



Polymerization of safflower oil in a diesel lubrication system
by John Walter Olson

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:

Oxidative addition polymerization of lubrication oil contaminated with safflower oil diesel fuel was investigated in laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Primary research objectives were the identification and testing of key additives which might suppress problems of excessive viscosity rise and alkalinity decline of lubrication/safflower oil mixtures.

Both commercial and base stock medium-speed locomotive lubrication oils were investigated with 5.0 weight percent safflower oil contamination. Oil mixtures were exposed to elevated temperature and were contacted by percolation with either oxygen or nitrogen to provide an oxidizing atmosphere and agitation or simply agitation. Copper, a known diesel engine wear metal, was introduced as a polymerization catalyst.

Lubrication oils were evaluated with and without safflower oil and additives. Both commercial and base stock oils with no safflower oil were found to polymerize at a moderate baseline level. Amines were found to show little alkalinity maintenance efficacy while performance by an overbased calcium phenate was relatively good. Numerous antioxidants were tested for ability to disrupt the mechanisms leading to polymerization. Two widely-used antioxidants, zinc dialkyldithiophosphate and zinc diamyl-dithiocarbamate, were found to promote polymerization of oil mixtures in this research. This unexpected result is almost certainly a result of promotion catalysis by zinc. A metal deactivator N-N'-disalicylidene-1,2-propanediamine retarded viscosity rise, apparently by chelating wear metal catalysts. This beneficial inhibition seemed to be prominent during the initiation phase of the addition polymerization mechanism.

Research demonstrated that the overbased calcium phenate and metal deactivator N-N'-disalicylidene-1,2--pro-panediamine could be combined to effectively delay viscosity rise and suppress alkalinity decline. Both compounds are strong candidates for inclusion in any commercial lube oil to be used with plant oil fuel.

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A thesis submitted in partial fulfillment
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of

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APPROVAL

of a thesis submitted by

John Walter Olson

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

Oxidative addition polymerization of lubrication oil contaminated with safflower oil diesel fuel was investigated in laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Primary research objectives were the identification and testing of key additives which might suppress problems of excessive viscosity rise and alkalinity decline of lubrication/safflower oil mixtures.

Both commercial and base stock medium-speed locomotive lubrication oils were investigated with 5.0 weight percent safflower oil contamination. Oil mixtures were exposed to elevated temperature and were contacted by percolation with either oxygen or nitrogen to provide an oxidizing atmosphere and agitation or simply agitation. Copper, a known diesel engine wear metal, was introduced as a polymerization catalyst.

Lubrication oils were evaluated with and without safflower oil and additives. Both commercial and base stock oils with no safflower oil were found to polymerize at a moderate baseline level. Amines were found to show little alkalinity maintenance efficacy while performance by an overbased calcium phenate was relatively good. Numerous antioxidants were tested for ability to disrupt the mechanisms leading to polymerization. Two widely-used antioxidants, zinc dialkyldithiophosphate and zinc diamyl-dithiocarbamate, were found to promote polymerization of oil mixtures in this research. This unexpected result is almost certainly a result of promotion catalysis by zinc. A metal deactivator N-N'-disalicylidene-1,2-propanediamine retarded viscosity rise, apparently by chelating wear metal catalysts. This beneficial inhibition seemed to be prominent during the initiation phase of the addition polymerization mechanism.

Research demonstrated that the overbased calcium phenate and metal deactivator N-N'-disalicylidene-1,2-propanediamine could be combined to effectively delay viscosity rise and suppress alkalinity decline. Both compounds are strong candidates for inclusion in any commercial lube oil to be used with plant oil fuel.

INTRODUCTION

The last twenty years have seen a full cycle of interest in alternative fuels. At first, during the 1960's, there was a period of declining real oil prices and increasing oil consumption. Petroleum-based fuels were perceived as cheap and plentiful and little attention was given to alternative fuels. Subsequently, the 1973 oil embargo emphasized not only the United States' dependence on imported oil but also the gradual depletion of world petroleum sources. Biofuels were proposed as an alternative source of energy and became the subject of intense research and development.

The 1980's have seen a collapse of oil prices and a waning of interest in alternative energy, including biofuels. However, the volatility of oil prices, continual political tension in the Mid-East, and knowledge that petroleum resources are finite should favor a renewed interest in alternative energy.

Seed oils such as safflower and sunflower have received considerable attention as direct substitutes or extenders for conventional diesel fuels. Their use dates back to 1900 when Dr. Rudolf Diesel was known to have fueled one of his

engines with peanut oil [1]. Factors favoring vegetable oils as transportation fuels include their physical nature as liquids and hence, their portability, their energy content (roughly 88% of diesel fuel), their ready availability, and the fact that they are renewable resources [2].

To date, vegetable oils have not been developed as diesel fuels due to technical and economic obstacles. The price and cost of processing of vegetable oils is at least twice that of conventional diesel fuel [3]. Technical problems abound and include 1) coking on injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, 2) carbon deposits on cylinder walls, 3) piston ring sticking, and 4) lubrication oil thickening and loss of alkalinity as a result of contamination with vegetable oil [4]. Furthermore, technical problems are compounded when one considers the vast array of diesel engine designs currently in use.

Prior research in this laboratory has focussed on problems associated with oilseed fuel contamination of engine lubrication oil. This study continues with that focus. Unburned or partially burned liquid fuel blows by the piston rings and dilutes the lubrication oil. Rewolinski demonstrated that thickening then takes place and is probably due to addition polymerization at points of unsaturation [5]. A 375% increase in viscosity is

considered a failure in lubrication oil tests [6]. In addition, occurrence of alkalinity loss is due to the oxidation of lubrication system components to acids [5]. These acids lead to excessive rates of engine corrosion.

Lubrication oil thickening could be reduced by either eliminating fuel dilution or by modifying the lubrication oil. Engine design modifications would be costly, even if possible. Alterations in the chemical makeup of lubrication oil may therefore be more feasible. Again, however, technical problems are compounded when one considers the variety of lubrication oils available, each being formulated to comply with the specifications of individual engine manufacturers.

Energy planners in Montana have proposed a strategy that would centralize the use of plant oil fuel in diesel locomotives during times of emergency shortage [7]. This would lessen the state's reliance on fossil fuels, provide a market for surplus crops, and free the general remaining diesel supply for agriculture and other transportation needs. Furthermore, technical problems would be isolated to only a few engine designs and lubricants.

Currently there are two U.S. manufacturers of diesel locomotives. A General Electric 4-cycle model accounts for approximately one third of the market whereas the General Motors Electromotive Division manufactures a 2-cycle model, accounting for the other two thirds of the market [8]. Both

models are classified as medium speed, indicating operating speeds between 250 and 1000 revolutions per minute [9].

