



Mechanism of lubricating oil degradation in presence of plant oil  
by Abhijit Dutta

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:

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Four antioxidants designed to influence different steps in an oxidative polymerization mechanism were tested for efficacy. A single compound zinc diamyl dithiocarbamate inhibited both polymerization and solids formation in contaminated base stock oil experiments. This antioxidant did not prove to be as effective with SAE 30 commercial oil, possibly due to adverse interactions(s) with additives in the commercial oil.

Zinc diamyl dithiocarbamate apparently inhibits polymerization by decomposing intermediate hydroperoxide species into forms other than free radicals. Zinc diamyl dithiocarbamate was not effective in experiments where a free radical initiator was used, showing that this compound does not appear to inhibit chain propagation.

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MONTANA STATE UNIVERSITY  
Bozeman, Montana

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## ABSTRACT

The mechanism of polymerization of lubricating oil contaminated with sunflower oil fuel was studied in a laboratory apparatus simulating the conditions in a diesel engine crankcase.

Oxidative polymerization of contaminated base stock lubrication oil was shown to proceed by a free radical mechanism by exclusion of oxygen and addition of a known free radical initiator. In trials using oxygen and contaminated base stock oil with no antioxidant, heavy solids generation was encountered within 10 hours. These solids appeared to be products of oxidative degradation rather than addition polymerization. Thickening of SAE 30 commercial oil contaminated with sunflower oil also appeared to proceed by a free radical polymerization mechanism catalyzed by copper. No solids build-up was observed in this case.

Four antioxidants designed to influence different steps in an oxidative polymerization mechanism were tested for efficacy. A single compound zinc diamyl dithiocarbamate inhibited both polymerization and solids formation in contaminated base stock oil experiments. This antioxidant did not prove to be as effective with SAE 30 commercial oil, possibly due to adverse interactions(s) with additives in the commercial oil.

Zinc diamyl dithiocarbamate apparently inhibits polymerization by decomposing intermediate hydroperoxide species into forms other than free radicals. Zinc diamyl dithiocarbamate was not effective in experiments where a free radical initiator was used, showing that this compound does not appear to inhibit chain propagation.

## INTRODUCTION

With the gradual depletion of world petroleum sources, provisions must be made for continuation of energy supplies for mechanized agriculture, most of which is powered by diesel engines. The most promising alternative fuels are those which can be used with no or minimal modification of existing engines. For the farm sector, which has become heavily dependent on diesel power [1], plant oils are attracting considerable attention as direct substitutes for diesel fuel. Vegetable oils are capable of providing all of the liquid fuel needed on a typical farm when 10% or less of the total acreage is devoted to fuel production [2,3]. The meal after plant oil extraction can be a source of high protein livestock feed. Further, farmers are already familiar with the type of equipment used in the extraction and processing of vegetable oils.

As far back as 1912, Rudolf Diesel, the inventor of the diesel engine, had tried using vegetable oil as a diesel fuel [4], but economics and design were unfavorable. However, the 1973 oil embargo and the diesel fuel price rise of 400% in the last ten years have rekindled research in the quest for alternative fuels. Among the advantages of vegetable oils as fuel are: their physical nature as liquids and, hence, their portability, their heat of combustion, their ready availability, and the fact that they are renewable resources. In reality, vegetable oil fuels used in U.S. farm tractors introduce a

number of problems, which can be ascribed to their high viscosity, low volatility, and the reactivity of the unsaturated hydrocarbon chains.

In short-term (<10 hours) engine performance tests, vegetable oils perform quite well. Problems show up only after the engine has been operating on vegetable oil for longer periods of time and are far more pronounced in direct-injection engines than in the less efficient engines having precombustion chambers (indirect-injection) [2,5].

Engelman et al. [6] tested waste soybean-diesel oil blends compared with the diesel fuel alone in short-term engine tests. They conclude that use of the blend is feasible, but long-term test data are absent.

Quick [3] and Hofman et al. [7] report on various tests using sunflower, safflower, and/or winter rape as fuels. Quick claims that blends of 20% sunflower oil-80% diesel could probably be used now. However, he warns against using plant oil fuels before testing is complete as severe engine damage and a voiding of manufacturer warranties could result.

