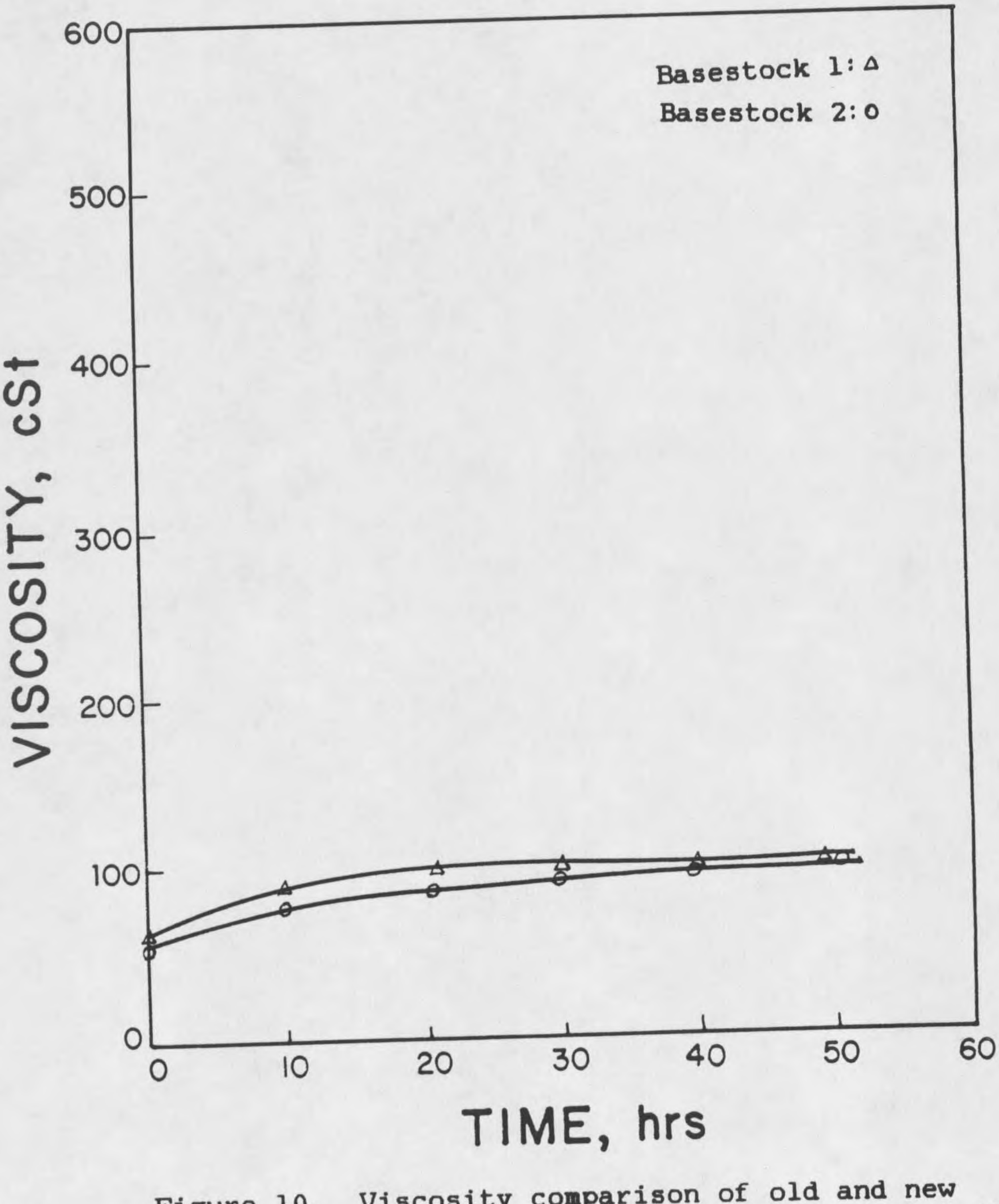


Figure 10. Viscosity comparison of old and new basestock oils and 5.0 % sunflower oil vs. time for standard conditions.

influence the polymerization or other oxidation of the sunflower oil [33] . Fourier transform infrared spectroscopy (IR) on the two samples were analyzed for differences in aromatics. [34] The aromatic region of IR showed no distinct differences between the two basestocks.

Differences between the two basestocks were not clearly definable using infrared spectroscopy or atomic emission data. Up to this point in the research, the current researcher assumed the basestock oil acted as an inert diluent for the sunflower oil because Dutta [12] showed that, when the basestock oil without the presence of sunflower oil was exposed to oxygen, copper and 150 C, viscosity did not rise and no gel formed. Surprisingly, different batches of hydrocarbon basestock appeared to cause sunflower oil to react differently at the experimental conditions of this work.

In attempting to answer the question of influence of different basestocks, there are a variety of possible explanations. Perhaps a trace agent such as a homogeneous refinery chemical was causing the difference. Different sources of crude may contain varying amounts of trace elements due to geographical differences [33] . These trace elements may not have been detectable in the atomic emission study because variations in results occur when attempting to detect metals in amounts of 10 parts per million or less.

Further speculation as to differences between the two basestocks was judged to be unproductive to the current work.

Because the new basestock oil gave different results from those found previously, any earlier research that was to be extended would need to be reproduced. The series of ZDTC and Lupersol 130 experiments that were previously discussed were reproduced (Runs 4-7) in the new basestock oil.

The first experiment with the new hydrocarbon basestock oil (Run 9) involved 5.0 weight percent sunflower oil, 1.0 weight percent ZDTC and 0.5 weight percent Lupersol 130 added every four hours. The mixture was exposed to oxygen, copper foil and 150 C. It was hypothesized that because sunflower oil in the new basestock oil produced gel at a later time than in the old basestock oil that ZDTC might be able to prevent oxidation of the polymers which contribute to gel. This was believed because there appeared to be a slower oxidation of polymers which contribute to gel in the new basestock (gel at 20 hours instead of at 10 hours as with the old basestock). Lupersol 130 might then be able to make polymers contributing to viscosity rise because the polymers might not be oxidized and become polar. When this experiment was performed, gel formation occurred within 20 hours. It was concluded that ZDTC did not act against the oxidation reactions that result in polar polymers. The ZDTC did not perform any better in this experiment with the new basestock oil than it did with the same conditions in the old basestock oil.

Next, the new basestock oil with Lupersol 130 added every four hours at 0.5 weight percent and standard conditions of oxygen percolation, copper foil and 150 C without ZDTC present (Run 10) were tested. This experiment also produced heavy gel in the twenty hour time frame. The polymers were again being oxidized and becoming polar.

The two key experiments that did not produce gel in the old basestock oil were repeated in the new basestock oil. The first experiment used 0.5 weight percent Lupersol 130 added every four hours, nitrogen, copper, 150 C and 5.0 weight percent sunflower oil. This experiment (Run 11) reproduced the results obtained in the old basestock oil. Viscosity rise was observed, and no gel formation took place. Comparison of the viscosity results can be seen in Figure 11. Viscosity rises of the two basestocks contaminated with 5.0 weight percent sunflower oil and exposed to Lupersol 130 and nitrogen are similar. Under a nitrogen environment, viscosity rise occurred in the same time frame.

