



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

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

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

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

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

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

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in

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APPROVAL

of a thesis submitted by

John Walter Olson

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

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ABSTRACT

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

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

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

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

INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

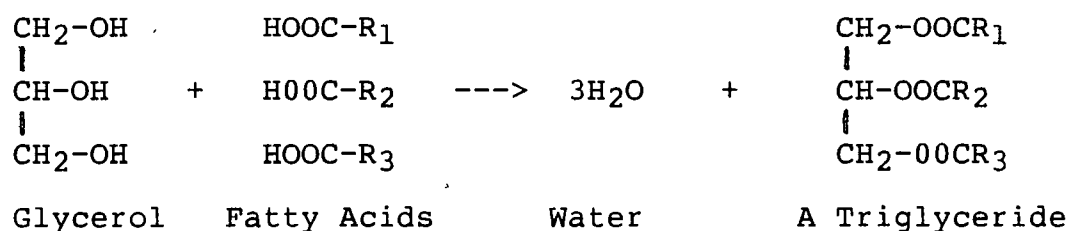
THEORY

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

Vegetable Oils

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

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



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

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

TABLE 1. Fatty Acid Distributions (Percent)

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

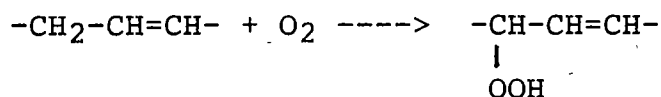
The primary constituents, oleic and linoleic acids, plus linolenic acid are unsaturated. Each of these acids contain 18 carbons and one, two, and three double bonds, respectively [11]. Accordingly, the high degree of unsaturation in vegetable oils, especially compared to only slight unsaturation in diesel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

Oxidative Polymerization of Vegetable Oil

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

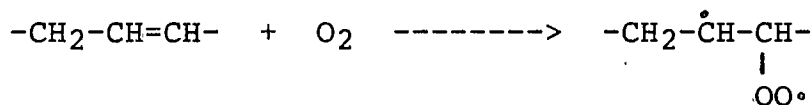
1. An induction period occurs, preceeding the initiation of the oxidative chain reaction, during which no visible physical or chemical properties are changed. It is assumed that natural antioxidants are consumed during this induction period.
2. Oxygen interacts with double bonds to form hydroperoxides.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

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

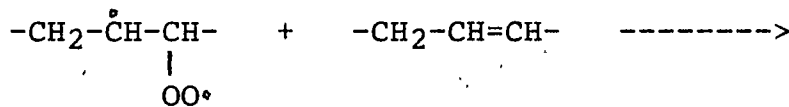


However, because of the high energy requirements, approximately 80 kcal/mole, required for rupture of the α -methylenic carbon-hydrogen bond, Bolland and Gee [19], Farmer [20], and Gunstone and Hilditch [21] almost simultaneously concluded that the initial point of oxidative attack was the double bond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

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

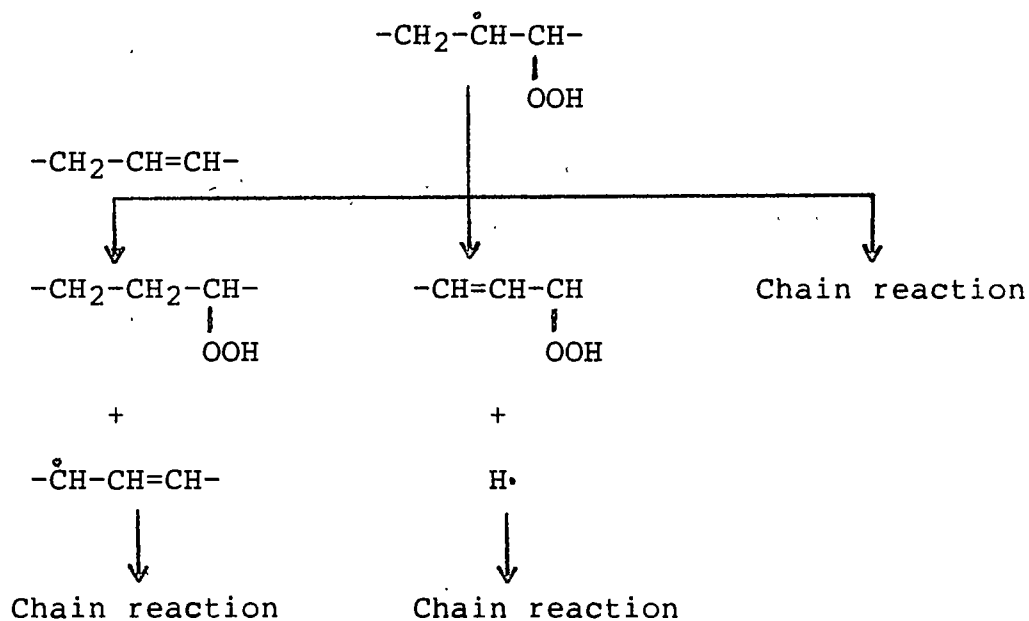


2. The diradical abstracts hydrogen from an α -methylenic carbon, producing two single radicals.

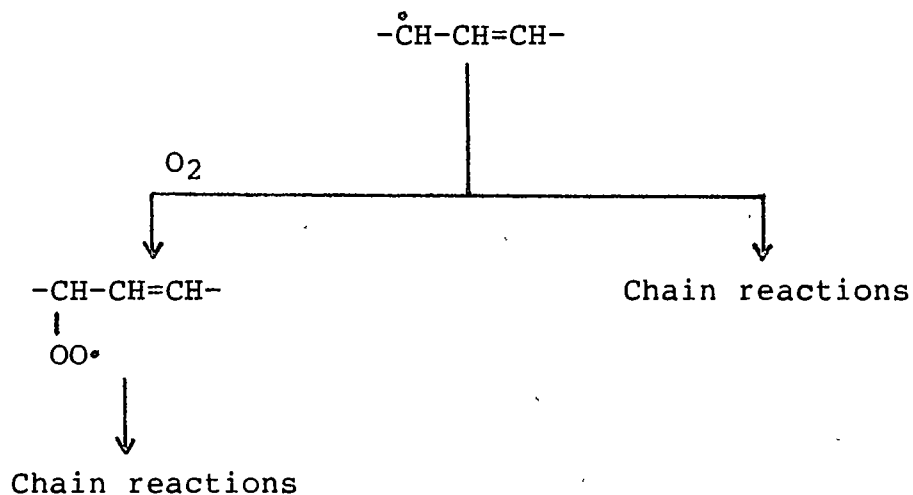


3. As shown below, these single radicals are subject to further reactions that can lead to other radicals or, as will be shown later, lead to vinyl polymerization.

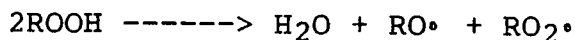
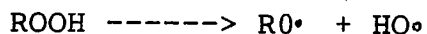
a)



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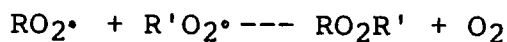
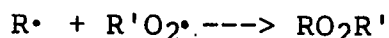
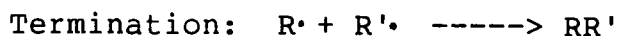
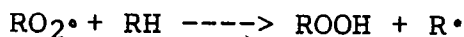
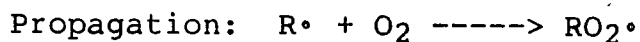


Once hydroperoxides are formed, even in trace amounts, they can play a significant role in autocatalysis [23].

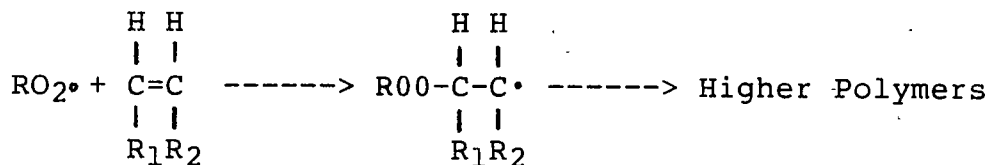
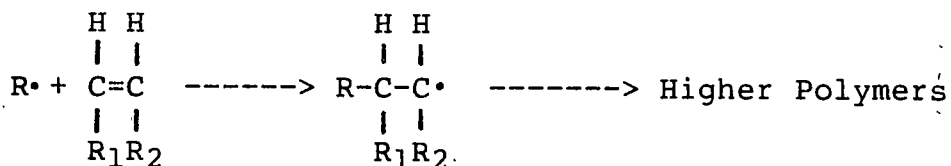


From a kinetic standpoint there are three stages in the autoxidation process [24]. The $\text{R}\cdot$ radical will be used as an example.

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



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



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

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

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

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

Catalysis

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

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

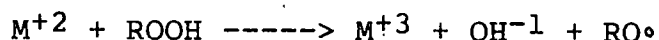
It is usually accepted that catalysts are unable to alter the course of reaction but merely participate in the formation of transitory intermediates. They may, however, direct the course of reaction by favoring the formation of one intermediate among several possible species.

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

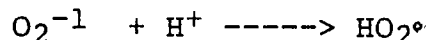
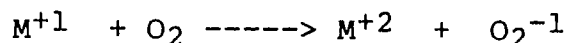
are that these active metals exist in at least two different valences, the higher being less stable, and that they are susceptible to being oxidized from the lower to higher valences.

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

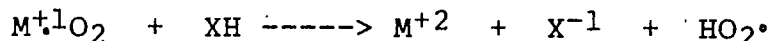
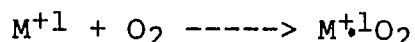
1. Trace hydroperoxides may shift the metal valences and produce free radicals.



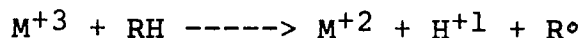
2. The oxygen and metal ion may react directly. The resulting O_2^{-1} then readily reacts with a proton to form $HO_2^{\bullet}$.



3. A metal/oxygen complex may form which subsequently forms the $HO_2^{\bullet}$ radical.

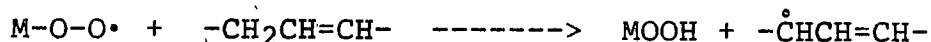
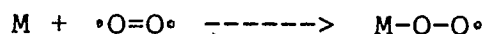


4. Electron transfer to the metal ion may result in the oxidation of the alpha methylenic group.

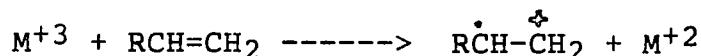


The metallic catalysts are believed to catalyze not only decomposition but also formation of hydroperoxides. While the activity in the creation of hydroperoxides is not clear, several possibilities exist. Metallic catalysts, M,

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



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



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

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

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

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

Lubrication Oil

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

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

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

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

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

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

Oxidation of Lubricating Oils

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

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

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

Antioxidants

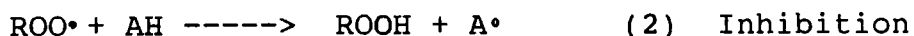
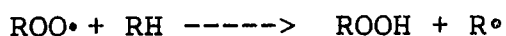
As previously discussed, oxidative reactions associated with vegetable oils are related to those associated with lubrication oils. This suggests that additives incorporated in lubrication oils might be effective in vegetable oils as well. Indeed, additives must be sought which are compatible with the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

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

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

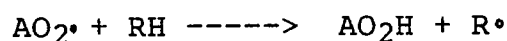
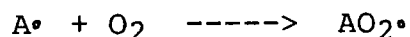
The literature on antioxidants, their use, and mechanisms of activity is voluminous. In fact, literally hundreds of natural and synthetic compounds have been shown to be effective antioxidants, depending upon the system involved [31]. However, there is a lack of complete agreement on their exact mechanism(s)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

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



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

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



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

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

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

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



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

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

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

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

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

Additive Interaction

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

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

PRIOR RESULTS

Development of Crankcase Simulation

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

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

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

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

Effect of System Variables with Commercial Oil.

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

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

Commercial Oil: Copper Study

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

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

Effect of System Variables with Base Stock Oils

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

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

Base Stock: Copper Study

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

Polar Gel Theory

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

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

Additive Study

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

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

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

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

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

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

RESEARCH OBJECTIVES

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

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

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

EXPERIMENTAL

Equipment

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

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

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

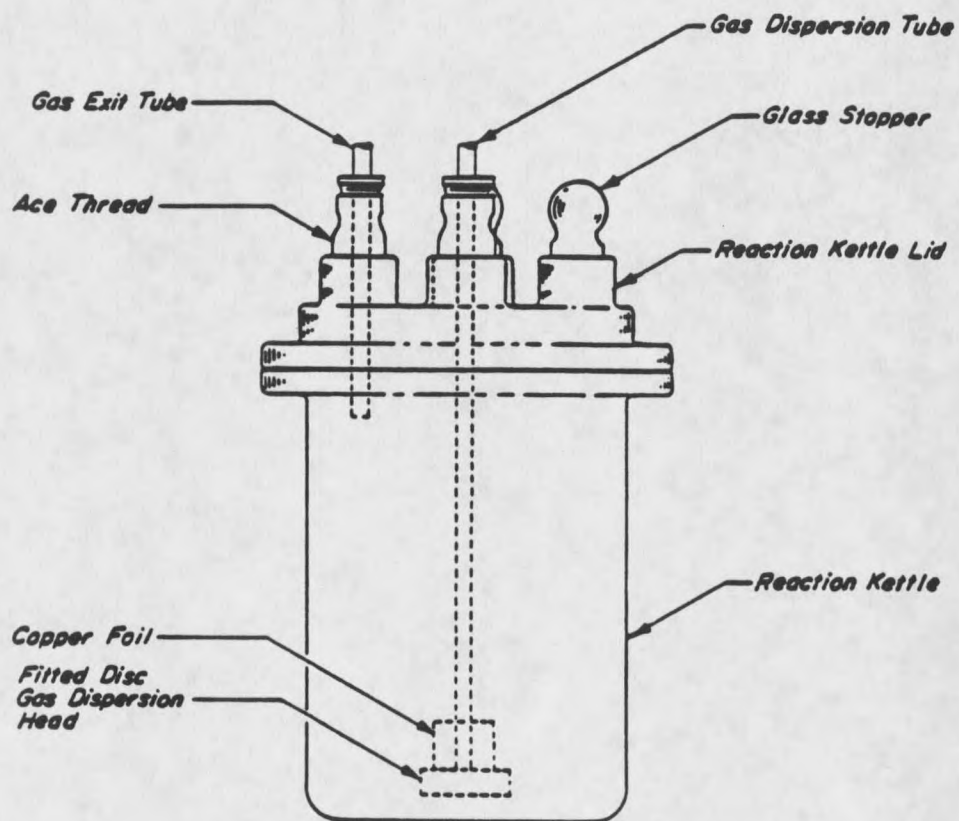


Figure 1. Reaction Kettle.

fourth kettle opening was closed with a ground glass stopper.