Deere and Company [8] reported injector deposits and filter plugging problems in their tests with sunflower and peanut oil and blends with No. 2 diesel fuel. They suggested that a trend to slightly higher hydrocarbon, CO, and particulate emissions was possibly a result of using a fuel system optimized for diesel fuel.

Extensive tests using vegetable oil fuels as well as other alternative fuels have been carried out by Caterpillar [9]. They have extended their warranty on some engines operating on up to 10% vegetable oil, but only in Brazil. This demonstrates acceptance by a major manufacturer of the general concept of vegetable oil-based blends.

Clark et al. [10] report significant reduction in gum formation and fuel filter plugging when methyl and ethyl soybean esters were used as compared to straight soybean oil. Quick [11], however, points out that the extra cost and high crystallization temperature (0°C) are problems with esters. Hugo [12] also expresses caution that incomplete removal of the catalyst used in the transesterification process will result in severe fuel system corrosion when the ester is used in the engine.

Pryde [13] summarizes research done by various investigators and notes two major problems as the results of using plant oils as a fuel or as a fuel blend. First, a thickening of crankcase oil has occurred which is attributed to the contamination of petroleum-based crankcase oil with unburned plant oil. Second, a build-up of carbon on and in the fuel injector nozzles was observed.

Van der Walt et al. [14] tried several minor engine modifications to reduce the coking problem. Their work concentrated on the injectors, since coking is first observed there. Modifications include injector retraction, water cooling of the injectors, and teflon coating of the injectors. None of these modifications had any effect. They also tested a number of commercially available fuel additives for elimination of the coking problem. Only a few have been found which show promise of mitigating the coking problem.

Lubricating oil sample analyses with sunflower oil, cottonseed oil, and a 25% blend of sunflower oil in diesel fuel were conducted by Darcy et al. [15]. Lubricating oil contamination, as evidenced by the percentage of total solids, was greatest for the sunflower oil blend.

Although total solids increased in some cases to dangerous levels, lubricating oil viscosities did not greatly increase.

Possibly as a result of incomplete combustion and increased chemical reactivity of some oils at elevated temperatures, engine lubricating oil contamination may be a major hindrance to these oils emerging as viable fuels for diesel engines. There have been several speculations as to why this contamination occurs. Bruwer et al. [16] suggested that incomplete combustion of plant oils may well be causing thickening by consuming antioxidants in the lubricating oil thus allowing polymerization of oxidized vegetable oil in the engine crankcase. Walton [17] surmised that oils with lower iodine numbers might be expected to undergo less polymerization. His lube oil analyses indicated some viscosity change and formation of insoluble carbonaceous material. More recently, up to 8% total solids were reported in lubricating oil samples by Yarbrough et al. [18].

Bauer et al. [19] attempted to simulate the lubricating oil environment within the engine and used ASTM D 943, "Oxidation Characteristics of Inhibited Steam Turbine Oils," as the basis for test development. Lubricating oil (API CD SAE 30) was intentionally contaminated with soybean oil and then exposed to heat, air, agitation, and various metals of engine construction. Samples contained in 25 mm glass test tubes were heated in a constant temperature oil bath. Oxygen was supplied through 2 mm glass tubes from high pressure cylinders. Flow rates of 1000 ml/hr gave sufficient agitation.

The parameter chosen to determine thickening was oil viscosity. Catalytic amounts of copper and iron together, molybdenum, manganese,

chromium, and nickel were tested to determine effect on rate of viscosity increase of 10% soybean oil in lubricating oil. The rate of viscosity increase with copper and iron was an order of magnitude higher than with the other catalysts. The range of soybean oil dilution levels tested was 0% to 10%. There was little difference in the rate of viscosity increase through 1%, with the rate at 3% slightly higher, and 10% significantly higher. The rate of viscosity increase was significantly higher at 100°C than at 120°C.

Results of endurance tests with soybean oil are reported by Adams et al. [20]. Soybean oil dilution levels from 0% to 50% and water levels from 1% to 10% were tested to simulate hardening and condensation in the crankcase. The solutions were held at 85° to 95°C and agitated by aeration. Catalytic amounts of cobalt and manganese were tested. Viscosity increase was independent of the amount of water present. No significant hardening was noticed in 240 hours without the added metals, but samples containing 10% or more soybean oil became highly viscous in 94 hours with addition of manganese and cobalt.