Typically, a railroad with 3000 locomotives will consume approximately six million gallons of engine lubricant per year. Up to 25% of this can be attributed to crankcase oil drains due to high viscosity. Railroad engine manufacturers typically recommend that the crankcase lubricant be drained when its viscosity at 40 °C increases 30% [10]. Of particular interest is that additional consumption of oil takes place by burning as much as 0.75 gallons of oil per 100 gallons of fuel [8]. This indicates that some thickening and loss of alkalinity may be tolerable due to high oil consumption of locomotives. This will inevitably change as new high-horsepower, low oil consumption (0.2 to 0.3 gallons of oil/ 100 gallons of fuel) and fuel-efficient locomotives are currently being introduced [8,10]. Furthermore, problems associated with vegetable oil fuels would place additional stress on engine lubricant quality.

Prior research has focussed on problem definition, quantification of thickening and alkalinity losses, and the role played by system variables. Current research shall continue this investigation with emphasis on resolving these problems. A number of commercial lubrication oils have been used (generally SAE 30) as well as their corresponding base stock oils. The base stocks were used to avoid the unknown

chemical nature of the additive package in the commercial lube oil. Sunflower oil was primarily used as the contaminating vegetable oil. The present research uses an SAE 40 medium speed oil and its corresponding base stock. This commercial formulation is the same oil which Burlington Northern currently uses in its diesel locomotives. The vegetable oil in use in this research is safflower oil grown locally in Montana.

While a considerable amount of work has been done, the general problems of 1) viscosity rise and 2) alkalinity decline still remain for lubrication oil contaminated with plant oil fuel. A theoretical discussion pertaining to the present research as well as a summary of prior research will be presented. From this, the objectives of the current research will be summarized.

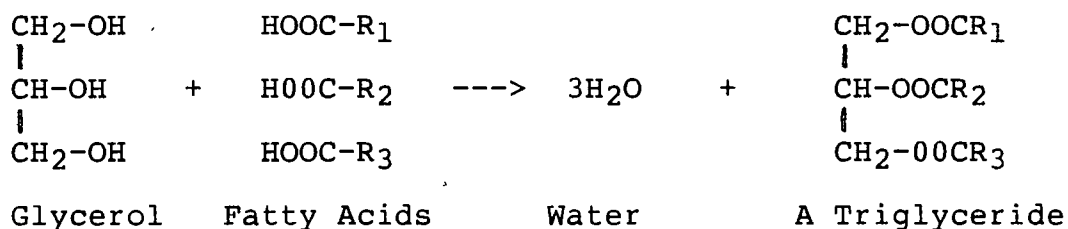
THEORY

The thickening and loss of alkalinity of lubrication oil contaminated with vegetable oil has been largely attributed to oxidative addition polymerization at points of unsaturation in the plant oil fuel [5]. This polymerization is known to be catalyzed by transition metals, some of which are common wear metals found in diesel lubrication oil. It is significant that the lubrication oil itself is more than just a diluent for the contaminant vegetable oil fuel. As will be discussed, lubrication oils have inherent properties which can dramatically influence the polymerization of the vegetable oil fuels. The following sections present the basic properties of both vegetable oil fuels and petroleum lubrication oils. This discussion includes a brief summary of their potential reaction mechanisms as well as a fundamental understanding of lubricant development.

Vegetable Oils

Vegetable oils are structurally different than petroleum-based diesel fuels. The latter are arranged in normal or branched chain structures, as well as aromatic

configurations and contain mostly carbon and hydrogen. Vegetable oils are predominantly composed of glyceryl esters of fatty acids, so-called triglycerides. Structurally, they can be thought of as a reaction product of glycerol and fatty acids [11].



In the above scheme, R_1 , R_2 , and R_3 represent even numbered hydrocarbon chains of fatty acids that are usually 16-22 carbons in length. The size of the chains and the number of double bonds depend upon the particular vegetable oil. The degree of unsaturation for one triglyceride molecule can vary from zero to nine double bonds. Typical molecular weights range from 650 to 970 with fatty acids contributing 94-96% of the total weight [11]. Thus, these acids predominantly influence both physical and chemical properties of the triglyceride.

In the past, research in this laboratory was conducted with sunflower oil as the contaminating oil [5,12-15]. Current research uses safflower oil. However, from Table 1 it can be seen from their fatty acid distributions that these two oils are similar and are therefore expected to give similar results [16].

TABLE 1. Fatty Acid Distributions (Percent)

<u>Fatty Acid</u>	<u>Sunflower Oil</u>	<u>Safflower Oil</u>
Palmitic	6.4	6.4
Stearic	1.3	3.1
Arachidic	4.0	0.2
Oleic	21.3	13.4
Linoleic	66.2	76.6-79.0
Linolenic	<0.1	0.04-0.13

The primary constituents, oleic and linoleic acids, plus linolenic acid are unsaturated. Each of these acids contain 18 carbons and one, two, and three double bonds, respectively [11]. Accordingly, the high degree of unsaturation in vegetable oils, especially compared to only slight unsaturation in diesel fuel, suggests that some fuel properties, e.g., oxidation resistance, would differ significantly from those of hydrocarbon fuels.

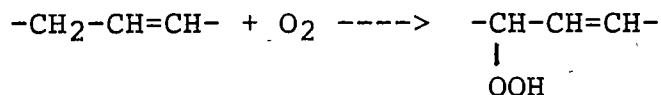
Oxidative Polymerization of Vegetable Oil

The attack of oxygen on the double bonds of the vegetable oil may produce a variety of reactions and is known as autoxidation since this attack is autocatalytic [11]. The polymerization reaction appears to be predominant and is thought to occur by a free radical, hydroperoxide

mechanism. Rheimich and Austin have described this process in the following way [17].

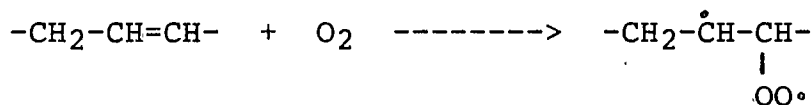
1. An induction period occurs, preceeding the initiation of the oxidative chain reaction, during which no visible physical or chemical properties are changed. It is assumed that natural antioxidants are consumed during this induction period.
2. Oxygen interacts with double bonds to form hydroperoxides. A considerable uptake of oxygen coincides with the beginning of a perceptible polymerization reaction.
3. The polyunsaturated species undergo conjugation of double bonds and isomerization of cis to trans forms.
4. The hydroperoxides decompose resulting in free radicals which in turn contribute to autocatalysis.
5. Production of high molecular weight cross-linked polymers and low molecular weight carbonyl and hydroxyl compounds occurs via free radical polymerization and scission reactions.

Farmer and Sutton demonstrated that the first isolatable product of the oxidation of an olefin was a hydroperoxide with an intact bond alpha to the site of oxidation [18].

