



Catalysis of sunflower oil polymerization in a diesel lubrication system
by Rajkumar Raman

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 sunflower oil diesel fuel was investigated in laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Primary research objectives were characterization of the catalytic roles of engine wear metals and testing of chemical additives which might suppress polymerization.

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Several commercial metal catalyst deactivators were investigated in this study. N,N'-disalicylidene 1,2-propane diamine (NNPD) was moderately effective in retarding polymerization, especially during the initiation phase, but its mechanism of action appeared to be more as an antioxidant than as a metal deactivator.

Attempts to reverse or inhibit copper catalysis by using excessive copper concentrations or adding polar acids to oil mixtures fail to succeed in any measure. However, all additive trials performed in this study were clouded by the unknown, proprietary commercial additives present in the diesel lubrication oils.

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requirements for the degree of

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in
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January 1989

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APPROVAL

of a thesis submitted by

Rajkumar Raman

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.

Dec 20, 1988
Date

D. L. Shaffer
Chairperson, Graduate Committee

Approved for the Major Department

Dec 20, 1988
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

January 26, 1989
Date

Henry Parsons
Graduate Dean

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ABSTRACT

Oxidative addition polymerization of lubrication oil contaminated with sunflower oil diesel fuel was investigated in laboratory apparatus simulating conditions prevailing in a diesel engine crankcase. Primary research objectives were characterization of the catalytic roles of engine wear metals and testing of chemical additives which might suppress polymerization.

Of the common wear metals in a diesel lubrication system, only copper displays a significant catalytic role for sunflower oil polymerization. Catalysis is dominated by dissolved copper species. The extent of oxidation of the metallic copper surface was determined to be critical in determining the extent of copper dissolution.

Several commercial metal catalyst deactivators were investigated in this study. *N,N'*-disalicylidene 1,2 propane diamine (NNPD) was moderately effective in retarding polymerization, especially during the initiation phase, but its mechanism of action appeared to be more as an antioxidant than as a metal deactivator.

Attempts to reverse or inhibit copper catalysis by using excessive copper concentrations or adding polar acids to oil mixtures fail to succeed in any measure. However, all additive trials performed in this study were clouded by the unknown, proprietary commercial additives present in the diesel lubrication oils.

INTRODUCTION

In the modern world of today, transportation plays an important role in the overall economic growth of any nation. Petroleum possesses the potential of being able to serve as a backbone to this progress. With the rise of crude oil costs in the early 1970's, efforts were made to search for alternate sources of liquid fuel.

Vegetable oils, being a replenishable source of energy, have attracted the attention of a number of researchers [1-8]. The fact that calorific values of plant oils are comparable to diesel fuel, posed them as a possible substitute. However, when used under standard operating conditions of a diesel engine, these oils tend to contaminate and thicken the lubricating oil system into a highly viscous mass [7].

In a diesel engine uncombusted fuel experiences a high temperature in the combustion chamber and a lower temperature in the engine crankcase. When vegetable oil is used as diesel fuel, a small part of the fuel remains uncombusted and seeps into the crankcase. Over a period of time the quantity of this unconsumed fuel in the crankcase increases. The lubricating oil/vegetable oil mixture thickens over a period of time making it impossible for the efficient working of the engine. This problem is related

to the structural chemical differences between vegetable oils and diesel fuel.

Extensive research has been and is being conducted to tackle this problem in this laboratory. The first step was to understand the various factors which might affect the thickening of the mixture. An experimental setup was constructed in order to study the various parameters. In order to simulate the conditions of a diesel engine, certain standard conditions had to be established. These may be summarized as temperature, metal catalyst concentration and chemical environment. Rewolinski [9] chose 150 C as a rough average temperature encountered by the oil as it travels through the combustion chamber and the engine crankcase. In a laboratory apparatus designed to simulate conditions of a diesel crankcase, he found that oxygen strongly influenced the thickening or polymerization of sunflower oil mixed with lubricating oil, while nitrogen did not. He also found that the rate of viscosity rise increased with increase in the concentration of vegetable oil in lubricating oil. In order to get a measurable viscosity rise within a reasonable period of time, Rewolinski standardized the oxygen flow rate percolating through the simulation apparatus to be 2.0 ml/sec and the concentration of vegetable oil to be 5.0 weight percent sunflower oil.

Jette [10] focussed his research on the role of copper as an important engine wear metal in the system. This metal was observed by Rewolinski to be more important as a polymerization catalyst than iron, another common engine wear metal. Jette found that copper was most active catalytically when present in a soluble form in the reactant mixture. This soluble form(s) was a result of copper species dissolved from a strip of copper foil present in the reactant mixture. He also found that copper acetylacetonate (CuAcAc) was effective in imitating closely the catalysis of the dissolved copper species from the immersed foil strip. He used copper foils of different sizes and found the viscosity rise due to polymerization increasing with increase in the size of the foil up to a maximum. A standard size of 2.0 cm X 5.0 cm was established for the metal foil. The probability of unwanted metal contamination was minimized by keeping the reactant mixture with the foil in a glass reactor.

Dutta [11] studied the mechanism of lubricating oil degradation in the presence of sunflower oil. He investigated the polymerization in hydrocarbon basestock oil as well as commercial lubricating oil. He primarily dealt with basestock oil to avoid the problem of the 'additive package' which is present in any commercial lubricating oil. This package typically contains numerous

chemical compounds whose chemistry is withheld by the suppliers as proprietary information.

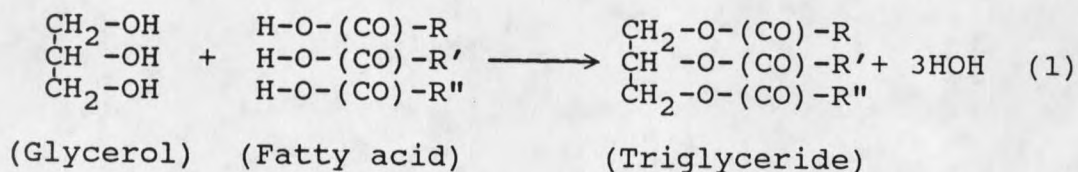
Thus, with this much prior knowledge, research on this lap of the project moved on to testing the inhibition and influence of copper and other important engine wear metals like lead, aluminium and silver, with a view to understanding the mechanism of catalysis in the sunflower oil/lubricating oil polymerization.

THEORY

General Background

Vegetable oils in general are structurally different from diesel fuels. The former possess a high degree of unsaturation by way of double bonds between two adjacent carbon atoms. They therefore have a tendency to be attacked by oxygen and undergo addition polymerization through a free radical mechanism. Oxygen may also induce cleavage on a vegetable oil molecule to form aldehydes and ketones. Diesel fuels on the other hand primarily contain straight chain paraffins and aromatic hydrocarbons. As a result these fuels show considerable resistance towards oxidation.

Vegetable oil molecules are hydrophobic in nature. They predominantly contain glyceryl esters of fatty acids, which are known as triglycerides. These esters may be formed by reacting a glycerol molecule with three molecules of fatty acids:



R, R' and R'' symbolize the even numbered hydrocarbon chains of fatty acids with a typical range of 16-22 carbons in length. Typically, these chains are different in length as well as in the degree of unsaturation. A triglyceride molecule is made up of a glyceryl portion (C_3H_5-) with a molecular weight of 41 and the remaining fatty acid units ($RCOO-$) having a molecular weight range from 600 to over 950. These fatty acid units can contribute 96% of the total weight of the triglyceride molecule and therefore greatly influence its physical and chemical properties [12].

Many vegetable oils mostly contain oleic, linoleic and linolenic acids. These acids each have a length of 18 carbon atoms. Sunflower oil has oleic and linoleic acids as its major components. Fuel properties like oxidation resistance are directly related to the fatty acid composition of plant oils. The markedly different composition of vegetable oils suggest their properties to be significantly different from fossil hydrocarbon fuels like diesel.

Oxidative Polymerization

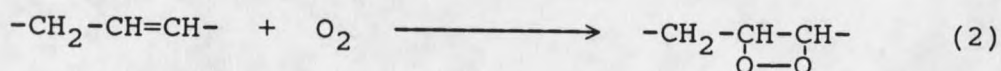
Plant oils undergo degradation by polymerization when exposed to heat and oxygen. The extent of

deterioration is a direct function of the degree of unsaturation of the fatty acid components. Atmospheric oxygen is capable of chemically attacking these oil molecules directly. This complex chemical attack is termed as autoxidation. A high degree of unsaturation in these oil molecules favors free radical polymerization to occur as a consequence of autoxidation. This oxidative degradation can be explained in the following sequential manner [13].

1. An induction period exists wherein no visible physical or chemical changes of the oil are observed. This is a result of natural antioxidants present in the oil being consumed.
2. Initiation of the oxidative chain reaction occurs. Oxygen interacts with the carbon-carbon double bonds forming hydroperoxides.
3. Conjugation of double bonds occurs followed by cis- trans isomerization.
4. Hydroperoxides decompose to form free radicals. The high concentration of these radicals makes the reaction autocatalytic.
5. High molecular weight cross-linked polymers and low molecular weight carbonyl and hydroxy compounds are

formed due to polymerization and scission reactions respectively.

The initiation mechanism of oxidative chain reactions has been a subject of controversy. Initially, this was thought to be due to the attack of oxygen on the carbon-carbon double bonds of the unsaturated fatty acids forming cyclic peroxides [14]:



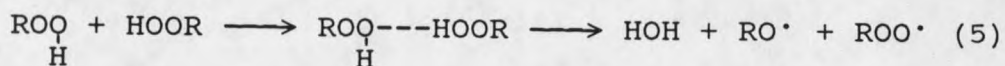
Later it was shown that the initial products contain noncyclic alpha-methylenic hydroperoxides with the double bonds still intact [15]. This suggested the alpha-methylenic carbon-hydrogen bond to be broken. However this bond has an energy of 80 kcal/mole, which is relatively strong when compared to the low availability of energy resources. Researchers have therefore concluded that the oxygen directly attacks the carbon-carbon double bond [16-19].

Autoxidation results in the formation of hydroperoxides, which when formed even in trace amounts act as catalysts. These hydroperoxides are formed as a result of the oxidative attack on the carbon-carbon double bond. As a result, rearrangement of electrons takes place with

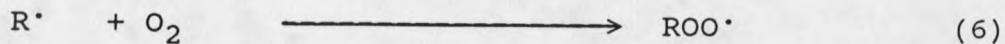
the shifting of the double bond. This shifting is referred to as conjugation [17-18]:



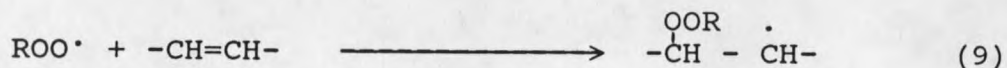
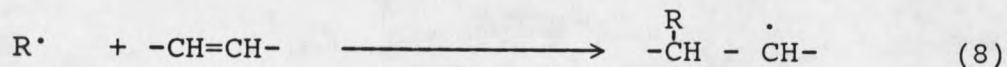
The hydroperoxides so formed may decompose to free radicals [16]:



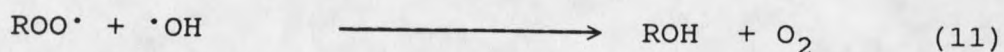
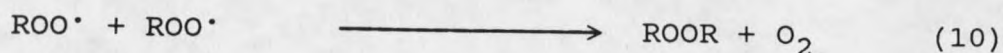
Chain propagation may occur in the following manner :



Free radicals may also attack carbon-carbon double bonds to form larger hydrocarbon free radicals [20]:



Termination reactions generally result in the formation of higher polymers from the constituent free radicals [16,20]:

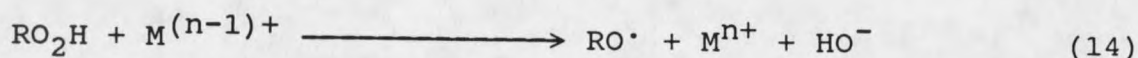


Transition Metal Catalysis

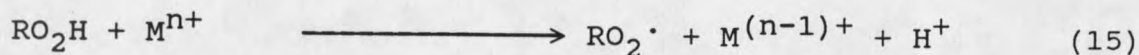
Sunflower oil forms alkyl hydroperoxides in presence of oxygen [11]. Active, soluble forms of copper catalyze this reaction [10]. An extensive literature survey was done in the process of hypothesizing a mechanism by which copper may influence the polymerization. Fortunately, substantial information was obtained with respect to the effect of transition metal complexes in nonpolar solvents and their reaction with alkyl hydroperoxides. Copper being a transition metal (valence states 1 and 2) is in this category with other common metals namely cobalt, manganese and iron.

The metal-catalyzed homolytic decomposition of alkyl hydroperoxidic intermediates is the most common pathway for the catalysis of liquid phase autoxidations. The two principal reactions of alkyl hydroperoxides with metal complexes are [21]:

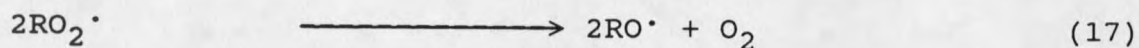
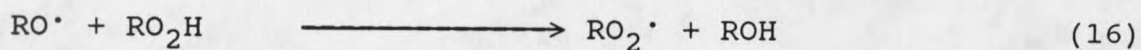
Reduction



Oxidation



In inert solvents, reaction (14) or (15) can be followed by the radical chain decomposition of the hydroperoxide, i.e. :

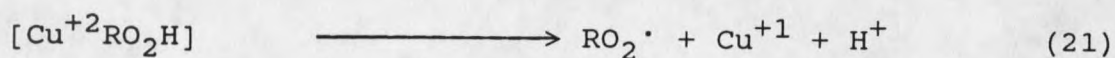
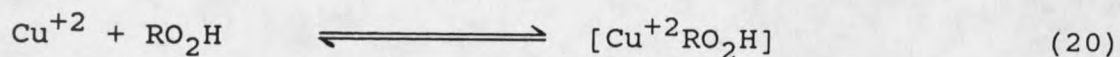
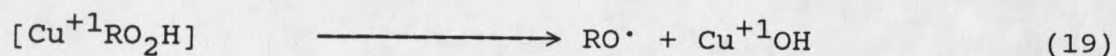
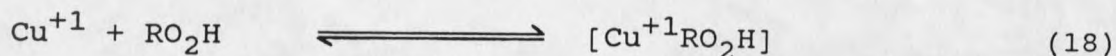


Under these circumstances, the metal ion acts as an initiator rather than as a catalyst. In general, the metal complexes catalyze autoxidations by generating chain-

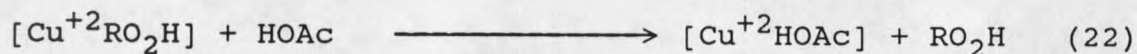
initiating radicals via reaction (14) or (15). When the metal has two oxidation states of comparable stability, reactions (14) and (15) can occur concurrently. Chain initiation during metal catalyzed autoxidations of hydrocarbons generates alkoxy and alkylperoxy radicals from the reaction of alkyl hydroperoxides with the metal catalyst as shown in equations (16) and (17).

Transition metal complexes, especially in media of low polarity such as saturated hydrocarbons, often behave as catalysts at low concentrations and as inhibitors at high concentrations. This phenomenon, referred to as catalyst-inhibitor conversion, manifests itself in the long induction periods often observed in metal-catalyzed autoxidation in nonpolar media [22-23]. In practice, an abrupt transition from catalysis to inhibition is generally observed for hydrocarbon autoxidations catalyzed by cobalt, manganese or copper [22,24]. Such puzzling kinetic phenomena associated with metal-catalyzed autoxidations have been analyzed by Black [25] on the basis of metal-hydroperoxide complexes. Chain initiation via the unimolecular decomposition of a transition metal-hydroperoxide complex has been generalized for several transition metals by Chalk and Smith [26]. There seems to be more experimental evidence in support of such complexes in the initiation of metal-catalyzed autoxidations [25,27].