Blackburn et al. [21] examined oxidation resistance of lubricating oil diluted with ethyl esters of soybean oil in a laboratory test. The laboratory test, ASTM D 2272, "Continuity of Steam-Turbine Oil Oxidation Stability by Rotating Bomb," used a bomb to measure time required for the oil to react with a given volume of oxygen at 150°C. Tests were performed on 20 lubricating oils for gasoline and diesel engines which were contaminated with ethyl soyate at a level of 17%. Oxidation life of uncontaminated oil ranged from 60 to 250 minutes, while the oxidation life of contaminated oil ranged from 20 to 75 minutes.

Korus et al. [22] studied the effect of three commercial antioxidant diesel fuel additives on oxidative polymerization of pure high erucic rapeseed oil. Samples were heated to 240°C in open glass beakers in a forced air convection oven. None of the additives tested reduced the rate of oxidative polymerization of rapeseed oil.

Romano [23] used 25 ppm butylated hydroxytoluene (BHT), a commercial food antioxidant, in a 50% mixture of lubricating oil and methyl esters of soybean oil. Samples were degraded by heating to 140°C and aeration with 30 L/hr air. At 100 hours the viscosity of the sample without BHT had risen one and one half times as much as the sample with BHT, while total base number in both samples was below acceptable limits. After 200 hours viscosity of the sample containing BHT had risen above that of the sample without BHT. The author concluded that BHT is not a proper antioxidant for this system.

Rewolinski et al. [24] report on possible mechanisms of lubricating oil degradation in the presence of plant oil. Samples of diesel lubrication oil contaminated with sunflower oil were exposed to 150°C and catalytic oxidation in a laboratory heater bath. Viscosity rise was shown to be a strong function of sunflower oil concentration, quantity of copper catalyst, and presence of oxygen. Total base number also was a function of amount of copper present in the system. The viscosity still rose in the same manner, when the total base number, and hence alkalinity, was kept constant using a commercial additive. When nitrogen was substituted for oxygen, and a commercial peroxide was added at intervals, viscosity rise was similar to the case with oxygen.

These results strongly suggest that oil thickening is not caused by free acidic species but rather proceeds by a free radical mechanism.

Lubricating oils have undergone significant changes from those used in early engines. Much research has been done to develop oils for engines operating under varied conditions. These lubricants now are specifically formulated for engine operating conditions and fuels used today. Since these oils were designed with common fuels used to date, it is not surprising that existing lubricating oils may create problems when new fuels such as plant oils are used. It is imperative to examine lubricating oil requirements with these fuels and develop characteristics which will eliminate problems that have been experienced.

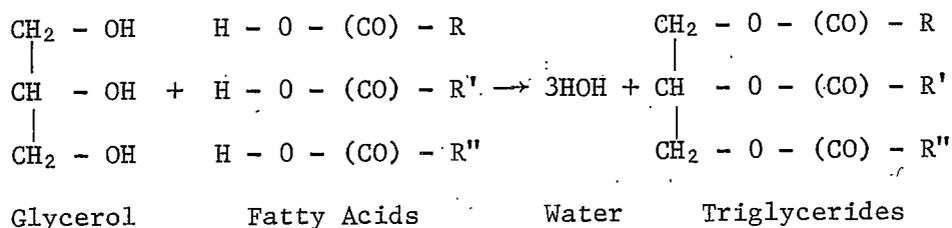
Lubricating oil contamination from using plant oils seems to be an unresolved problem. Some researchers have tried to circumvent this problem by using short oil change intervals. However, this does not seem to be a long-range solution since lubricating oil changes are relatively expensive. Another answer to this problem may be to determine what lubricating oil properties are required to better serve plant oil fuels. Production of a lubricating oil which would alleviate contamination and polymerization by these fuels would add to the overall feasibility of plant oils as fuels for diesel engines.

## THEORY

General Considerations

Petroleum-based diesel fuels have different chemical structures than vegetable oils. The former contain mainly carbon and hydrogen atoms which are arranged in normal (straight-chain) or branched-chain structures as well as aromatic configurations. The normal structure is preferred for better ignition quality [25]. Diesel fuel can contain both saturated and straight or unbranched chain unsaturated hydrocarbons, but the latter are not present in large enough amounts to make fuel oxidation and subsequent polymerization a problem. The aromatics that are present generally are oxidation resistant and their presence would not cause a fuel polymerization problem.

