



Polymerization of sunflower oil diesel fuel
by Joan Patricia French Keller

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

The 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.

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.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

December 1986

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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.

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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.

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

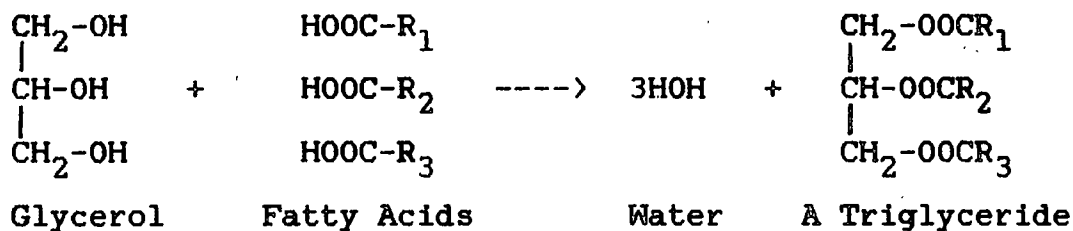
The presence of oxygen in a diesel lubrication system contaminated with vegetable oil may produce a variety of chemical reactions. One of these reactions is oxidative polymerization where oxygen interacts with the double bonds of vegetable oils to initiate the formation of addition polymers. Other oxidation 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.



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] .

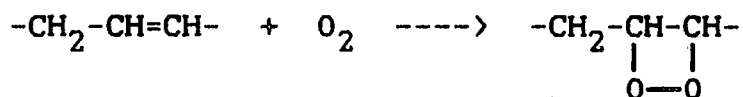
1. The initiation of the oxidative chain reaction is preceded by an induction period which has been attributed to the presence of natural antioxidants. There are no detectable changes in the vegetable oil physical or chemical properties. The induction period may be eliminated by adding a small quantity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

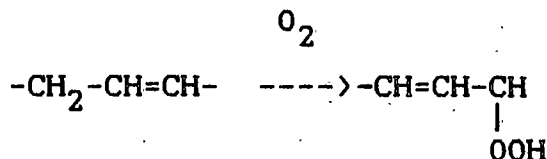
The initiation of the radical chain reaction is a controversial topic. The autoxidation of vegetable oils was first thought to consist of an initial attack on the double bonds of the unsaturated fatty acids to form cyclic peroxides [17] . This reaction is depicted below.



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].

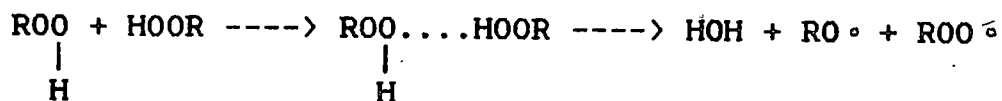
Only a few of the carbon-carbon double bonds need be attacked to produce hydroperoxides. Once formed, even in trace amounts, hydroperoxides can act as catalysts. At this point, it should be mentioned that the initiation of autoxidation may be due to metal catalysts since most fatty esters contain metal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

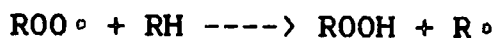


Hydroperoxides may decompose by several mechanisms. When hydroperoxides decompose, the following groups can be

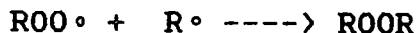
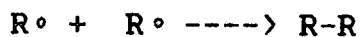
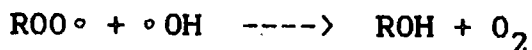
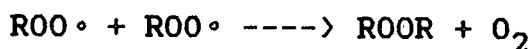
produced: tertiary radicals, hydroxyl radicals, carbonyls and a carbon-carbon cleavage. The hydroperoxides may decompose to form free radicals in the following manner [19] .