Using copper as an example, initiation is assumed to involve the following steps [25]:



In media of low polarity, copper is tied up as a complex with the alkyl hydroperoxide in excess. As the concentration of copper is increased, however, a point is reached at which $[\text{Cu}] > [\text{RO}_2\text{H}]$, and the equilibrium concentration of the uncomplexed $\text{Cu}(+1)$ increases suddenly to the point at which the oxidation can no longer proceed. In polar protic solvents such as acetic acid, the catalyst is mainly associated with the solvent molecules present in much higher concentrations than RO_2H :



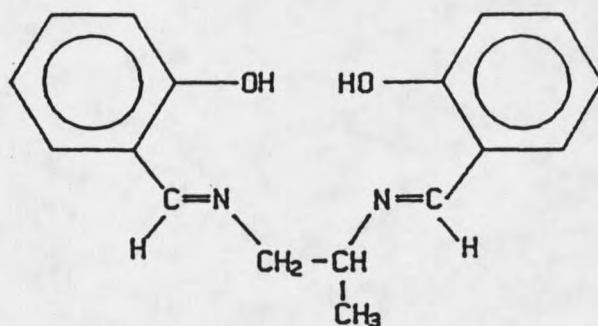
Consequently, the phenomena of abrupt catalyst-inhibitor conversion and long induction periods are generally restricted to media of low polarity.

Another kinetic observation associated with metal-catalyzed autoxidations is the phenomenon of limiting rate, whereby reaction rates ultimately level off at some limiting values. This behavior was attributed by Tobolsky [28] to the attainment of a steady-state concentration of alkyl hydroperoxides in which the rate of decomposition is counterbalanced by its rate of formation as shown by Woodward and Mesrobian [29-30] for the case of cobalt. However, other investigators have found that, in media of low polarity, the hydroperoxide concentration increases steadily throughout the region of maximum rate [24,31-33]. This apparent anomaly has also been rationalized by Black [25] to be a consequence of the formation of metal-hydroperoxide complexes.

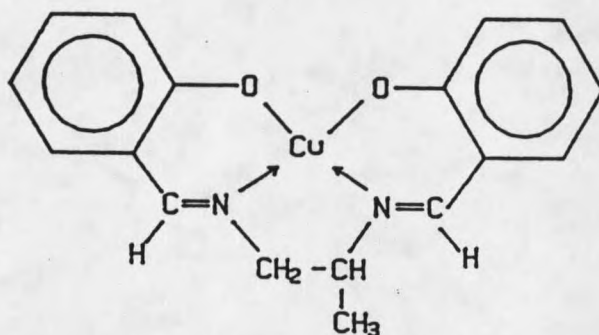
Chelation

Chelating agents or deactivators may sequester the active metal species in the experimental system. These agents operate by several mechanisms. They may form an insoluble metal complex by modifying the redox potential of the metal ions, or may sterically hinder the metal ions by forming a metal ion-hydroperoxide complex [26]. This process of deactivation is, however, not always effective and may sometimes enhance metal ion activity, especially

when the coordination is incomplete, resulting in an unfavorable change in the redox potential [26,34]. Some of the typical chelating agents are *N,N'*-disalicylidene 1,2-propane diamine (NNPD), oxalyl bis-(benzylidenehydrazide), and ethylene-diamine-tetraacetic acid (EDTA) and its sodium salts. NNPD has the following chemical structure [35]:



It may act as a copper ion deactivator by forming a metal ion complex in the following manner:



Certain bisphenols like, 2,2'-methylene-bis (4-methyl-6-tert-butylphenol) and a few secondary arylamines, such as *N,N'*-di-(beta)-naphthyl-p-phenylenediamines are also known to be effective copper ion deactivators in

certain chemical systems. The mechanism(s) by which they deactivate copper is not clearly understood.

RESEARCH OBJECTIVES

Sunflower oil contamination undergoes oxidative polymerization in a lubricating oil system. This reaction has been shown to be strongly catalyzed by solubilized copper [10]. In order to use plant oil instead of diesel fuel, the problem of polymerization causing lubricating oil viscosity rise has to be eliminated.

The initial goal in this lap of the project was to explore the possibility that engine wear metals other than copper might be influencing the reactant oil mixture. Once this was done studies would be conducted on the wear metals (including copper) which affect the contaminated oil system catalytically. Emphasis was to be given to the mechanism by which these wear metals may influence the process of oxidation. This would help in devising means to overcome part of the problem, namely catalysis in oxidative degradation.

In order to achieve the goals of this research the following paths were to be taken.

1. The theory of inhibitory characteristics of transition metal complexes in nonpolar solvents was to be applied to the work.

2. The effects of certain known chelating agents or commercial metal deactivators were to be investigated to inhibit wear metal catalysis.

EXPERIMENTAL

Apparatus and Procedures

Simulated conditions of the crankcase of a diesel engine were achieved in the laboratory. Two identical reaction kettles (500 ml in volume) were used. Each had a glass top with four entrance ports (Figure 1). The entrance ports in the center and one of the sides were threaded to screw fit a gas inlet and outlet pipe, respectively. These pipes were held securely by means of a gasket and a screwable cap. The other entrances were basically used for gaining access to the reaction mixture (taking samples, adding chemical compounds) during the course of a run. These two entrances were plugged by glass stoppers. All four entrance ports were affixed to the glass top of the reaction kettle by means of silicon grease, which made the whole system leakproof. This airtight atmosphere was necessary to obtain a controllable environment.

The entering gas tube was connected to a 30 mm glass frit disc used for gas percolation and keeping the temperature constant within the reaction mixture. The frit was placed in the bottom center of the kettle. If a metal catalyst was used in the experiment, then a 2.0 cm X 5.0 cm

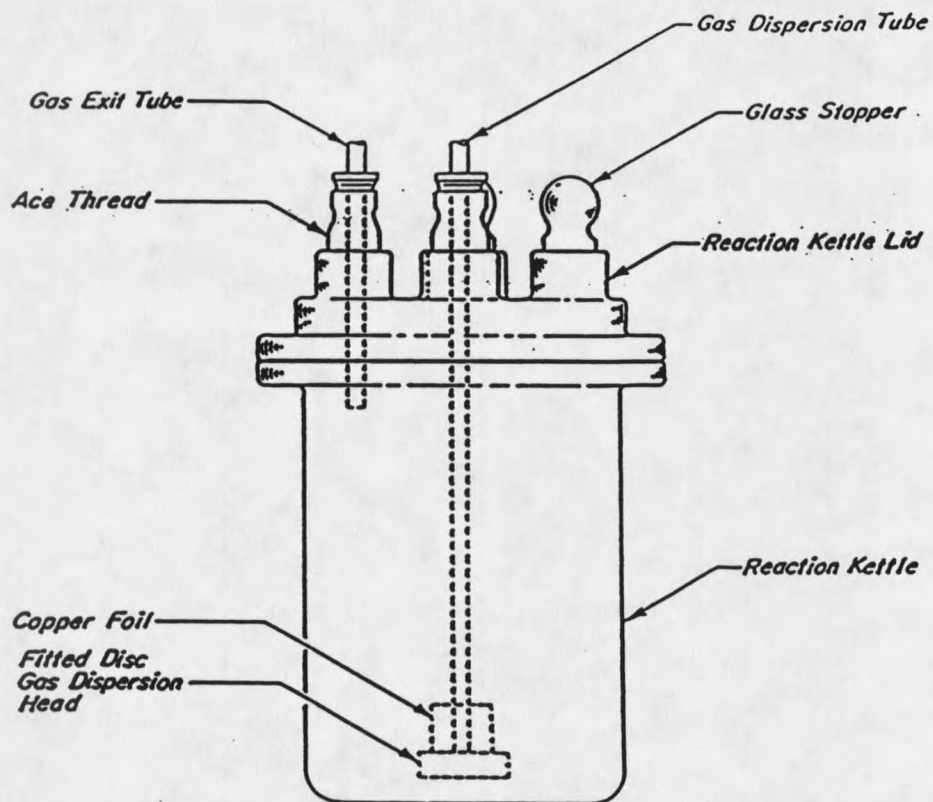


Figure 1. Reaction Kettle

foil strip with a thickness of 0.125 mm was cut out and placed on top of the frit like a hollow cylinder (Figure 1). The exiting gas tube was connected to a soap film bubble flow meter by means of tygon tubing. The flow rate was normally adjusted to 2.0 ml/sec.

The reaction kettle(s) was placed in a paraffin oil bath (Figure 2) maintained at a temperature slightly above 150 C so that the temperature of the reaction mixture in the kettle(s) would read exactly 150 C. The bath was mixed thoroughly at the above designated temperature by means of a Polyscience Model 73 immersion circulator. This apparatus kept the temperature constant with an error of ± 0.2 C and circulated approximately 13 liters of heating oil per minute. The oil bath was well insulated with approximately 2 inches of vermiculite insulation between steel plates that made up the sides and the bottom of the bath. A tight fitting steel lid covered the vapor space above the kettle(s) and the paraffin oil. The whole system described so far was operated under a venting hood for general safety reasons.

The gas supply to the reaction mixture (oxygen or nitrogen, as the case may be) was provided by means of cylinders fitted through regulators connected by stainless steel tubing. Tubing entered a four-position gas header mounted on a steel frame placed beside the oil bath. Two

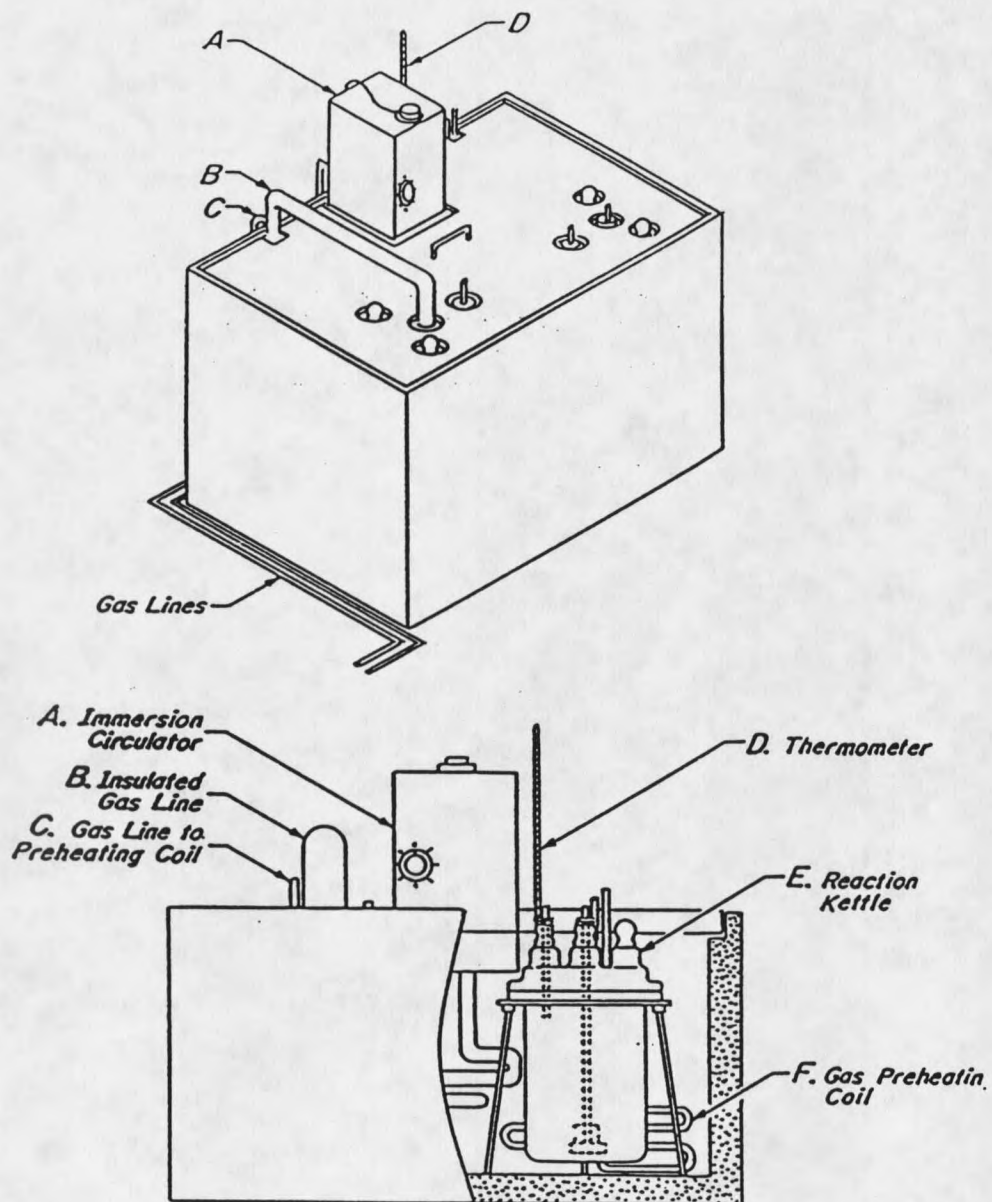


Figure 2. Oil Bath and Reaction Kettle

precision needle valves were connected to the headers to control gas flow to the reaction kettles. The gas was preheated by passing it through a stainless steel coil immersed in the oil bath. Insulated teflon tubes connected the preheating coil to the glass stem of the frit. The operating diagram for the system is shown in Figure 3.

Generally speaking, during the course of a run, 8 ml samples were taken periodically and their viscosities were measured by calibrated Cannon-Fenske viscometers. Various specific viscometers were used as oil viscosities increased during an experiment. The oil samples were emptied into the viscometer, which was immersed in a constant temperature water bath, maintained at 40.0 C by another Polyscience Model 73 immersion circulator. The oil samples were pipetted out of the reaction mixture by placing the pipette eight inches below the surface of the steel lid of the oil bath. Viscosity readings were taken twice for each sample and the average value was noted. Then the sample was promptly returned to the reaction kettle.

Atomic emission spectroscopy studies were sometimes conducted (depending on the intent of a particular experimental run) on 90 ml oil samples from the reaction mixture. These samples were sent to Case Lubricant Analysis Service in Indianapolis, Indiana, to

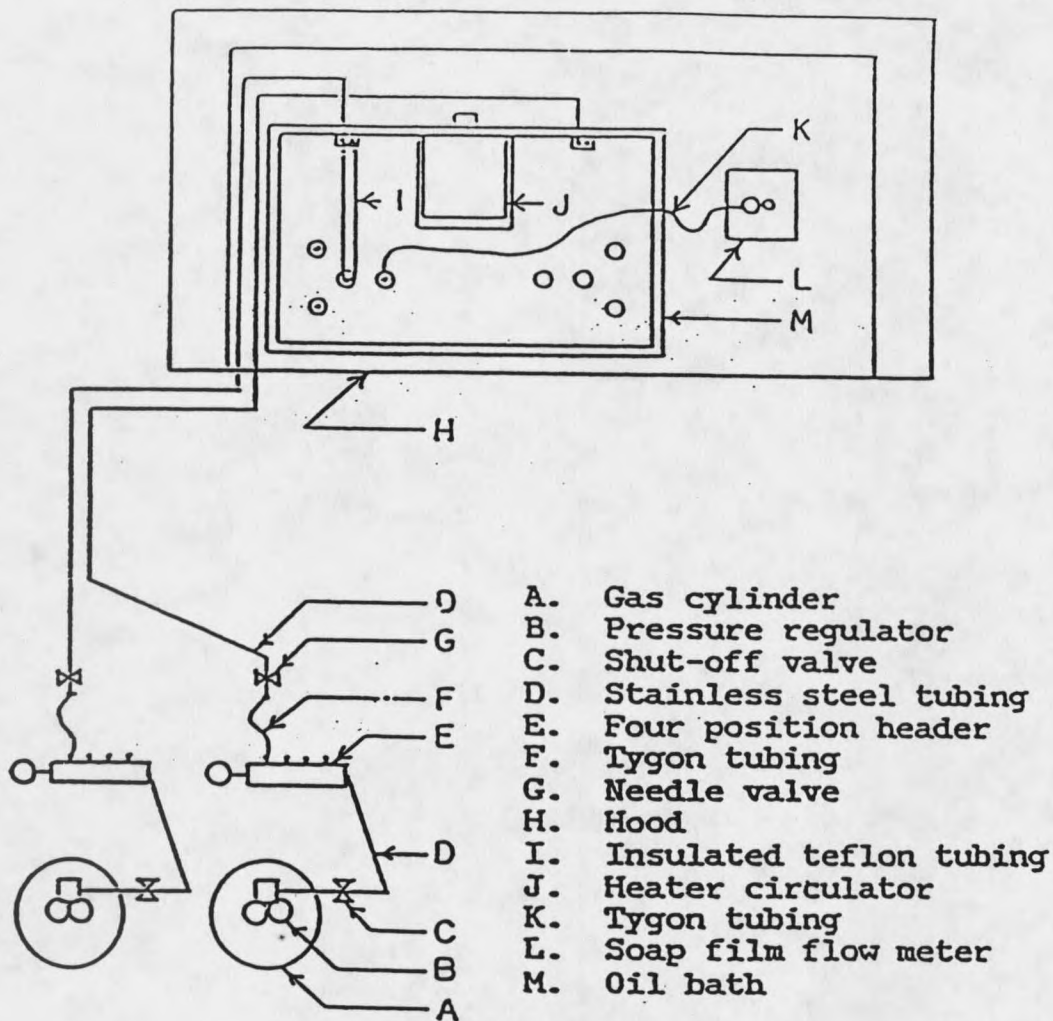


Figure 3. Oil Bath and Operating Diagram

obtain the concentration levels of wear metals in parts per million. The error on the reported values was estimated at $\pm 20\%$, based on the procedure used for testing.