The second experiment that produced no gel in the old basestock was 1.0 weight percent ZDTC, oxygen, copper, 150 C

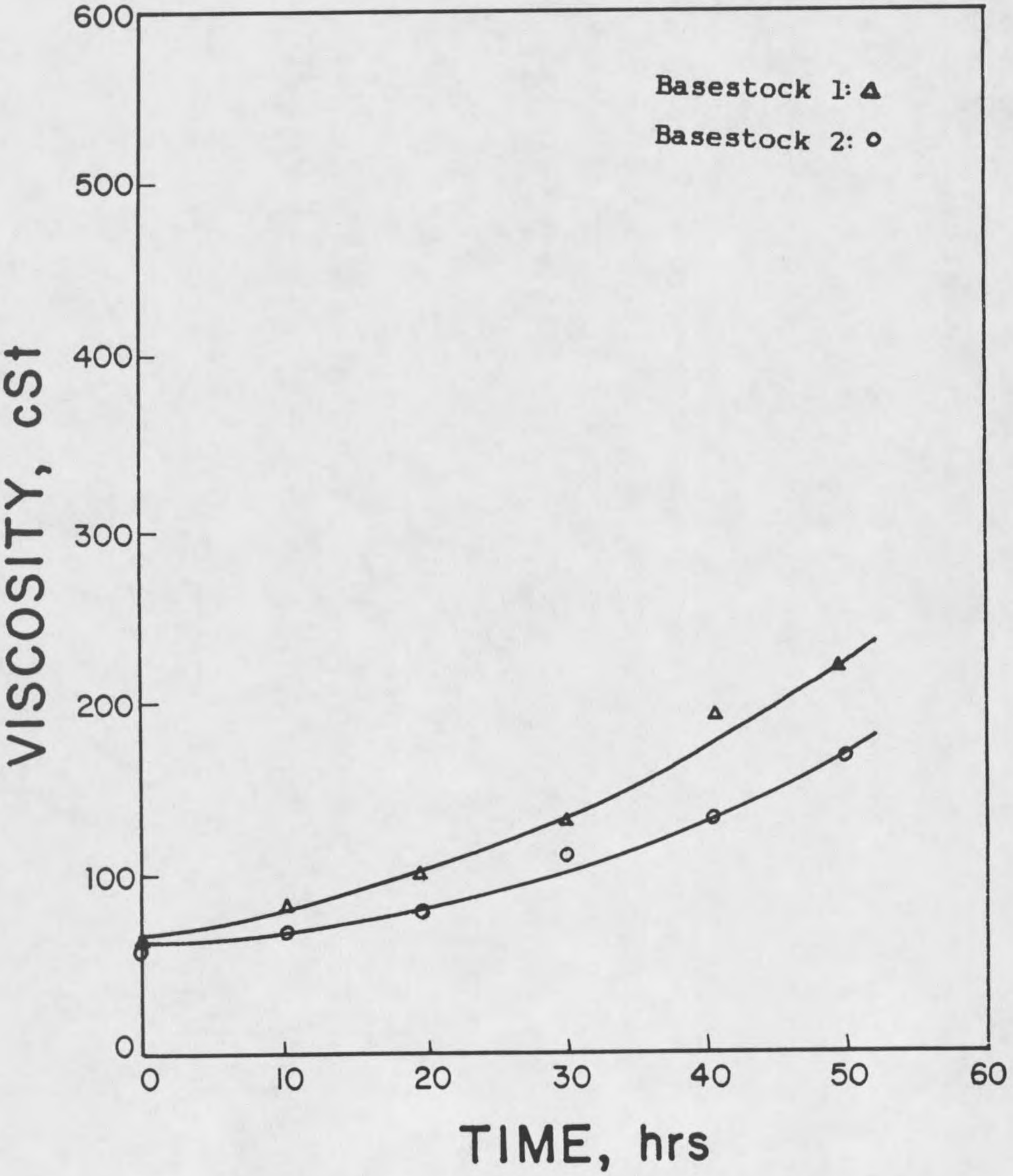


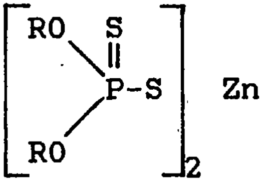
Figure 11. Viscosity comparison of old and new basestock oils and 5.0% sunflower oil vs. time for standard conditions with nitrogen and additions of 0.5% Lupersol 130 every 4 hours.

and 5.0 weight percent sunflower oil. These same conditions were tested with the new basestock (Run 12). With the new basestock, gel formation occurred between 15 and 20 hours. The amount of gel formation at 20 hours in the new basestock oil with ZDTC present was comparable to the amount of gel formation at 10 hours in the old basestock oil without ZDTC present. The amount of gel formed with ZDTC present in the new basestock oil was also similar to the amount of gel formed in the new basestock oil without the presence of ZDTC. ZDTC appeared to be ineffective since gel formation occurred in the same time frame as standard conditions (around 20 hours).

Because ZDTC was so effective in minimizing gel formation in the old basestock oil (exposed to an oxygen atmosphere) and was considered a key to future research, the exact same ZDTC experiment (Run 13) was repeated. Gel formation again occurred in significant amounts at 20 hours. There appeared to be no improvement when using the new basestock oil in conjunction with ZDTC.

The new basestock oil may have some metal or contaminant compound that is deactivating the ZDTC and making it ineffective. Some difference(s) between the two basestocks causes ZDTC to perform differently in each.

From the beginning of the sunflower oil experiments in this laboratory, it was known that ZDTP, zinc dialkyl dithiophosphate, was the most commonly used antioxidant in the lubricant industry [32] . ZDTP supposedly inhibits the initiation stage of autoxidation by decomposing intermediate hydroperoxides to nonradical products. It may also inhibit the propagation step by reacting with the peroxy radical. The structural formula of ZDTP is given below.



Dutta [12] showed 1.0 weight percent ZDTC blocked gel formation and viscosity rise in the old basestock oil/5.0 weight percent sunflower oil mixture exposed to oxygen percolation, copper foil and 150 C. One weight percent ZDTP was ineffective when used under the same conditions. The current research indicates ZDTC may not be a superior antioxidant. However, it may remain in the system while ZDTP decomposes. Jette [11] showed the concentration of zinc (presumably from ZDTP) in a commercial lubricating oil/5.0 weight percent sunflower oil system decreased with time. Based on these results, a decision to test ZDTP in the new basestock was made.

Dutta's results with 1.0 weight percent ZDTP in the old basestock oil/5.0 weight percent sunflower oil were reproduced with the new basestock oil/5.0 weight percent sunflower oil under standard conditions (Run 14).