Vegetable oils are water-insoluble, hydrophobic substances which consist predominantly of glyceryl esters of fatty acids, so-called triglycerides. Structurally, a triglyceride is the reaction product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride:



R, R', and R'' symbolize the even numbered hydrocarbon chains of fatty acids that are usually 16 to 22 carbons in length. Depending on the particular oil R, R', and R'' may be the same, but are typically different not only in chain length, but in the number of double bonds. The degree of unsaturation on one triglyceride molecule can vary from zero to as high as nine double bonds. The molecular weight of the glyceryl portion ( $C_3H_5$ ) of a triglyceride molecule is 41. The remainder of the molecule, the fatty acid units ( $RCOO^-$ ), have a typical molecular weight range from 650 to 970. The fatty acids contribute 94-96% of the total weight of the molecule and consequently greatly influence both the physical and chemical properties of the triglycerides.

The unsaturated fatty acids most commonly found in vegetable oils are oleic, linoleic, and linolenic acids. They each have a chain length of 18 carbons, but the number of double bonds they possess are one, two, and three, respectively. Oleic and linoleic acids are documented as being major components in such vegetable oils as sunflower and safflower. Linolenic acid is found in certain varieties of rapeseed along with erucic acid. Erucic acid, like oleic acid, has only one double bond but its chain length is 22 carbons. Some fuel properties, e.g., oxidation resistance, are markedly influenced by the fatty acid composition of vegetable oils. The large size of vegetable oil molecules (typically three or more times larger than hydrocarbon fuel molecules) and the presence of oxygen in the molecules suggest that some fuel properties of vegetable oils would differ significantly from those of hydrocarbon fuels.

### Oxidative Polymerization

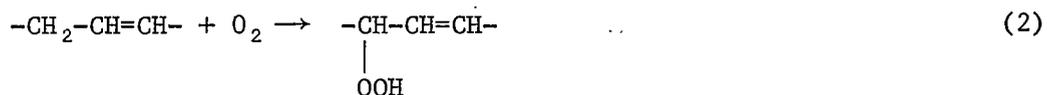
Polyunsaturated vegetable oils are more susceptible to deterioration by polymerization upon exposure to heat and oxygen than diesel fuel. The oxidation of vegetable oils involves a direct chemical attack by oxygen of the air, generally termed as autoxidation. With highly unsaturated fatty acids autoxidation is usually accompanied by polymerization. Oxidative polymerization occurs by a free radical, hydroperoxide mechanism, in which the primary reactions are the formation of unsaturated ester hydroperoxides, the decomposition of these materials, and their subsequent cross linking. The major changes that occur during oxidative polymerization are as follows [26]:

1. The initiation of the oxidative chain reaction is preceded by an induction period. During this period no visible changes in physical or chemical properties of the oil are observed. Natural antioxidant compounds are consumed during this period.
2. The reaction becomes perceptible and oxygen uptake is considerable. Oxygen interacts with double bonds forming hydroperoxides.
3. Conjugation of double bonds occurs accompanied by isomerization from *cis* to *trans* unsaturation.
4. Decomposition of the hydroperoxide forms a high free radical concentration and the reaction becomes autocatalytic.
5. Polymerization and scission reactions begin to yield high molecular weight cross-linked polymers and low molecular weight carbonyl and hydroxy compounds.

The autoxidation of simple unsaturated compounds was at first thought to consist of an initial attack on the double bonds of a particular system to form cyclic peroxides [27].



Farmer and Sutton [28], however, demonstrated that the first product of the oxidation of an olefin is a hydroperoxide with an intact double bond alpha to the site of oxidation.



An early kinetic survey established that the hydroperoxides were formed in substantially quantitative yield during the primary stages of the autoxidation process [29]. The unsaturated linkage, although still intact, was shown to be transformed from the cis form to the trans geometric isomer [30,31], which is the more stable form. Privett et al. [32] concluded that at least 90% of linoleate hydroperoxide preparations are conjugated. When oils containing linoleate or more highly unsaturated acids are oxidized, the concentration of conjugated diene increases at about the same rate as oxygen uptake and peroxide formulation as measured by ultraviolet absorption at 2340 Å [33].