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

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

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

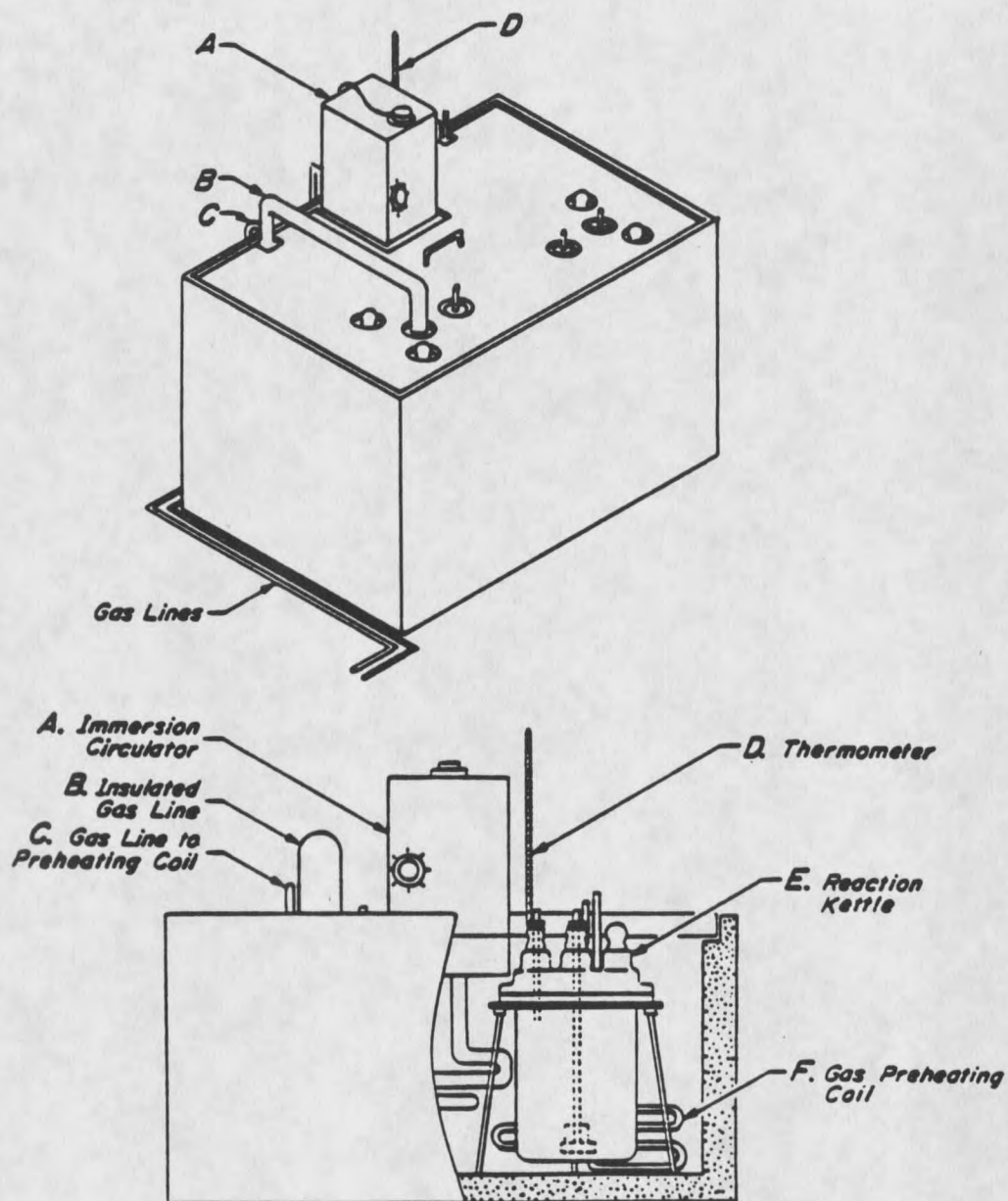


Figure 2. Oil Bath.

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

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

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

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

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

Materials

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

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

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

Company, Inc. of Norwalk, Connecticut. Zinc dialkyl-dithiophosphate (ZDTP) was supplied under the tradename Lubrizol 1395 by Phillips Petroleum Company of Bartlesville, Oklahoma. N,N'-disalicylidene-1,2-propanediamine (NNPD) was supplied by Dupont Petroleum Chemicals Division. All other chemicals were reagent grade.

Experimental Procedures

Approximately 475 gm of lubricating or base stock oil was added to a reaction kettle and weighed to the nearest 0.01 gm. This oil was diluted with safflower oil to obtain a 5.0% by weight safflower oil in lube oil mixture. Appropriate amounts of additives, if any, were then added. If cupric acetylacetonate was used, it was always added last. This mixture was then thoroughly stirred using a glass stirring rod. Occasionally the oil mixture was heated to increase solubility of additives. The total volume of mixture was typically slightly over 500 ml.

The glass gas dispersion tube, with or without copper foil, was immersed in the oil. The lid was placed on the kettle with the gas dispersion tube protruding from the center opening and the glass stirring rod protruding from a side opening. Appropriate adapters or stoppers were fitted into lid entrances. All ground glass surfaces were greased with Dow Corning high vacuum grease.

The sealed reaction kettle and its contents were immersed in the oil bath by resting the kettle flange on a matching tripod standing on the bottom of the oil bath tank. The bath cover was placed in position and the teflon gas flow tube was attached to the stem of the gas dispersion tube. Gas flow rates were adjusted to 2.0 ml/sec as measured by the rotameter.

Samples were periodically removed during each run to determine viscosity of the oil mixture. One of the glass stoppers was removed and a graduated pipet was inserted 8.5 inches below the surface of the bath cover into the oil mixture. An 8.0 ml sample was pipetted and then transferred to the viscometer. The sample was allowed to equilibrate for ten minutes before measuring viscosity. Following the viscosity measurement the sample was prepared for a Total Base Number (TBN) titration, returned to the reaction kettle, or discarded when appropriate.

In an attempt to determine rate of solids formation, care was taken to note when solids were first observed. Methods of observation included 1) inspecting the solid glass rod frequently during the run, 2) noting solid particles when determining viscosity, and 3) occasionally lifting the gas dispersion tube and inspecting the fritted glass head. Experiments were terminated either when glass surfaces were thickly covered with solids or when the viscosity exceeded 450-500 cst.

Total base number quantifies alkalinity of an oil sample. TBN values were determined potentiometrically according to ASTM D 2896 [42]. The back titration method was employed as it is the suggested technique for used oil samples. Excess standard acidic solution was added to the prepared sample. The excess was then back titrated with a standard basic solution. The resulting sigmoidal shaped curves gave clear end points.

Iodine values indicate relative degrees of unsaturation. These values were determined according to ASTM Standard 1959-69 [43]. This is the Wijs procedure for determination of unsaturation in drying oils and is applicable to vegetable oils and their fatty acids.

Structural analysis of selected samples was done using Carbon-13 NMR. This technique provides information on the functional groups attached to carbon. A 0.5 ml sample of oil was mixed with a 0.5 ml sample of chloroform-d. The resulting highly concentrated sample gave good results. The primary area of interest in the NMR spectrum was the unsaturation region which occurs at a relative shift in magnetic field strength of 110-140 parts per million as related to the internal standard, tetramethylsilane.

Nitrogen content analysis of selected samples was investigated using combustion-gas chromatography. Oil samples (1.0 to 2.0 mg) were spotted on 8.0 cm diameter glass filters. These filters were previously combusted at

500 °C to remove volatile components. The oil-containing filter was then placed on the center of a small (approximately one inch square) piece of aluminum foil. Edges of foil were folded over until the oil/filter sample was neatly wrapped. Samples were analyzed according to manufacturers guide-lines [44]. Aluminum was cleaned with hexane/acetone prior to use. All material was handled with clean instruments to avoid any contamination.

RESULTS AND DISCUSSION

Standard Conditions

To begin the current research, several initial experiments were executed using the standard conditions of past research. These conditions were 5.0 weight percent vegetable oil contamination, 2.0 ml/sec oxygen flow rate, 150 °C, and the presence of a 2.0 cm x 5.0 cm strip of copper foil. Current research used safflower oil and SAE 40 lubrication oil as opposed to use of sunflower oil and SAE 30 oil in prior research [5,12-15]. Therefore, a first goal of this work was to compare the differing oils.

Viscosity rise versus time for the SAE 40 commercial lube oil contaminated with 5.0 weight percent safflower oil (Run 1) is given in Figure 3. The viscosity rise is of the expected exponential form based upon earlier work with SAE 30 diesel lube oil. The rate of rise is also comparable to earlier sunflower oil contamination results although the starting viscosity is roughly 50% higher. The run was terminated when kinematic viscosity exceeded 500 cSt.

Figure 4 presents total base number (TBN) decline for Run 1. Values of TBN start at above 14 mg KOH/g and fall somewhat asymptotically to near 8 mg KOH/g at the end of the

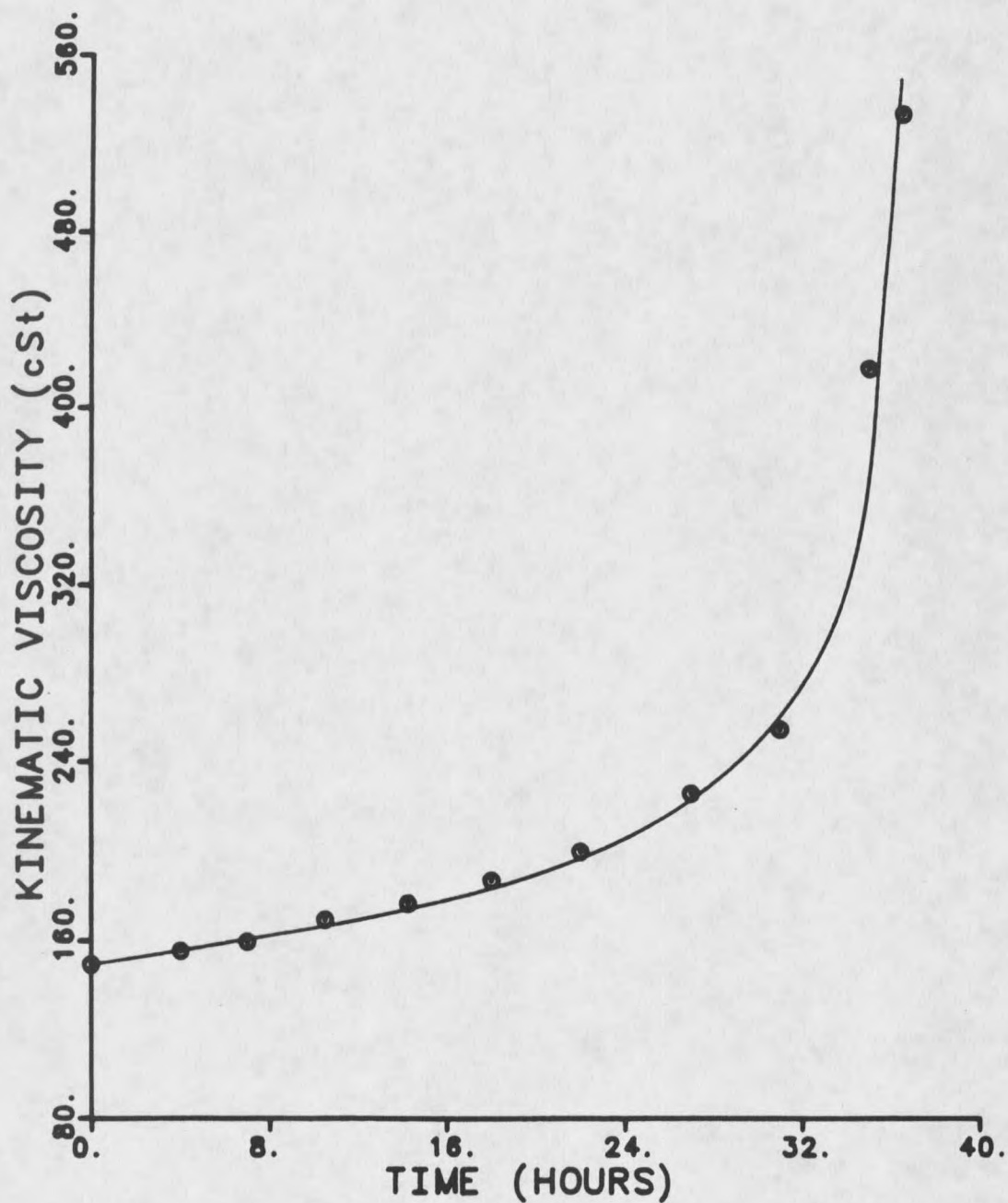


Figure 3. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions of prior research.

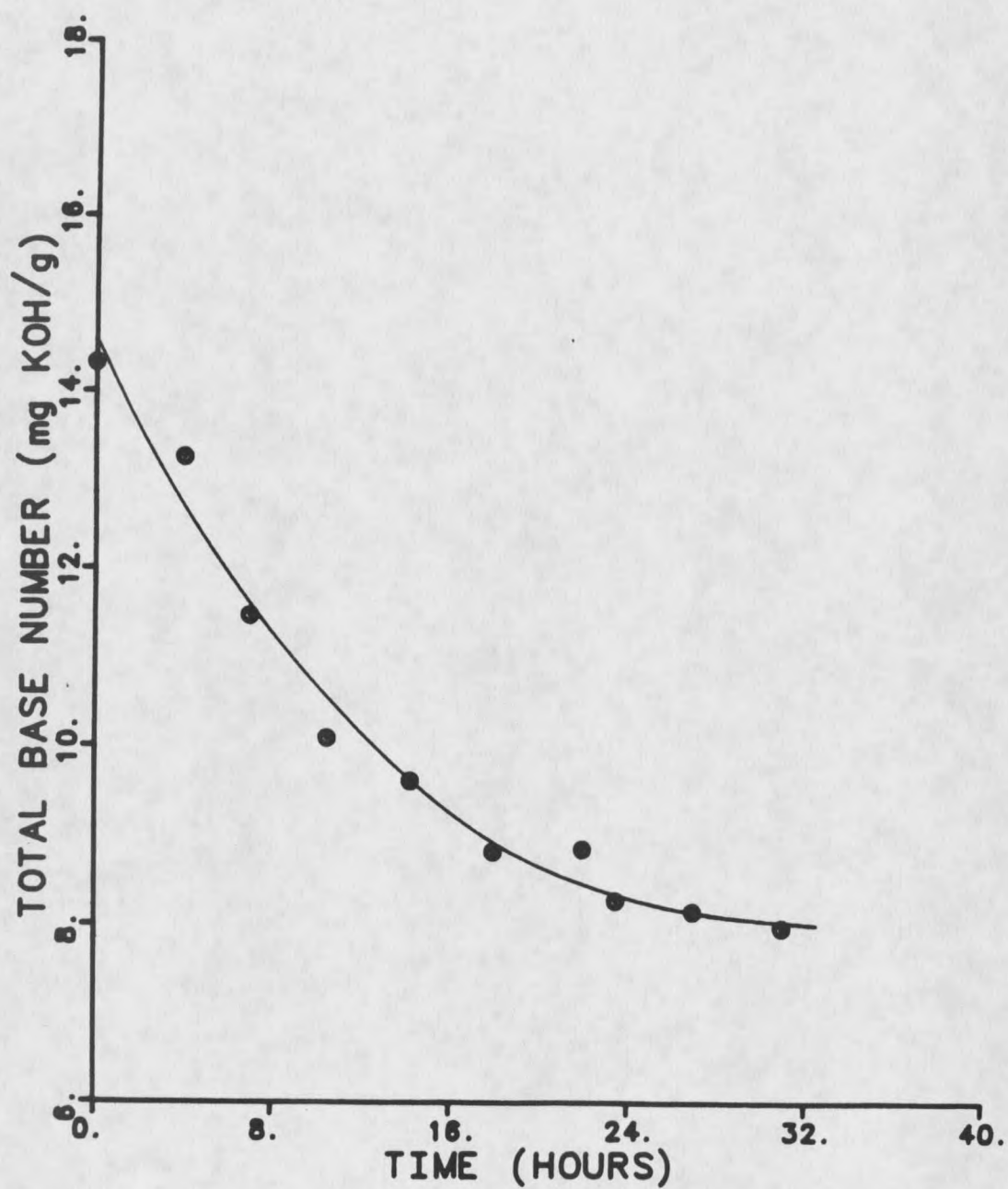


Figure 4. Total base number of commercial/safflower oil mixture versus exposure time for standard conditions of prior research.

run. The absolute value of this initial TBN is roughly twice that of 5.0% sunflower oil in SAE 30 commercial oil. This difference is primarily due to the higher buffering of the locomotive oil. Again, the loss of TBN is similar to earlier work.