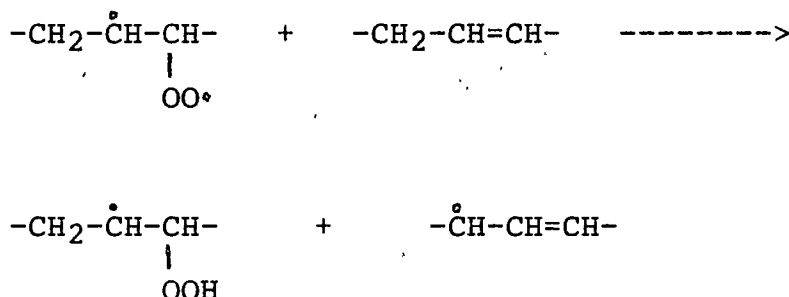


However, because of the high energy requirements, approximately 80 kcal/mole, required for rupture of the α -methylene carbon-hydrogen bond, Bolland and Gee [19], Farmer [20], and Gunstone and Hilditch [21] almost simultaneously concluded that the initial point of oxidative attack was the double bond and not the α -methylene group. Bolland and Gee proposed a limited attack at the double bond to produce radicals in sufficient amount to initiate the chain reaction through the α -methylene carbon [19]. This mechanism can be seen in the following scheme where both hydroperoxides and radicals are produced directly [22]. As will be shown later, hydroperoxides may then decompose to produce other radicals.

1. Oxygen attacks a double bond to produce a diradical.

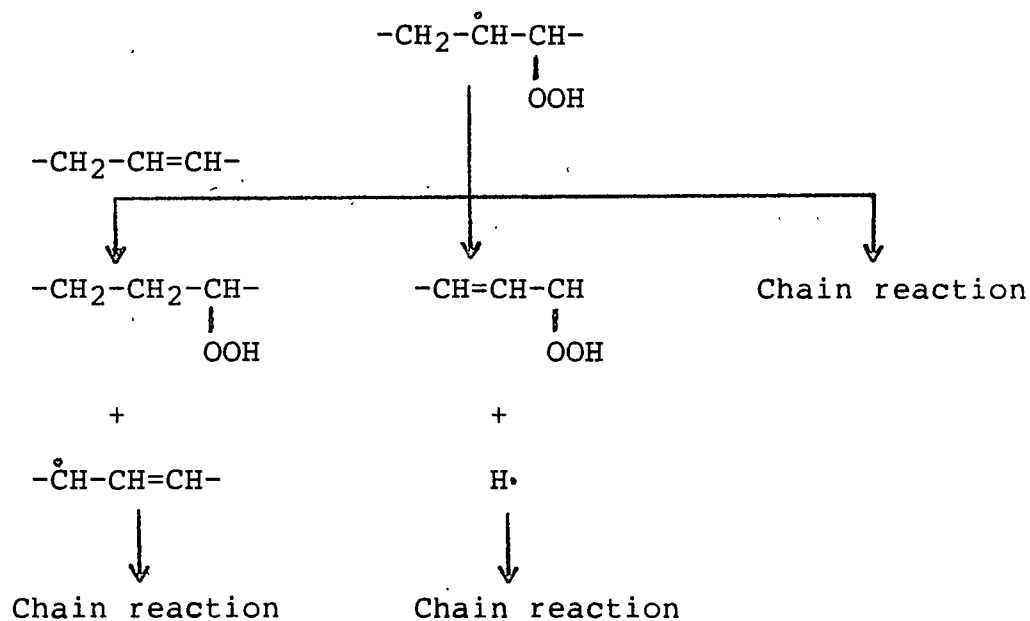


2. The diradical abstracts hydrogen from an α -methylene carbon, producing two single radicals.

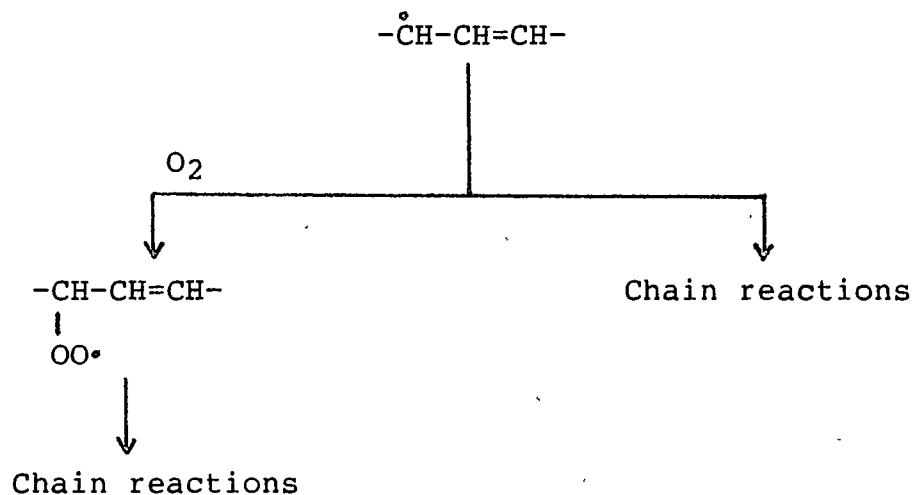


3. As shown below, these single radicals are subject to further reactions that can lead to other radicals or, as will be shown later, lead to vinyl polymerization.

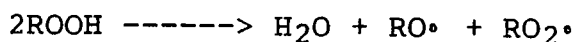
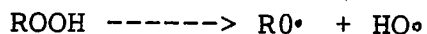
a)



b)

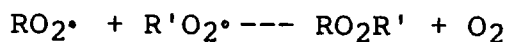
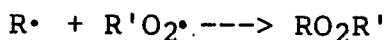
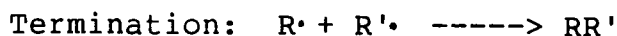
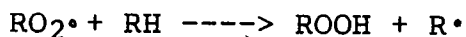
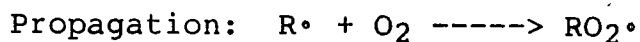


Once hydroperoxides are formed, even in trace amounts, they can play a significant role in autocatalysis [23].

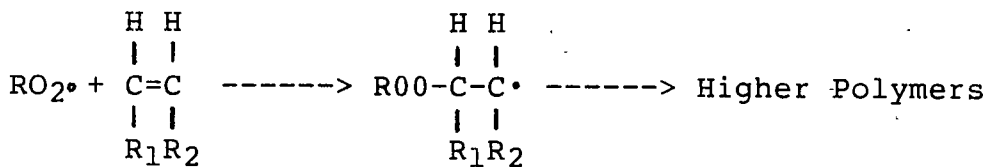
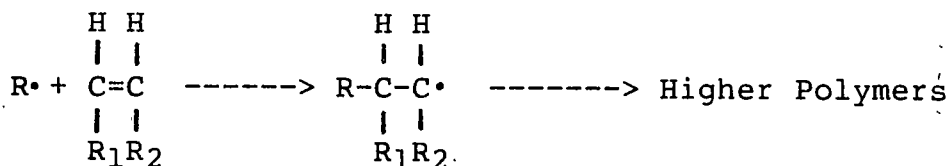


From a kinetic standpoint there are three stages in the autoxidation process [24]. The $\text{R}\cdot$ radical will be used as an example.