The lack of a satisfactory source of the energy required for the rupture of an  $\alpha$ -methylene carbon-hydrogen bond, which is 80 kcal/mole, has led various investigators to propose that the hydrogen is removed

through reaction with a free radical [33]. Thus a radical  $A^\bullet$ , abstracts a hydrogen from a molecule of linoleate,  $RH$ , to form the radical  $R^\bullet$ .



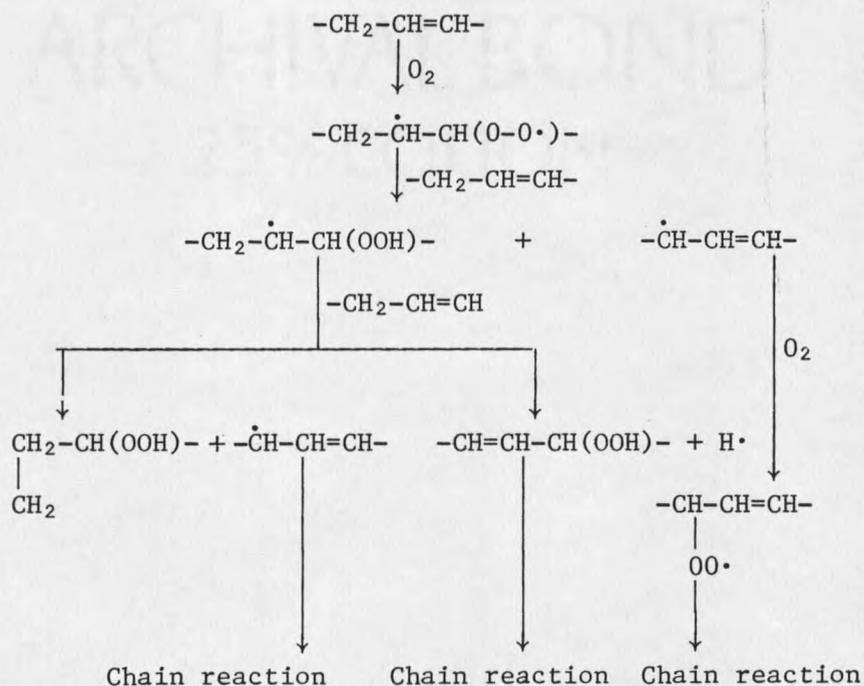
The chain propagation reaction then continues as follows [34]:



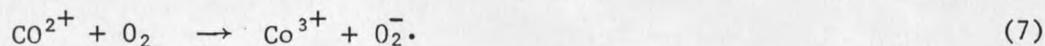
The primary reaction to produce the radicals (indicated as  $A^\bullet$  above) responsible for initiation of the chain reaction is subject to some controversy. Originally Farmer et al. [35] held the view that hydroperoxides are the initial products of autoxidation. But because of the high energy requirement for rupture of the  $\alpha$ -methylene carbon-hydrogen bond, Bolland and Gee [36], Farmer [37], and Gunstone and Hilditch [38] almost simultaneously postulated that the initial point of oxidative attack was the double bond and not the  $\alpha$ -methylene group. Bolland and Gee proposed a limited attack at the double bond to produce radicals in sufficient quantity to initiate the chain reaction through the  $\alpha$ -methylene carbon. A diradical is formed by the action of oxygen on the double bond followed by subsequent rearrangement and further reaction.

Khan [39] has shown by the use of isotopes that during the autoxidation of the methyl esters of oleic acids the initial attack by oxygen apparently takes place at the double bond during the induction period. This is followed by a steady-state period during which the

reaction propagation is carried out by attack upon the methylenic group in the position adjacent to the double bond.



Uri [34] argues that the direct attack of oxygen on the double bond has low thermodynamic probability, and he maintains that trace metal contaminants like copper, iron, or cobalt catalyze the initiation of autoxidation by producing free radicals through electron transfer. The possible mechanisms of radical formation could be by reduction activation of trace hydroperoxides, direct reaction of a metal ion with oxygen, or oxidation by electron transfer of the  $\alpha$ -methylene group by the metal ion [33].