Significant viscosity rise was not observed, and gel formation occurred within 20 hours. The viscosity results are shown in Figure 12 with Dutta's results depicted by a dotted line. There was no improvement with ZDTP present over the standard conditions case with no ZDTP. Gel formation occurred at a later time than in Dutta's experiment and in a time frame similar to a standard conditions experiment.

Since Jette [11] showed the concentration of zinc declined with time and ZDTP may be decomposing in this laboratory system, progressive additions every four hours of 1.0 weight percent ZDTP were made to the new basestock oil/5.0 sunflower oil mixture. Again, the system was exposed to oxygen, copper foil and 150 C (Run 15). When this experiment was run, significant gel formation occurred within 15-20 hours. The ZDTP added either initially or periodically was not effective in the given system.

Neither ZDTC nor ZDTP had worked in the new basestock, yet one of the earlier speculations was that antioxidants in the commercial lube oil were stopping oxidation to gel. Perhaps there was an interaction between the antioxidants and some other material in the commercial lube oil. At this time, an ongoing review of the literature revealed copper stearate might have a synergistic effect with the

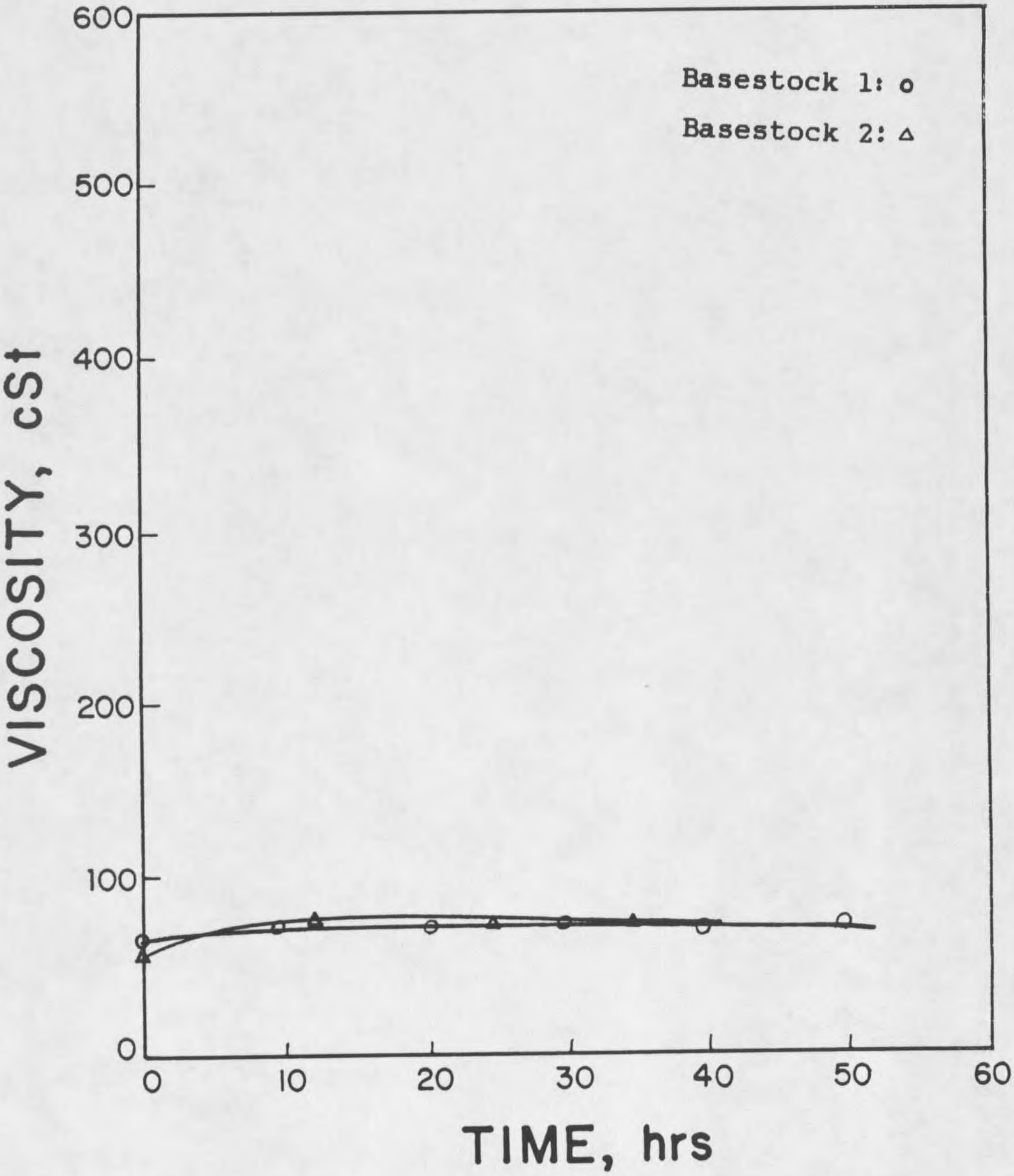


Figure 12. Viscosity comparison of old and new basestock oils and 5.0% sunflower oil vs. time for standard conditions with initial addition of 1.0% ZDTP.

antioxidants [35] . The structure of copper stearate is as follows:

$$(C_{17}H_{35}COO^{-})_2\ Cu^{+2}$$

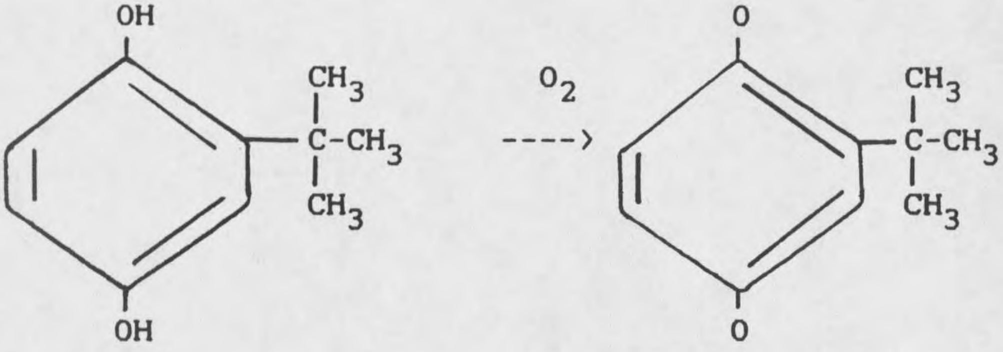
Perhaps the old basestock contained a material that activated the ZDTC whereas the new basestock did not. Copper was a known catalyst for the addition polymerization reaction and may be a catalyst for gel-forming oxidation reactions. Dutta's [12] copper and no-copper experiments could not distinguish any differences in the rate of gel formation. He concluded copper was not a catalyst for the gel-forming reaction(s). The current researcher felt gel formed so rapidly in the old basestock oil that the role copper played was undefinable. In the new basestock oil where gel formation occurs at a slower rate, the role of copper with respect to gel may become clearer.