Initiation: Production of $\text{R}\cdot$ radicals.



All free radical species can lead to higher molecular weight polymers through vinyl polymerization [23].



It is well known that rates of vinyl polymerization vary with number and degree of conjugation of unsaturated linkages. For example, the number of double bonds of the fatty acid should affect the reactivity, and it has been

shown that the rate of oxidation of films of triolein, trilinolein, and trilinolenin was in the order of 1:20:330 [25]. However, the actual ratios of reactivity are the subject of some disagreement as other workers believe the relative rates of oxidation of methyl oleate, methyl linoleate, and methyl linolenate to be either in the order 1:12:25 or 1:2:4 [26].

It is possible that other functional groups of the triglyceride may accelerate or decelerate the rate of oxidative polymerization. For example, Miyashita and Takagi recently proposed that the higher oxidative rates of free fatty acids than that of their methyl esters could be due to the catalytic effect of the carboxyl groups on the formation of free radicals by the decomposition of hydroperoxides [27]. Thus, it is conceivable that the position of double bonds with respect to carboxyl groups may explain the above disagreements.

In addition to oxidative polymerization there exists a number of other oxidation mechanisms. Privett and co-workers found that even in the early stages of oxidation only 90% of the products could be accounted for as hydroperoxides [28]. In addition to the numerous volatile compounds, e.g., carbon dioxide and water, there are a number of relatively nonvolatile secondary oxidation products [23]. These include aldehydes, ketones, carboxylic acids, anhydrides, esters, et cetera.

Catalysis

As discussed above, addition polymerization is believed to occur via a free radical mechanism. While there is considerable agreement concerning propagation and termination, there is uncertainty as to formation of the original free radical necessary for initiation in the reaction sequence.

Heaton and Uri [29] contend that the direct attack of oxygen on the double bond has low thermodynamic probability, and they propose that trace metal contaminants catalyze the initiation of autoxidation by producing free radicals through electron transfer. Indeed, even the most highly purified fatty esters contain trace metal catalysts [22].

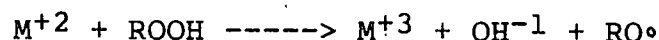
It is usually accepted that catalysts are unable to alter the course of reaction but merely participate in the formation of transitory intermediates. They may, however, direct the course of reaction by favoring the formation of one intermediate among several possible species.

It is known that certain metal compounds increase the rate of oxidative addition polymerization and have been classified into two groups. The first group, the participating catalysts, include such metals as cobalt, lead, and manganese, which are the most active, as well as other such metals as cerium, copper, chromium, iron, tin, vanadium, and zirconium [22]. Seemingly important criteria

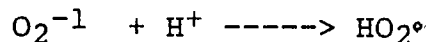
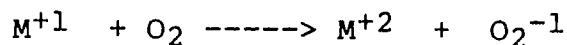
are that these active metals exist in at least two different valences, the higher being less stable, and that they are susceptible to being oxidized from the lower to higher valences.

The catalytic activity of these metals, M, may involve several alternative pathways [23]:

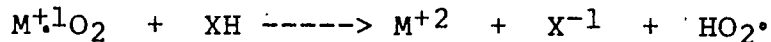
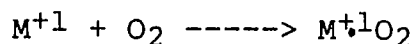
1. Trace hydroperoxides may shift the metal valences and produce free radicals.



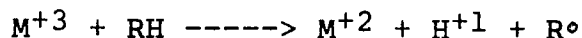
2. The oxygen and metal ion may react directly. The resulting O_2^{-1} then readily reacts with a proton to form HO_2° .



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

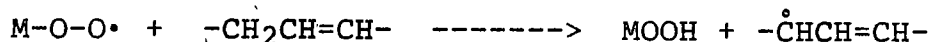
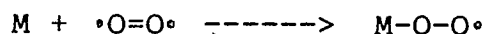


4. Electron transfer to the metal ion may result in the oxidation of the alpha methylenic group.

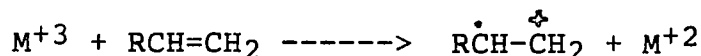


The metallic catalysts are believed to catalyze not only decomposition but also formation of hydroperoxides. While the activity in the creation of hydroperoxides is not clear, several possibilities exist. Metallic catalysts, M,

may act as oxygen carriers, thereby aiding the stability of the oxygen molecule [22].



There could be a direct attack of a metal ion upon an olefinic double bond [22].



Although this reaction produces a more complicated product, the ion radical may possibly form a hydroperoxide to help initiate autoxidation.

In addition to participation catalysts there exists a second class, promoter catalysts, which include such metals as aluminum, calcium, zinc, and lead [22]. The mechanism of these catalysts is not known for certain but it appears to be of a physical or mechanical nature, such as arranging the disperse phase polymers into a coherent order or by aiding in the mobility of the participating catalysts. Of considerable importance is that combinations of catalysts from both groups sometimes exhibit synergistic action. For instance, the combination of cobalt and lead was found to be greater than that of cobalt, a participator, which was found to be greater than lead, a promoter, when used in a drying reaction [22].

Uri maintains that the kinetic and thermodynamic probabilities for formation of free radicals by the metal-catalyzed reactions are considerably more favorable than the

Bolland and Gee proposal of diradicals by direct oxidation of a double bond [24].

Lubrication Oil

Lubricating oils are generally prepared from crude oils according to the following scheme [30]:

1. Distillation, to adjust the viscosity and flash point.
2. Refining, to improve the aging tendency and the viscosity-temperature characteristics.
3. Deasphalting of the residue from vacuum distillation.
4. Dewaxing, to improve the low-temperature properties.
5. Blending of different base stocks and addition of additives, to give the finished product the required properties.

Molecular weights of lubricating oil fractions range from about 300 to 800 with various hydrocarbons represented [30]. These include aromatics, naphthenes, paraffins, but only occasionally olefins. The properties and quality of lubricants depend on the source and viscosity range of the base stock, the production processes and refining intensity, as well as the blending and formulation of additives. Base stocks of different origin but of the same type are similar but by no means identical.

Many properties of modern lubrication oils are achieved by the addition of chemicals, without which the present-day

requirements could not be met. These additives can improve oxidation resistance, low-temperature and wear properties, corrosion resistance, and viscosity-temperature behavior. They can also give properties to the oils which they did not initially possess. These include dispersancy, detergency, extreme pressure characteristics, emulsifying properties, et cetera.