The degree of unsaturation of the sunflower oil used was determined by conducting an iodine value test. This value was determined according to ASTM Standard 1959-69 which is applicable to plant oils and their fatty acids [36].

Safety precautions were adequately taken by placing the experimental setup containing the hot oil under a venting hood. Safety glasses, aprons and gloves were used when handling hot oils and chemicals. All waste chemicals considered hazardous were disposed of through the Chemical and Hazardous Waste Department of Montana State University.

Materials

The sunflower oil used at the beginning of this project was obtained from Continental Grain Company of Culbertson, Montana. It had an iodine value of 140. When this initial stock of oil was exhausted, a new supply was obtained from Cargill Incorporated in Fargo, North Dakota. This latter sunflower oil had an iodine value of 144. Hydrocarbon basestock as well as commercial lubricating oil

was provided by Phillips Petroleum in Bartlesville, Oklahoma. Two different batches of basestock oil as well as corresponding commercial lubricating oils were obtained. The second batch of commercial lubricating oil was shipped under the company name of AMOCO. The commercial lubricating oils used were of the grade API CD SAE 30.

Lubrizol 5955 A, a metal deactivator, and zinc dialkyl dithiophosphate (ZDTP), supplied under the trade name Lubrizol 1395, both were supplied by Phillips Petroleum Company of Bartlesville, Oklahoma. DuPont Metal Deactivator (NNPD) was obtained from DuPont U.S.A. Reagent grade metals like lead, aluminium and silver were used in a few experiments. All other chemicals used were reagent grade.

RESULTS AND DISCUSSION

Considerable research has been done in this laboratory towards the use of sunflower oil as a substitute for diesel fuel. Up to this point in the project, successful attempts have been made in the following :

- 1) categorizing the various parameters that affect plant oil polymerization in the contaminated lubricating oil system [9,10],
- 2) understanding the importance of hydroperoxide formation in the pathway to the polymerization of sunflower oil in lubricating oil [11],
- 3) establishing copper as a catalyst when present in certain active soluble forms [10].

This lap of the project started off with an aim of looking further into the catalytic activity of copper and other active engine wear metals, if any. The first step taken was to be on par with the results obtained by the previous workers. Thus, two standard runs (Runs 1 and 2) were conducted using commercial lubricating oil, Super HD II low ash MIL-L-2104C API CD SAE 30. A standard run consisted of a 5.0% mix (by weight) of sunflower oil with commercial lubricating oil in the presence of a

2.0 cm X 5.0 cm copper foil strip (0.125 mm thick) and oxygen percolation at a flow rate of 2.0 ml/sec. The reaction mixture was subjected to a temperature of 150 C. The results from both the runs were observed to be similar to that obtained by Jette [10] (Figure 4). Variations between the viscosity rise curves of Runs 1 and 2 are a result of typical experimental error. This error is primarily caused by the following reasons:

- 1) temperature of the reactant oil mixture fluctuates closely around 150 C,
- 2) oxygen flow rate is checked every four hours and hence may vary between two successive monitoring times,
- 3) error introduced during weighing the reactant mixture containing sunflower oil and lubricating oil.

Thus an "average" viscosity rise curve is sketched in and shown in Figure 4, which will be used as reference in later runs. At this point it must be mentioned that any experimental run conducted hereafter will have the basic parameters set according to the standard run, unless otherwise mentioned. Also, any quantity of added chemical expressed as percent refers to the weight percent with reference to the weight of the reaction mixture at the time of addition.

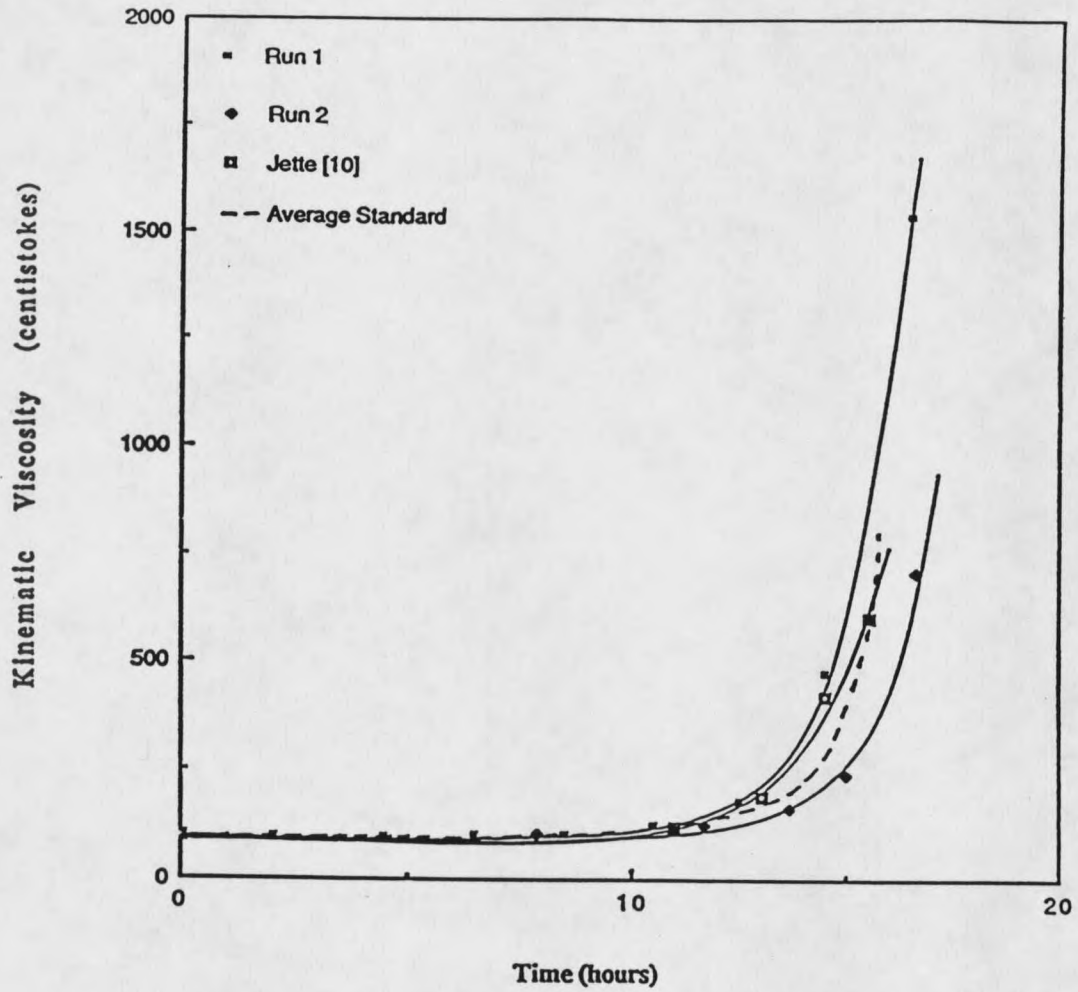


Figure 4. Kinematic viscosity versus exposure time for commercial lubricating contaminated with 5% sunflower oil under standard conditions

In a first scouting trial a commercial metal deactivator, Lubrizol 5955-A, was evaluated for impact on copper catalysis. No literature was available regarding the chemistry (proprietary) or mechanism of copper metal inhibition for Lubrizol 5955-A, but its use was suggested by industry contacts. This deactivator was used in Run 3. In this run 0.10% of the deactivator was added to the reaction mixture at the start of the run. The viscosity rise curve did not appear to be significantly different from that of the standard run. It is possible that the deactivator vaporized during the course of the run and escaped with the exiting gas. Therefore Run 4 was conducted by adding 0.10% at the beginning and also after 9.5 hours. The viscosity rise results of this run did not vary much from the standard run either. The results of Runs 3 and 4 are plotted with the standard run in Figure 5. With these experiments it can be safely concluded that the recommended commercial deactivator in question does not seem to show any significant effect in the system under consideration.

The role of some prominent engine wear metals other than copper was looked at in the next work. The metals employed were in the form of a foil with the same dimensions as of the copper foil. The first metal used was lead. This foil was used in Run 5 instead of copper.

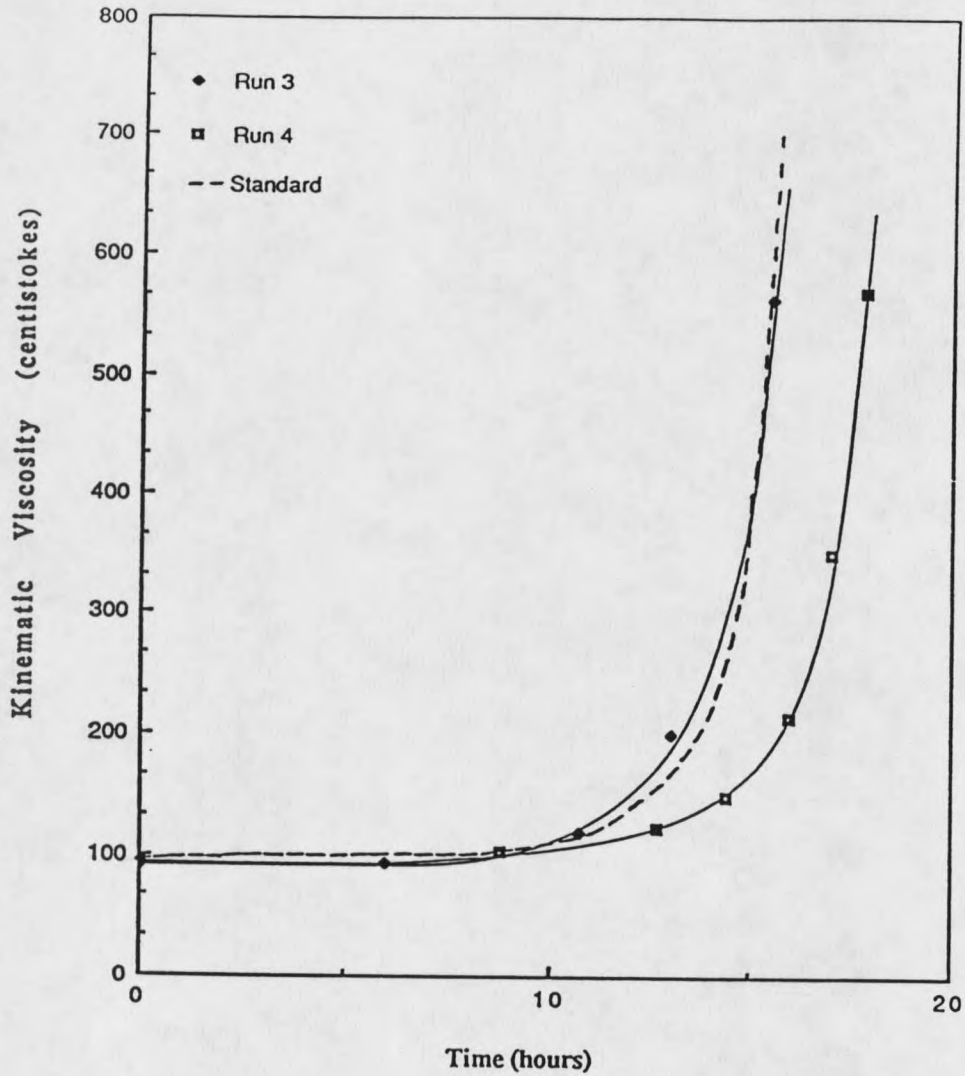


Figure 5. Kinematic viscosity versus exposure time for Runs 3 and 4 conducted with the addition of Lubrizol 5955-A once and twice respectively

Similarly Runs 6 and 7 were conducted subsequently with aluminium and silver foils, respectively. Results of these metal substitution trials are given in Figure 6.

The immediate results in terms of the viscosity rise curves showed great similarity among the three runs, and a slower rise compared to the standard run with copper foil. In order to more fully understand the role of these metals (as in their present metallic foil state), another run was conducted (Run 8) without the inclusion of any metal foil in the system. The viscosity rise curve obtained matched closely those of Runs 5, 6 and 7. This indicates an inert catalytic nature for the three metals as against the catalytic effect of copper. Figure 6 also shows a plot of Run 8.

Atomic emission spectroscopy results indicated no detectable lead or aluminium dissolving in the system. No sample from Run 7 was sent to Case Lubricant Analysis Service. Thus, based on this set of runs it can be safely stated that some prominent engine wear metals, namely lead, aluminium and silver, while in their metallic forms, do not affect the behavior of the reaction mixture.