To establish a control, 10 ppm copper stearate replaced copper foil in an experiment of new basestock oil/5.0 weight percent sunflower oil exposed to oxygen and 150 C (Run 16). It was speculated that copper stearate might dissociate and yield Cu^{2+} ions in the system. However, significant gel formation occurred in Run 16 within 5 hours which was faster than with standard conditions. This was not unexpected because Jette [11] showed soluble copper was the most active form of catalyst in this system. When using copper foil, the copper first had to dissolve to form active species.

With direct addition of copper stearate, the copper was already in a soluble form.

Next copper stearate (10 ppm) and 1.0 weight percent ZDTC were both added at otherwise standard conditions (Run 17). ZDTC appeared to be effective for a short period of time, but significant gel formed by 16 hours. Both copper stearate experiments seemed to produce gel faster than the standard conditions case.

The ongoing literature search suggested phenols might work as antioxidants in the present system. Quinones which are oxidized phenols might destroy free radicals and thereby terminate radical reactions [36] . High levels of phenols might increase the induction period and delay the oxidation process. Dutta [12] tried 4,4'-methylenebis (2,6-di-tert-butylphenol) in his research. It was believed Dutta's phenol might not have been converted to the quinone which may be the functional form responsible for antioxidant action [37] . The tertiary butyl groups might have hindered the hydroxyl group and the quinone structure might not have been active. Tertiary butyl hydroquinone (TBHQ) is a simpler molecule and might be easily oxidized to the quinone form. This conversion is shown on the following page.



tertiary butylhydroquinone tertiary butylquinone

When 0.5 weight percent TBHQ was used in the current system with new basestock oil, 5.0 weight percent sunflower oil, copper foil, oxygen and 150 C (Run 18), significant gel was formed within 20 hours. There was no improvement with the addition of TBHQ.

The complex chemistry associated with using oil additives such as antioxidants was again reviewed, and it was decided that some simpler chemistry must be understood and more fundamental experimental variables examined. At this time, Raman [38] found removal of the copper foil from the commercial lubricating oil system at four hours still resulted in a viscosity rise similar to the standard conditions where the copper was left in the mixture for the duration of the experiment.

In the new basestock system, more insight into the chemistry might be obtained by manipulating the environment to which the oil mixture was exposed. From Raman's results, it was hypothesized that long-lived radicals might be formed early in the experiment and keep producing addition polymerization. If the new basestock system were exposed to oxygen for four hours and then subjected to a nitrogen environment, viscosity rise might take place without gel formation. The initial oxygen environment might produce the long-lived radicals that lead to viscosity, and the gel might not form because the oxygen would not be present to polarize the addition polymers.

A standard experiment of new basestock oil/5.0 weight percent sunflower oil exposed to copper foil and 150 C was run with oxygen for four hours and then nitrogen for the remainder (Run 19). No viscosity rise was detected in 48 hours (4 hours of oxygen and 44 hours of nitrogen). A small amount of gel formed due to the initial exposure to oxygen. Because viscosity rise was not detected and minimal gel formed, the theory of long-lived radicals seems improbable. It appears more likely that Raman's result with removing copper after four hours is due to soluble copper species that remain in the system after the copper is removed.

The body of experimental data gathered so far indicated oxygen was attacking the double bonds in the addition polymers and making these polymers polar. The polar addition polymers are then not soluble in the nonpolar lubricating oil. If the carbon-carbon double bonds were converted to addition polymers by Lupersol 130 in a nitrogen atmosphere, the large materials that dissolved in neutral solvent might produce viscosity.

Next, three experiments were performed exposing the basestock/sunflower oil mixture to 1.0 weight percent Lupersol 130 added every two hours and a nitrogen atmosphere. The first (Run 20) subjected the oil mixture to Lupersol 130, nitrogen, copper foil and 150 C until reaching a viscosity of 500 centistokes. Nitrogen percolation was then switched to oxygen (28 hours) to produce a viscosity rise to 1278 centistokes in an additional 24 hours. These viscosity results are shown in Figure 13. The experiment ran for another 44 hours where viscosity measurements were not taken and frequent observations were made to see if gel formation was occurring. No apparent gel formation took place. However, the oil mixture became so viscous that it was a solid at room temperature; therefore, gel might not have been detected even if it were present. The tentative conclusion was drawn that the polymerized material did not convert to gel. The most accessible double bonds were converted to addition polymers by the Lupersol 130, and few were left for oxygen to attack to form gel.

The second experiment (Run 21) involved the same conditions as Run 20, and a viscosity of 215 centistokes at 20 hours was measured before switching to oxygen. Viscosity continued to rise for the next 20 hours until reaching 500 centistokes. These results are also shown in Figure 13. The experiment ran for an additional 22 hours while checking for gel formation. An apparent gel phase was present at 62 hours, but it could not be separated from the viscous supernatant phase. When the mixture cooled to room temperature, attempts to separate the two phases by decanting were unsuccessful. The result of this experiment leads to the conclusion that moderately polymerized material converts to gel only very slowly. The most accessible double bonds were converted by the Lupersol 130 to addition polymers, and few were left for oxygen to attack to form gel.

In the third experiment (Run 22), the viscosity reached 110 centistokes at 12 hours before switching to an oxygen environment. Viscosity results are also shown in Figure 13. Significant gel was formed within 15 hours after switching to oxygen. The amount of double bonds consumed in going from 60 to 110 centistokes may not have been high enough to prevent gel formation after oxygen introduction.

The theory that oxygen was simultaneously cleaving double bonds to yield polar compounds while addition polymerization was proceeding appears to be valid. To further test this hypothesis, a compound that might react with carboxylic acids and prevent gel formation was tested.