The final commercial products are prepared by blending of the appropriate base stocks and additives, which then determine jointly the oil properties such as viscosity, viscosity-temperature behavior, aging, and special structural features.

Oxidation of Lubricating Oils

The oxidation of petroleum hydrocarbons proceeds according to a radical chain mechanism via alkyl and peroxy radicals [30]. That is, hydrocarbon radicals are formed, as discussed earlier, which either further react with oxygen, terminate, or proceed in vinyl polymerization. An induction period exists which depends on the refining treatment. That is, adequately refined mineral base stocks contain "natural inhibitors" in the form of sulfur and nitrogen compounds. Over-refined oils do not contain these natural inhibitors or contain them in only small quantities. On the other hand, refining generally improves the response of an

oil to synthetic inhibitors or additives [30]. These facts are generally recognized by refiners who exercise great care in controlling the degree of extraction and may indeed often add back aromatic extract in the course of final formulation.

As with vegetable oils, further reaction of the peroxy or other radicals lead to alcohols, ketones, carboxylic acids and similar molecules, all of which can be the basis for a condensed, oxygen containing compound with higher molecular mass. Depending upon the conditions, resinous, sludge-like or also lacquer-type substances are built up which after further aging and oxidation can lead to sludge and carbon deposits. Furthermore, as with vegetable oils, metallic catalysts can play an important role in accelerating autoxidation.

Antioxidants

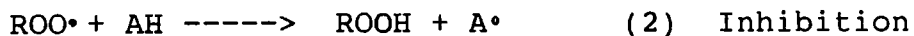
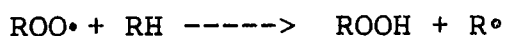
As previously discussed, oxidative reactions associated with vegetable oils are related to those associated with lubrication oils. This suggests that additives incorporated in lubrication oils might be effective in vegetable oils as well. Indeed, additives must be sought which are compatible with the lubrication oil in use.

All naturally occurring oils, to include vegetable oils as well as lubrication base stocks, contain "natural

inhibitors" which serve the specific purpose of protecting the oil from deterioration. Vegetable oils contain the phenolic compound tocopherol (vitamin E) as their primary antioxidant whereas the inhibitors found in base stock oils are generally in the form of sulfur and nitrogen-containing compounds [15,30]. The remarkable characteristic of these antioxidants is their great effectiveness at low levels of concentration. Natural antioxidant concentrations are usually less than a few hundredths of one percent.

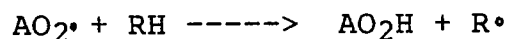
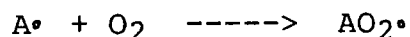
The literature on antioxidants, their use, and mechanisms of activity is voluminous. In fact, literally hundreds of natural and synthetic compounds have been shown to be effective antioxidants, depending upon the system involved [31]. However, there is a lack of complete agreement on their exact mechanism(s) of action. Shelton claims there is evidence for at least five different classes of oxidation inhibitors based on differences in the mechanism by which they appear to inhibit oxidation [32]. However, for purposes of this study, antioxidant behavior shall be limited to three types.

The first type, the chain breaking agents, suppress propagation by removal of peroxy radicals in a reaction involving either electron or hydrogen transfer. Phenols or amines of specific structures function as radical acceptors by transfer of a hydrogen atom from the oxygen or nitrogen atom to the alkyl radical [33].



where R^\bullet is an alkyl radical and AH is an antioxidant.

In contrast, the relative ease with which these antioxidants oxidize is also responsible for the initiation of new chains. This may occur either through reaction with oxygen or by engaging in chain transfer [34].

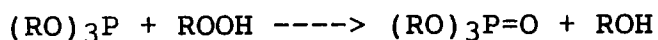


The occurrence of these oxidation-promoting reactions during inhibited autoxidation seems to be more important with amines. Furthermore, it suggests that there may be some optimum antioxidant level.

Among the numerous phenolic inhibitors, typical agents include the naphthols, sterically hindered monohydric, dihydric, and trihydric as well as sterically hindered dinuclear, trinuclear, and polynuclear phenols. Typical amines include p-p'-dioctyldiphenylamine, phenyl- α -naphthylamine, and diphenylamine. These nitrogen-containing inhibitors are suited predominantly for temperatures below 120 °C but can sometimes be used above 150 °C; their

efficacy depends essentially on the degree of refining of the oil [30].

The second type of antioxidant, the peroxide decomposers, function by decomposing hydroperoxides through polar reactions. This type of activity has been found with a variety of sulfur, phosphorus, sulfur/nitrogen, and sulfur/phosphorus-containing compounds [30]. These include dialkyl sulfides and polysulfides, diaryl sulfides, modified thiols, mercaptobenzimidazoles, thiopene derivatives, xanthogenates, metal dialkyldithiocarbamates, and metal dialkyldithiophosphates. The exact mechanism of peroxide decomposition is yet unknown. While it has been proposed that sulfur-containing compounds are converted into the ultimate oxidation product, sulfur dioxide, which is the final catalyst for peroxide decomposition, the phosphates are thought to function as stoichiometric decomposers [35].



The metal salts of certain dithioacids such as the carbamates, xanthates, and phosphates have received considerable attention as hydroperoxide decomposers [30]. In fact, metal salts of thiophosphoric acids are used predominantly as oxidation inhibitors for motor oils. Again, however, their exact mode of action has not been established. Colclough and Cunneen have proposed that the zinc dialkyldithiophosphates actually act as chain-breaking agents and propose they function by electron-transfer from

an electron-rich sulfur atom to a peroxy radical [36]. Burn claims that the zinc salt itself, not a decomposition product, removes peroxy radicals [37]. Howard, et al, believe peroxy radicals react at the metal center [38]. On the other hand, Dutta found that zinc dialkyldithiocarbamate is not a very good scavenger of free radicals and concluded this antioxidant functions primarily by hydroperoxide decomposition [14]. Scott claims hydroperoxides are destroyed in ionic, generally Lewis acid-catalysed, reactions [39]. Al-Malaika et al. maintain that the final catalyst responsible for decomposition of hydroperoxides is sulfur dioxide [40]. Thus, it seems these compounds may inhibit both initiation and propagation.

Finally, the third type of antioxidants are metal deactivators. These may function by (1) combining with the metal to form a stable nonionic complex, (2) an electronic effect which preferentially stabilizes one of the metal oxidation states, or (3) sterically hindering the hydroperoxide from the coordination sites [31]. In contrast, these compounds can sometimes enhance metal ion activity, particularly if coordination is incomplete and causes an unfavorable change in redox potential [41]. Compounds such as triethylenediamine, N,N'-disalicylidene-ethylenediamine, ethylenediaminetetraacetic acid, phosphoric acid, citric acid, and gluconic acid can be effective chelating agents [30]. Zinc dialkyldithiophosphates and

dialkyldithiocarbamates can also be effective metal passivators and operate by formation of layers on metal surfaces which prevent dissolution of metal ions in the oil phase.