Due to the unknown chemical nature of the additive packages in commercial oils (most commercial additive packages are proprietary), past researchers have chosen to use hydrocarbon base stock as the participating lubrication oil [14,15]. By this, the possibility of additive interaction could be avoided when testing individual additives for efficacy as well as mechanism. Again, however, any final oil additive formulation must be determined for the current commercial oil in use.

Run 2 was conducted to establish a baseline for the 40-weight base stock. Again, the oil mixture was exposed to the standard conditions of past research. Initial viscosity of this mixture at 40.0 °C was 136 cSt. At two hours exposure time the viscosity measurement was erratic, somewhere near 145 cSt. Formation of very small insoluble particles (referred to as gel or solids) was noted at this time in the viscometer capillary, indicating viscosity measurements were suspect at best. The experiment was continued with visual observations of mixture samples and kettle components made at half hour intervals. Solids formation was noted on the glass rod at 2.5 hours. By five

hours total exposure time, heavy gel occluded liquid samples and coated all wetted surfaces in the resin kettle reactor. The run was terminated at this point.

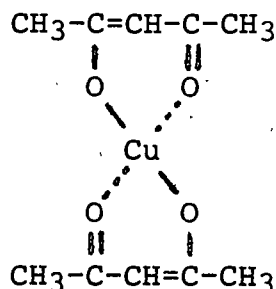
The insoluble gel build-up was somewhat more rapid than observed earlier for 5.0% sunflower oil in two different SAE 30 lube oil base stocks (heavy gel at 8-10 hours and 15-16 hours). Whether this difference is due to the vegetable oil change or the lube oil or both is not known. None the less, the order of magnitude of gel build-up was similar to that seen in earlier work.

Total base number for the base stock mixture was initially 1.3 mg KOH/g, reflecting the lack of buffering additives in the base stock. At one hour exposure this value had fallen to 1.1 mg KOH/g. Subsequent measurements were not attempted since 1) samples which represented the entire mixture were difficult to obtain and 2) solid particles were difficult to dissolve in the solvents used for TBN analysis.

At this point in the research a decision was made to switch to 10 ppm copper via cupric acetylacetonate (CuAcAc) as the active copper catalyst. Jette established that soluble copper dominates catalysis of polymerization as opposed to solid metallic copper [11]. Jette also found 10 ppm copper to yield approximately the same rates of polymerization and alkalinity decline as the standard foil strip. Furthermore, problems associated with the metallic

copper, e.g. oxidation and "gel blanketing," would be avoided as soluble copper species are chemically complexed and should also be largely unaffected by the formation and precipitation of insoluble gel.

Chemically, CuAcAc has the following structure [45]:



This copper complex is generally quite soluble in many organic systems and appeared to dissolve readily in the oil mixture at room temperature. The thermal stability of CuAcAc at 150 °C is unknown, but similar metal complexes seem to exhibit at least moderate stability at such temperatures. Should the copper be released by decomposition of the complex, the acetylacetonate fragment should evaporate. Furthermore, CuAcAc has the ability to complex additional molecules, simultaneously altering its coordination number [45]. Thus, the complexed copper may participate in the catalysis in a similar fashion to metallic copper.

Figure 5 presents a comparison of a standard case exposure using copper foil (Run 1 shown as a dotted line) and 10 ppm copper via CuAcAC. Viscosity rise curves are initially similar in each case with the CuAcAc trial (Run 3)

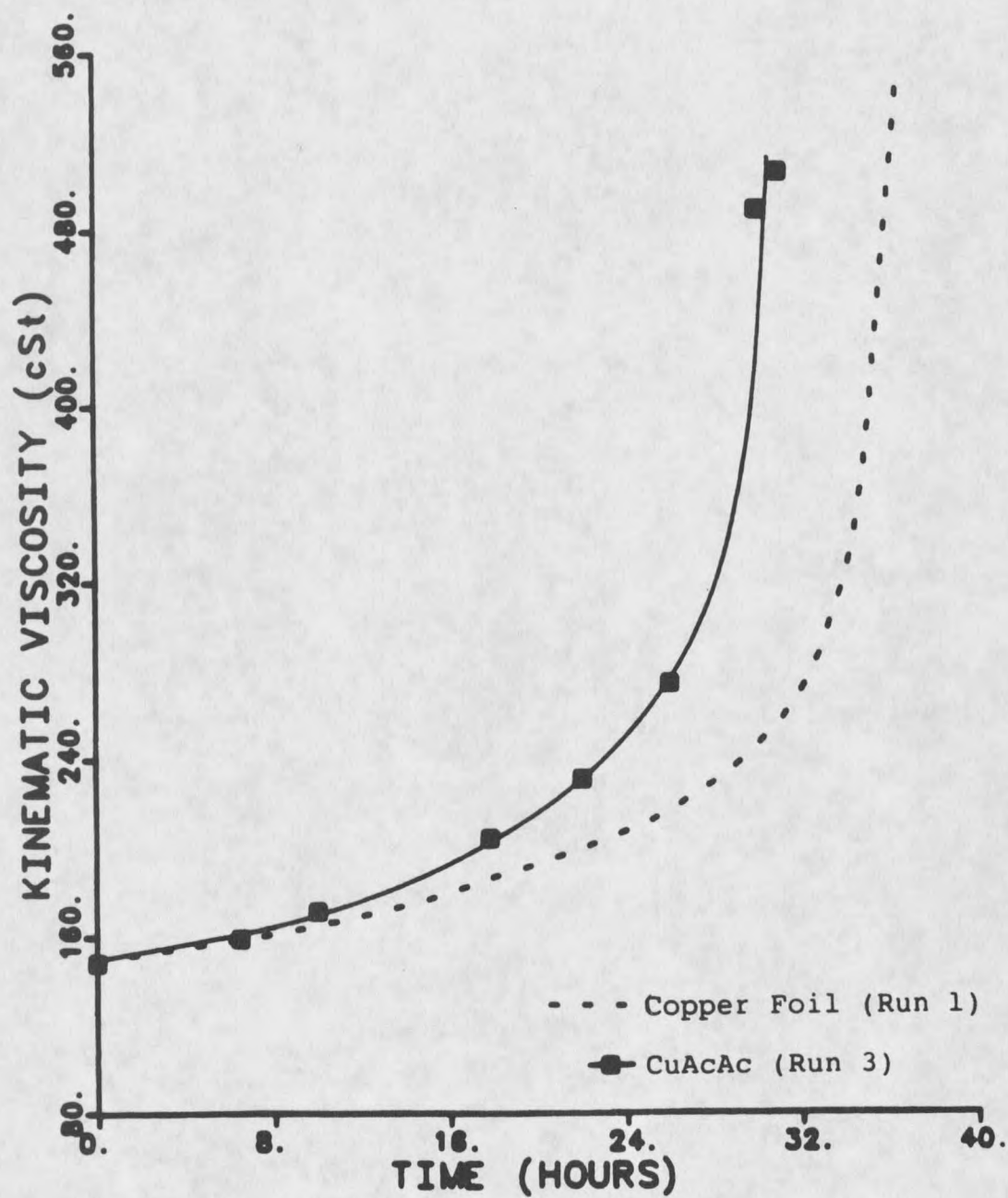


Figure 5. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with CuAcAc as the copper catalyst.

rising more rapidly late in the run, perhaps due to less influence of gel. However, gel formation was similar (low levels) in each trial. It may be that the initial high concentration of soluble copper from CuAcAc accelerates the initiation of addition polymerization. That is, based on Jette's conclusions, copper is most active catalytically when soluble and must first dissolve from the copper foil. In addition, these results suggest, as Jette concluded, that copper is more important during initiation than propagation.

Alkalinity loss curves for the two trials are given in Figure 6. As with viscosity, these curves are similar. This result is expected since past research has shown that formation of acidic species runs parallel to an increase in viscosity.

Results of Run 4, base stock at standard conditions except with CuAcAc, were similar to the above results in that lube oil degradation took place slightly faster than that in foil trials. Solids were noted on the glass rod one hour earlier with heavy solids formation by 4-5 hours.

Potential interactions of CuAcAc with other additives to be tested are unknown. However, this compound seems to interact similarly (if at all) with additives in the commercial lube oil as does the soluble form(s) of copper produced by the foil. This behavior, shown in Figures 5 and 6 as well as by the results of Run 4, is the basis for the

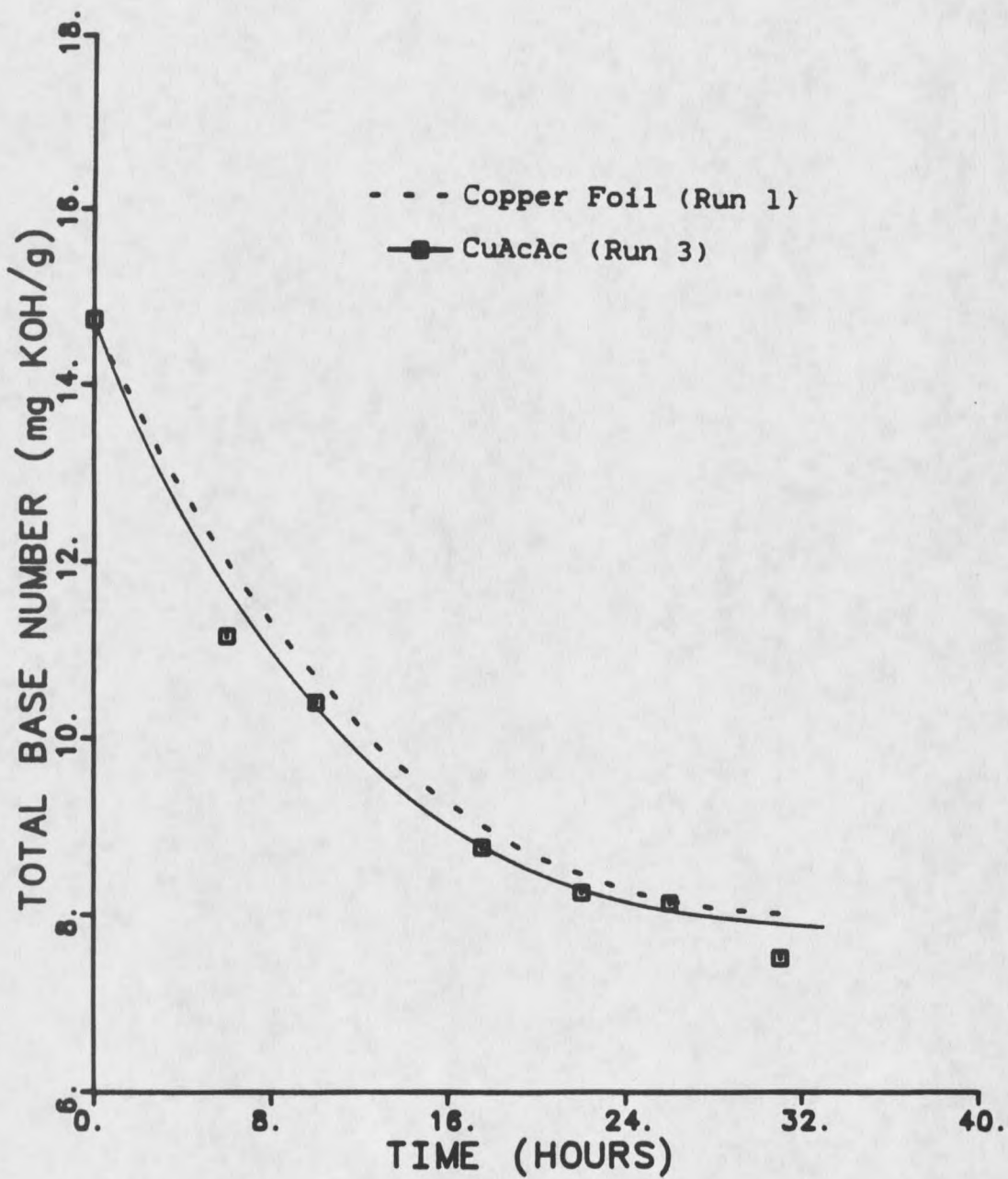


Figure 6. Total base number of commercial/safflower oil mixture versus exposure time for standard conditions with CuAcAc as the copper catalyst.

switch from copper foil to CuAcAc as the active catalyst. Hereafter the conditions of Runs 3 and 4 shall be the standard conditions. These conditions are 10 ppm copper via CuAcAc, 2.0 ml/sec oxygen flow rate, 150 °C, and 5.0% safflower oil contamination.

Base Stock: Antioxidant Study

The experience of past research indicates that the most effective antioxidant polymerization inhibitors were those of a peroxide-decomposing or metal-deactivating nature. Specifically, the most effective were N,N'-disalicylidene-1,2-propanediamine (NNPD) and zinc diamyldithiocarbamate (ZDTC). Zinc dialkyldithiophosphate was also found to show some promise as an effective antioxidant. Thus, all three additives are considered likely candidates for retesting in the current system.

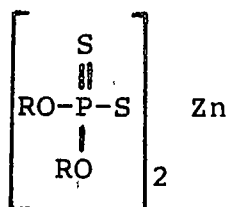
At this point in the research an ongoing literature review revealed that zinc is highly corrosive to the silver wrist pin bushings found in General Motors Electromotive Division locomotives [8]. As a result, Burlington Northern strictly forbids the use of any zinc-containing oil formulations; a zinc content up to 25 ppm is generally allowed, however [46]. Although the commercial ban of zinc appears to be a dilemma for future research, it is recognized that testing of the noted zinc compounds would

actually be practical for a variety of reasons. First, these compounds are readily available and testing could begin immediately. Second, depending upon their success, antioxidants of the ZDTC and ZDTP type that are based on other cations would be sought for evaluation. Finally, in general any insight gained from these additives would be used to guide future research.