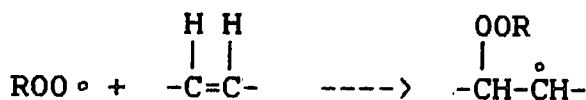
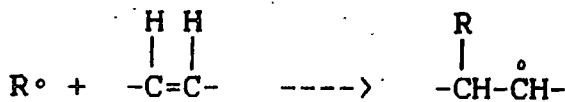
The mechanism of chain propagation is agreed upon among investigators [25] . The initiation products may be oxidized or may combine with another hydrocarbon to produce the following reactions.



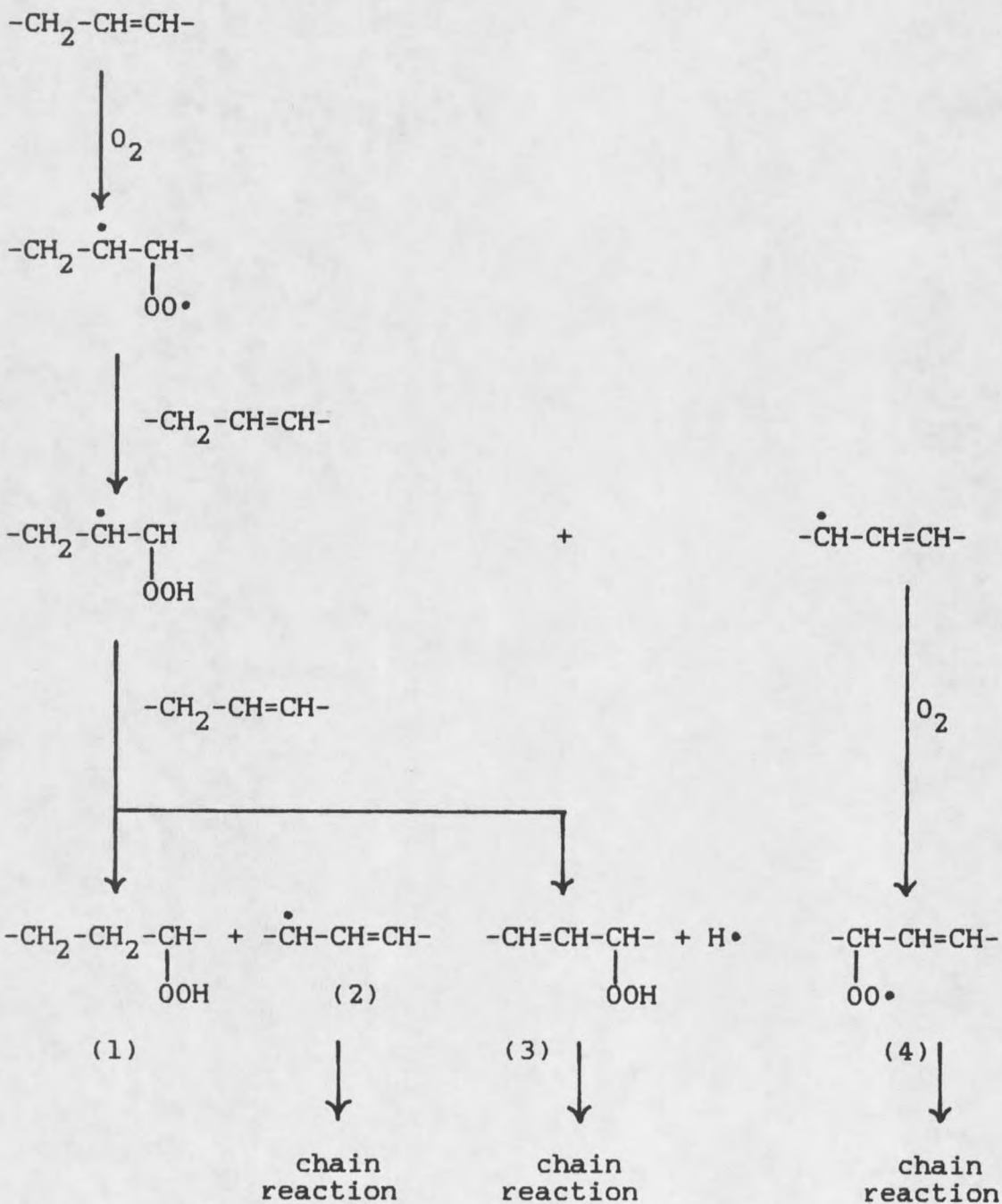
Termination reactions generally consume free radicals and often yield polymers. Some of these reactions are shown below [19,25] .