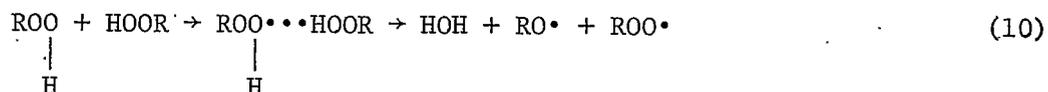
According to Uri [34] the kinetic and thermodynamic probabilities for formation of free radicals by the metal-catalyzed initiation reaction are considerably more favorable than direct oxidation of a double bond. This is possible since even the most highly purified fatty esters contained traces of metal catalysts [34].

The possibility exists that different mechanisms might operate at various temperatures. In the oxidation of methyl oleate, the attack might be at the allylic hydrogen at 20°C, whereas at higher temperatures, combination with the double bonds could occur [40]. Based on the rate of change in the viscosity of autoxidized linseed oil, apparent differences in the course of the reaction in the temperature ranges below 84°C, between 84°C and 130°C, and above 130°C were noted [41].

Once the hydroperoxides are formed, even in small amounts, they can play an important role in the autocatalysis. Decomposition of the hydroperoxide can occur in a monomolecular mode producing two free radicals:



or in a more likely bimolecular reaction proceeding through intermediate hydrogen bonding:



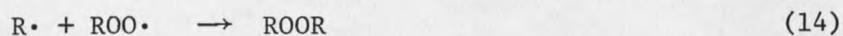
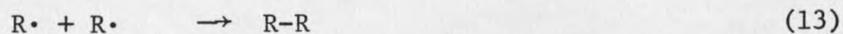
Either decomposition mechanism serves to introduce new radicals into the reaction to initiate the chain reaction of autoxidation.

Kinetically, there are three stages in the autoxidation process [33,34]:

Initiation: production of free radicals.

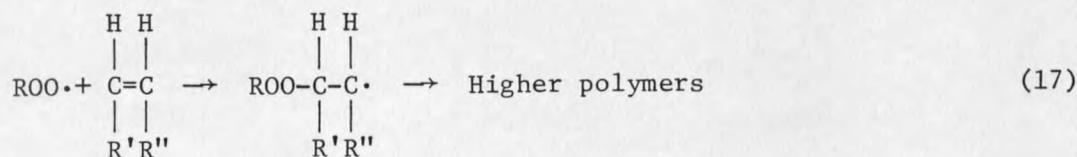
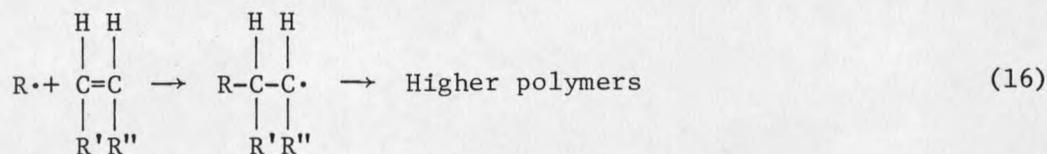


Termination: polymers are formed by the combination of free radicals in this stage:



Extensive review of the kinetics of autoxidation reactions has been given by Uri [34].

In addition to the dimers formed by combination of free radicals, higher molecular weight polymers are formed through vinyl polymerization:



The rate of oxidative polymerization varies with the number and degree of conjugation of the unsaturated linkages. The rate of autoxidation of methylene-interrupted polyunsaturated systems like linoleates, the esters of linoleic acid, is significantly higher than that of monounsaturated systems due to the activation of the methylene group by adjacent double bonds. The actual ratios of reactivity of different unsaturated systems, however, are not unanimously agreed upon [42]. For instance, it has been shown [43] that the rate of oxidation of films of triolein, trilinolein, and trilinolenin was in the order of 1:20:330. In contrast, Kartha [44] noted that the relative rates of oxidation of methyl oleate, methyl linoleate, and methyl linolenate were either 1:12:25 or 1:2:4.

#### Antioxidant Action

Certain naturally occurring accessory substances in the fat or oil are capable of influencing the rate of oxidation to a great extent. Those substances that favor the oxidation are termed prooxidants; those suppressing oxidation are known as antioxidants or inhibitors. All natural fats and oils contain characteristic antioxidants. A remarkable feature of antioxidants is their great effectiveness at low concentrations in the oil. The natural antioxidant concentration of an oil usually does not exceed a few hundredths of 1% [46].