The first antioxidant to be tested was zinc dialkyldithiophosphate (ZDTP). Raman found that repeated additions of this compound slightly inhibited viscosity rise in a 30-weight commercial/sunflower oil mixture [12]. While this performance is not overly impressive, the fact remains that ZDTP is used as the primary antioxidant in most motor oils. Furthermore, ZDTP may yield benefits in the current oil mixture system.

Zinc dithiophosphates are prepared by the reaction of P_2S_5 with the respective higher alcohols (e.g. hexyl, 2-ethylhexyl, octyl alcohols), followed by a reaction with zinc oxide [30]. Their solubility in hydrocarbon oils increases with the increasing number of carbon atoms of the alkyl residues and is satisfactory with the diamyl compounds and higher. Metal dithiophosphates may act not only as antioxidants, but also as corrosion inhibitors and extreme

pressure additives according to vendor claims [48]. They have a typical structure of:

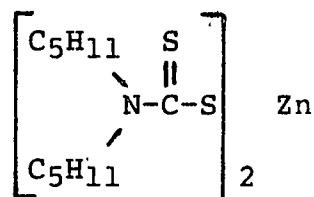


Although ZDTP's have been widely used as antioxidants for many years, their exact mechanism of action is not clear. However, it is clear that they can be efficient peroxide decomposers as they have been shown to accelerate the decomposition of both t-butyl and cumene hydroperoxide to non-radical products. In addition, they have been shown to inhibit oxidation by acting as chain-breaking agents [37].

The recommended level of usage is 0.65% to 1.3% by weight in suitable base stocks. ZDTP was added at 1.0 weight percent to an otherwise standard base stock/safflower oil mixture exposure in Run 5. At seven hours exposure time a thick (approximately 1.5 inch) layer of foam was noted above the oil mixture surface. At 9.5 hours exposure time the foaming had subsided, leaving behind hard, brittle solids on the kettle wall. These solids were found to be distinctly different from those generally found in base stock experiments. During this period, relatively little change had occurred in oil mixture viscosity. At twelve hours heavy formation of solids was noted and the run was terminated.

This antioxidant seemed to suppress the oxidation reactions leading to viscosity build-up and solids formation for a brief period of time. Whether or not the efficacy of ZDTP was hindered by the foaming action is yet unknown. However, the presence of ZDTP seems to be the causal factor for foaming to occur. The literature indicates that the foaming stability of an oil is a function of viscosity and surface tension [30]. Furthermore, surface-active substances such as detergents, extreme pressure agents, and corrosion inhibitors (several characteristics of ZDTP) strongly affect surface tension and as a result significantly increase the foaming tendency of oils. It was concluded that foaming occurred due to the presence of ZDTP and its surface-active properties.

The second antioxidant to be tested in base stock/saf-flower mixtures was zinc diamyldithiocarbamate (ZDTC). This additive has found use in diesel lubrication oil as an extreme pressure agent, oxidation inhibitor, corrosion and wear inhibitor, and also as a detergent [30]. Chemically, ZDTC has the following structure:



The metal dialkyldithiocarbamate antioxidants are generally of the peroxide decomposing type. Recently, Al-Malaika, et al. proposed that the antioxidant activity of

ZDTC may be due to its oxidation by hydroperoxides to give sulfur acids which are thought to be ionic catalysts for the decomposition of hydroperoxides [47].

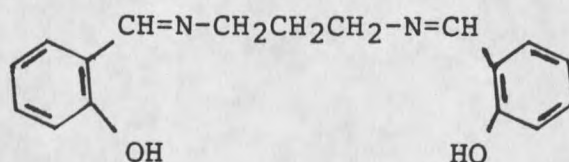
The recommended level of ZDTC usage in diesel lube oil ranges from 0.25% to 1.5% by weight [48]. Run 6 was conducted with 1.0 weight percent ZDTC added to a standard base stock oil mixture. Initial TBN was boosted from 1.3 to 1.9 mg KOH/g due to ZDTC addition. At eleven hours exposure the viscosity remained unchanged. However, during this period, TBN dropped to 1.5 mg KOH/g. At nineteen hours exposure time the viscosity was up about 8 cSt. At this time solids were first observed. Heavy solids formation occurred between 20 and 24 hours.

It is interesting that foaming did not occur with ZDTC. After all, it, like ZDTP, has several surface-active characteristics. Perhaps ZDTC has some anti-foam characteristics. On the other hand, it was not surprising that ZDTC performed much better than ZDTP. This same difference in efficacy occurred in prior research with 30-weight base stocks and remains subject to speculation. It is theorized that ZDTP may be acting as a chain breaking agent and forming hydroperoxides. These may then decompose to radicals and the polymerization continues. Literature from R.T. Vandervilt implied that ZDTP as the only inhibitor may not control viscosity increase [49]. Holdsworth, et al. stated, "Of considerable practical importance is the

synergism shown by peroxide decomposing antioxidants when used in combination with chain-breaking agents [33]."

The approach of Run 7 was to combine a potential chain breaking agent, ZDTP, with a hydroperoxide decomposer, ZDTC. It was speculated that ZDTC might also suppress the foaming tendency of ZDTP. One percent by weight of each additive was added to a standard base stock oil mixture. Foaming occurred as before and a considerable amount of solids formation was noted by 15 hours exposure time. It was concluded that 1) ZDTC does not possess appreciable anti-foam characteristics in this case and 2) ZDTP, perhaps due to oil foaming, was antagonistic towards ZDTC.

The final antioxidant to be tested in base stock was the metal deactivator N,N'-disalicylidene-1,2-propanediamine (NNPD). This is a known chelating agent for metal ions, especially copper, and functions by preventing their participation in oxidation reactions as well as the precipitation of insoluble metal compounds [30]. Chemically, NNPD has the following structure:



The suggested concentration of NNPD ranges from 0.01 to 0.5 weight percent [50]. However, Raman found that increasing NNPD concentration improved performance [12]. Therefore, the conditions for Run 8 were 40-weight base

stock, standard conditions, and 1.0 weight percent NNPD. Due to the amine functionality, NNPD increased initial TBN from 1.3 to 3.7 mg KOH/g. At 30.5 hours exposure the viscosity had increased from 129 to 143 cSt and TBN dropped to 2.5 mg KOH/g. While oil appearance remained virtually unchanged, a few very small solids were observed. Viscosity and TBN evaluations were continued, although suspect. Heavy solids formation was noted between 58.5 and 61 hours.

NNPD distinctly slowed viscosity rise and solids formation versus standard conditions. Earlier work with SAE 30 lubrication oil indicated NNPD might function not only as a catalyst deactivator but also by some other antioxidant mechanism [13]. To check this behavior, Run 9 was conducted without NNPD using base stock and standard conditions except without copper. Throughout the exposure of Run 9, precipitation of solids was gradual beginning at 30 hours. Termination of the experiment at 48 hours found kettle surfaces covered with heavy solids formation.

The NNPD case was clearly better than the no-copper trial and at first glance, indicates an additional antioxidant capability of NNPD. However, it may be that NNPD is either deactivating trace metals or perhaps has dispersant characteristics and thus, keeps solids from precipitating. The exact role of NNPD remains unclear and further work in commercial 40-weight may clarify the NNPD mechanism.

Metal deactivators show strong synergistic effects when used with other antioxidants [30]. To test this possibility, Run 10 was conducted with 1.0 weight percent NNPD, 1.0 weight percent ZDTC, base stock/safflower oil mixture, and standard conditions. Both of these compounds effectively delayed oil degradation at 1.0 weight percent concentration levels when used separately. At nineteen hours exposure time viscosity had increased 5.0 cSt and light formation of solids was noted on the glass rod. Recall that this is approximately the same time that heavy solids formation occurred in the ZDTC run (Run 6). Also, this level of solids formation was not noted until 30 hours in the NNPD run (Run 8). Heavy solids formation occurred between 48 and 51 hours exposure time, or about 10 hours earlier than the NNPD run.

The NNPD/ZDTC combination was not only not synergistic but appeared to be antagonistic. A plausible explanation is that NNPD may be complexing with ZDTC (or zinc) and is therefore hindered from completely deactivating the copper catalyst. After all, approximately 600 ppm zinc is introduced into the system via ZDTC. Future work in commercial oil may shed more light on this subject.

Consumption of additives by base stock lubricating oil was thought to be minor compared to that by vegetable oil. After all, the iodine value for safflower oil, 148, was much higher than the value 4.9 determined for 40-weight base

stock. Nuclear magnetic resonance also confirmed that there was very little unsaturation in the base stock oil, especially compared to that in safflower oil. However, to check for oxidation of base stock species, Run 11 was conducted with base stock and standard conditions except no safflower oil was present. At 2.75 hours exposure time, viscosity increased from 157 to 173 cSt. TBN dropped from 1.0 to 0.45 mg KOH/g as well. At this time, very small solids were noted in the viscometer capillary. Viscosity and TBN measurements were continued, although suspect at best. Viscosity continued to increase and TBN continued to decrease.

Solids formation, like the no copper trial, was gradual and at 80 hours exposure time the experiment was terminated. While solids formation was not as extensive as a standard case with safflower, a notable amount of solids was observed. The conclusion drawn from this experiment was that base stock, itself, underwent notable oxidation.

It was still unclear, however, as to the extent base stock might consume a particular antioxidant. Run 12 was conducted with one percent by weight ZDTC in base stock. Conditions were standard except the safflower oil was not introduced into the kettle until 24.0 hours exposure time.

Throughout the initial 24.0 hours exposure time the lube oil appeared to be non-degraded and retained its original yellowish coloring. However, by 23.0 hours

exposure time, total base number had dropped from 1.9 to 1.0 mg KOH/g, indicating some formation of acidic species in the lube oil. At 24.0 hours exposure time safflower oil was added and observations were continued. Seven hours later, or 31.0 hours exposure time, heavy formation of solids was noted and the experiment was terminated.

The antioxidant ZDTC clearly slowed solids formation as before. However, the lasting benefit of ZDTC was not nearly as good as the case when safflower oil and ZDTC were both added at the onset of the experiment (Run 6). That is, heavy solids formation occurred only 7.0 hours after introduction of safflower compared to formation of heavy solids at between 20.0 and 24.0 hours in Run 6. Volatility of ZDTC may be disregarded since this additive has been found to be effective for up to 60 hours in another base stock oil mixture at 1.0 weight percent. Thus, it was concluded that lube oil species are oxidizing as well as consuming antioxidant.

Commercial Oil: Safflower Sensitivity Study

As a basis for further work, commercial SAE 40 oil was evaluated for sensitivity to safflower oil content since base stock studies indicated significant oxidation of

lubrication oil may be taking place. Figure 7 gives viscosity rise curves for SAE 40 commercial oil with no safflower present. The two cases presented are for copper foil (Run 13) and CuAcAc (Run 14) catalysis. Also presented for reference is the standard CuAcAc case with safflower (dotted line). Viscosity rise for the standard case is clearly more rapid, but the two trials containing no safflower show remarkable increases in viscosity. When similar experiments were performed with SAE 30 commercial lube oils, there were no detectable viscosity rises for 70 hours. As shown, the foil case rises slower than CuAcAc at first and then speeds past the CuAcAc case. Perhaps soluble copper concentration, originally small in the foil trial, may have exceeded the 10 ppm copper content of the CuAcAc trial, therefore, accelerating polymerization in the foil trial.

TBN decline curves for the no-safflower trials as well as the control case (dotted line) are given in Figure 8. There are several key points of interest in this figure. First, TBN decline seems insensitive to catalyst form. Second and more significant, the TBN declines observed in both no-safflower cases are very similar to the control case. This result, like the viscosity rise, was unexpected in light of earlier work with SAE 30 lube oil where only 2.0 mg KOH/g were lost in over 65 hours of exposure with no plant oil present. The buffering power of the alkaline

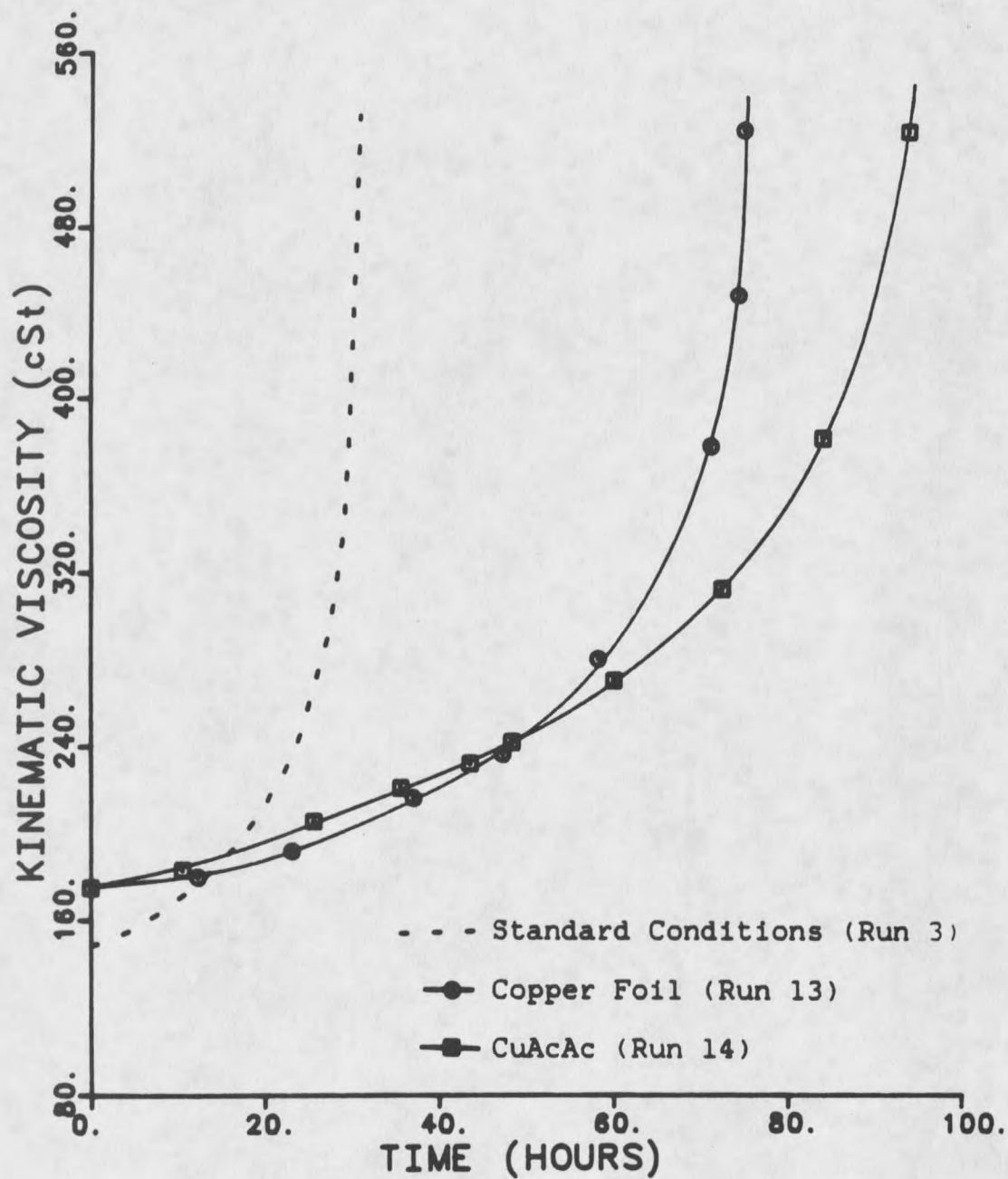


Figure 7. Kinematic viscosity of commercial oil versus exposure time with copper metal foil and with CuAcAc as catalysts.