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

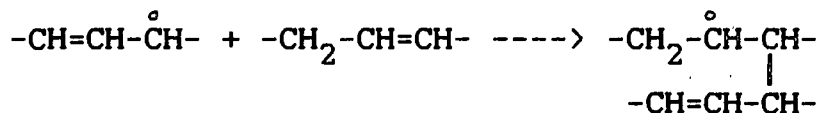


The following general scheme describes oxidative attack of the double bond, formation of hydroperoxides, hydroperoxide decomposition, chain reactions and termination reactions [19,24] .

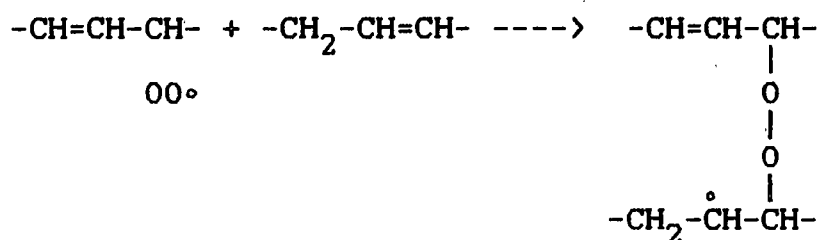


Each of the radicals may react with a variety of compounds [19,25]. These are detailed below.

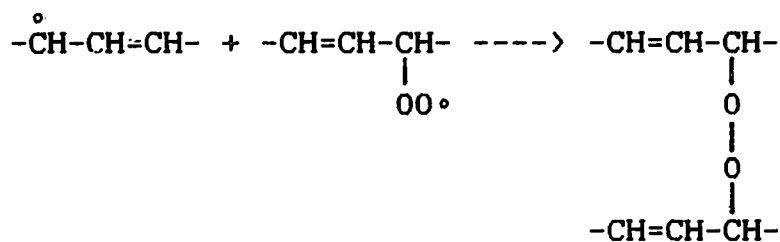
Radical (2) may react with a carbon-carbon double bond and polymerize to form another radical. This is the primary polymerization pathway.



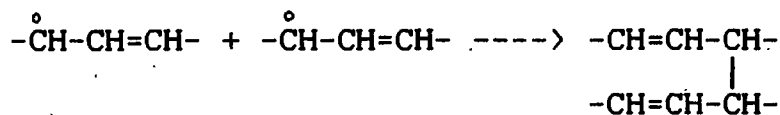
Radical (4) has the capability to attack a carbon-carbon double bond to produce polymer products and continue the chain reaction.



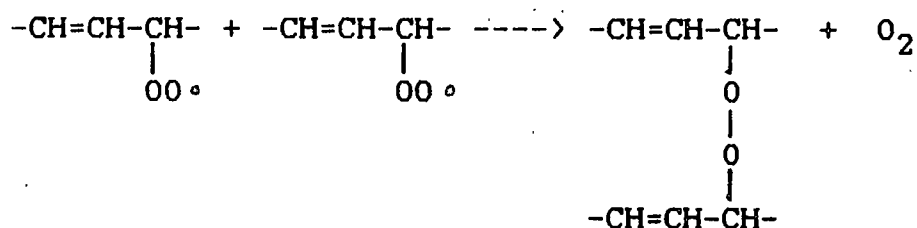
Radical (2) may also combine with Radical (4) and polymerize to a nonradical polymer.