Next, two runs were conducted with basestock oil in the absence of any sunflower oil. Run 9 dealt with bubbling oxygen through basestock oil in the presence of a copper foil for 48 hours. Run 10 dealt with the same

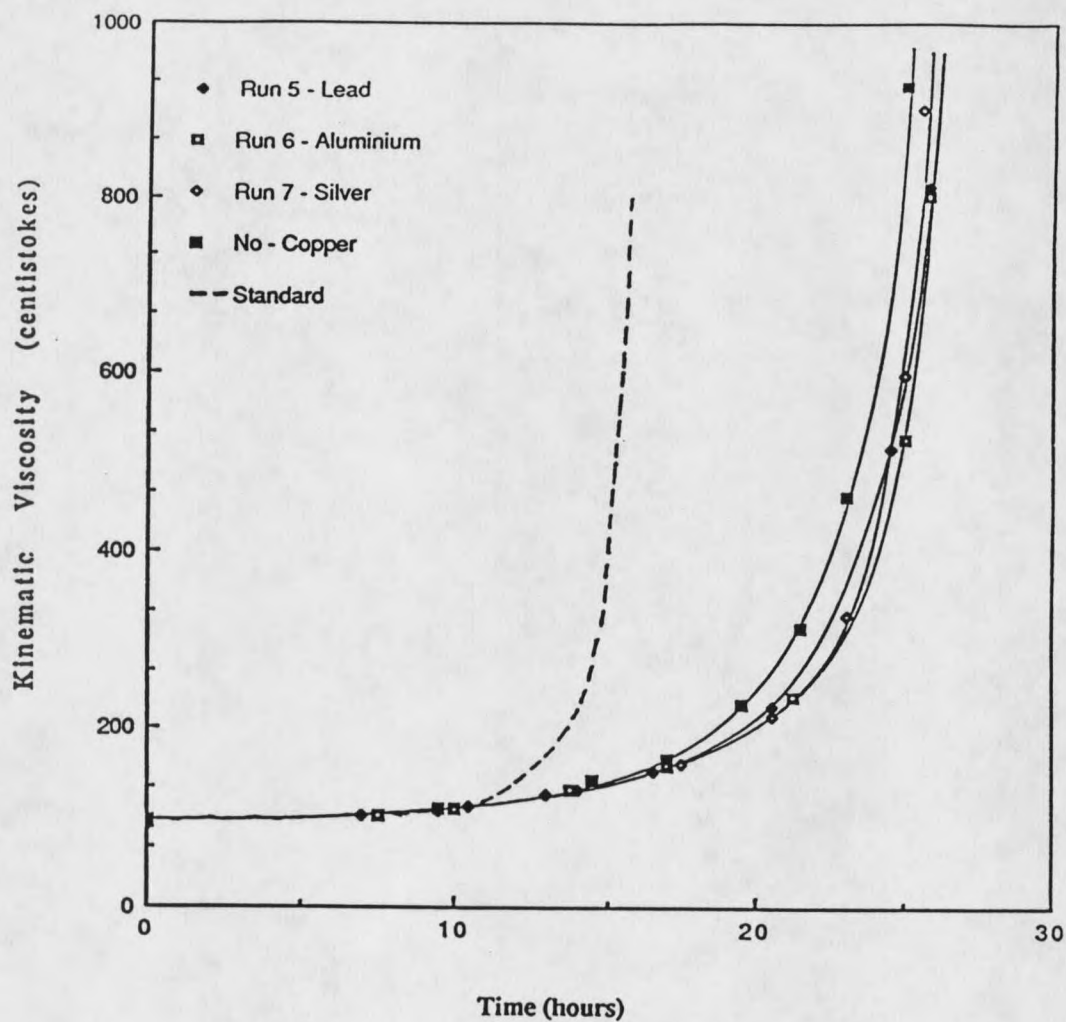


Figure 6. Kinematic viscosity versus exposure time for three different engine wear metals compared against a copper run and a no-copper run

conditions except with the use of nitrogen instead of oxygen. Oil samples were taken from each of the two runs at 24 and 48 hours and sent to Case for atomic emission studies. The results obtained gave the following copper concentrations in parts per million:

Table 1. Atomic emission results (ppm) for the effect of oxygen and nitrogen on copper dissolution.

Run	Gas Used	24 hours	48 hours
9	Oxygen	5,5	6,7
10	Nitrogen	1	2

The above results (duplicates for Run 9) indicate the effect of oxygen in the dissolution of copper in the system. These results were compared with those of Jette [10], who conducted similar (no sunflower) runs with commercial lubricating oil, instead of basestock oil. His results indicated higher concentrations of dissolved copper in both cases. Jette found 28 ppm dissolved copper at 48 hours using oxygen percolation and 14 ppm copper at 48 hours using nitrogen. Jette's results suggest a promoting action of the additive package in the commercial lubricating oil for the dissolution of copper.

Any commercial lubricating oil generally contains an additive package. This package contains a number of antioxidants and metal inhibitors of unknown (proprietary)

chemistry. Dutta [11] suggested zinc dialkyl dithiophosphate (ZDTP) and zinc dialkyl dithiocarbamate (ZDTC) as probable antioxidants in an additive package. Looking at the atomic emission results at the end of a standard run, an interesting observation was made. Zinc and phosphorus concentrations drop drastically at the end of the run when compared with the corresponding values at the start of the run as shown:

Table 2. Dissolved metal concentrations (ppm) at the beginning and the end of a standard run.

	Cu	Si	Ba	B	Ca	Mg	P	Zn
Metal ppm at the start of a standard run	0	6	1	64	43	1321	1276	1217
Metal ppm at the end of a standard run	5	8	2	65	47	913	963	1003

If one could replenish the loss of zinc and especially phosphorus during the course of the run, polymerization might be retarded considerably. Based on Dutta's studies on ZDTP [11], the compound was chosen as a potential source for the two metals. Run 11 was conducted with the addition of 1.0% ZDTP every 8 hours. No ZDTP was added initially, as the commercial lubricating oil itself probably contained antioxidants similar in nature to ZDTP in the additive package. A plot of the viscosity rise

curve for Run 11 is shown against the standard run and the no-copper situation in Figure 7. The viscosity rise curve showed substantial delay when compared with the standard run. In fact, one can actually see breaks in the curve at 8 and 16 hours, indicating the retarding effect of the compound. After 24 hours of the run, addition of ZDTP did not make much of a difference, probably because the polymerization had proceeded to quite an advanced stage by then.

Thus, replenishing zinc and phosphorus in this manner did not stop the viscosity rise, but did however highlight the potential of ZDTP as an antioxidant. ZDTP could be added more frequently and even in greater quantities in an attempt to delay the viscosity rise substantially. However, looking at the situation from the practical point of view, such a procedure would be quite impractical as this would change the nature of the lubricating oil to a large degree. Thus, the viscosity rise problem still remained unsolved.

An extensive literature survey conducted prior to this experimental work suggested a large increase in the active soluble copper species in the system might reverse the role of copper from catalytic to inhibiting in nature [24]. The concentration of the soluble copper species to be employed was indicated to be 0.1 gm mole / liter.

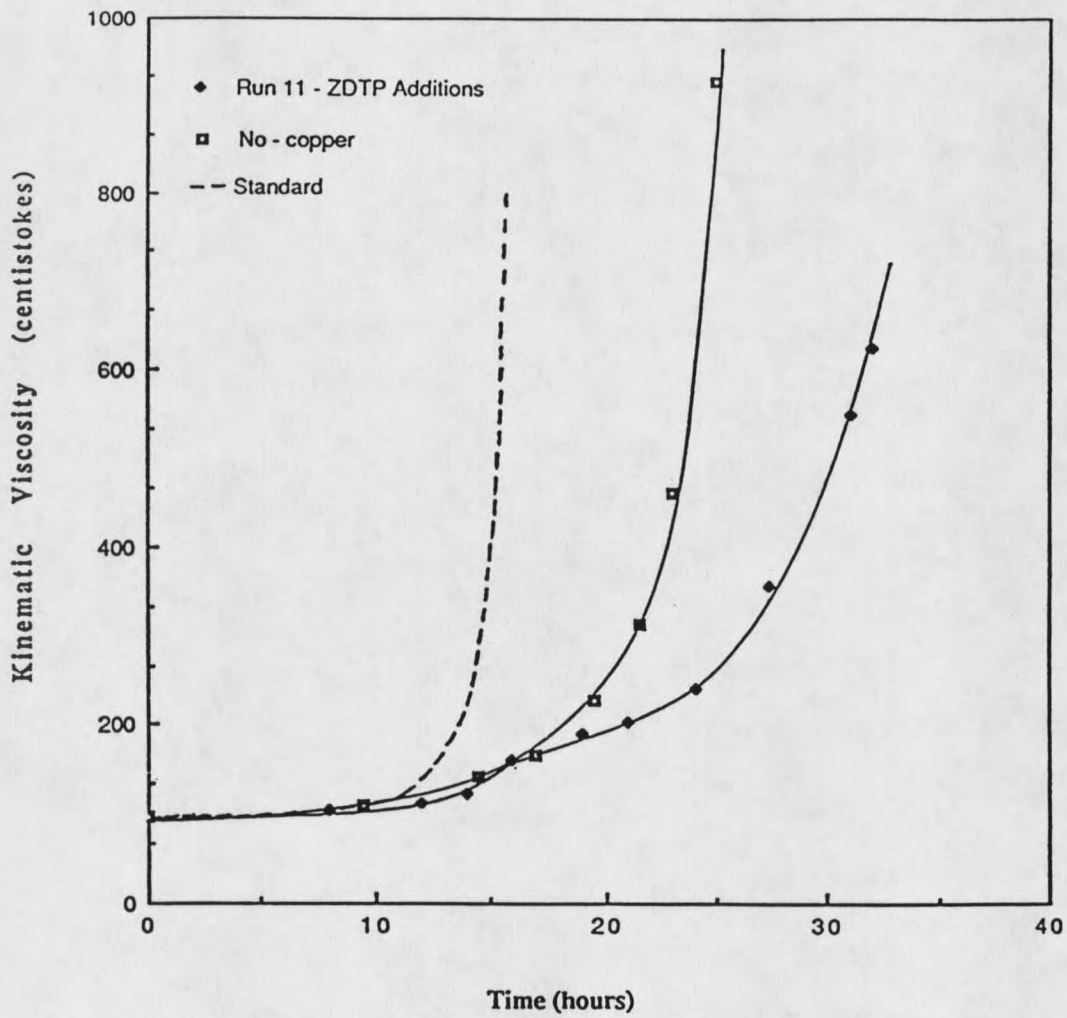


Figure 7. Kinematic viscosity versus exposure time for the addition of 1.0% ZDTP every eight hours

Copper acetylacetonate, established to be a good source for such active species [10], was used to test this theory of reversal of activity. The chemical (powder) was mixed thoroughly in the reactant oil mixture at the above specified concentration and was used in Run 12. This run showed much faster viscosity rise than that of the standard run as shown in Figure 8. This result contradicted the inferences from the literature survey regarding the active copper species in this system. However, the results obtained from Run 12 followed the same pattern as those of Jette [10], obtained with varying amounts of copper acetylacetonate.

At this point an attempt to combat the vegetable oil polymerization problem was made by resorting to commercial metal deactivators once again.

A potential copper deactivator, N,N' -disalicylidene, 1,2-propane diamine (NNPD) was obtained from DuPont USA. As has already been mentioned, the structure of NNPD purportedly facilitates sequestering the active copper species by forming a coordinate complex with the copper metal ion.

Run 13 was conducted with 0.50% NNPD added at the start of the run. The viscosity rise curve was delayed when compared with the standard run as shown in Figure 9. This encouraged the scheduling of Runs 14 and 15, at higher

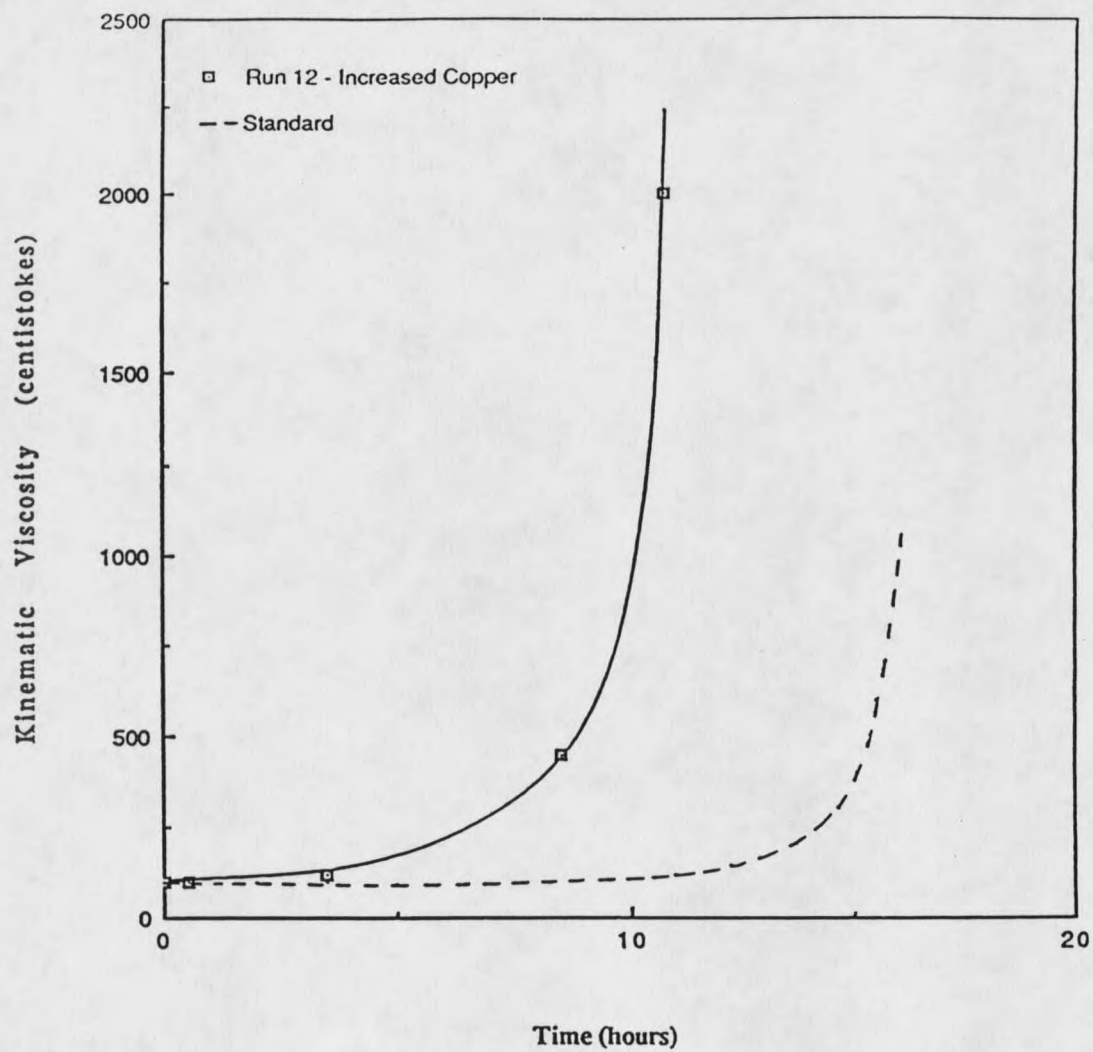


Figure 8. Kinematic viscosity versus exposure time for Run 12 conducted with a dissolved copper concentration of 0.1 gmole/l

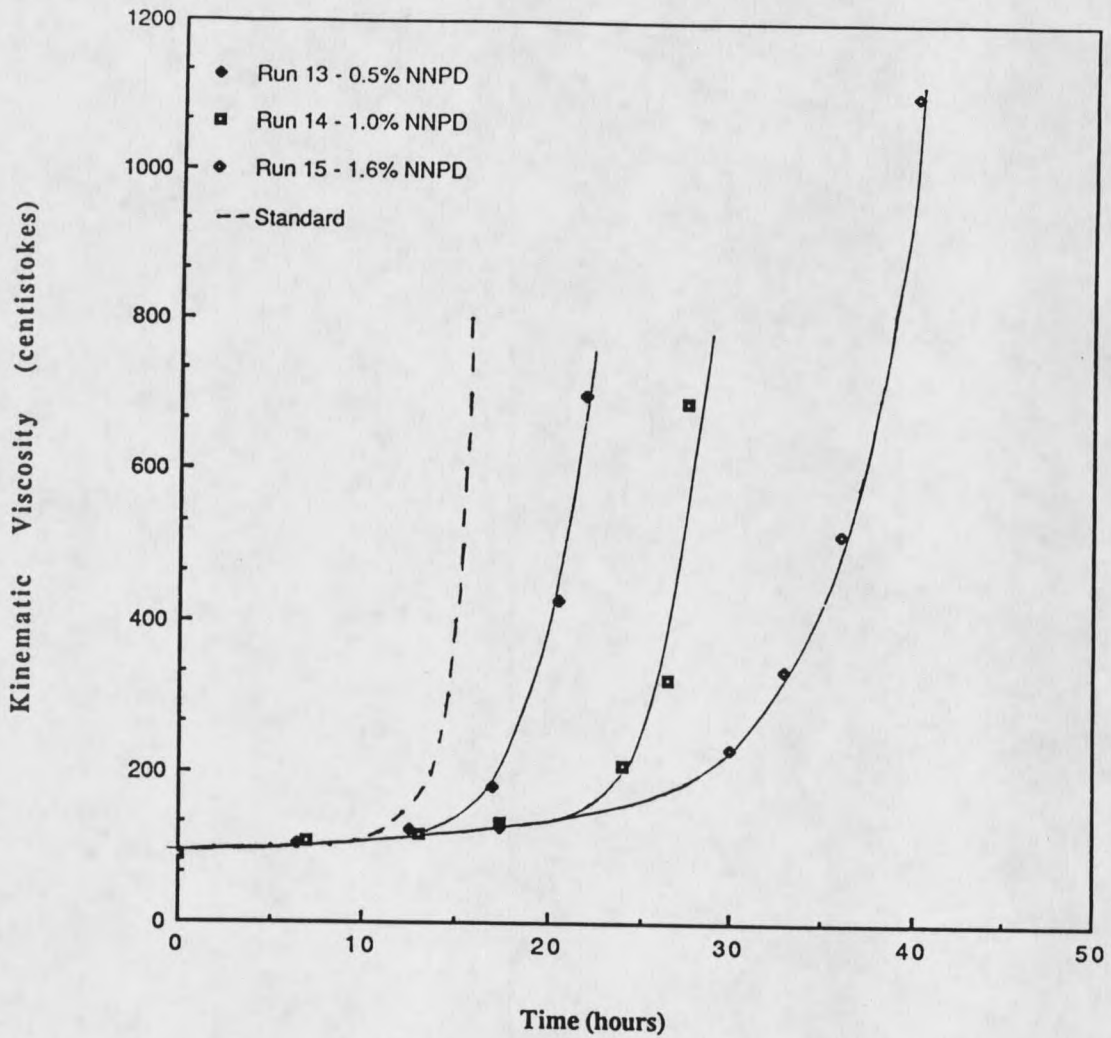


Figure 9. Kinematic viscosity versus exposure time for three runs conducted with different initial additions of NNPd

NNPD concentrations of 1.0% and 1.6%, respectively, added initially. Both these runs again showed substantial viscosity rise delays when compared with the standard run. The delay in the viscosity rise seemed to increase with increase in the amount of NNPD added at the start, as shown in Figure 9. However, it must be pointed out that, in all three cases polymerization did occur eventually, thereby increasing the viscosity beyond acceptable limits for the working conditions of a diesel engine [37]. This led to hypothesizing the possibility of NNPD being lost to the atmosphere or being consumed in some manner during the course of the run, thus allowing the viscosity rise.