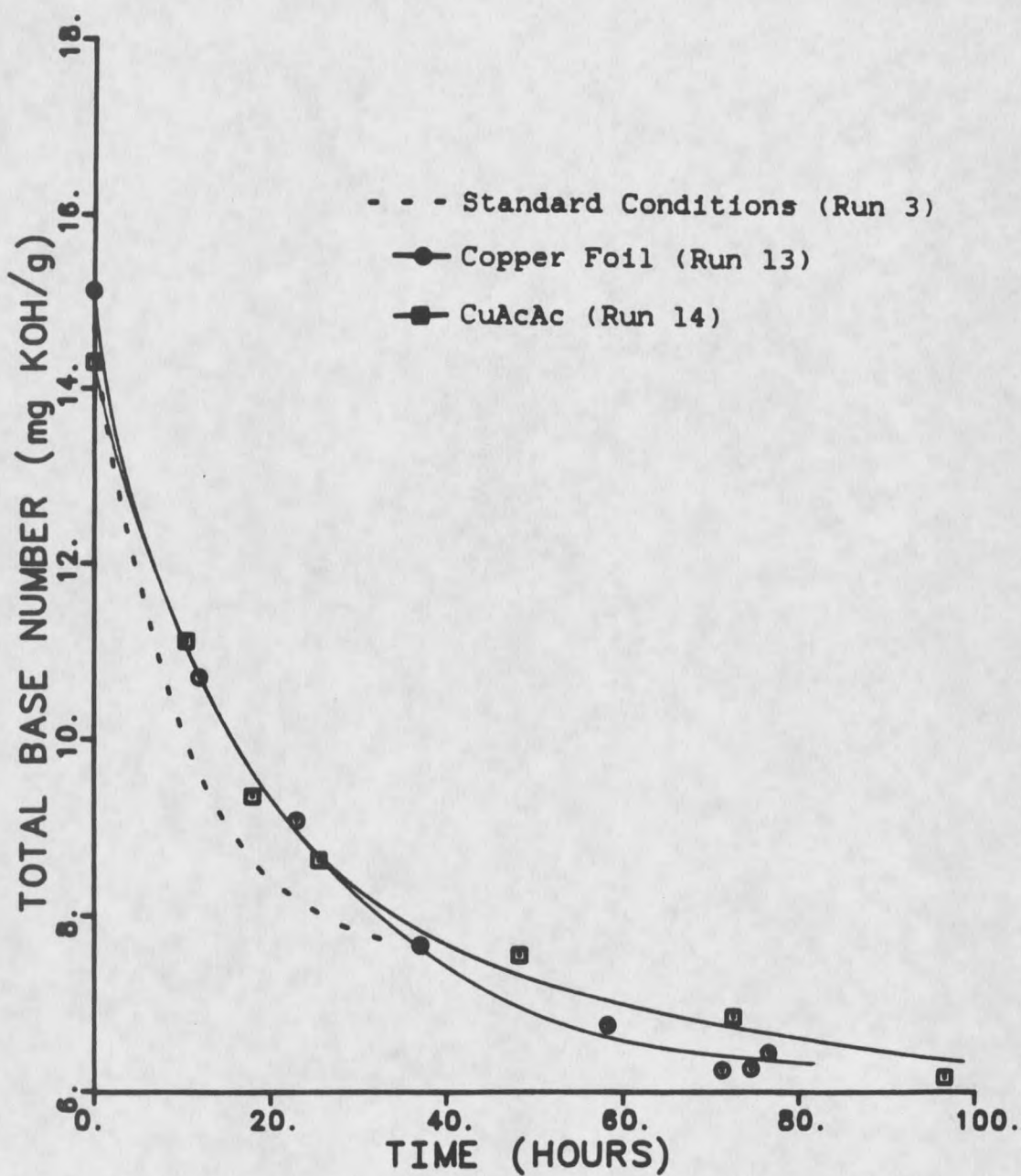


Figure 8. Total base number of commercial oil versus exposure time with copper metal foil and with CuAcAc as catalysts.

maintenance additives in the 40-weight locomotive oil appears quite weak compared with that of the SAE 30 oil.

It appeared probable that the level of unsaturation of the SAE 40 medium speed locomotive oil was significantly higher than that of the SAE 30 oil, resulting in some addition polymerization of the lube oil alone. Iodine values for the two commercial oils, their corresponding base stocks, and those for safflower and sunflower oil are shown in Table 2.

TABLE 2. Iodine Values

<u>Oil</u>	<u>Iodine Value</u>
SAE 30 Commercial	4.8
SAE 40 Commercial	5.7
SAE 30 Base Stock	5.6
SAE 40 Base Stock	4.9
Sunflower Oil	142
Safflower Oil	148

As shown in Table 2 the difference between commercial oils, as well as base stocks, is slight and values for all are significantly less than those of the vegetable oils. The iodine values, however, should be taken with some reservation since the test is not very satisfactory for

conjugated double bonds [42]. Therefore, Carbon-13 nuclear magnetic resonance (NMR) was used to confirm these results. This analytical technique provides structural information, i.e. information on the functional groups attached to carbon. Spectra obtained from the NMR analysis confirmed the iodine value analysis, and it was concluded that the variation in viscosity rise was probably not due to differences in unsaturation.

Perhaps the 40-weight oil contains more volatiles and thus thickens more rapidly as these materials are lost. Logan, et al. found lubricant viscosity increased approximately 2.0% for each 1.0% mass evaporated [10]. To test this, commercial oil with no safflower oil was exposed with nitrogen percolation rather than oxygen. All other conditions were standard. As with past work with SAE 30 oil, no physical (viscosity) or chemical (TBN) changes were noted in the oil. However, one observation was made which had appeared relatively unimportant in past experiments. The exit ports of the kettle reactor were void of any oily residue. That is, oil deposits had always formed on exit ports during oxygen runs. The significance of this is that lube oil/vegetable oil components were evidently being oxidized to lighter, more volatile components, the extent of which is unknown.

While a certain amount of lube oil species may become volatile, it seems unlikely that the significant viscosity increase for commercial oil was entirely due to evaporation. It was felt that new insight might be gained if an elemental analysis were performed on the lubrication oil. Commercial 40-weight samples were sent to Lubricon Laboratory of Indianapolis, Indiana for atomic emission (AE) analysis. The results for this analysis as well as those for a SAE 30-weight commercial oil used in earlier research are shown in Table 3.

TABLE 3. Atomic Emission Data (ppm)

<u>Element</u>	<u>30-weight Oil</u>	<u>40-weight Oil</u>
Aluminum	0	1
Boron	34	0
Calcium	7	3841
Copper	0	0
Iron	10	6
Lead	1	0
Magnesium	1280	0
Phosphorus	1157	13
Silicon	8	0
Sodium	6	43
Zinc	1118	3

The additives appear to be significantly different, and one may only speculate as to the identity of individual additive compounds. High levels of zinc and phosphorus normally indicate the presence of an antioxidant like ZDTP. This is not unexpected as ZDTP is a very common additive. Compounds with the alkaline earth/alkali metals, e.g. barium, calcium, magnesium, and sodium, are typically used in detergents and dispersants and usually have alkalinity-boosting characteristics [30].

The additive package in the SAE 30 appears rather well rounded and contains perhaps an antioxidant as well as several detergents and/or dispersants. On the other hand, the 40-weight oil appears to contain mostly additives of the detergent/dispersant type. In fact, it contains more than twice the alkaline earth/alkali metal as that in SAE 30. Recall that the TBN of SAE 40-weight oil was approximately twice that of the SAE 30-weight oil. It may be that antioxidants of the amine/phenol variety or ZDTC/ZDTP type except with other cations, e.g. calcium and sodium, are in this package. However, based on viscosity increase and TBN decline, one could also speculate that the 40-weight oil does not contain any antioxidants.

Since oil additive packages are proprietary, the exact formulation of these commercial oils may never be known. The AE analysis does suggest, however, that SAE 40 lube oil oxidation may be largely due to deficiencies in the additive

package. Whether locomotive lube oil oxidation is due to unsaturation, volatility, additive deficiencies, or perhaps a combination of all three is not completely known. However, it may not be statistically important and may even suggest that some oil instability may be tolerable due to higher oil consumption of locomotive engines.

Commercial Oil: Alkalinity
Maintenance Study

As reported above, TBN decline observed for commercial oil without safflower oil was very similar to the control case. The significance of this is that alkalinity loss does not seem to be a major problem for the use of plant oil fuel in a diesel locomotive. In fact, this issue (of alkalinity decline) now seems a secondary matter to viscosity rise. None the less, research on alkalinity maintenance was continued and several compounds were examined for efficacy.

First, octadecylamine (ODA), an eighteen-carbon saturated hydrocarbon with an amine functional group at one end, was examined for its impact on alkalinity. Rewolinski found this compound to be soluble in a SAE 30 lubrication/sunflower oil system [5]. Figure 9 gives TBN decline for a standard case exposure of 5.0% safflower/95.0% commercial SAE 40 oil mixture with periodic additions of ODA (Run 16). The standard control case is shown as a dotted line. The

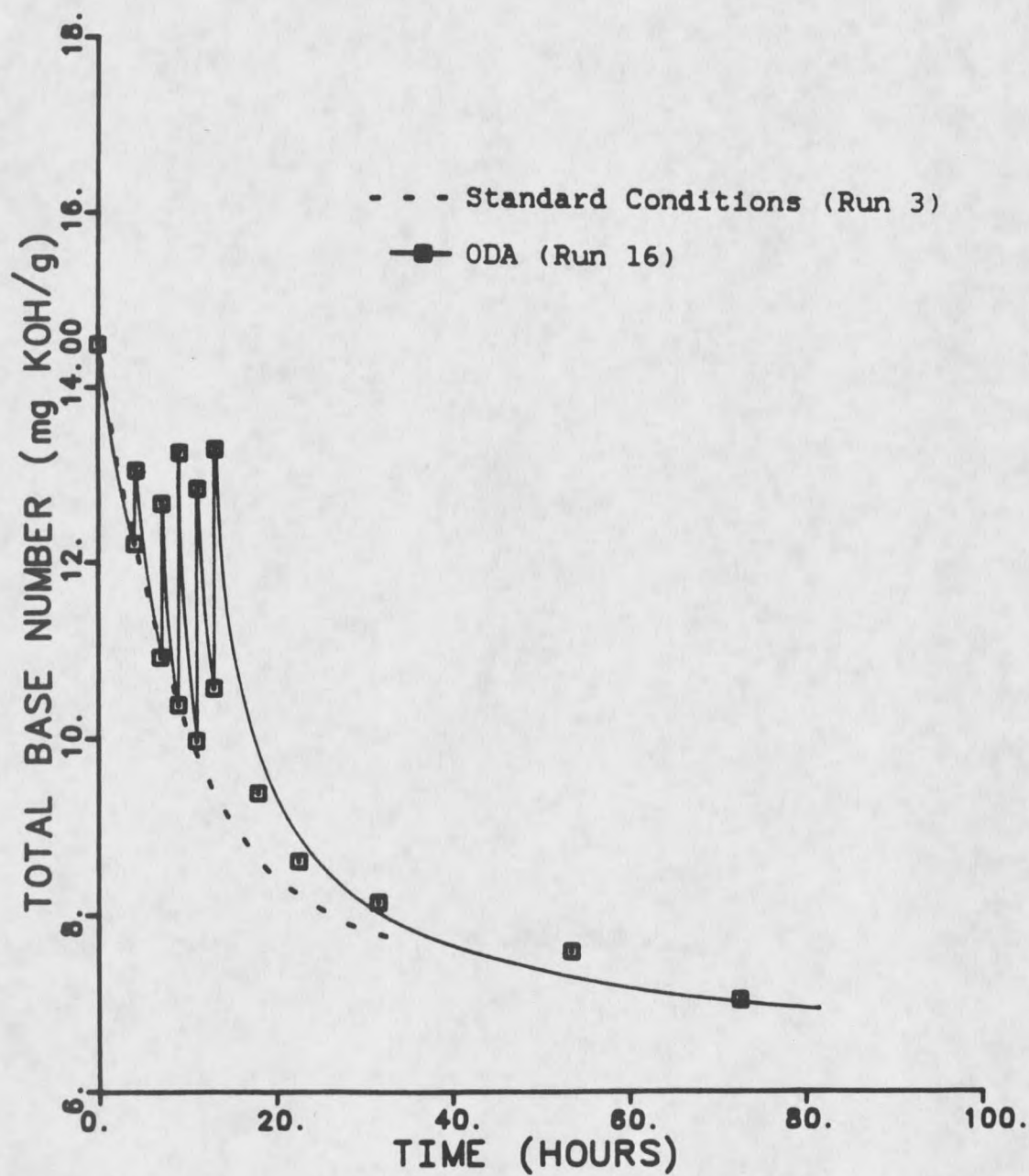


Figure 9. Total base number of commercial/safflower oil mixture versus exposure time for standard conditions with periodic additions of ODA.

quantities of ODA added ranged from 2.5 to 11.3 grams as TBN was repeatedly restored to about 13 mg KOH/g. As Rewolinski found with commercial SAE 30 mixtures, ODA temporarily raised TBN to high levels, but alkalinity loss subsequent to the ODA addition was very rapid. Following suspension of ODA addition at about 30 hours, alkalinity loss tracked the curve for the 40-weight lube oil with no ODA additions. It was concluded that while ODA was effective at boosting alkalinity, it was not an effective alkalinity maintenance additive.

A second compound, an overbased calcium phenate (OCP), was tested for its ability to suppress alkalinity decline. This compound is made by the reaction of phenol with an excess of metal oxide or hydroxide (particularly of calcium or barium). The term overbased indicates the phenate contains (for example) seven times the amount of metal present in a normal phenate. Besides its neutralization power, OCP possesses good dispersant properties. The main incentive for the use of overbased phenates is, besides the better neutralizing power, cheaper production in comparison with the normal phenates [30].