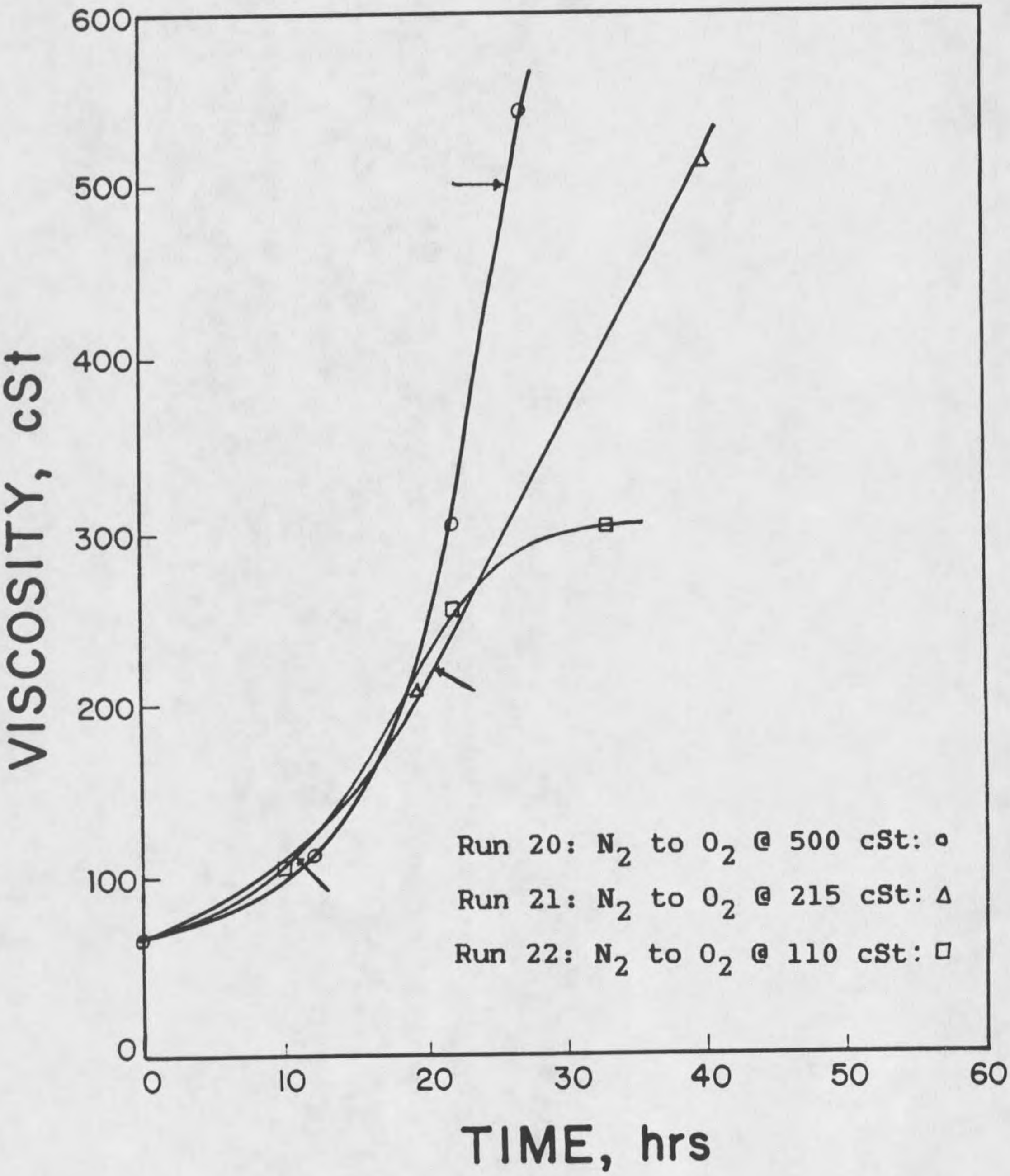


Figure 13. Viscosity of new basestock oil and 5.0% sunflower oil vs. time for standard conditions with nitrogen and additions of 0.5% Lupersol 130. Nitrogen switched to oxygen at times indicated by arrows.

Octadecylamine (ODA) is an eighteen carbon amine with the following formula.

$$CH_3(CH_2)_{17}NH_2$$

The amine should react with the acids to form long chain amides which would be less polar than the acids and remain soluble in the nonpolar lubrication oil. As the carbon-carbon double bond is being cleaved to form acid groups, the ODA might react with the acids. The product molecule should be a triglyceride with an eighteen carbon amide which should be somewhat larger than the original triglyceride molecule and might remain in solution due to its overall nonpolar character.

Fifteen grams octadecylamine was initially added at the beginning of a basestock oil/sunflower oil experiment and exposed to copper foil, oxygen and 150 C (Run 23). Viscosity at 20 hours was 147 centistokes in Run 23 while at 20 hours it was 309 centistokes in a standard commercial oil experiment. Viscosity results were difficult to take after 20 hours because gel formation occurred and gel particles plugged the viscometer. Viscosity rise occurred at a slower rate than with a standard commercial lubricating oil experiment as can be seen in Figure 14. Slight gel formation was detected at twenty hours. The experiment ran for an additional 16 hours, and the amount of gel present did not appear to increase. The final quantity of gel