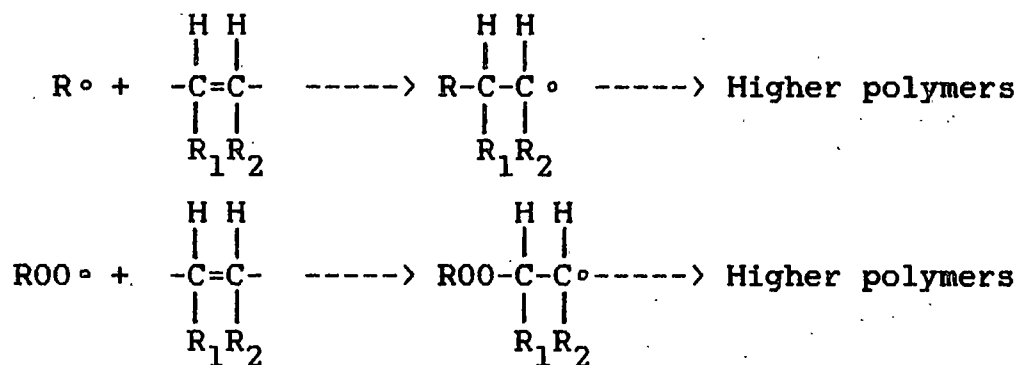
Two Radical (2)'s may polymerize to a nonradical polymer.



Two Radical (4)'s may polymerize.



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

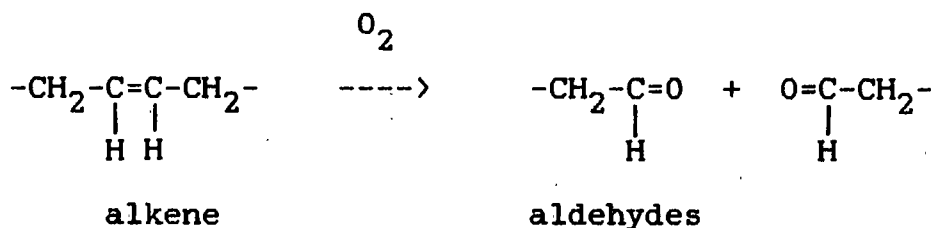


This predominant polymerization pathway to higher polymers is known as vinyl polymerization.

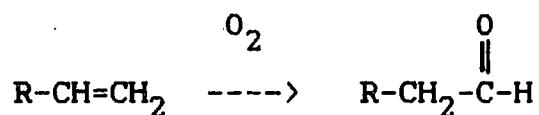
Other Oxidation Reactions

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] .

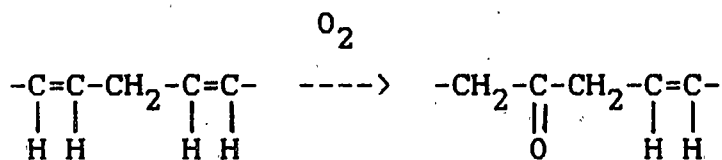
The products of cleavage each contain a carbon-oxygen double bond with the oxygens attached to the carbons present in the original carbon-carbon double bond [27] .



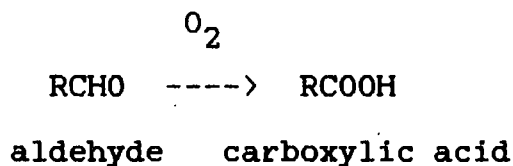
Aldehydes may also be formed without cleavage of the carbon-carbon double bond. If a hydrocarbon molecule contains a terminal double bond, this bond may be attacked; and an aldehyde may be formed [26] .



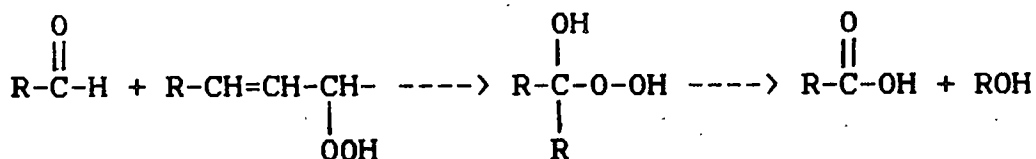
Oxygen may open the hydrocarbon chain (without cleavage of the double bond) in the following manner to form ketones [26,27] .