Another run (Run 16) was performed with 0.50% NNPD added initially and every 4 hours thereafter. Interestingly enough, the nature of viscosity rise for this run matched closely with that of Run 13, where 0.50% NNPD was added only at the beginning of the run as shown in Figure 10. This indicated that the role of NNPD as a metal deactivator occurs predominantly during the initial stages of the polymerization process. It was theorized that, during the initial stages of a standard run, the plant oil molecules present in the system have relatively short chain lengths. Therefore, the resistance to mass transfer for copper dissolution from the foil to the reactant mixture is small. Thus, while polymerization is still in its

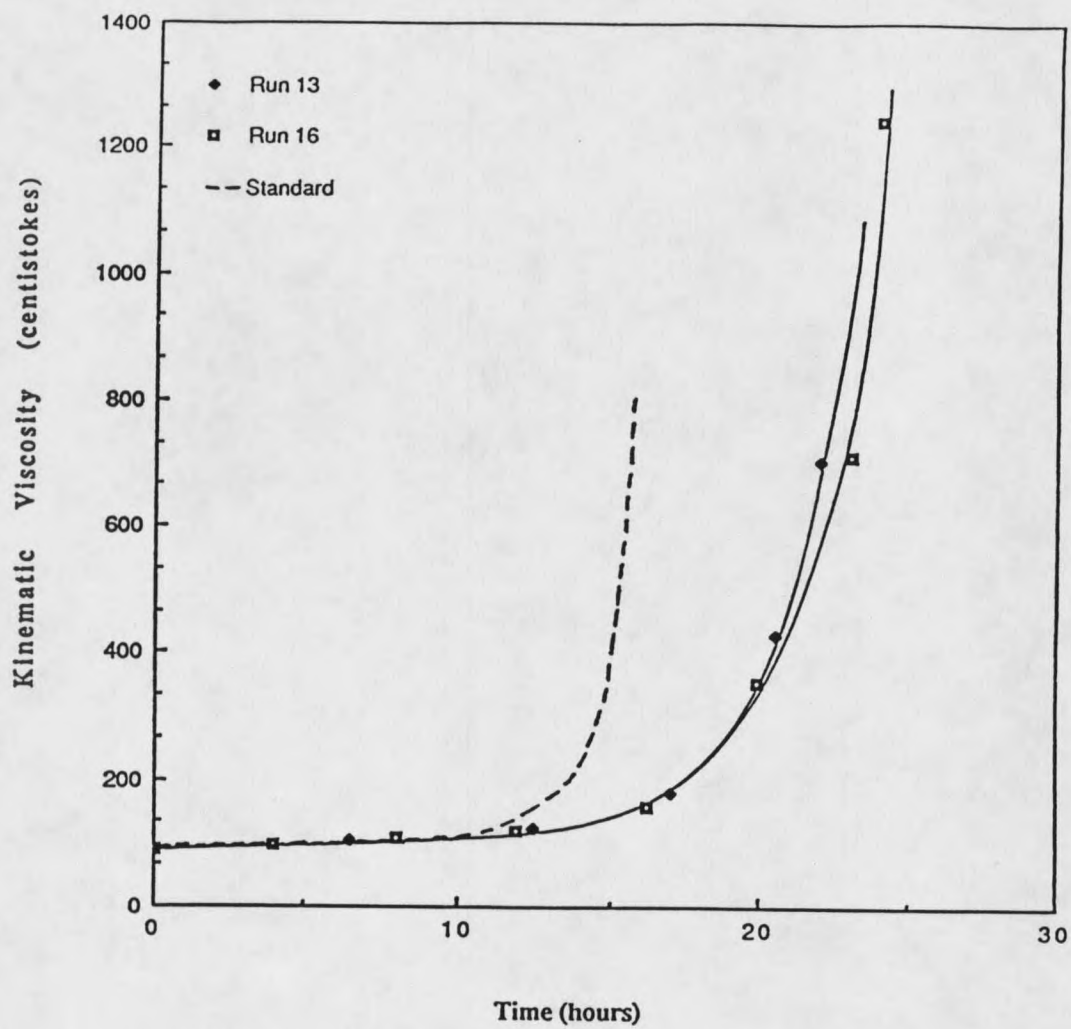


Figure 10. Kinematic viscosity versus exposure time showing the effect of addition of 0.50% NNPD initially (Run 13) and every 4 hours (Run 16)

elementary stages, active copper species readily dissolve into the system and take part as an initiator in the polymerization. After having actively taken part in the initiation, copper species may not catalyze the propagation phase [10]. The propagation phase however brings about an increase in the mass transfer resistance in the reactant mixture caused by the increasing lengths of the polymer molecules. This may retard the dissolution of copper species from the foil into the reactant mixture. The effectiveness of NNPD during the initial stages of a run could be postulated as due to its ability to successfully reduce the activity of the soluble copper species or to reduction in the rate of dissolution of the species into the system.

Runs 17 and 18 were conducted to further test the role of NNPD in deactivating dissolved active copper species. Based on the work done by Jette [10] two routes could be adopted to get these active species in the system:

- (1) Conduct an exposure of commercial lubricating oil and the copper foil in the absence of sunflower oil at 150 C, with nitrogen bubbling through the system for 48 hours. At the end of 48 hours soluble active copper species will be available in the system. This point could be taken as the start of a run with the

removal of the copper foil and addition of 5.0% sunflower oil and 1.0% NNPD.

- (2) Use copper acetylacetonate as a source of active soluble copper species in the system. Add a measured quantity of it at the start of the run with 1.0% NNPD.

Route (1) was used in Run 17 and route (2) in Run 18. The viscosity rise results of Run 17 are shown in Figure 11 compared with an analogous run conducted by Jette [10] without any NNPD added to the system. The point of addition of sunflower oil was taken as the start of the run in both cases. Run 17 showed considerable delay in the viscosity rise when compared with its corresponding run conducted by Jette. This indicated that NNPD was probably successful in retarding the activity of the dissolved copper species present in the reactant mixture.

Run 18 was conducted with the addition of 10 ppm of copper acetylacetonate (CuAcAc) and 1.0% NNPD at the start of the run. The value of 10 ppm was chosen because Jette's viscosity rise curves seemed to approach a maximum at a CuAcAc concentration corresponding to 10 ppm of copper or higher [10]. The viscosity rise curve of this Run 18 is compared with that of a similar run conducted by Jette [10] in the absence of any NNPD in Figure 11. Atomic emission spectroscopy results indicated a copper concentration of

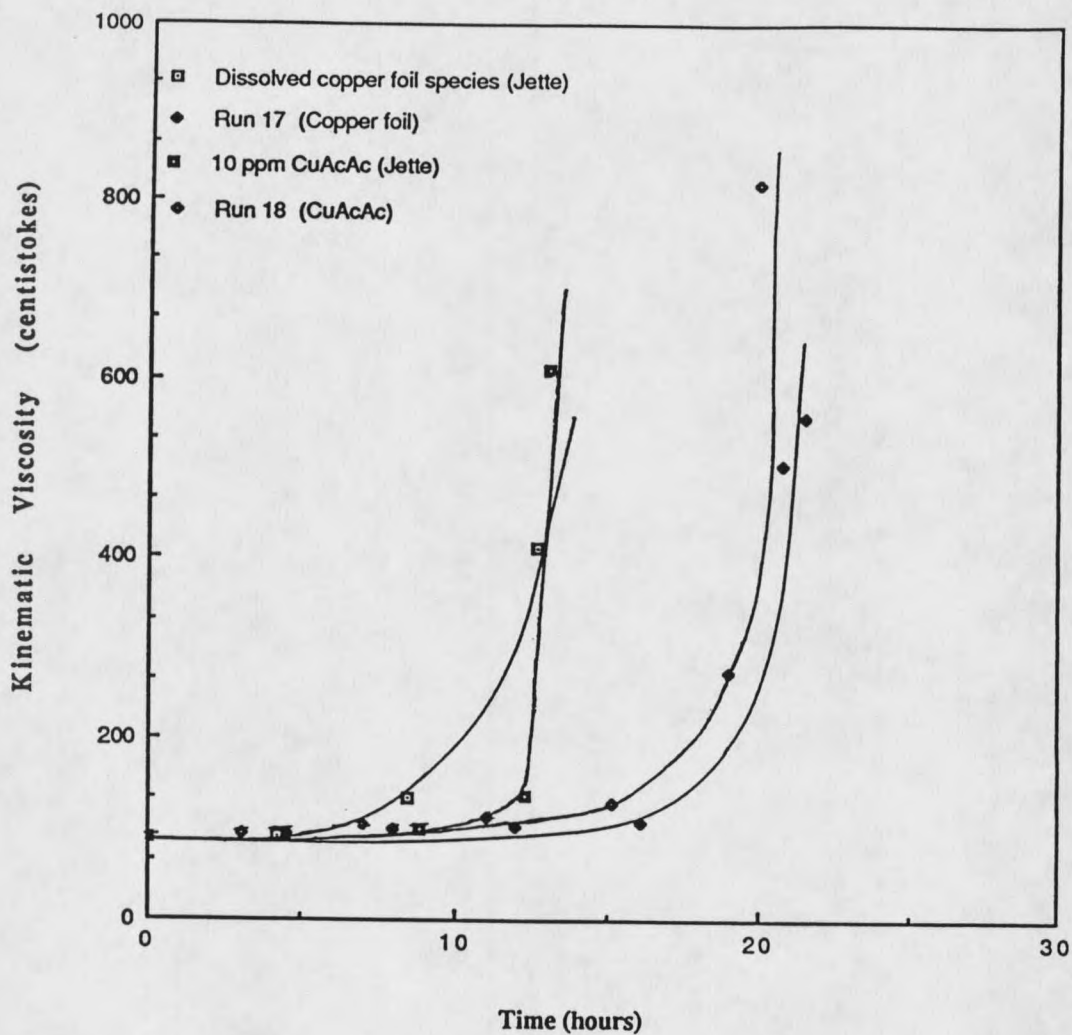


Figure 11. Kinematic viscosity versus exposure time showing the effect of 1.0% NNPD on dissolved forms of copper species

12 ppm for Run 18. Again, the NNPD seems to impose a considerable delay when compared to Jette's results for the experiment conducted without NNPD.

The experiments conducted with NNPD so far seem to highlight it as a good dissolved copper metal deactivator. It would however be interesting to know the effect of NNPD in the absence of any source of copper. If in this situation the viscosity rise curve matches that of the no-copper situation, it could be safely said that the commercial compound was solely a copper metal deactivator. Thus Run 19 was conducted with the addition of 1.0% NNPD at the start of the run in the absence of any copper. The viscosity rise curve obtained was substantially slower than the no-copper situation without the NNPD. This suggested that NNPD might be an effective antioxidant, however nothing in the literature survey indicated a role of NNPD as an antioxidant. Figure 12 shows a plot of Run 19 with the no-copper trial and Run 14 with 1.0% NNPD added initially in the presence of copper foil.

Thus, the results obtained based on the runs conducted with NNPD up to this point indicate it to be an antioxidant although its role as a copper metal deactivator cannot be neglected. The next step was to analyze whether NNPD played any role in the dissolution of copper species from the foil into the system. Two commercial lube oil

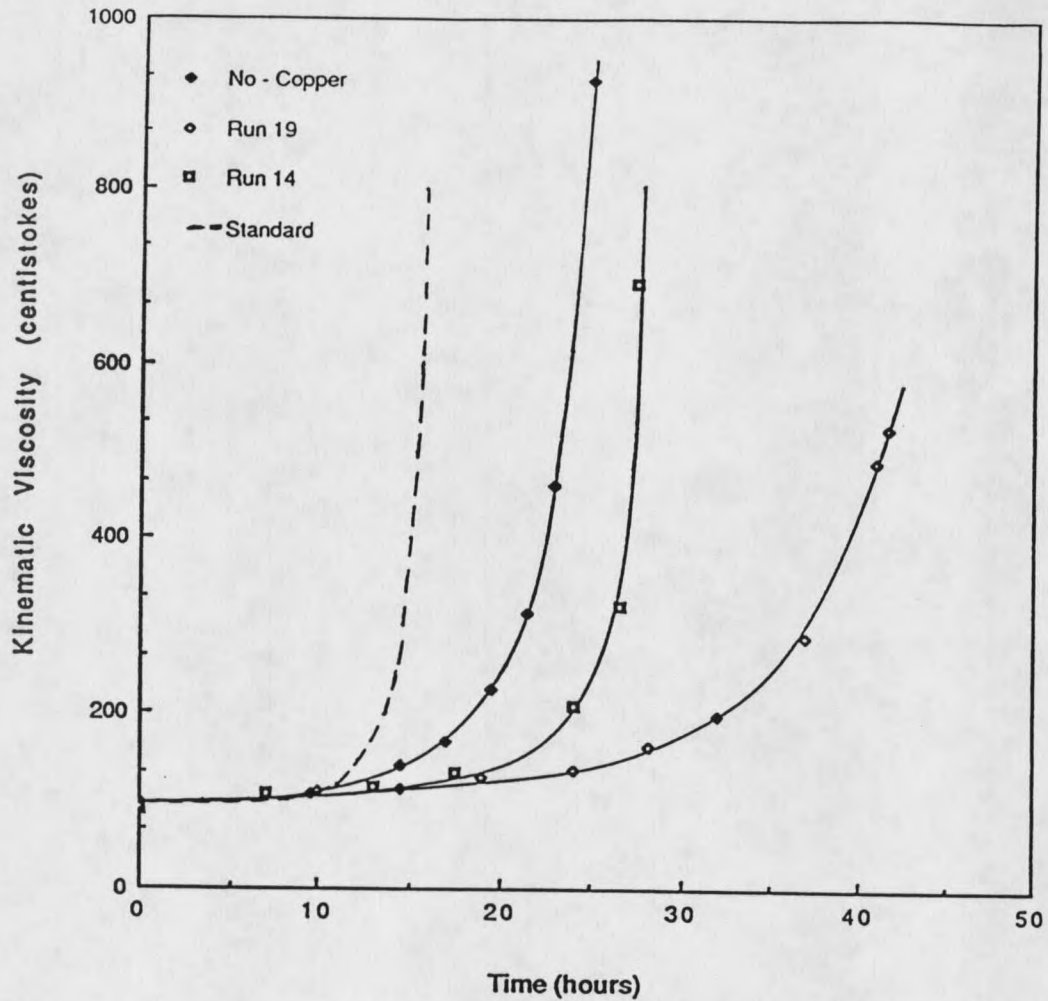


Figure 12. Kinematic viscosity versus exposure time showing the effect of 1.0% NNPD addition at the start of Runs 14 and 19 in presence and absence of copper respectively

runs were conducted one after the other in the absence of sunflower oil and in the presence of oxygen and copper foil. Run 20 was conducted with the addition of 1.0% NNPD initially and every 12 hours thereafter for a total run time of 48 hours. Oil samples for atomic emission spectroscopy studies were taken at the time of addition of the NNPD including at the beginning. Run 21 was conducted on the same grounds, but without the addition of NNPD. The idea behind these two runs was to compare the copper concentrations at several different periods in the system with and without the effect of NNPD, keeping oxygen as a common factor. In this way an attempt was made to understand solely the role of NNPD as a copper metal deactivator.