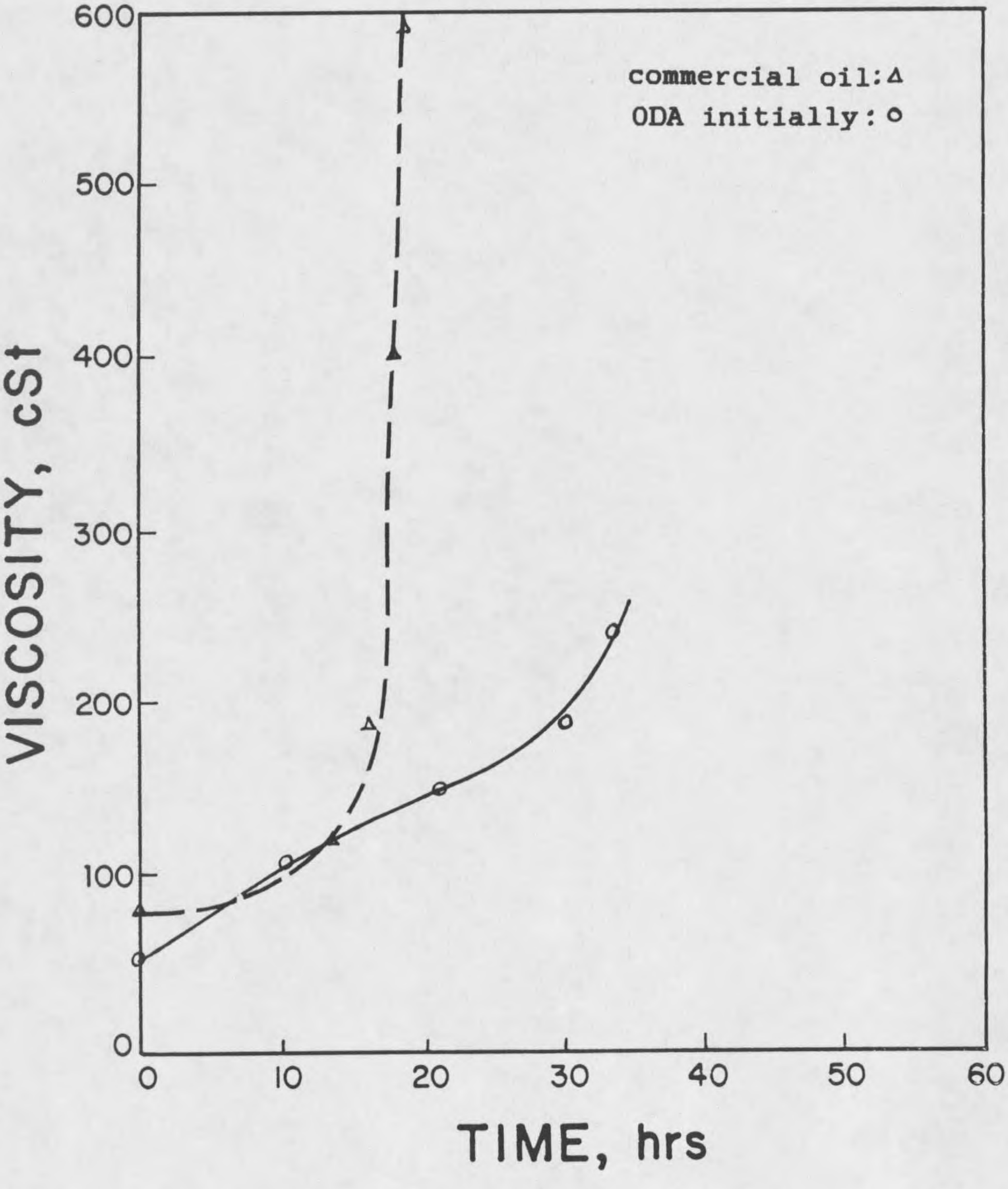


Figure 14. Viscosity of new basestock oil and 5.0% sunflower oil vs. time for standard conditions with 15 g ODA added initially.

formed was substantially less than the amount of gel formed in a standard conditions experiment with basestock.

It was hypothesized ODA might be evaporating from the system; therefore, periodic additions were tried. When 0.7 grams ODA were added every four hours to basestock oil/5.0 weight percent sunflower oil and exposed to copper, oxygen and 150 C (Run 24), gel formation was prevented. The experiment ran for 32 hours with ODA additions every four hours. An additional 18 hours of exposure resulted in no gel formation. The ODA appeared to be reacting with acids as they formed. Viscosity rise was similar to a standard experiment as shown in Figure 15.

The total base numbers (TBN's) for Run 24 are shown in Figure 16. Two TBN samples were taken every four hours. The first sample was taken immediately prior to adding the ODA. The second sample was taken 25 minutes after adding the ODA. An average TBN of approximately 0.3 was maintained. These results indicated the ODA was keeping the system from becoming increasingly acidic.

To test the polar compound hypothesis further, it was speculated the ODA might solubilize gel that had already been formed. A reaction kettle with 36 grams new basestock oil, 4 grams gel from a standard basestock experiment and 4 grams ODA was heated to 150 C. After six hours, the gel "dissolved", and a viscosity measurement was taken.

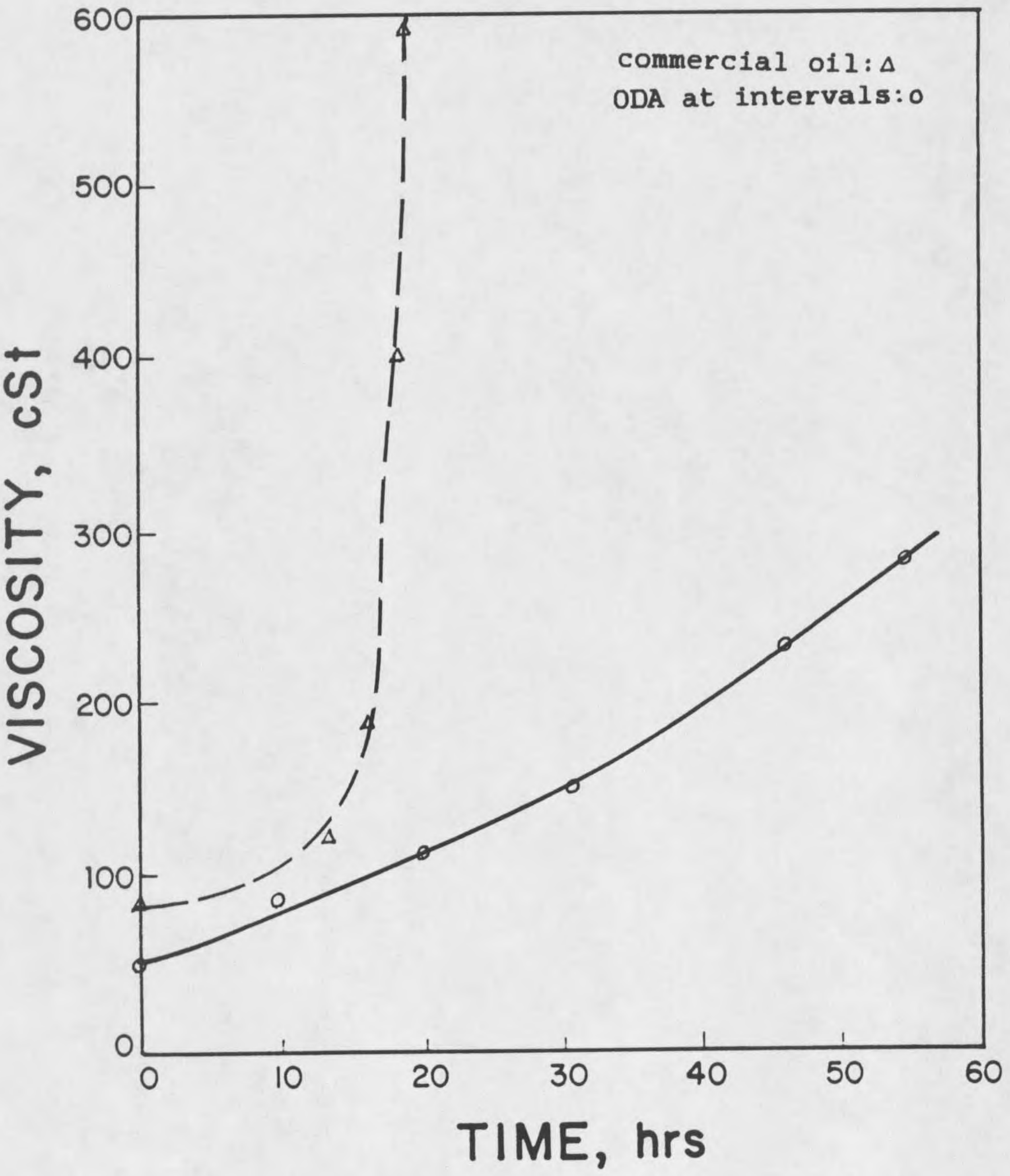


Figure 15. Viscosity of new basestock oil and 5.0% sunflower oil vs. time for standard conditions with additions of 0.7 g ODA every 4 hours.