There is no universally accepted mechanism which can explain how traces of a foreign substance are able to exert so powerful a retarding effect on autoxidation [45]. The possible inhibitory effect of

hydroquinone and similar compounds including the tocopherols, may be as follows [46], where

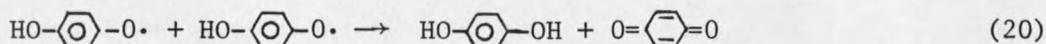
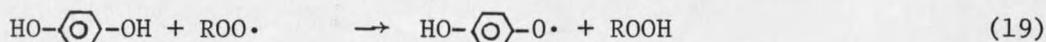
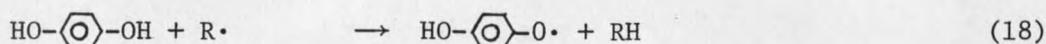
RH = the activated linoleic pentadiene system with H as  
the labile hydrogen of the methylene group,

R• = free radical,

ROO• = oxygenated free radical,

ROOH = primary oxidation product (hydroperoxide), and

HO--OH = hydroquinone:



Thus the antioxidant species supplies hydrogen atoms (eq. 18) to terminate both the initiating and propagating steps in the autoxidation chain reaction. Because of the energy required to remove H from RH to form R•, this step would be slow, and if the antioxidant were present before many radicals and chain carriers were formed, it is easily seen how trace amounts of antioxidant could greatly retard the progress of autoxidation even though the antioxidant is eventually destroyed. Autoxidation can thus be inhibited at the initiation and propagation steps. In fact, antioxidants are often classified on the basis of their ability to do either or both [47].

Two main categories of antioxidants inhibit the initiation step in autoxidation. The peroxide decomposers operate by decomposing hydroperoxides to nonradical products through polar reactions. Metal

deactivators are strong metal ion complexing agents and thus do not allow the metal to react with the hydroperoxide.

Antioxidants that decompose hydroperoxides include sulfides, such as dialkyl thiodipropionate ( $[\text{RO}_2\text{CCH}_2\text{CH}_2]_2\text{S}$ ), aryl and alkyl phosphites ( $[\text{RO}]_3\text{P}$ ), and metal salts of certain dithioacids such as zinc dithiocarbamates ( $[\text{R}_2\text{NCS}_2]_2\text{Zn}$ ), and zinc dithiophosphates ( $[(\text{RO})_2\text{PS}_2]_2\text{Zn}$ ) [47].

Much progress has been made in elucidating the mechanism of hydroperoxide decomposition by sulfides through studies of di-tert-butyl sulfide [48]. Oxidation, followed by elimination and condensation reactions (eq. 21), gives tert-butyl sulfenic acid and tert-butyl thiosulfoxylic acid which are reported to be the efficient hydroperoxide decomposers.



The exact mechanism of their action is yet unknown. However, it is believed [47] that  $\text{SO}_2$  is the ultimate oxidation product and peroxide decomposition catalyst. The phosphites are believed to function as stoichiometric peroxide decomposers (eq. 22) [49].



Hydroperoxide decomposition by zinc salts of dithioacids can also be very effective, and various mechanisms have been proposed for their action [50,51]. Colclough et al. [52] proposed a mechanism involving electron-transfer from an electron-rich sulphur atom to a peroxy radical by which zinc dialkyl dithiophosphates act as chain-breaking

inhibitors. Burn [50], however, postulated that the electron-transfer mechanism involves a stabilized peroxy intermediate which, on attack of a second peroxy radical, leads to intramolecular dimerization of the incipient dithiophosphate radicals before addition to a double bond can occur. Holdsworth et al. [53] claim that all sulphur-containing antioxidants eventually evolve sulphur dioxide, which acts as a catalyst for the peroxide decomposition reaction.

The deactivation of metal ions by chelation can operate by more than one mechanism. The chelating agent may act by forming an insoluble metal complex, by modifying the redox potential of the metal ion, or by sterically hindering the metal ions thereby preventing the formation of metal ion-hydroperoxide complexes [54]. However, chelation is not always effective and can sometimes enhance metal ion activity, particularly if coordination is incomplete and causes an unfavorable change in redox potential [54,55]. Typical chelating agents are N,N'-disalicylidene-1,2-propanediamine, oxalyl bis-(denzylidenehydrazide), and ethylene-diamine-tetraacetic acid (EDTA) and its sodium salts. Some secondary arylamines, such as N,N'-di- $\beta$ -naphthyl-p-phenylenediamine and certain bisphenols, such as 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) are also known to be effective copper ion deactivators.