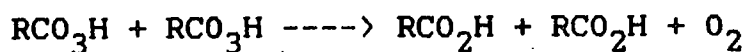
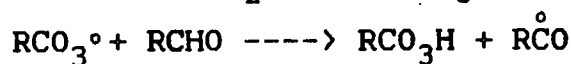
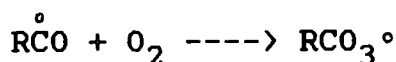
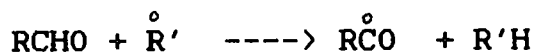
Aldehydes can undergo further oxidation with extreme ease. They are readily converted to carboxylic acids by copper and heat [26] .



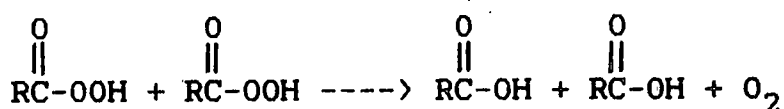
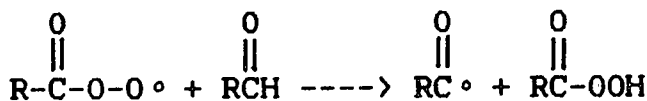
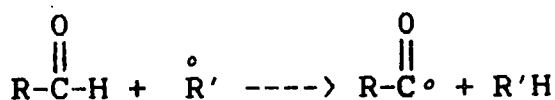
Another mechanism by which aldehydes are converted to carboxylic acids and alcohols may be [26,27]



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] .



The mechanism for these reactions may be as follows:



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].

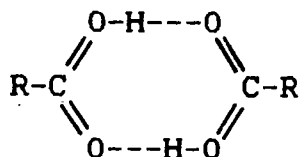
The carbonyl group contains a carbon-oxygen double bond. The pi electrons pull strongly toward oxygen and make carbonyl carbon electron-deficient and carbonyl oxygen electron-rich. Because the carbonyl group is flat, it is susceptible to unhindered approach from above or below. Approach is perpendicular 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.

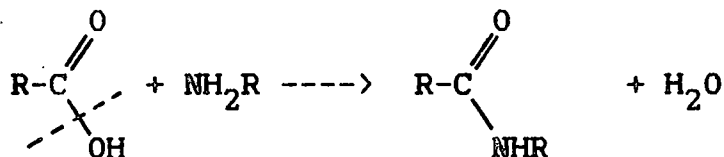
For example, carboxylic acid molecules are polar and can form hydrogen bonds with each other. Two carboxylic acids can strongly hydrogen bond in the following manner: [26]



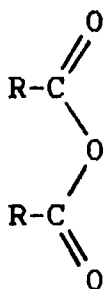
In this case, the carboxylic acid molecules are held together by two hydrogen bonds. Carboxylic acids readily hydrogen bond in hydrocarbon solvents. Once hydrogen bonded, they are less likely to react with other chemical species in the system.

Carboxylic acids were given their name because their most characteristic property is acidity. 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] .

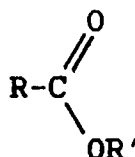
Formation of amides involves cleavage of the C-OH bond of the acid: [26]



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



anhydride

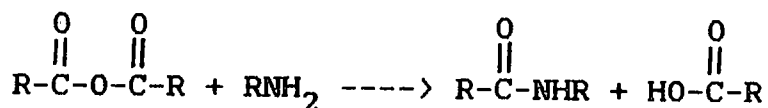
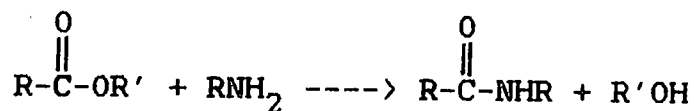
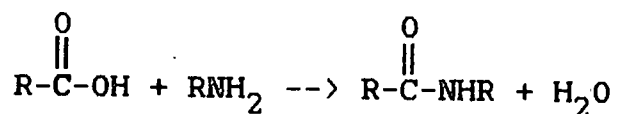


ester

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] .