Theoretically, the efficacy of antioxidants would be expected to be directly proportional to concentration. However, this is seldom the case except perhaps within limited ranges for a few antioxidants [11]. In general, successive additions of antioxidants yield steadily diminishing returns. At higher concentrations an appreciable amount of antioxidant is consumed by side reactions. It is also possible that in some cases decomposition of the antioxidant may yield substances with a prooxidant effect.

Additive Interaction

The development of a lubrication oil calls for a wide knowledge of additive technology. In addition to the complexity of the mechanism of each individual additive, the complexity of the system must be overcome. The requirements placed upon the lubrication oil are many and include 1) good oxidation and thermal stability, 2) ability to retain alkalinity, 3) good detergent properties and 4) adequate protection against wear [9]. The difficulties are compounded by the conflicting demands. For example, many

good corrosion inhibitors are either nullified in the presence of alkaline compounds and/or are soluble in water. Indeed, powerful antagonistic results may occur among some additives. These represent but a few of the problems to be resolved. Finally, the only reliable way of determining final performance is through first, empirical observation in laboratory testing and second, actual engine assessment.

PRIOR RESULTS

Development of Crankcase Simulation

Prior to work done in this laboratory, most research on the problem of plant oil contamination of diesel lubrication oil has involved problem definition in extended engine testing. This led to high experimental costs due to the destructive evaluation of new engine components. Laboratory scale simulation of conditions prevailing in a diesel engine crankcase allows for more precise control of system variables than is possible in engine tests. Furthermore, the high costs of engine testing can be avoided.

Past researchers in this laboratory were able to simulate crankcase conditions in glassware immersed in a specially designed, hot oil bath [5,12-15]. Glass tubes [5] or kettles [12-15] containing lubrication oil, vegetable oil, and any additive(s) were immersed in the oil bath. Temperatures to slightly over 150 °C were possible. Fritted glass dispersion tubes provided the means by which either preheated oxygen or inert gas could be percolated through the oil mixture. In addition to providing a proper oxidizing atmosphere, sparge gas minimized mass transfer

limitations by gently agitating liquid samples. Gas flow rates were precisely controlled. Common wear metals known to exist in used crankcase oil were introduced either in metallic form, i.e. foil strips, or in soluble form via soluble metallic compounds.

Essentially two types of data were accumulated. One, the kinematic viscosity, was used to determine physical changes in the oil mixture. Viscosity measurements, taken at 40 °C were measured using calibrated Cannon-Fenske viscometers. Second, Total Base Number (TBN) was measured to indicate chemical changes in the oil mixture system. TBN indicates alkalinity of the oil mixture and was determined according to ASTM Standard Method D-2896 [42].

Effect of System Variables with Commercial Oil.

Simulation parameters which were considered important included temperature, chemical environment, and the percent of vegetable oil contamination. Rewolinski studied these factors and developed a standard set of conditions which has been used throughout the research [5]. He found that an increase in temperature led to an increase in viscosity rise. A temperature of 150° C was chosen as a compromise between the crankcase temperature (100-150 °C) and the temperature encountered in the combustion areas (200-350 °C)

of a diesel engine [30]. Rewolinski also showed that polymerization was strongly influenced by the presence of oxygen. An increase in oxygen flow rate was found to only slightly influence the rate of viscosity rise. A flow rate of 2 ml/sec of oxygen percolating through 500 ml of oil mixture was chosen as a standard condition. The use of nitrogen did not affect the system. Increasing the concentration of vegetable oil resulted in a rise in the rate of viscosity increase. A concentration of 5.0% vegetable oil was chosen as the standard condition.

Commercial Oil: Copper Study

Rewolinski showed that copper, a common wear metal in engines, had a significant catalytic effect on viscosity rise. Jette went on to determine that soluble copper was the most important catalyst form [12]. He was able to simulate the effect of metallic copper by using soluble copper in the form of cupric acetylacetonate (CuAcAc). He also determined that copper was important for initiating the polymerization reaction and that an increase in the rate of viscosity rise resulted from an increase in copper. As a result of these findings, a 2 cm X 5 cm piece of copper foil was chosen as the standard amount of metallic copper catalyst.

In later studies, Raman discovered that the influence of copper varied significantly from batch to batch of commercial oil. In one commercial/sunflower oil mixture, exposures with copper and with no copper yielded terminal viscosity at 16 and 23 hours, respectively. However, in a second commercial/sunflower oil mixture, less than a 50% viscosity rise was observed at 90 hours exposure with no copper present. The viscosity of this second commercial/sunflower oil mixture with copper increased roughly 500% in less than 30 hours. Something in the commercial additive packages was either promoting or deactivating the copper in the various oils. He also found that the rate of viscosity rise decreased as oxidation of the copper foil increased. As a result, subsequent copper foils were thoroughly sanded with emery cloth before using.

Effect of System Variables with Base Stock Oils

Hydrocarbon base stock oils were used in prior research to avoid the influence of additives in the commercial oil and thus, study the mechanisms of individual additives. However, instead of observing a significant viscosity rise, Dutta encountered the rapid formation of solids [14]. The timeframes in which this occurred ranged from 4-5 hours to 15-16 hours for various base stocks.

Throughout these tests there was a problem of quantifying the amount of solids formed. A number of techniques were tried including homogenizing the solids in the liquid phase with subsequent viscosity measurement and centrifuging the solids for weighing. However, a number of different solids have been observed. Some are occluded with liquid and gel-like whereas others are drier and compacted. Some stick to the surfaces of the reaction vessel while others do not. As a result of these differences, analysis of solids formation has been mostly qualitative.

Base Stock: Copper Study

It was initially thought that solids may be "blanketing" the copper foil and therefore eliminating the catalyst action [14]. However, as with the commercial oils, the presence of copper was important with some base stocks and not with others. Furthermore, the use of soluble CuAcAc resulted in identical results as those with metallic copper.

Polar Gel Theory

Keller conducted research to determine the mechanism of insoluble solids formation [15]. She hypothesized that simultaneous oxidation of addition polymers in the base stock yielded polar compounds which would then precipitate

from the non-polar lubricating oil. Experiments including the use of infrared spectroscopy supported this theory. She went on to find an additive, octadecylamine (ODA), which inhibited solids formation in base stocks and gave viscosity increases much like those in the commercial oil.

Additive Study

Throughout the research a number of different additives have been used in both base stock and commercial oils. These additives have included antioxidants, dispersants, and alkalinity enhancers.

Of the variety of antioxidants used, only one agent, zinc dialkyldithiocarbamate (ZDTC), gave any significant improvement. At a 1.0 weight percent concentration level, it prolonged solids formation and viscosity increase from 10 hours to 60 hours for one base stock and from 4 hours to 20 hours for another. Unfortunately, it had no effect on another base stock oil and gave only slightly improved performance in commercial oil.