Figure 10 gives TBN as a function of exposure time where OCP was added periodically to a standard SAE 40 commercial/safflower oil mixture (Run 17). For reference, the dashed curve is that of the standard control case. Addition quantities averaged 0.4 weight percent as TBN was

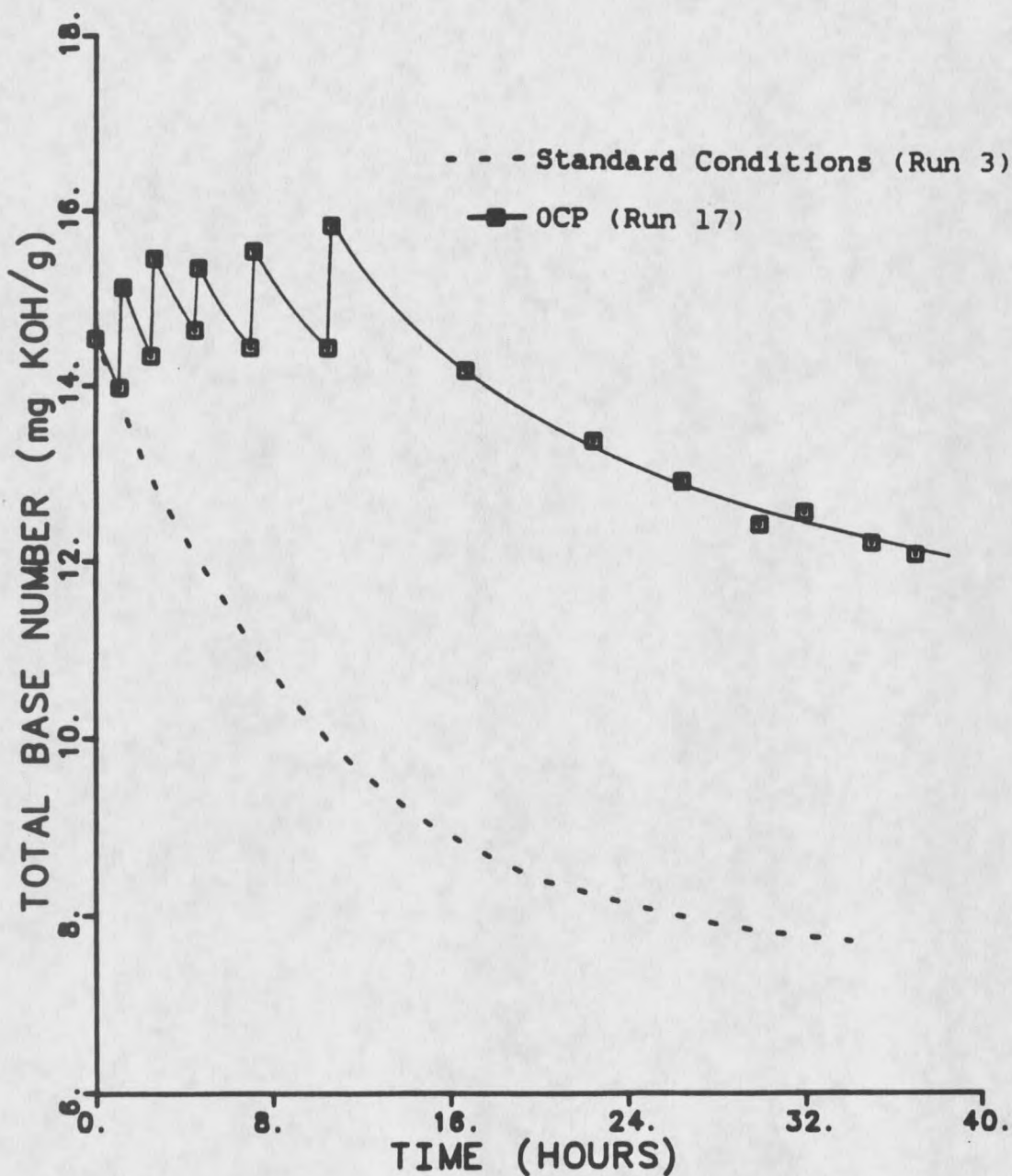


Figure 10. Total base number of commercial/safflower oil mixture versus exposure time for standard conditions with periodic additions of OCP.

maintained near the initial value of 14.5 mg KOH/g. Of special significance is that TBN remained quite high for over 24 hours after OCP additions ceased.

The lack of lasting benefit from ODA additions and the success of OCP is suspected to be due to additive volatility or thermal stability with the additive OCP perhaps superior on each count. Run 18 was conducted to test for ODA losses due to evaporation. An otherwise standard commercial/safflower oil experiment was conducted except 5.0 gm of ODA was added at the one-hour mark. Thereafter, a 3.0 ml oil sample was collected every twenty minutes for three hours. The goal was to follow nitrogen loss with time since the basic component of ODA is its terminal amine group. Nitrogen content of oil samples was analyzed using Carlo Erba gas-combustion chromatography. Unfortunately, nitrogen concentration was below the instrument detection limit and it was impossible to even estimate whether nitrogen (and hence ODA) was declining with increasing exposure time.

Whether or not the poor performance of ODA is due to additive instability remains unknown. Perhaps, as Rewolinski suggested, ODA may be reacting with something other than the desired free acidic species [5]. In any case, performance of OCP was relatively good and this additive compound is a strong candidate for inclusion in any commercial lube oil to be used with plant oil fuels.

Commercial Oil: Antioxidant Study

The remarkable performance of NNPD in the base stock experiments provided sufficient incentive to explore its impact on polymerization of safflower/commercial oil components. That of ZDTP and ZDTC was marginal to fair at best. However, the additives in the commercial oil may or may not interact well with these two potential antioxidants. Perhaps anti-foam agents are present which will allow ZDTP to be a more efficient antioxidant. Therefore, it was concluded that these antioxidants, like NNPD, remained likely candidates for oxidation inhibition in the SAE 40 commercial/vegetable oil mixture.

Figure 11 presents viscosity rise versus time for a standard SAE 40 commercial/safflower oil mixture trial with 1.0 weight percent ZDTP added at the onset of the experiment (Run 19). The standard control case curve is given as a dotted line. As shown, ZDTP shows no efficacy in the commercial/safflower oil mixture, in fact just the opposite. The ZDTP case actually thickens faster than the control. Foaming did not occur and was therefore not a hindrance to ZDTP performance. However, the unknown interactions among ZDTP and the lube oil additives are undoubtedly involved here.

ZDTC was evaluated next at a 1.0 weight percent concentration level in the standard commercial oil mixture (Run

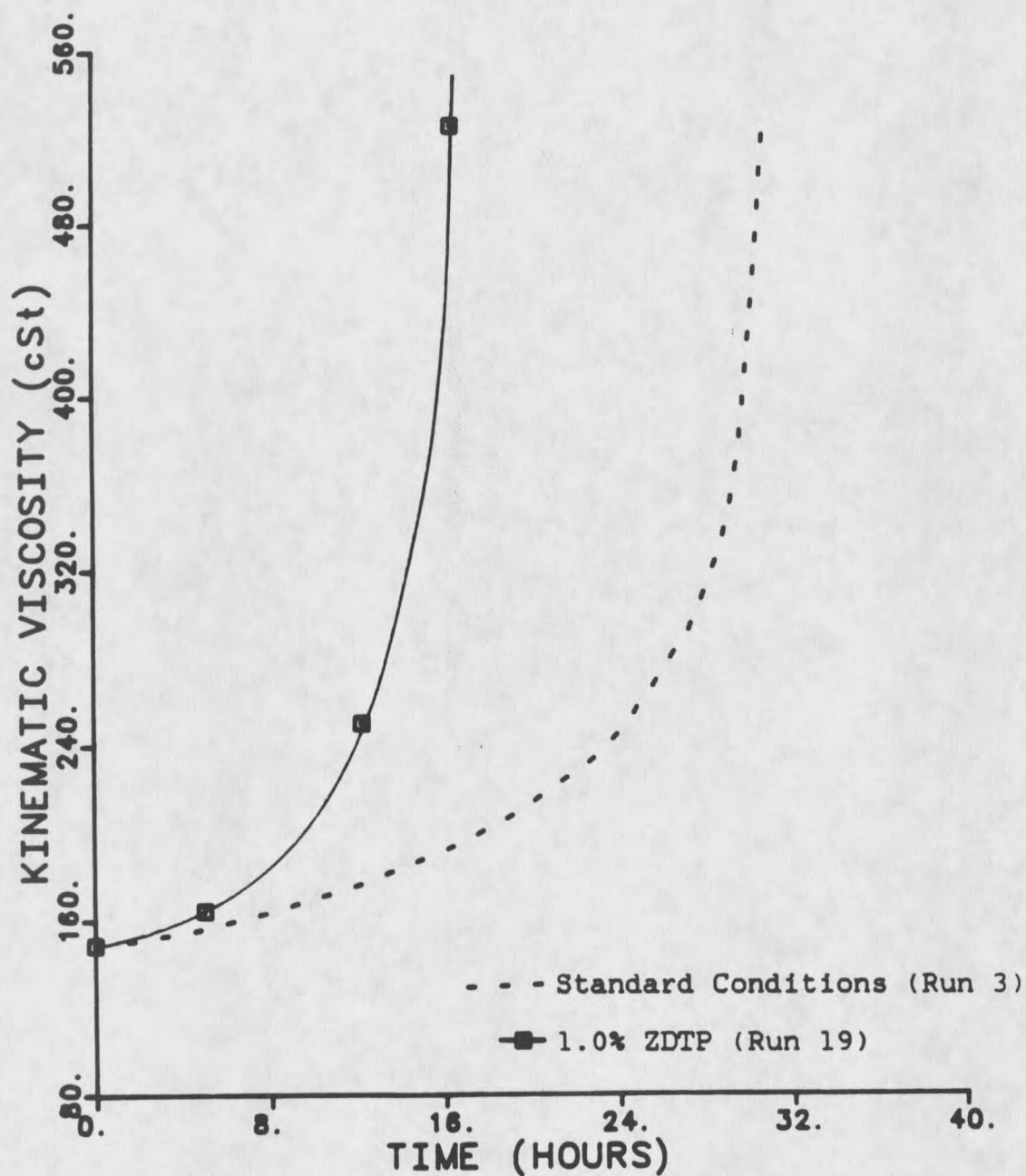


Figure 11. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 1.0 weight percent ZDTP.

20). The viscosity rise as well as that for the standard control are given in Figure 12. Once again, as with ZDTP, the ZDTC fails to retard viscosity rise, and in fact accelerates it as did ZDTP. The lack of any success from ZDTP and ZDTC was clearly disappointing.

The reader should keep in mind that these antioxidants were not designed to inhibit oxidative addition polymerization. Rather, these compounds are general antioxidants which were developed to stop viscosity breakdown and formation of corrosive acids in lubrication oils where few double bonds exist. While it is hoped that these compounds would also suppress oxidative addition polymerization at sites of unsaturation, it is no great surprise that ZDTC/ZDTP do not work well in the presence of a safflower oil contaminated system.

The third likely candidate, NNPD, was evaluated next at a 1.0 weight percent level in a standard commercial oil mixture (Run 21). As shown in Figure 13, NNPD distinctly slows viscosity rise versus the control case (dashed line). Also shown in Figure 13 is an otherwise standard trial using no copper (Run 22). NNPD is shown to slow viscosity rise to roughly the midrange level between copper and no-copper cases. This result is interesting as NNPD was found to inhibit oxidation of oil mixture species beyond that of the no-copper case in base stock. Raman, as well, found NNPD in commercial SAE 30 to perform better than the otherwise

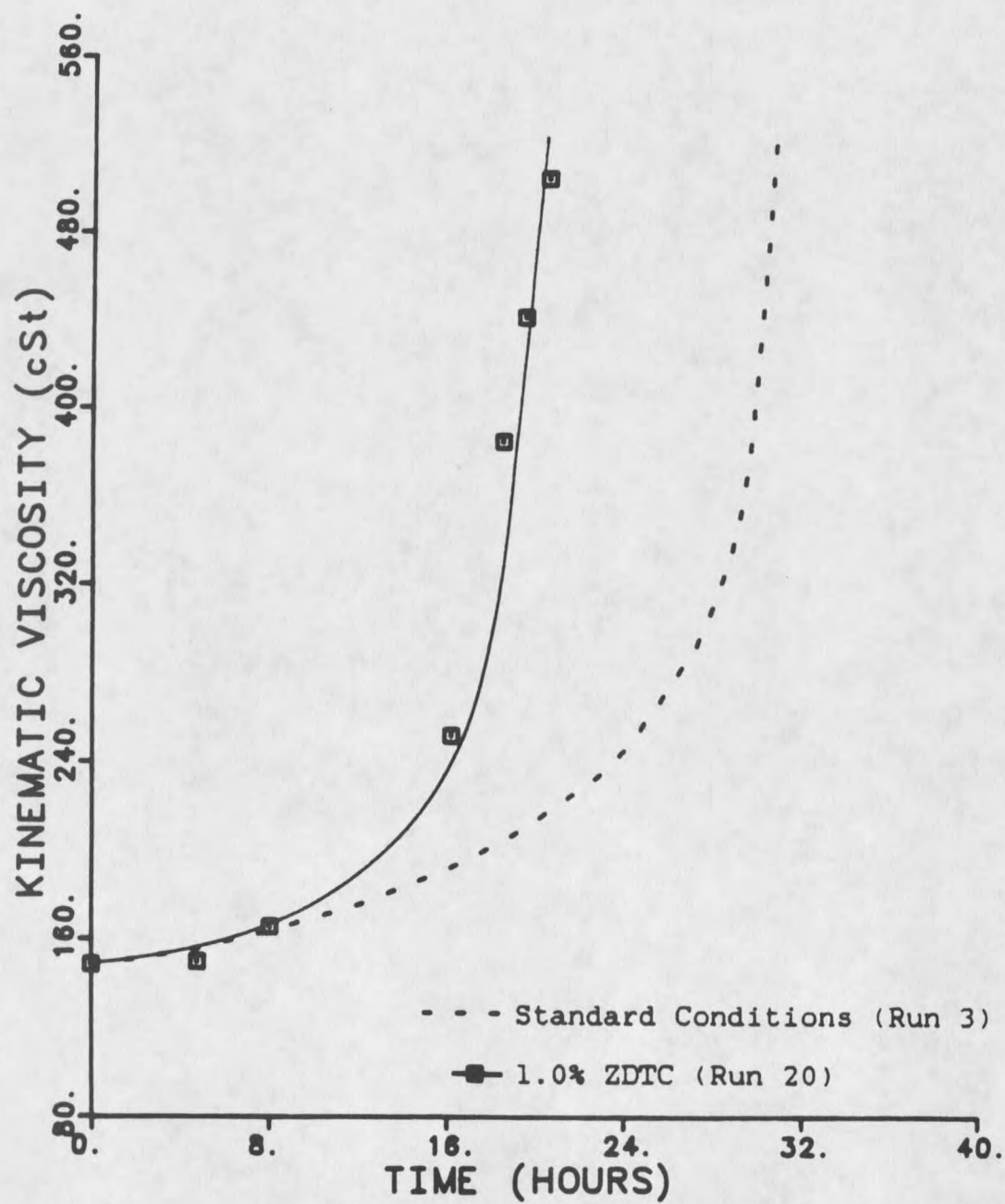


Figure 12. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 1.0 weight percent ZDTC.