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. Airtight 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 cm² 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.

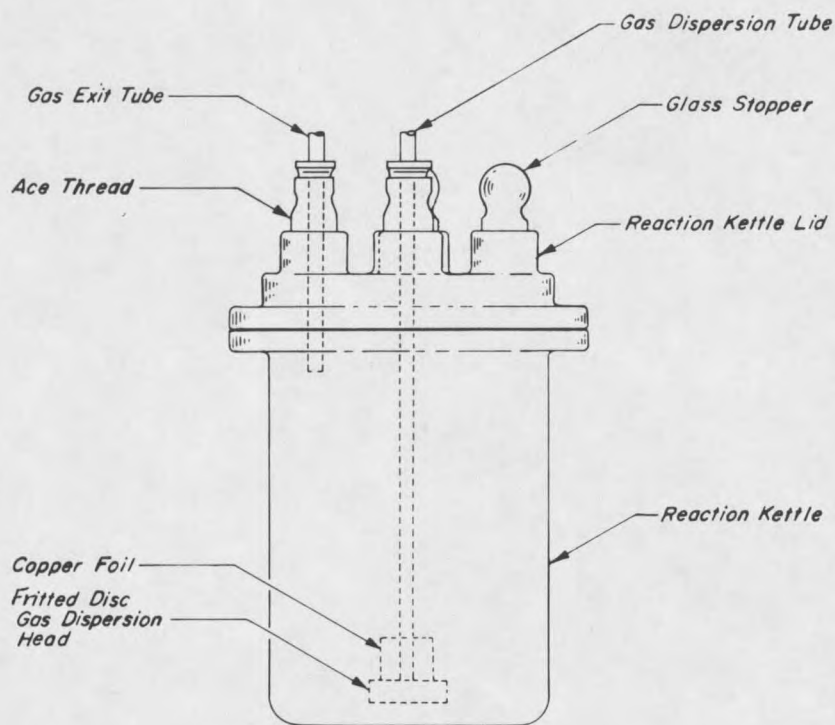


Figure 1. Reaction Kettle

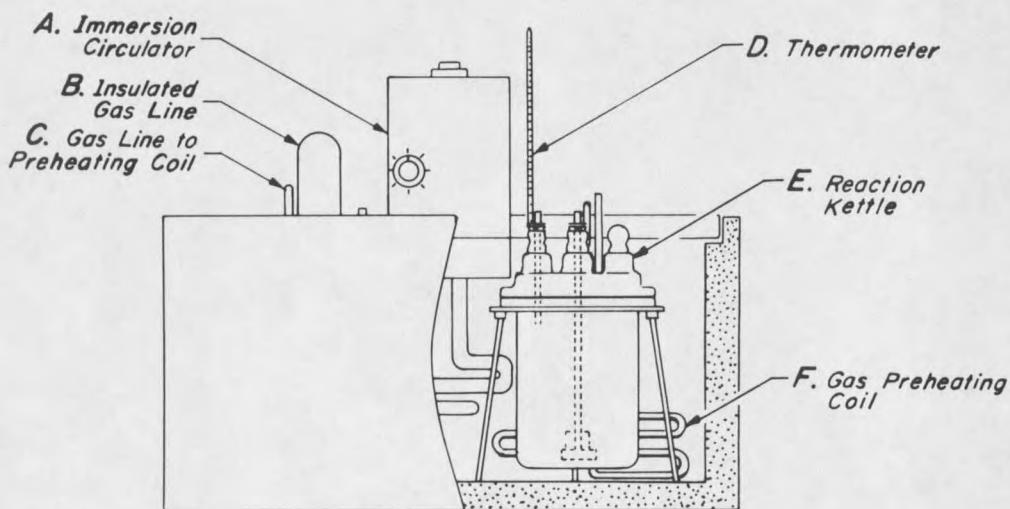