Slight inhibition of viscosity rise was also found in one commercial oil when Raman made frequent additions of zinc dialkyldithiophosphate (ZDTP) [13]. However, no improvement was found with the corresponding base stock and ZDTP. These results were surprising since ZDTP is one of the most widely used antioxidants in the oil industry.

Rewolinski tried several additives to deactivate the copper catalyst [5]. These included a disulfide to poison the catalyst and 2,2'-dipyridyl, a chelating agent. Negative results were observed when the rates of viscosity rise increased. Raman tried Lubrizol 5955A, which is known to be a metal deactivator [13]. Again, the result was negative. However, Raman found favorable results from a metal deactivator from DuPont, N,N'-disalicylidene-1,2-propanediamine (NNPD). Addition of this component gave slightly improved performance in the commercial oil system.

Keller used an organic dispersant, Paronox 107, at a 3.0 weight percent concentration level in the basestock to keep the solids dispersed [15]. The performance was only slightly improved and she concluded that solids formation was more than just a physical separation. That is, viscosity-forming species and the solids-forming species were chemically different.

Finally, Rewolinski used several agents to enhance the alkalinity of the lubrication oil. Both compounds, an overbased calcium phenate (OCP) from Amoco and octadecylamine (ODA), gave favorable results. However, frequent additions were necessary to maintain alkalinity.

RESEARCH OBJECTIVES

This research is undertaken to better understand and then solve the problems of 1) excessive viscosity rise and 2) alkalinity decline of lubrication oil when contaminated with plant oil diesel fuels. Polymerization of SAE 40 medium-speed lubrication/vegetable oil mixtures will be investigated in a laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Both hydrocarbon base stock and commercial lubrication oils will be used.

A primary goal of this work is the identification of key additives (antioxidants and alkalinity enhancers) which will suppress the above mentioned problems. Based on their performance, these additives will be combined to formulate a final additive package which will be recommended for optimization and subsequent diesel engine testing.

Also a goal of this work is to better understand and then propose mechanisms for individual additives as well as mechanisms for the interactions among various additives. These results will be used to identify a suitable course for future research.

EXPERIMENTAL

Equipment

Crankcase conditions were simulated in 500 ml pyrex resin kettles. Each kettle (Figure 1) was fitted with a four post entrance lid. The 24/40 standard tapered joints and kettle flanges were finely ground to ensure gas tight seals when greased.

Preheated gas was percolated through oil mixtures using immersed 6 mm glass tubes with 30 mm diameter fritted glass heads. The fritted glass was centered at the bottom of the kettle to provide maximum gas-to-liquid contact. Gas exited through a stainless steel tube and was passed through tygon tubing to a Brooks rotameter. The rotameter was frequently checked for accuracy by a Varian Aerograph soap film meter. Entering and exiting tubes were held in place with "Mini" Ace-Thred Adapters fitted with O-rings and threaded nylon bushings.

A third kettle opening housed a 6 mm by 10.5 inch solid glass rod. The rod was inserted 7 cm into the oil mixture at the beginning of each experiment. Like the gas tubes, it was held in place with a "Mini" Ace-Thred Adapter. The

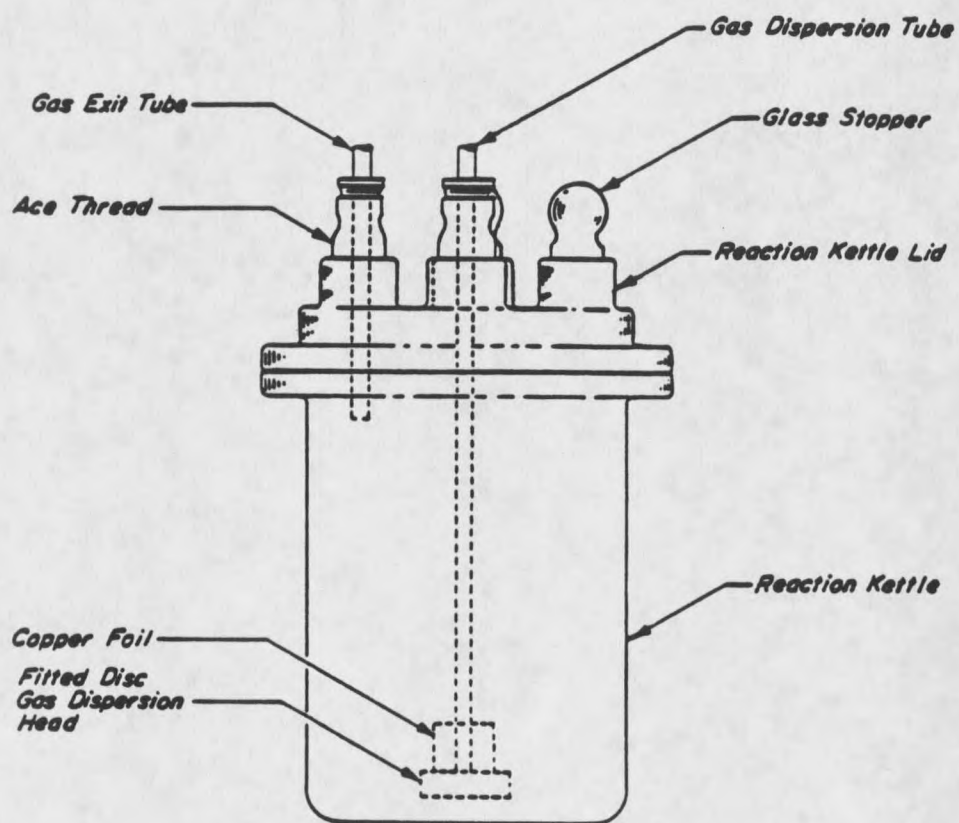


Figure 1. Reaction Kettle.

fourth kettle opening was closed with a ground glass stopper.

Metallic copper catalyst, 0.125 mm thick, was provided in several experiments as a 2.0 X 5.0 cm foil strip rolled into a 1.6 cm diameter cylinder and mounted just above the fritted glass disk. Copper foils were thoroughly sanded with emery cloth and cleaned with hexane and acetone prior to use.

An oil bath (Figure 2) capable of housing two reaction kettles was used to maintain oil mixture temperatures inside the kettles at 150 °C. The steel bath was insulated with 1.5 inch vermiculite insulation on the sides and bottom and fitted with a sheet metal cover to minimize heat loss. Paraffin oil was used as the heating medium and maintained at a level higher than the oil mixture levels inside the kettles. A Polyscience Model 73 immersion circulating heater was used to heat the oil. Temperatures were maintained with an accuracy of ± 0.2 °C, and oil was circulated at a rate of 13 liters per minute. The oil bath was placed in a venting hood to remove any noxious vapors.