The atomic emission spectroscopy results of Runs 20 and 21 did not show any substantial difference (considering the error involved) when compared at the corresponding periods of sampling as shown:

Table 3. Effect of 1.0% NNPD addition on the rate of dissolution of copper species.

Hour of Sampling	12	24	36	48
Run 20, Copper ppm	26	25	26	32
Run 21, Copper ppm	31	27	27	29

The results shown in Table 3 indicate a reduced probability of NNPD retarding the rate of copper dissolution into the system. At this point in time the commercial lubricating oil stock was almost exhausted. Sufficient quantity was available for just one more experiment before a totally new batch was put into use.

NNPD was found to be effective during the initial stages of a run based on the previous results. Assuming that it was a copper metal deactivator of unknown degree, besides being an antioxidant, it could be hypothesized that the dissolution of active copper species takes place very early in time during the course of a run. This idea was tested by conducting a standard run and removing the copper foil after 4 hours from the start (Run 22). The viscosity rise results were amazingly close to that of the standard run. This run therefore strengthened the possibility of the idea which was put to test. A plot of Run 22 along with the standard run is shown in Figure 13.

Having run out of the initial commercial lubricating oil a fresh batch (from AMOCO) of grade API CD SAE 30 was used to continue on with the project. A standard run (Run 23) and a no-copper run (Run 24) were conducted to establish the basis for comparison with the runs to be conducted in the future. These runs showed a substantial delay compared to the old commercial

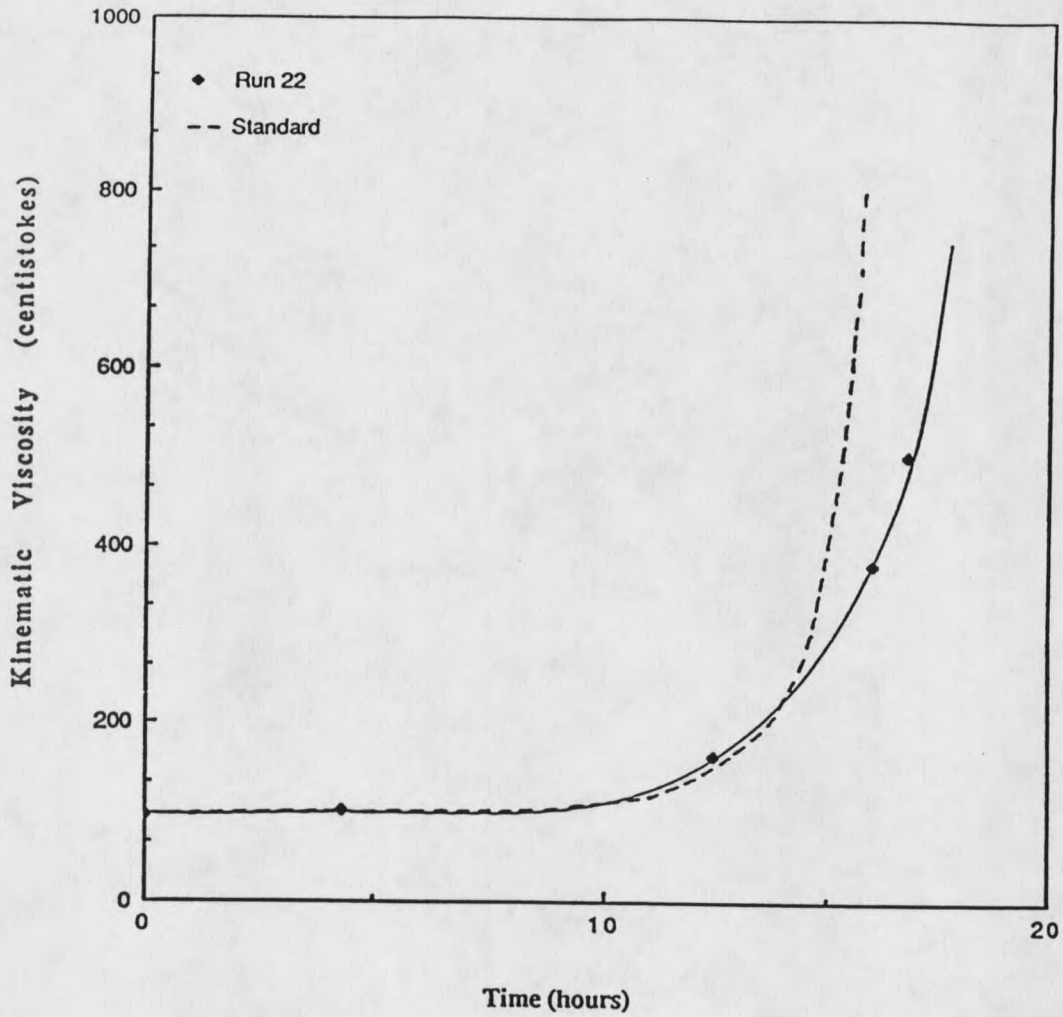


Figure 13. Kinematic viscosity versus exposure time showing the effect of copper foil removal after 4 hours in Run 22

lubricating oil as shown in Figure 14. Atomic emission spectroscopy results were obtained for the standard run conducted on the new lubricating oil. These results showed different constituent metal concentrations when compared to the old stock. Thus the additive packages of the two stocks of oil most probably contained different concentrations of antioxidants and metal deactivators in the form of organometallics. These organometallic compounds themselves may be of different chemistry in the two different additive packages. The following table gives the metal concentrations in parts per million of the two stocks of commercial lubricating oil:

Table 4. Dissolved metal concentrations (ppm) of old and new commercial lubricating oils.

Metals	Si	Ba	B	Ca	Mg	P	Zn
Old Lube, ppm	6	1	64	43	1321	1276	1217
New Lube, ppm	14	1	85	1499	470	1181	1377

The above results show strikingly different concentrations of magnesium and calcium in the two different stocks of commercial lubricating oils. This result was however not deeply probed into, as attempts were primarily being made towards the activity of copper as a catalyst.

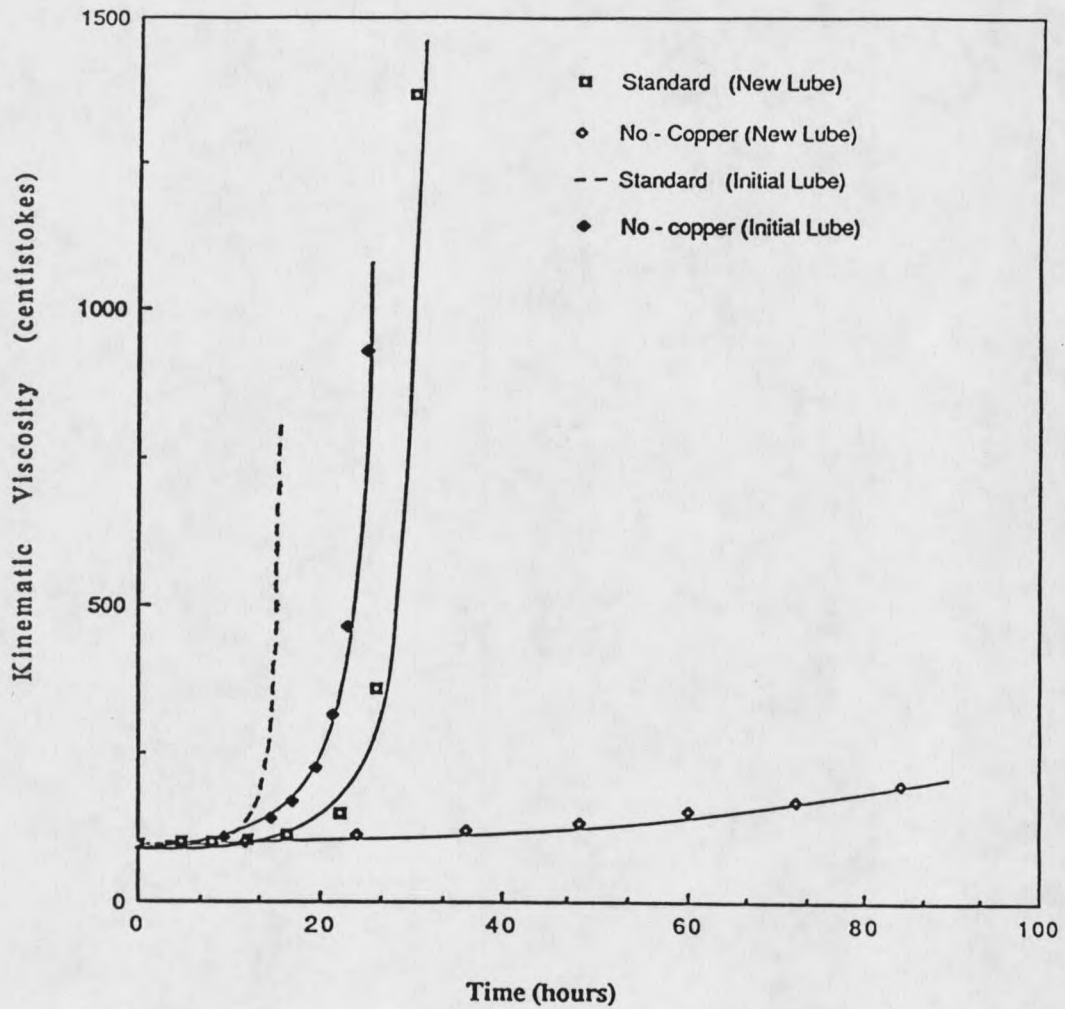


Figure 14. Kinematic viscosity versus exposure time for the new stock of commercial lubricating oil

Having obtained an interesting result in Run 22 (early copper removal), attempts were made to reproduce it in the new commercial lubricating oil (hereafter referred to as 'new'). Run 25 was conducted with the copper foil removed at 4 hours. The viscosity rise curve for Run 25 seemed to be more similar to the no-copper situation than the standard run. Two subsequent runs, 26 and 27, were conducted with the time of copper foil removal being after run times of 8 and 16 hours, respectively. Run 27 approaches the viscosity rise curve of the standard run, but is still distinctly slower. A plot of these runs is shown with the new standard run and the new no-copper situation in Figure 15. This significant change in the behavior of the results when compared with those of the old lubricating oil is almost surely a result of the change in the additive package. Atomic emission results of Runs 25, 26 and 27 were compared with that of Run 23 as shown:

Table 5. Effect of copper foil exposure time on the dissolution of copper species.

Run	23	25	26	27
Exposure Time (hours)	Standard	4	8	16
Dissolved Copper (ppm)	6	0	0	3

The results shown in Table 5 highlight the role of the additive package which is a major factor in the dissolution of copper. Runs 22 and 25 are analogous in

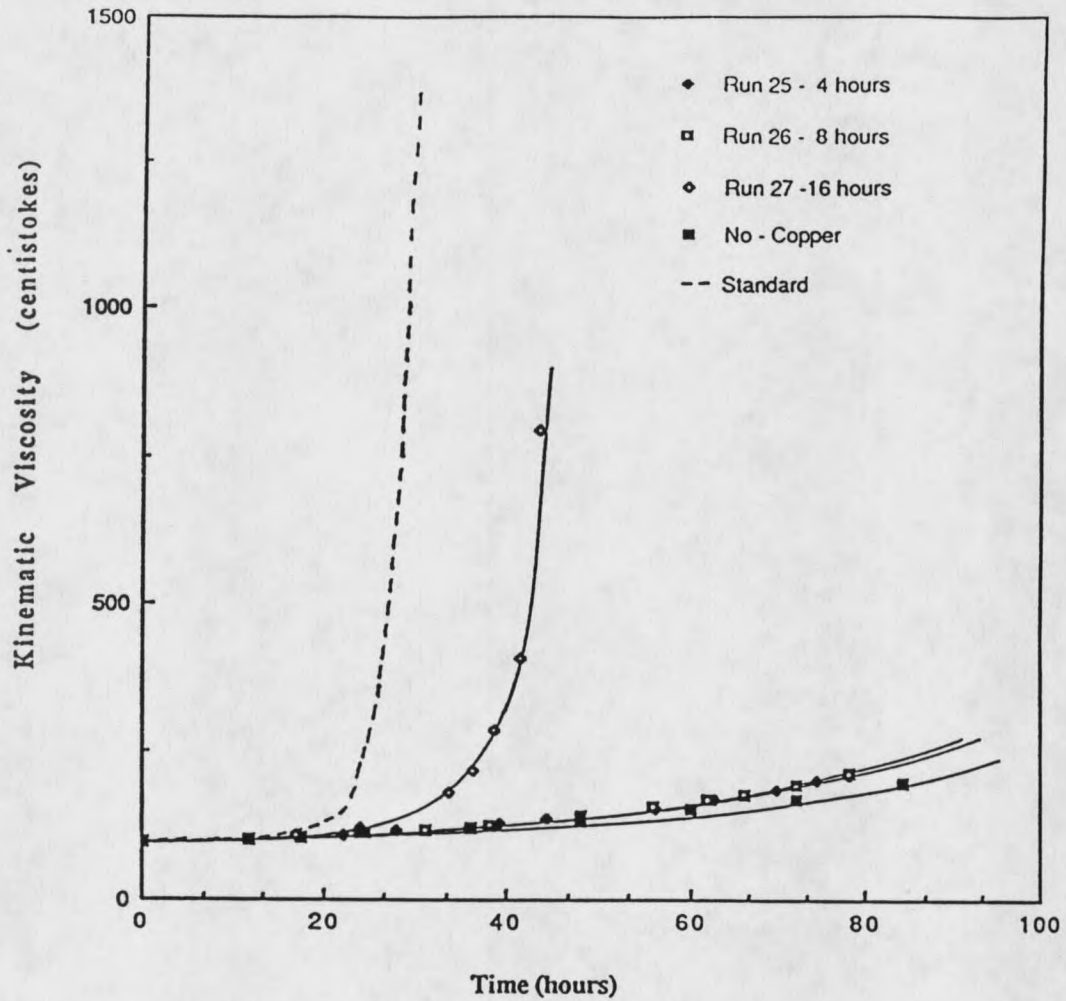


Figure 15. Kinematic viscosity versus exposure time showing the effect of copper foil removal at different times

nature but conducted with different stocks of commercial lubricating oils. The different additive packages in the two stocks is responsible for a faster viscosity rise in Run 22 as against the slower rise in Run 25. This may well be due to the lower copper concentration at the end of Run 25 (0 ppm) as against a predicted value of the copper concentration of Run 22 close to that of 5 ppm of the corresponding standard run.