Figure 2. Oil Bath and Reaction Kettle

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

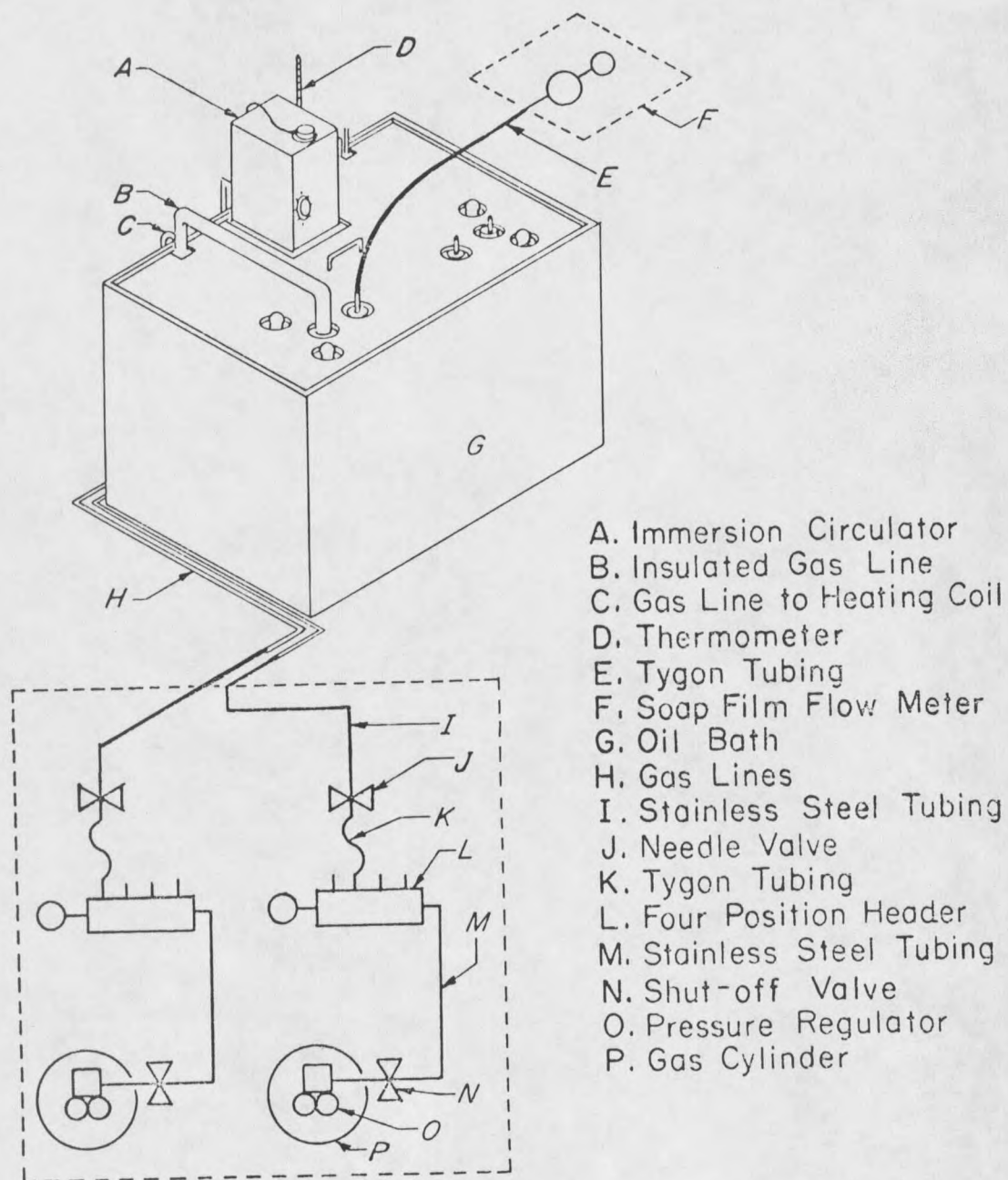


Figure 3. Oil Bath and Operating Diagram

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 cm² copper foil, 150 C and 2