High pressure cylinders supplied gas (oxygen/nitrogen) to the reaction kettles. Nominal 1/4 inch stainless steel tubing connected single stage regulators on cylinders to a four position header equipped with a 0-30 psi pressure gauge. Precision needle valves were linked to header positions via tygon tubing and used to control gas flow to

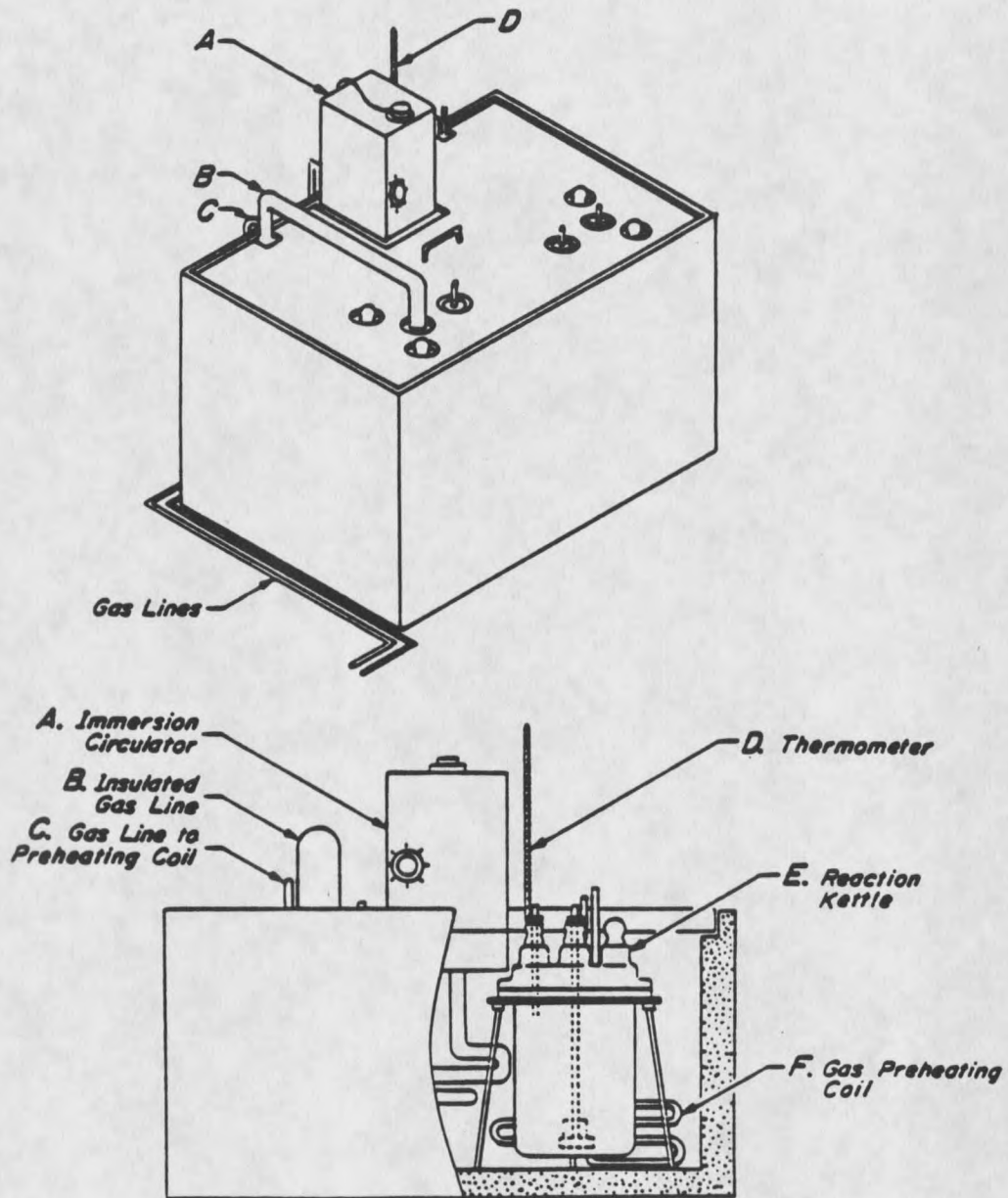


Figure 2. Oil Bath.

the reaction kettles. Each valve was connected by stainless steel tubing to stainless steel preheating coils immersed in the oil bath. Insulated teflon tubing connected the coils to kettle gas dispersion tubes.

Cannon-Fenske viscometers with ranges from 120 to 1200 centistokes were employed to measure kinematic viscosity of lubrication/vegetable oil mixtures. Viscometers were immersed in a constant temperature water bath maintained at 40 ± 0.2 °C using a Polyscience Model 73 immersion circulating heater.

Alkalinity of oil samples was determined according to ASTM D 2896, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration" [42]. An Orion Research Model 901 Microprocessor Ionalyzer was employed to determine end points using 1) a Corning sleeve-type calomel saturated glass electrode and 2) a Corning Ag/AgCl glass membrane electrode.

Carbon-13 nuclear magnetic resonance (NMR) spectra were obtained for selected samples. A Bruker WM-250 NMR machine with an Aspect 2000 computer was used for sample analysis. The solvent, chloroform-d, was used to relate data to the common standard, tetramethylsilane.

Selected samples were analyzed for nitrogen content using combustion-gas chromatography. A Carlo Erba 1106 machine was used for elemental analysis. Whatman Microfibre glass filters were used to absorb oil samples.

Materials

Vegetable oil used in this research was mill run safflower oil from Continental Grain Company in Culbertson, Montana. The oil was freshly extracted from mixed seeds from a number of common varieties grown as far east as Minot, ND and as far west as Geraldine, MT. The safflower oil was raw, having no fine filtering or chemical treatment and was kept in refrigerated storage.

Diesel locomotive lubrication oils used were a 40 weight, medium-speed commercial oil and its solvent refined base stock containing no additives. The commercial formulation was UNOCAL Heavy Duty SAE 40 oil. Both oils were obtained from UNOCAL Science and Technology Division, Brea, CA at the request of Burlington Northern Railroad.

Cupric acetylacetonate (CuAcAc), aluminum acetylacetonate (AlAcAc), octadecylamine (ODA) and sodium diethyldithiocarbamate (NaDTC) were obtained from Aldrich Chemical Company. Zinc acetylacetonate (ZnAcAc) was obtained from Alfa Products Division of Morton Thiokol, Inc. An overbased calcium phenate (OCP) under the tradename Amoco 9231 was provided by Amoco Petroleum Additives Corporation. Antimony dialkyldithiocarbamate (SbDTC), zinc diamyldithiocarbamate (ZDTC), 2-mercaptobenzothiazole (MBT), and p,p'-dioctyldiphenylamine (PDDP) were provided by R.T. Vanderbilt