At this point in the research another attempt was made to test one of the aspects of information obtained from the literature survey. Theories have been laid out explaining the ability of polar protic solvents like acetic acid to deactivate copper species, especially when the polar solvent is at a high concentration [21]. Rewolinski [9], looking into acid catalysis, had tried using an inorganic acid (phosphoric) in the current system, and the viscosity rise curve showed tendencies to be delayed when compared with the corresponding standard run as reproduced here in Figure 16. Therefore, it was decided to try using a long, straight chain acid which should easily dissolve in the present system and would also be moderately polar in nature. Lauric acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$, was added at 1.0% at the start of Run 28, and the viscosity of the reactant mixture was recorded during the course of the run. The data obtained from these recordings yielded a

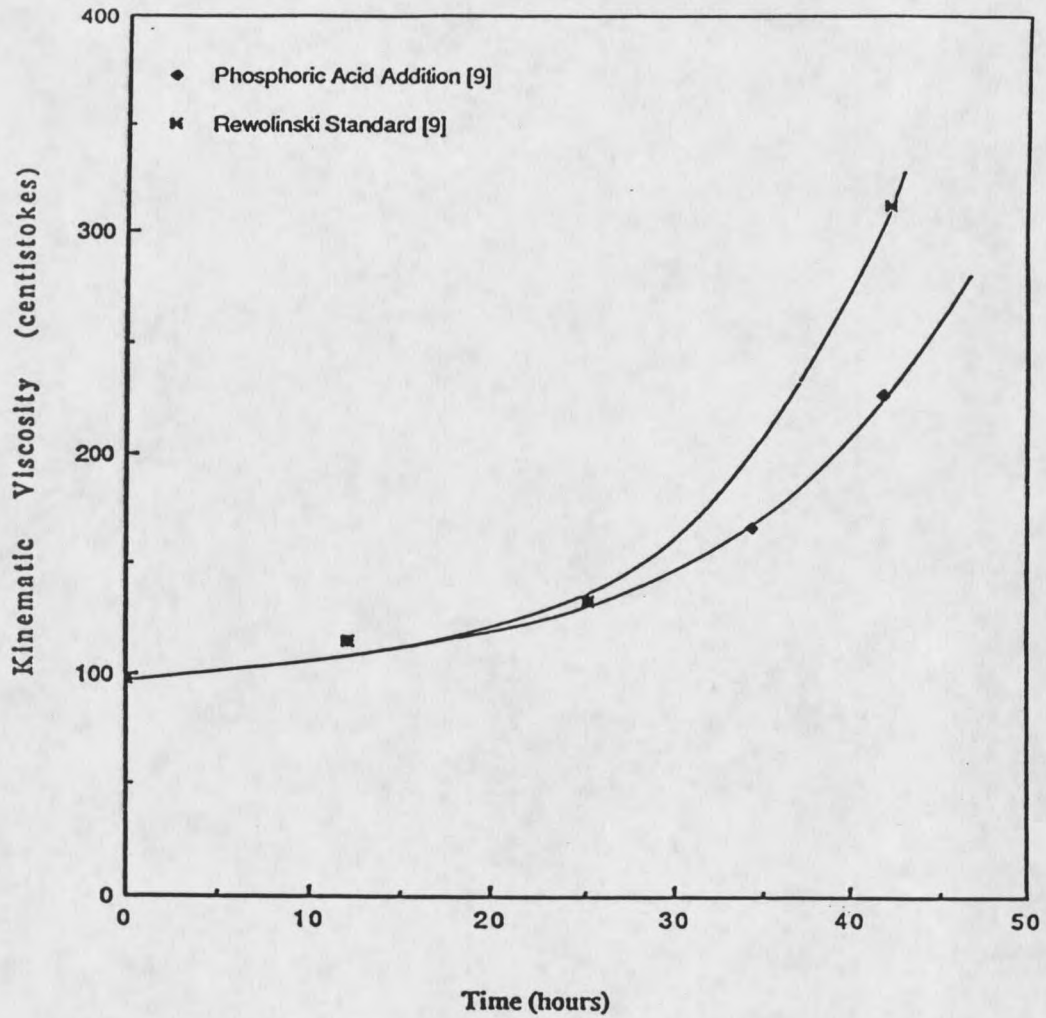


Figure 16. Kinematic viscosity versus exposure time showing runs made by Rewolinski [9] under standard conditions and with the addition of phosphoric acid

faster viscosity rise compared with that of the standard run as shown in Figure 17. Atomic emission spectroscopy results at the end of the run indicated a copper concentration of 3 ppm higher than the standard run. Thus, it appears that an acidic environment might increase the dissolution of copper species in the present system.

A final attempt was made with NNPD to understand its properties as a metal deactivator. It was assumed that the nature of the copper foil surface could be an important parameter in determining the concentration of dissolved copper species present in the reaction mixture at the end of a standard run. An experiment was conducted to test whether NNPD might increase the resistance of this surface regarding the dissolution of copper. A copper foil was immersed in NNPD at room temperature for 11 hours. The foil with a thin film of NNPD adhering to it (even after shaking the foil vigorously) was used in Run 29. The viscosity results obtained showed a quicker rise than the standard run, as shown in Figure 18. Atomic emission spectroscopy results indicated a higher concentration of copper (10 ppm) than a typical value for the standard run (6 ppm). Thus, NNPD may actually speed dissolution of the copper foil with long periods of contact. This experiment therefore seems to add a score against the use of NNPD as a copper metal deactivator.

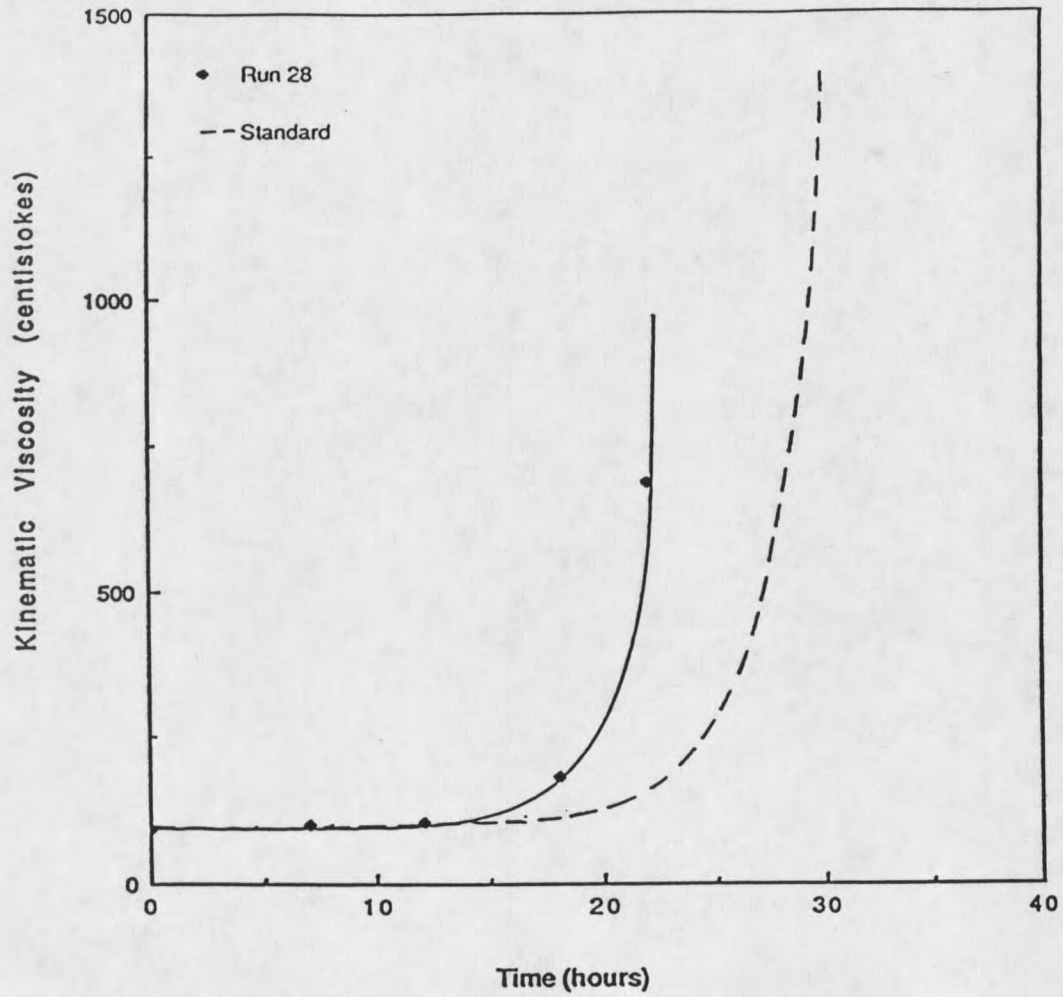


Figure 17. Kinematic viscosity versus exposure time showing the effect of addition of 1.0% lauric acid at the start of Run 28

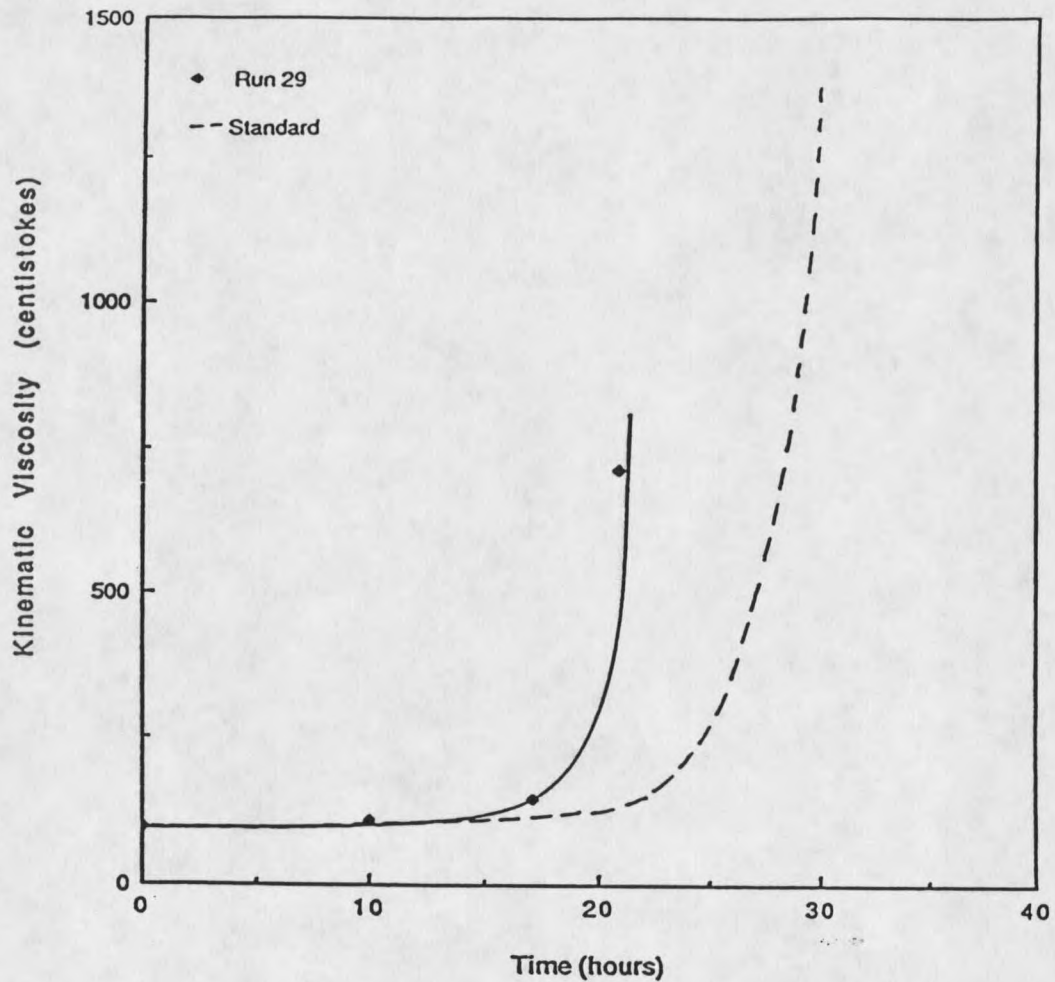


Figure 18. Kinematic viscosity versus exposure time showing the effect of copper foil immersed in NNPD for 11 hours at room temperature and then used in a standard run

During the course of a standard run, it is well established that copper species dissolve into the oil mixture system. It could be that these species dissolve more slowly towards the end of a run. This could be due to either one of the following reasons :

- 1) An increase in the external mass transfer resistance caused by the large polymer molecules in the latter stages of the polymerization reaction.
- 2) An increase in the surface resistance of the foil, reducing the dissolution of copper species in the oil mixture system.

A standard run was carried to completion, and the copper foil (darkened in appearance) from this run was used in place of an unused strip in Run 30. Interestingly enough, the viscosity rise curve for Run 30 closely matched the no-copper situation. This result seems to indicate that the initial exposure of the copper foil leads to an increase in its surface resistance, perhaps by forming an oxidized coating by the end of a standard run. This idea was tested further by making another related run. An unused copper foil was placed in a ceramic crucible and kept red hot in an open atmospheric oven for 33.5 hours. This was done to completely oxidize the metal surface. The

oxidized foil (almost black in appearance) was used in Run 31 instead of a typical foil sample. The viscosity rise curve obtained matched closely those of Run 30 and the no-copper situation. A plot of Runs 30 and 31 with the no-copper run is shown in Figure 19. Atomic emission spectroscopy results for Runs 30 and 31 indicated copper concentrations of 1 ppm and 0 ppm, respectively. This strengthened the theory of the oxidized copper foil being largely inert in the oil mixture system. Thus, during the course of a standard run, the copper foil probably gets oxidized and shows negligible tendencies to yield dissolved copper species towards the end.