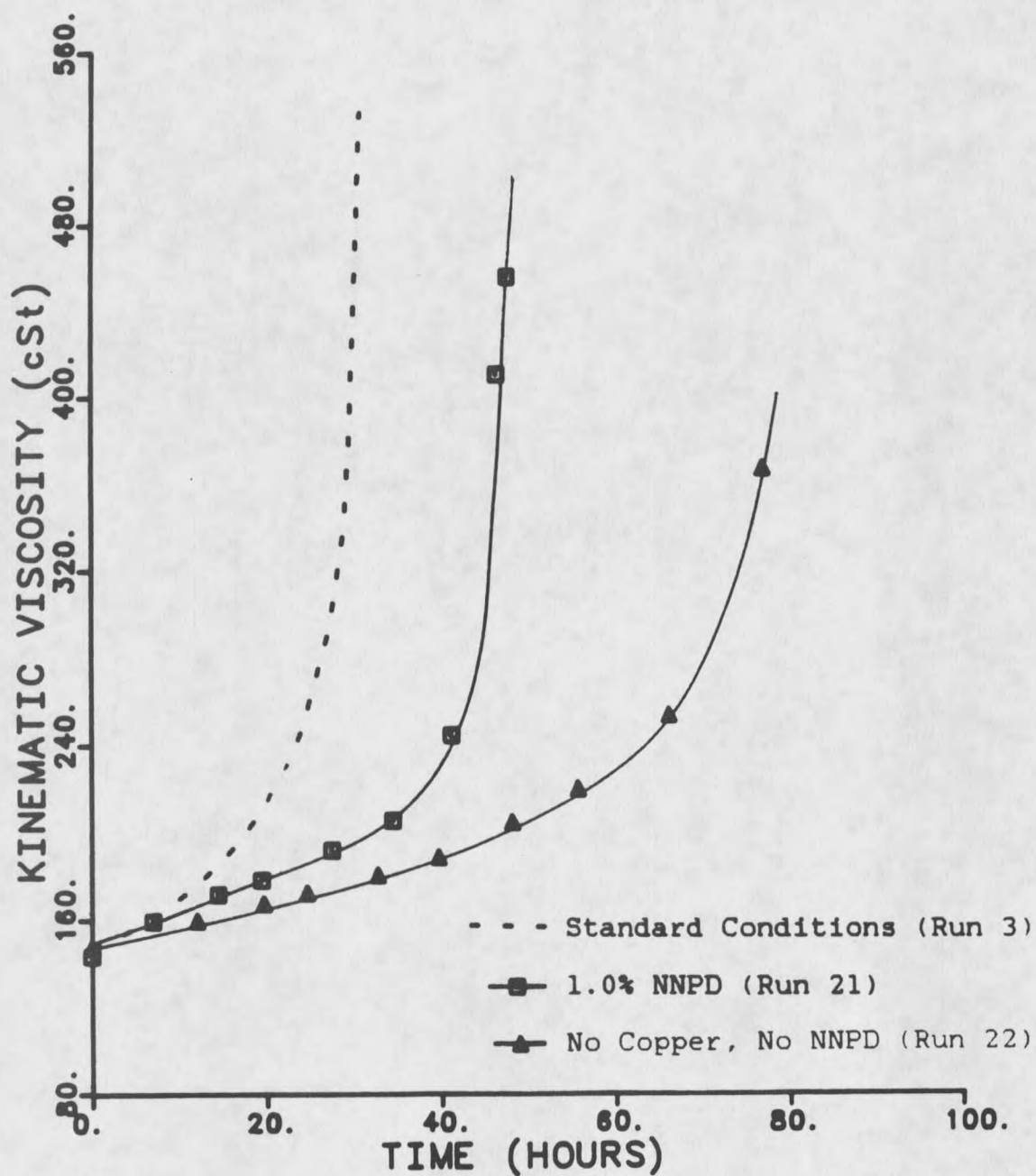


Figure 13. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 1.0 weight percent NNPD and for standard conditions with no copper.

standard SAE 30-weight commercial/sunflower no-copper case [12]. However, in Raman's case, presence of copper accelerated the system only 7-9 hours as opposed to at least 45 hours in the SAE 40 commercial oil mixture. Therefore, the SAE 40 oil "allows" NNPD more time to evaporate, decompose, or complex with species other than copper. Indeed, NNPD may be complexing with other additives and thereby hindering their (or its own) beneficial action. This type of behavior was demonstrated when NNPD was combined with ZDTC in Run 10.

To further elucidate this behavior, another trial was performed using NNPD at 1.0 weight percent in a standard commercial mixture but with no copper present (Run 23). This result along with the curves of Figure 13 are given in Figure 14. The significance of Figure 14 is that NNPD does not seem to inhibit polymerization as an oxidation inhibitor. In fact, it seems to promote polymerization versus the trial with no copper and no NNPD. A plausible explanation is that NNPD both inhibits and promotes polymerization by having separate impacts on two different steps in the polymerization mechanism. Pedersen found that while NNPD effectively deactivated copper, it activated iron, manganese, and cobalt by 43%, 103%, and 833%, respectively. He states, "Because these compounds (metal deactivators) form chelate compounds with the metals, the mere formation of a chelate compound is no criterion of metal deactivation" [41]. Therefore, NNPD may chelate

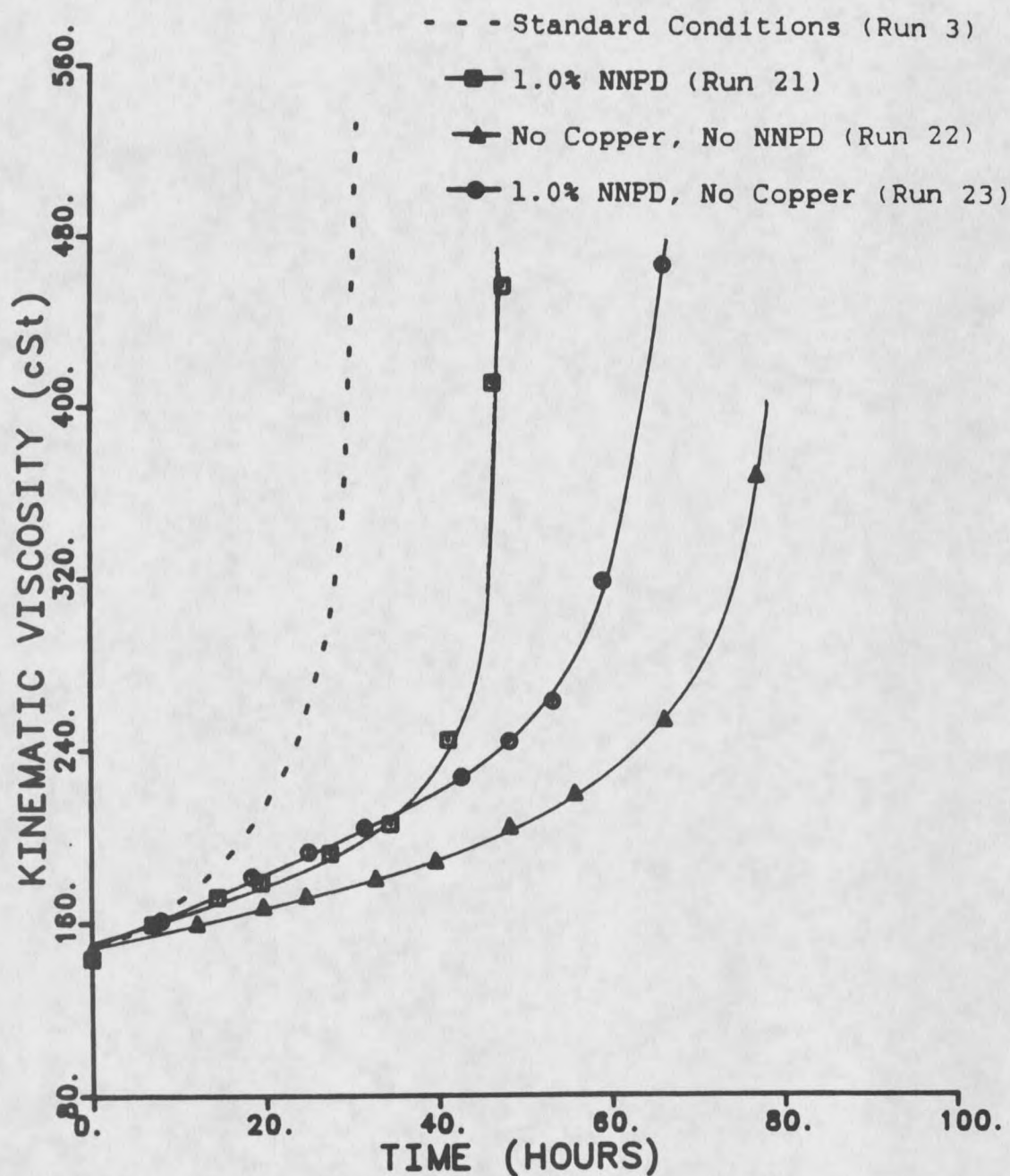


Figure 14. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for 1.0 weight percent NNPD with no copper, for standard conditions with 1.0 weight percent NNPD, and for standard conditions with no copper.

copper catalyst, but at the same time activate an otherwise inactive catalytic metal. The net effect would be better than the NNPD no-copper trial but worse than the no-copper only trial as shown in Figure 14.

The favorable performance of NNPD in the SAE 40 commercial/safflower oil mixture seems to insure its use in any final additive formulation. However, it was desirable to find additives with other antioxidant characteristics and thus, replace ZDTC/ZDTP. The viscosity rise data of the octadecylamine trial of Run 16 provides some insight to perhaps guide the choice of future antioxidants. This curve along with the standard case trial (dotted line) is given in Figure 15. The ODA curve is similar to the standard case up to about 200 cSt but rises distinctly slower thereafter. Based on TBN response it was suspected earlier that ODA may be evaporating or thermally unstable.

Working on the premise that amines can, in theory, act as chain breaking agents and also maintain TBN at elevated levels if volatility and thermal stability are not problems, a second amine was tested. This compound, p-p'-dioctyldiphenylamine (PDDA), was originally tested by Dutta in a SAE 30 base stock/sunflower oil mixture [13]. It was judged ineffective and thus not originally considered a candidate for testing in SAE 40 lubrication oils.

This antioxidant can be used in a variety of petroleum lubricants where an ashless oxidation inhibitor of good high

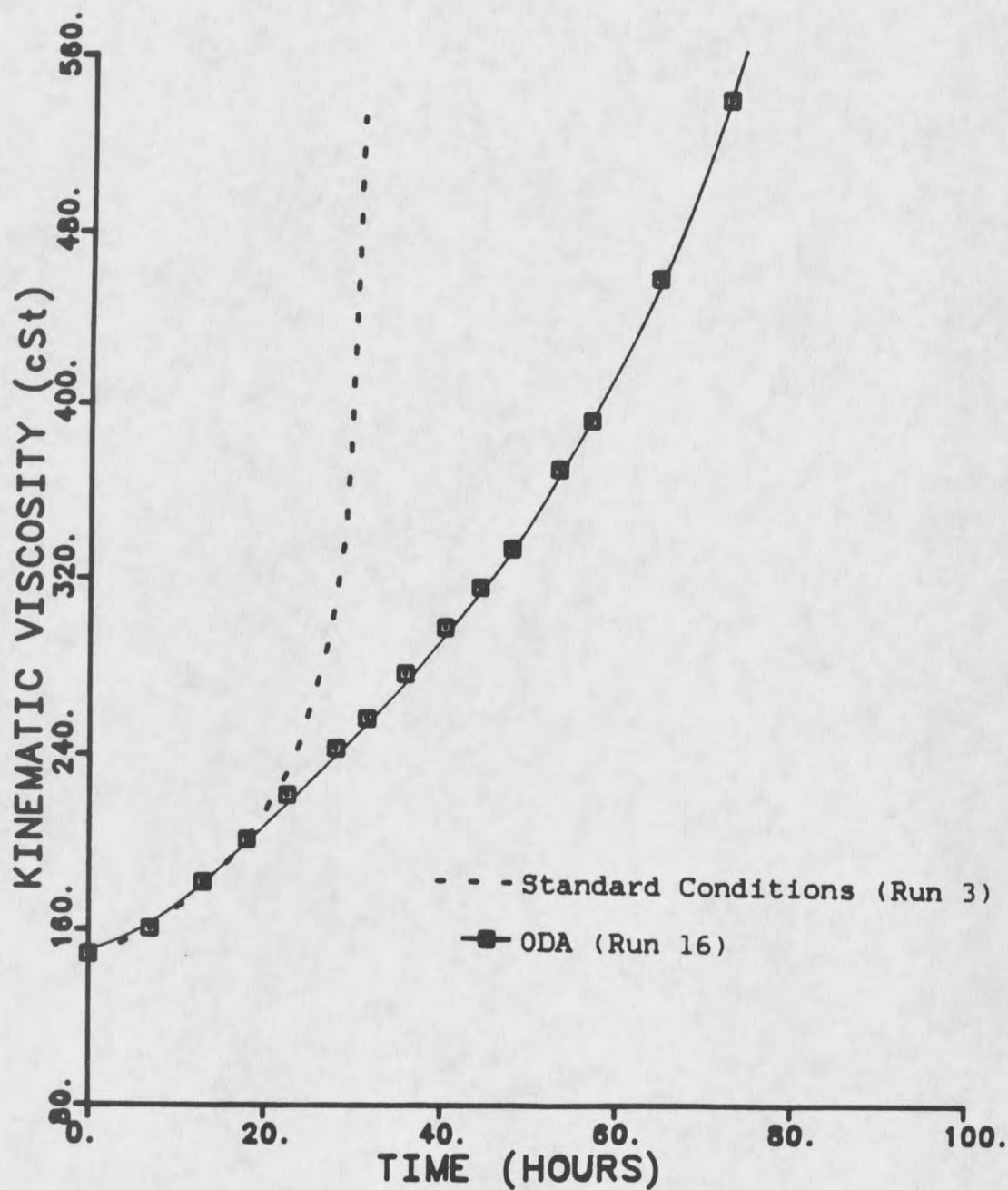
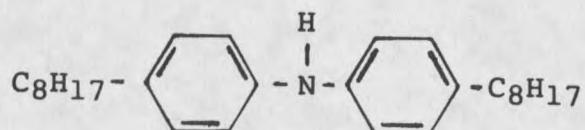


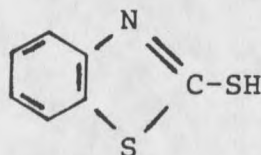
Figure 15. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with periodic additions of ODA.

temperature stability is needed [48]. Also, due to its higher molecular weight, volatility should be lower than ODA. Chemically PDDA has the following structure [48]:



Suggested levels of PDDA concentration range from 0.5 to 2.0 weight percent [48]. A standard 5.0% safflower/commercial oil exposure, where 1.0 weight percent PDDA was added at the onset of the trial, was employed to test this additive (Run 24). An immediate boost in TBN was seen versus the control case, but TBN fell as if no additive were present. Furthermore, as shown in Figure 16, viscosity rise was slightly faster than the control case. It was concluded that this compound was not effective in the present system.