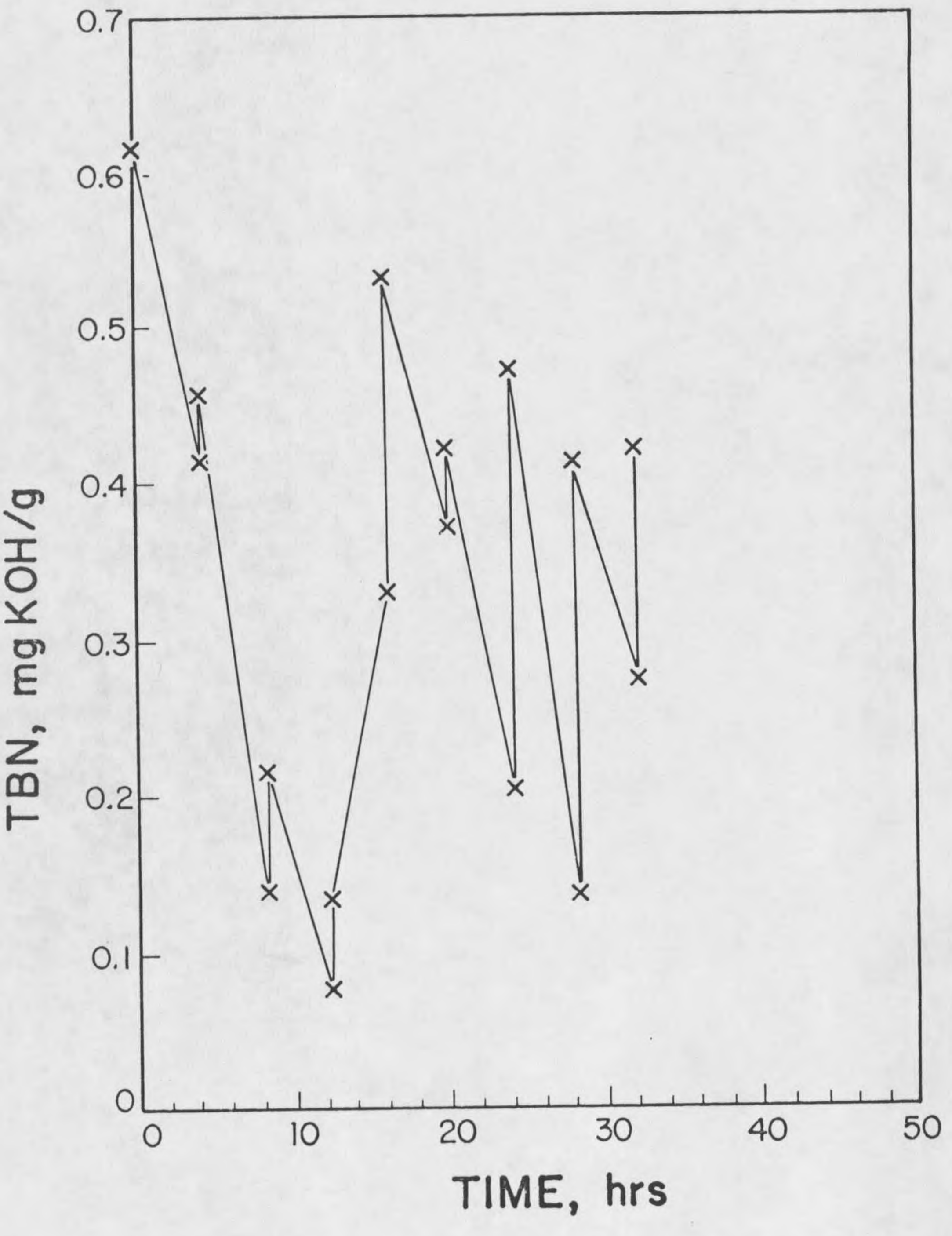


Figure 16. Total base number of new basestock oil and 5.0% sunflower oil vs. time for standard conditions with additions of 0.7 g ODA every 4 hours.

Basestock oil viscosity was 60 centistokes while dissolving the gel into the basestock gave a viscosity of 75 centistokes. Another experiment using the same proportions of gel, ODA and oil was run using commercial lubricating oil. The gel also "dissolved" within six hours. Viscosity increased from 95 to 155 centistokes.

The acidic gel hypothesis appeared to be valid. To further confirm this, Fourier transform infrared spectroscopy was used. This method should show relative amounts of carbonyl compounds and allow for sample comparisons. It was believed the gel material was more polar and was thus more oxidized than the sunflower oil by itself or the same amount of sunflower oil in a degraded oil mixture that had been converted to addition polymers. Sunflower oil in degraded lube oil would probably be more oxidized than pure sunflower oil. The order of increasing degree of oxidation might be pure sunflower oil, sunflower oil converted to addition polymers and sunflower oil converted to gel.

Since the gel from any given experiment was highly swollen with supernatant, it was necessary to obtain reasonably pure gel. The swollen gel from a standard conditions experiment (Run 16) was washed at room temperature with octadecane and hexane and then vacuum dried at room temperature for two or three minutes. This procedure was repeated until the gel was dry and crumbly. The gel was then subjected to a warm nitrogen atmosphere for 30 minutes to remove any occluded solvents. The gel was then dissolved in ortho-chlorophenol (OCP) which is a common solvent for dissolving complex polymers.

Three samples were analyzed with each sample containing the same concentration of sunflower oil. The three samples were 1) pure sunflower oil, 2) gel from a standard conditions experiment and 3) commercial lubricating oil/sunflower oil from a standard conditions experiment thickened to 300 centistokes. All samples were dissolved in OCP. Next the three samples, containing the same concentration of sunflower oil were analyzed by FTIR.

As expected, the gel was the most oxidized and contained more carbonyl groups than the other two samples. The degraded lubrication oil contained more carbonyl groups than the pure sunflower oil, another anticipated result. Figure 17 gives the FTIR spectra. Areas under each of the curves was determined. The degraded lube oil had 1.7 times as many carbonyl groups as pure sunflower oil while the gel had 4.2 times as many carbonyls as pure sunflower oil. These results were consistent with the "polar gel" theory and other experiments.

A tabulated review of all experiments performed is given in Table 4 of the Appendix.