Chemical character of the copper foil surface seems to be an important factor in the dissolution of copper species. Any fresh copper foil used was always cut from a large roll which had been exposed to the atmosphere for a long period of time. As a matter of interest, the tightly wrapped roll was opened up halfway to analyze the nature of the copper surface in the interior portions. It was observed that the interior surface regions had a much brighter shine than the outer, more dulled portions. Oxygen in the atmosphere has maximum access to the outermost portions. This is undoubtedly the reason for the change in the character of the foil as one proceeds deeper into the core of the roll. Copper foils cut from only the

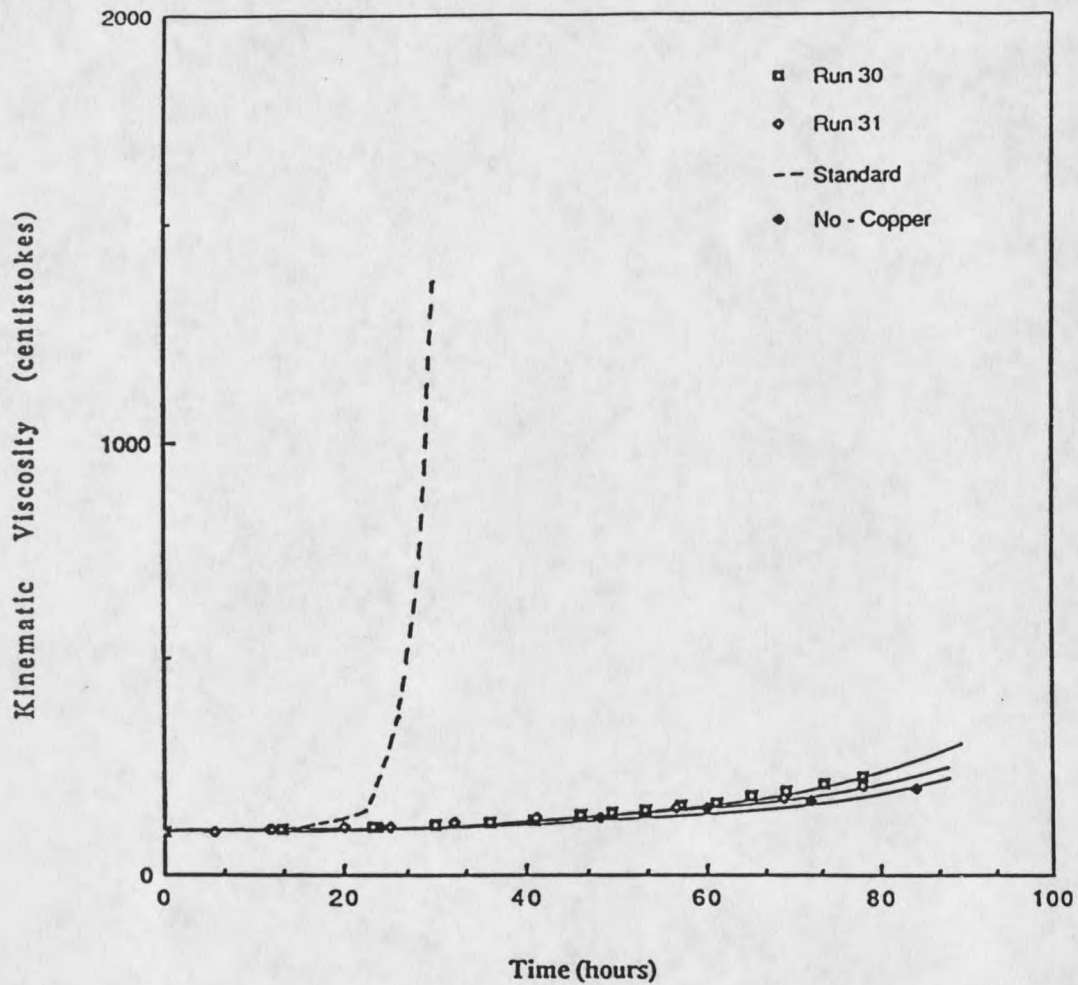


Figure 19. Kinematic viscosity versus exposure time showing the effect of oxidized copper foil obtained from a standard run and used in Run 30 as against a copper foil subjected to 33.5 hours of oxidation in an atmospheric oven and used in Run 31

most easily accessible (outermost) portions have been used in all experiments so far. One of such copper foils, presumably subjected to slow and prolonged atmospheric oxidation at room temperature, was rubbed with emery cloth to expose the inner layers of the foil with the brighter shine. In this process copper powder was obtained which was blown off the foil. This pretreated foil was immediately used in Run 32 in order to test the behavior of this uncontaminated form of the foil. This special strip of foil was not subjected to the standard cleaning process (hexane followed by acetone). The viscosity rise curve obtained for this run was found to be faster than the standard run and is shown in Figure 20. An oil mixture sample was sent to Case for atomic emission testing. While waiting for the spectroscopy results, it was postulated that the faster rise in viscosity of Run 32 could be due to adhering copper powder which might more readily dissolve in the oil mixture system. Therefore, another run (Run 33) was conducted with the same pretreatment of the copper foil. However, this time any adhering copper powder was carefully wiped off with a cotton swab dipped in commercial lubricating oil. This foil was then used in Run 33 and the results obtained were found to have a somewhat slower viscosity rise than of the previous run (Figure 20). The

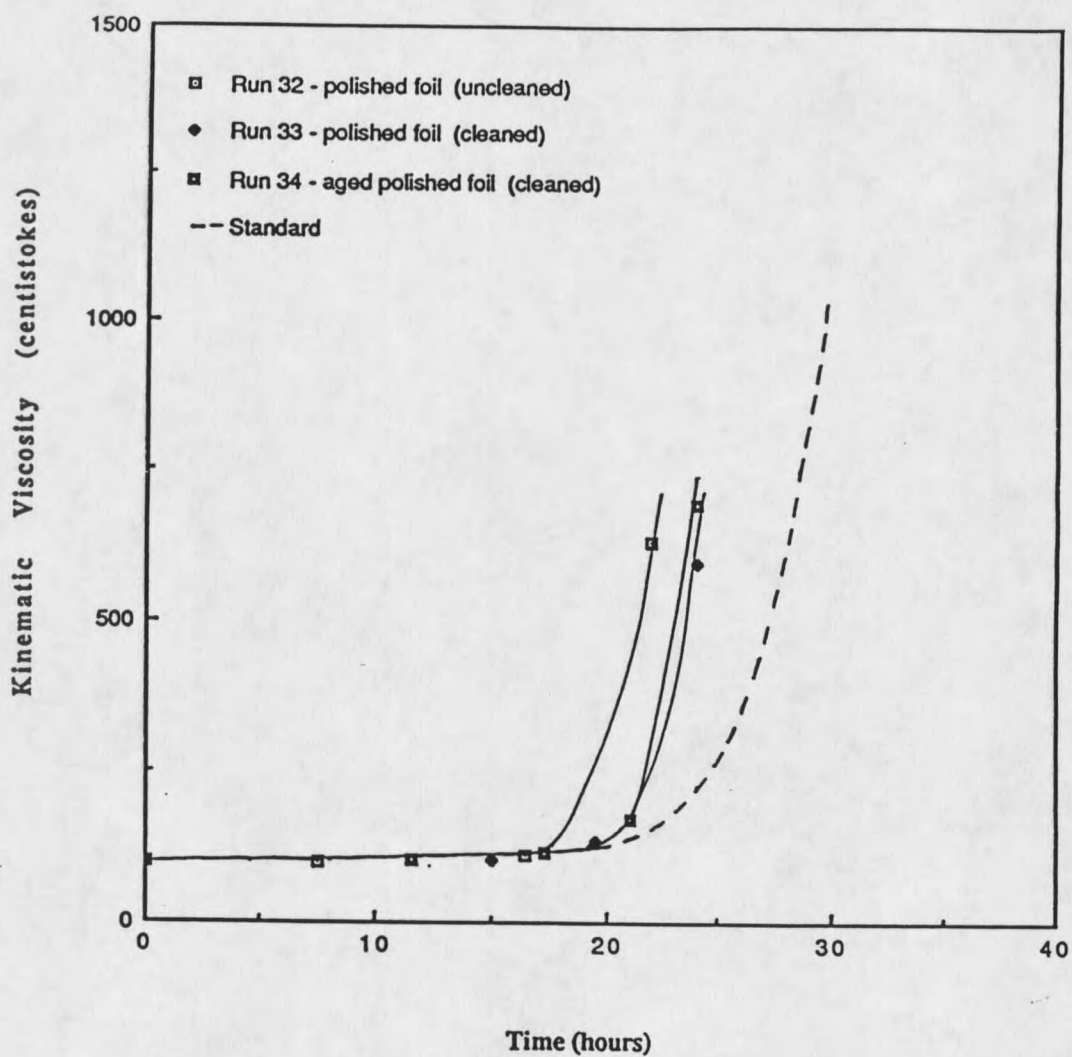


Figure 20. Kinematic viscosity versus exposure time showing the effect of copper foil surface subjected to three different treatments

atomic emission result for this latter run was 17 ppm copper versus 23 ppm for Run 32.

These results seem to confirm the possibility of copper powder being dissolved in Run 32. The viscosity rise curves show little difference, perhaps because at these higher copper concentrations, catalyst quantity is not a limitation [10].

In the next run the copper foil was given the same pretreatment as Run 32 but was then exposed to the atmosphere (at room temperature) for four days. The aged copper foil, still very bright in appearance, was cleaned of any adhering copper shavings in a manner similar to Run 33. The aged and cleaned copper foil was then used in Run 34. The viscosity rise curve was observed to be similar to that of the previous two runs as shown in Figure 20. However, the atomic emission result (18 ppm copper) matched closely to that of Run 33, again indicating a possible effect of copper powder.

From these experiments it can be safely stated that the process of atmospheric oxidation of the copper foil surface is a slow one at room temperature. However substantial variations in viscosity rise would probably be observed among different copper foil samples depending on the degree of oxidation.

It has been established that the copper foil has a decreased impact on the system at the end of a standard run. It would be interesting to conduct a run similar to Run 30, but with the use of nitrogen. Here, nitrogen could be bubbled through the reaction mixture in the presence of copper foil for a run time equal to that of the standard run. This used foil could then be employed instead of a fresh piece in a standard run with oxygen. This was done exactly in Run 35. The viscosity rise curve obtained was found to be quite similar to that of a standard run. This result is expected and strengthens the theory of oxygen creating a less active copper surface. A plot of Run 35 is given with the standard run in Figure 21.

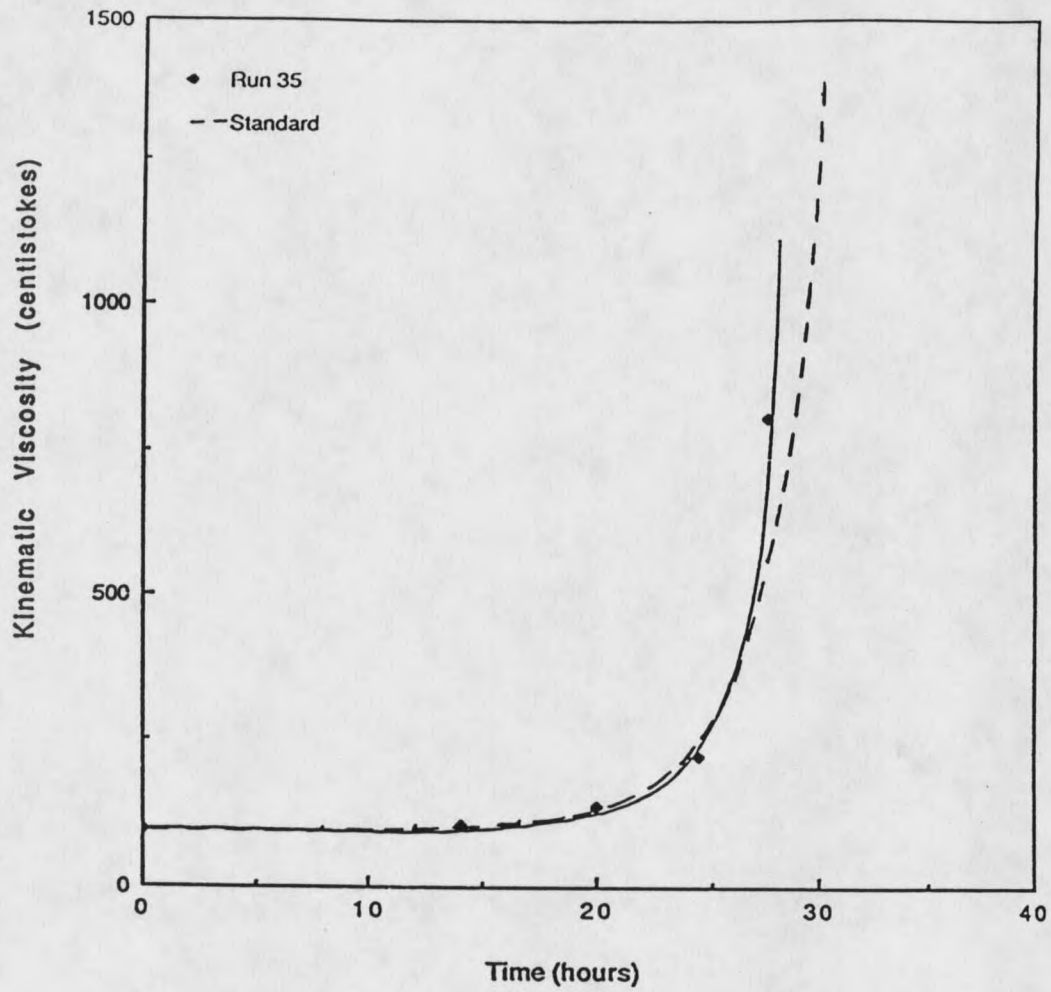


Figure 21. Kinematic viscosity versus exposure time showing the effect of a copper foil subjected to prior nitrogen percolation under standard conditions

SUMMARY

Research done in this lap of the project started off with the main aim of understanding the mechanism of the catalytic activity of copper and other important engine wear metals (if any) in the polymerization of sunflower oil contamination in diesel lubrication oil. Lead, aluminium and silver were tested in their elemental metallic forms and were found to be largely catalytically inert in the reaction system. This narrowed down the research to copper as the prominent catalytic wear metal.

The effect of commercial metal deactivators was examined by testing several potential deactivators, namely, Lubrizol 5955-A and NNPD. The first compound was found quite ineffective, but the second one showed substantial delay in viscosity rise when added to the system at the start of a run. This result directed the research to probe more deeply into the role of the compound as a potential deactivator. After having conducted a number of experiments, it was concluded that the compound behaves more effectively as an antioxidant than as a copper metal deactivator.

Meanwhile experiments were conducted with basestock oil, and it was found that the additive package

was a primary factor in enhancing the dissolution of copper species in the reactant oil mixture.

Information obtained from the literature suggested the use of an excess concentration of copper to observe a reversal of activity from catalysis to inhibition in the inherently nonpolar system. This was tested by means of adding copper acetylacetonate to amount to a copper concentration of 0.1 gmol/liter in the reactant mixture. Also, the effect of a weakly polar acid (lauric acid) was tried with a view to sequester the soluble and active copper species. Neither approach resulted in reduced copper catalytic activity.

The surface characterization of the copper foil was found to be an important parameter in determining the activity of the metal. An oxidized piece of the metal foil was found to be catalytically less active in the reactant oil mixture, whereas a freshly polished piece (having a bright unoxidized shine) was found to be more active. These results favored the theory of the copper foil showing a very low tendency to dissolve copper species in the system towards the end of a standard run.

Further research is indicated to understand the role of this important wear metal with an eye on the precise chemical nature of the copper foil used.

CONCLUSIONS

1. Of the common diesel engine wear metals, only copper plays an important catalytic role in polymerization of plant oil fuel. Other metals tested, including lead, aluminium and silver, appear to be catalytically inert in their pure metallic forms.
2. Surface character of copper foil is a key parameter in determining copper dissolution rate and hence catalytic activity. Oxidized copper foil seems to inhibit dissolution, while polished metallic surface dissolves more readily.
3. The role of copper in plant oil polymerization may be primarily as an initiator catalyst since copper foil shows little tendency to dissolve in the contaminated lube oil mixture or to participate catalytically during the final stages of polymerization.
4. The additive package in commercial lubricating oil seems to influence the dissolution of copper species in the lube oil mixture. The amount of dissolved copper may be directly related to individual chemical components in the additive package.

5. A commercial metal catalyst deactivator, N, N'-disalicylidene 1, 2-propane diamine, inhibits plant oil polymerization and may function more as an antioxidant than a metal deactivator.

6. Use of high concentrations of dissolved copper or attempts to polarize the dissolved copper foil species in the lube oil mixture to inhibit plant oil polymerization proved contrary to literature results for other reaction systems.

SUGGESTIONS FOR FUTURE RESEARCH

1. Future research must hurdle the problem of the propriety aspect of additive packages in commercial lubrication oils. Either the package composition must be determined (analytically or otherwise) or "artificial" packages must be formulated and used in basestock oils.
2. Future research should use surface science techniques to more fully characterize the role of copper metal surface nature on dissolution and subsequent catalysis in plant oil lube oil mixtures.
3. Research should continue to seek chemical additives that sequester or otherwise deactivate dissolved copper species.
4. A better kinetic model for catalyzed plant oil polymerization should be sought that fits the accumulated data for this system. Such a model may highlight key system parameters other than those presently known.

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For continuing work done in this area the interested reader may refer to : " Polymerization of Safflower Oil in a Diesel Lubrication System ", Olson, John Walter, Thesis, Montana State University, Bozeman, MT 59717, (1988).

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