Propagation inhibitors are mostly hindered phenols and secondary alkylaryl- and diarylamines. Their high efficiency is partly attributed to their low volatility. This class of antioxidants act by hydrogen atom transfer to the peroxy radical in a rate-controlling step (eq. 23).

The antioxidant radical is fairly stable and reacts with a peroxy radical or dimerize (eq. 24-25) [47].



AH = phenol, secondary amine

Since the hydrogen transfer step oxidizes the antioxidant (eq. 23), a correlation can be expected between antioxidant effectiveness and their oxidation potential. However, an antioxidant which is very easily oxidized can actually promote initiation of new chains through a reaction with molecular oxygen (eq. 26). In some cases, the antioxidant radical, A·, might also engage in chain reaction (eqs. 27-29).



Zinc salts of dithioacids appear to inhibit the propagation step by electron rather than hydrogen transfer, thereby reducing the peroxy radical to a peroxide anion,  $\text{ROO}_2^-$  [47]. Thus, these substances inhibit both initiation and propagation. However, the exact mechanism of electron transfer is still unresolved [47].

Based on the chain reaction theory, one might expect that the inhibitory effect of an antioxidant would be directly proportional to

its concentration in the fat or other substrates. Such, however, is seldom the case. In general, the successive addition of an antioxidant yields steadily diminishing returns in terms of increasing the stability of the substrate [46]. Presumably, at higher concentrations a substantial amount of the antioxidant is consumed by side reactions, and thus does not function as a free radical terminator. As discussed before, it is also possible that in some cases decomposition of the antioxidant may produce substances with a prooxidant effect.

In summary, various antioxidants show potential for retarding autoxidation chain reaction. These antioxidants operate by different mechanisms and hence their efficacy will be, to a large extent, dependent on the mechanism of lubricating oil thickening in the presence of plant oil. Based on the performance of these additives, a possible mechanism of plant oil polymerization could be theorized. Once the reaction scheme is clearly understood, an additive package would be relatively easy to formulate to inhibit the detrimental effect of vegetable oil. Discretion must be exercised in choosing additives, since compatibility and thermal stability are important factors for the antioxidant to be effective.

## RESEARCH OBJECTIVE

The purpose of this research is to elucidate the mechanism of lubricating oil degradation in the presence of plant oil. Polymerization of hydrocarbon base stock oil as well as commercial oil will be investigated in a laboratory apparatus simulating the crankcase environment in a diesel engine.

Various antioxidants which inhibit autoxidation reaction by different mechanisms will be tested for their effectiveness. Based on their performance with the base stock oil, these antioxidants will be used with the commercial oil.

A commercial free radical initiator will be used in conjunction with the antioxidants which give good performance with the base stock oil.

The catalytic action of a solubilized form of copper will be investigated with the suitable antioxidants.

## MATERIALS AND METHODS

Materials

Edible grade sunflower oil which was supplied by Continental Grain Company in Culbertson, Montana, was used in all experiments. Lubricating oil used was Super HD II low ash MIL-L-2104C API CD SAE 30 obtained from Phillips Petroleum Company in Bartlesville, Oklahoma. Phillips also provided the hydrocarbon base stock oil (without any additives). All chemicals used for analytical purposes were reagent grade.

Equipment

The main equipment items were comprised of the reaction kettles, viscometers, and other analytical apparatus. The oil bath (Figure 1) housing the reaction kettles was a steel tank 16" long by 14" wide by 11" high, insulated with 1 1/2" vermiculite insulation on the sides and bottom, and pressed between steel plates welded to the steel tank. Paraffin oil was used as the heating medium so as to allow reaching the desired temperature without smoking and a fire hazard. This oil filled the steel tank to a level higher than the level of oil mixtures in the reaction kettles. A Polyscience Model 73 immersion circulating heater was used to heat the oil. Maximum temperature obtainable was 150°C, with an accuracy of  $\pm 0.1^\circ\text{C}$ . Power output varied from 10 to 1000 watts, and pumping rate was 13 liters per minute. A mercury





























































