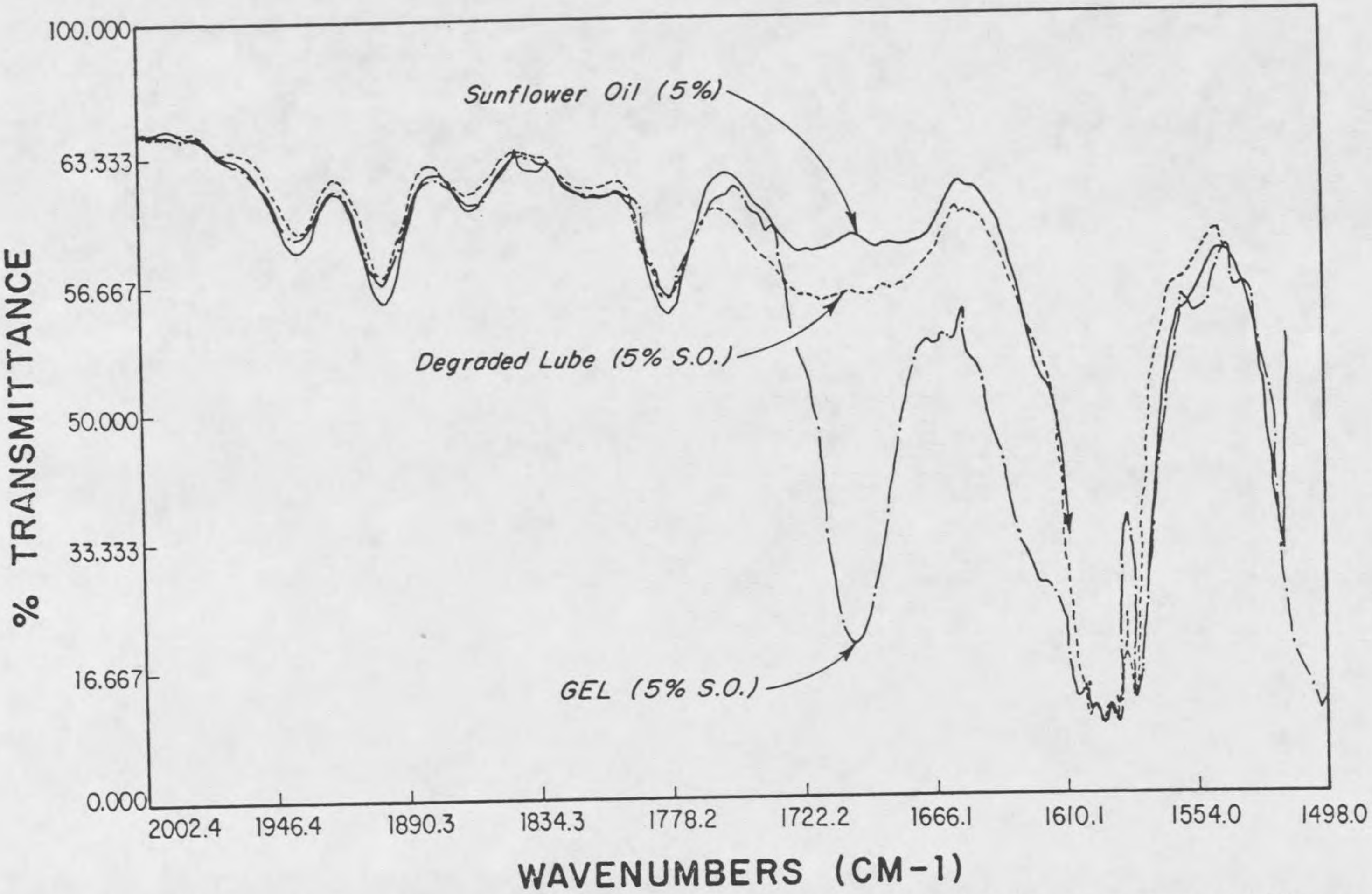


Figure 17. Infrared spectroscopy of equal concentrations of pure sunflower oil, addition polymerized sunflower oil and insoluble gel from sunflower oil.

SUMMARY

The mechanism of gel formation in basestock lubricating oil needed to be clarified at the conditions of this work. The experiments performed in this research provided insight into the differences between gel formation and addition polymerization of sunflower oil. Addition polymerization and gel formation appear to occur simultaneously and only exlude each other as double bonds are consumed.

Once a polymer is polarized to a certain degree by competing oxidation reactions, it has less affinity for the nonpolar lubricating oil. The difference in affinity causes a two phase system. Small molecules that are polarized may still remain in solution, so it should be kept in mind that addition polymerization to large molecules occurs simultaneously with polarization to acidic species. The addition polymers that become polarized appear to contribute to gel formation.

Attempts to make the system less polar by the addition of a long chain amine were successful in dissolving gel. When the acidic polymers were converted to less polar amides, the oil mixture existed as a single phase. Total

base number results showed the system was no longer as acidic. Infrared spectroscopy showed the gel contained more carbonyl groups than pure sunflower oil or degraded sunflower oil. All these results confirm that the polymers resulting from addition polymerization are polarized by oxidation to form the separate gel phase.

These results now facilitate the way for future research in hydrocarbon basestock oil without the presence of gel.

CONCLUSIONS

1. Insoluble gel formed from sunflower oil in basestock lubricating oil appears to be due to simultaneous addition polymerization and other oxidation reactions. These other oxidation reactions also take place at points of unsaturation to yield polar carbonyl groups, especially acids. These polymers then lose affinity for the nonpolar lubricating oil and form a separate phase.

2. The formation of insoluble gel requires the presence of oxygen at the conditions of this work. Sources of peroxy free radicals other than oxygen do not yield insoluble gel.

3. Insoluble gel formation can be prevented by reaction with long chain amines to yield amides which reduce overall molecular polarity by addition of a long chain polar component. Other long chain basic species should show similar gel-retarding behavior.

4. The antioxidant, zinc dialkyl dithiocarbamate (ZDTC), appears to retard gel formation by blocking addition polymerization and not by inhibiting the oxidation reactions that yield polar species.

SUGGESTIONS FOR FUTURE RESEARCH

1. A new standard experimental procedure needs to be devised where gel-forming species are converted to soluble species which can be quantified by viscosity rise.

2. Further confirmation of the theory that acidic species contribute to gel formation should be gained by alkalinity studies of gel and gel-forming systems.

3. Thin layer or gel permeation chromatography should be investigated to determine the relative polymeric natures of insoluble gel and soluble addition polymers.

4. Copper is known to promote addition polymerization, and hence viscosity rise. The formation of gel may also be copper promoted. The role of copper with respect to gel formation needs to be clarified. Other metals need to be tested for their ability to catalyze gel formation.

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APPENDIX

Table 4: Operation Parameters for Oil Bath Runs

Run	Oxygen	Nitrogen	Copper	%S.O.	Temp.	Additives
1	yes	no	foil	25	150	none
2	yes	no	foil	25	135	none
3	yes	no	foil	5	150	Paranox
4	yes	no	foil	5	150	ZDTC
5	no	yes	foil	5	150	Lupersol
6	yes	no	foil	5	150	Lupersol
7	yes	no	foil	5	150	Lup, ZDTC
8*	yes	no	foil	5	150	none
9*	yes	no	foil	5	150	Lup, ZDTC
10*	yes	no	foil	5	150	Lupersol
11*	no	yes	foil	5	150	Lupersol
12*	yes	no	foil	5	150	ZDTC
13*	yes	no	foil	5	150	ZDTC
14*	yes	no	foil	5	150	ZDTP
15*	yes	no	foil	5	150	ZDTP adds
16*	yes	no	stearate	5	150	none
17*	yes	no	stearate	5	150	ZDTC
18*	yes	no	foil	5	150	TBHQ
19*	4 hrs	44 hrs	foil	5	150	none
20*	28 hrs	68 hrs	foil	5	150	Lupersol
21*	20 hrs	42 hrs	foil	5	150	Lupersol
22*	12 hrs	21 hrs	foil	5	150	Lupersol
23*	yes	no	foil	5	150	ODA
24*	yes	no	foil	5	150	ODA adds

* indicates new basestock