At this time in the research another purported metal deactivator became available. This compound, 2-mercapto-benzothiazole (MBT) is used as a corrosion inhibitor, metal deactivator, and as an extreme pressure inhibitor [48]. Chemically, MBT has the following structure:



Having both an amine as well as sulfur-containing functionality, it was surmised that this compound may also be an effective oxidation inhibitor of either the chain breaking

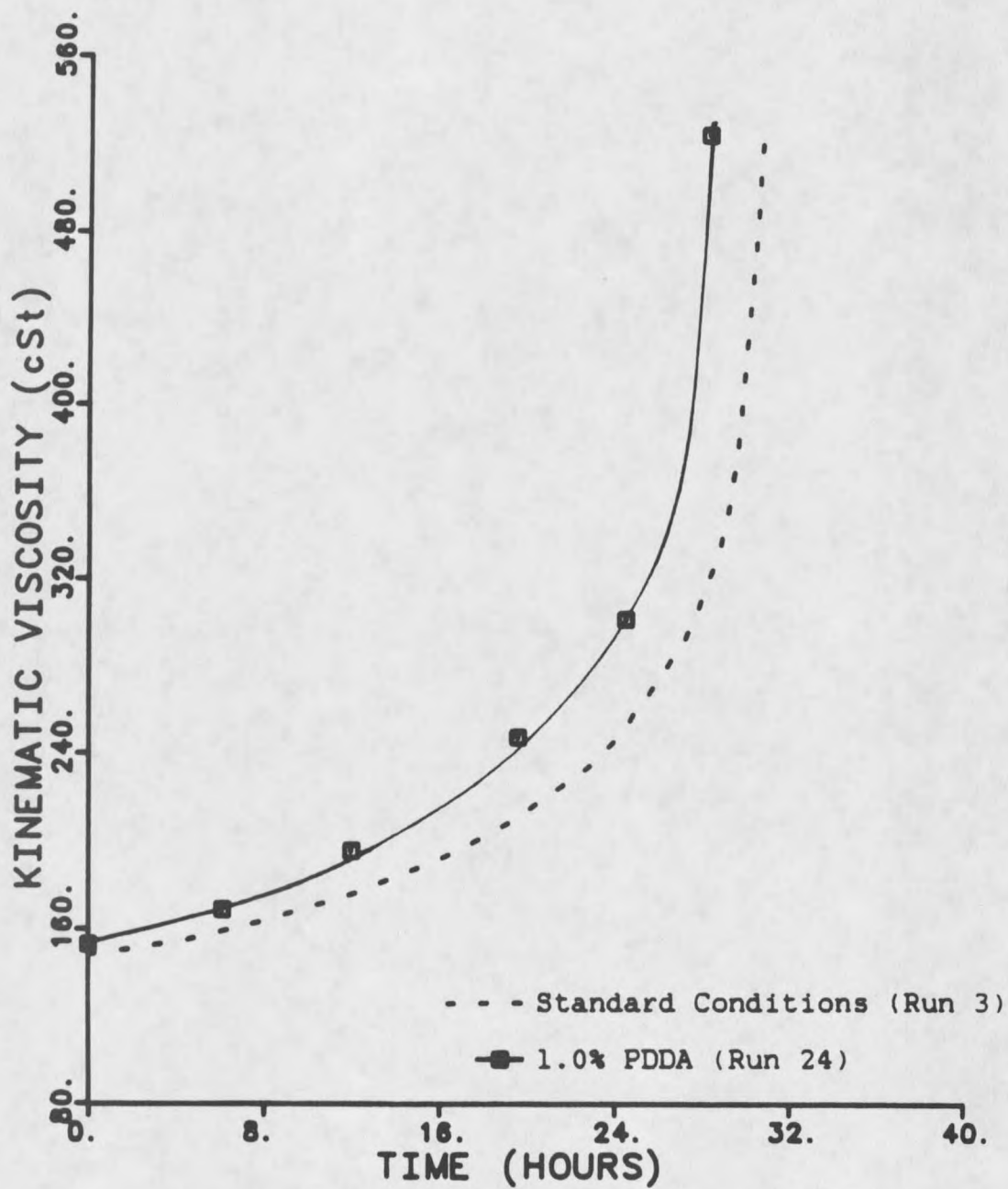


Figure 16. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 1.0 weight percent PDDA.

or peroxide decomposing type. Thus, the incentive for testing this additive was that it may possess several anti-oxidant characteristics.

Level of concentration for this compound is recommended between 0.0002 and 0.25 weight percent [48]. Run 25 was conducted with 0.25 weight percent in an otherwise standard commercial oil mixture. As shown in Figure 17, by 28 hours exposure time the viscosity had exceeded 500 cSt, a situation slightly worse than that of the control case. As with PDDA, this compound accelerated rate of viscosity rise. Whether additive interaction is involved in these two trials is unknown. In any case, it was concluded that MTB showed no prospect as a replacement for NNPD.

Zinc Catalysis Study

In an attempt to explain why ZDTC and ZDTP failed to show any antioxidant efficacy, zinc was suspected as a polymerization catalyst. A review of the literature revealed that zinc can be a polymerization catalyst, usually of the promoter catalyst type. These catalysts are thought to function by arranging disperse phase polymers into a coherent film or by aiding in the mobility of the participating catalysts, in this case copper.

To test this hypothesis a soluble zinc compound was sought which would yield results similar to those of ZDTC

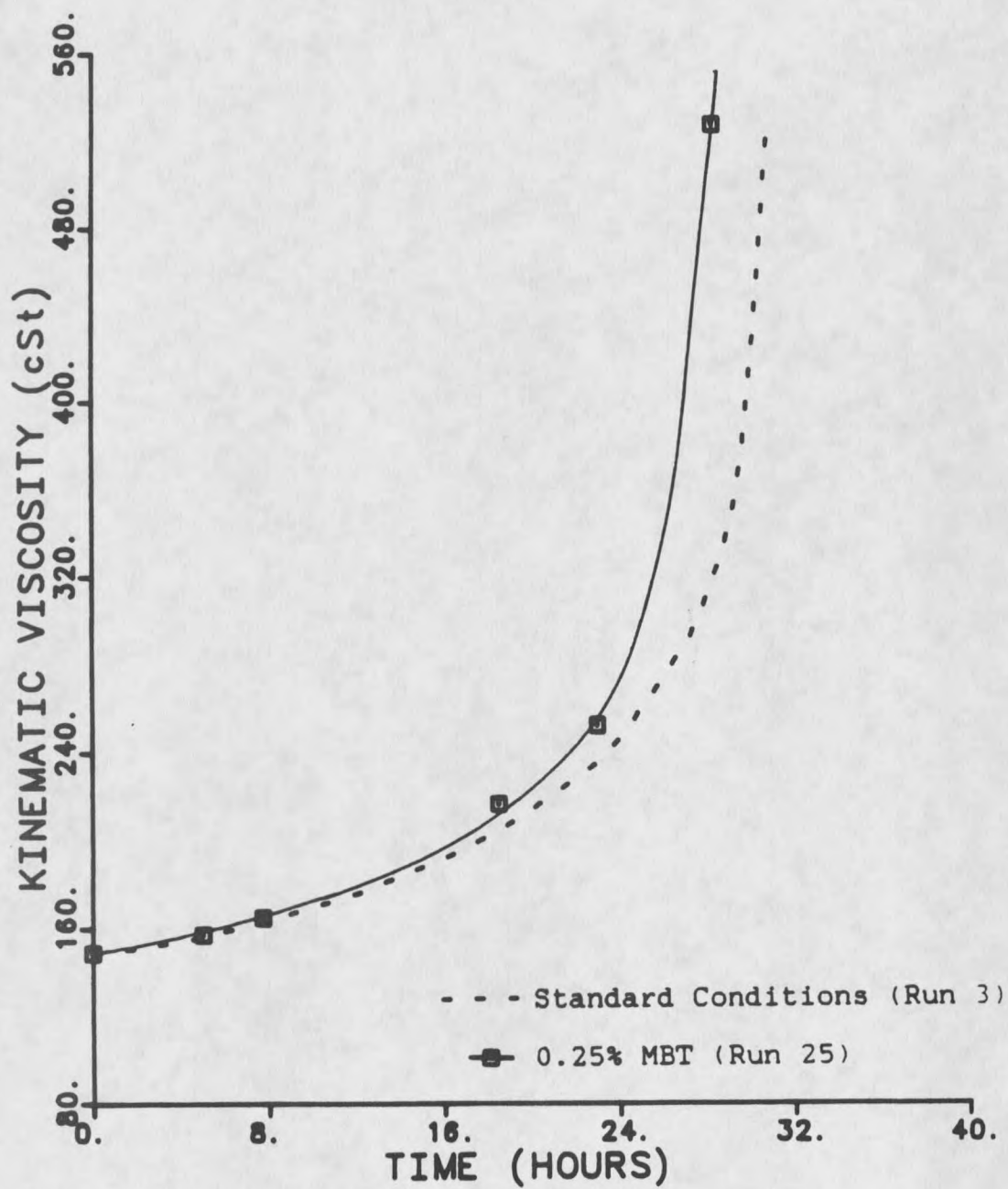


Figure 17. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 0.25 weight percent MBT.

and ZDTP. Introduction of soluble copper via CuAcAc had been successful and hence a similar compound, zinc acetylacetonate (ZnAcAc), was acquired. Chemically, this compound has the following structure:

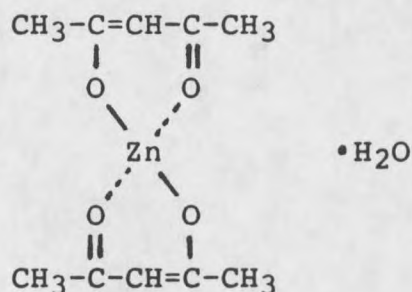


Figure 18 gives viscosity rise curves for several levels of ZnAcAc. In one trial (Run 26) 615 ppm zinc via ZnAcAc was added to a standard SAE 40 commercial/safflower oil mixture. Also given in Figure 18 are curves for the standard control (dotted line) and for 1.0% ZDTC (dash-dot line). As shown, the 615 ppm zinc curve falls roughly half way between the control and 1.0% ZDTC curves. This was somewhat surprising since quantity of zinc at 615 ppm is roughly the same as that at 1.0% ZDTC. However, at the onset of the experiment, dissolution and mixing-in of ZnAcAc had been difficult (preheating the oil mixture was required) and therefore it may be that not all of the ZnAcAc dissolved. The experiment was repeated using 1230 ppm zinc via ZnAcAc (Run 27). As before, dissolution problems were initially encountered. Also in Figure 18, this level of ZnAcAc is seen to yield a sharper curve that is very similar to the 1.0% ZDTC curve. Disregarding the discrepancies

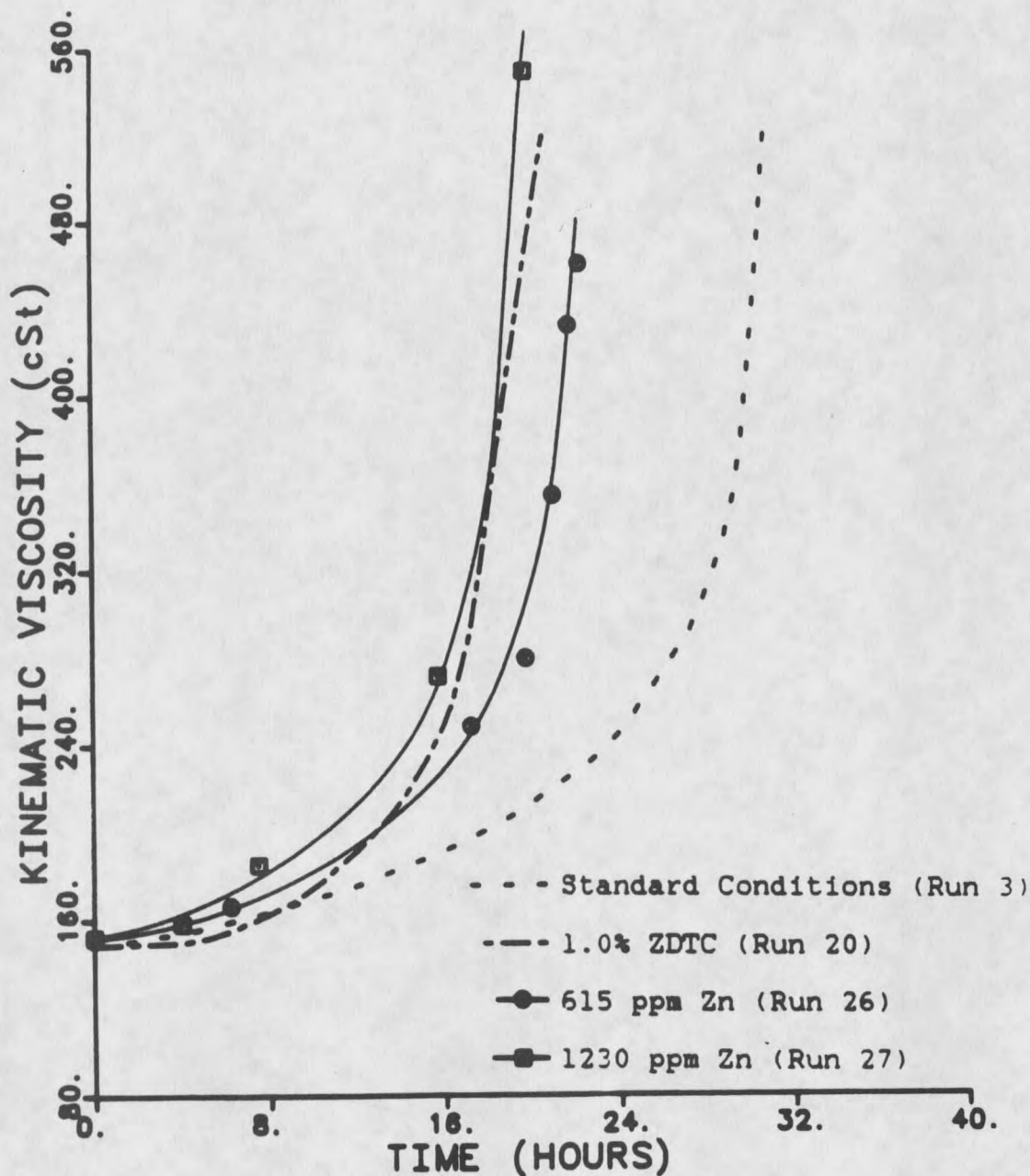


Figure 18. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with varying levels of ZnAcAc and for standard conditions with 1.0 weight percent ZDTC.

between zinc via ZDTC and zinc via ZnAcAc, there exists a definite trend that as the amount of dissolved zinc increases the rate of viscosity rise also increases. This result supports the zinc catalyst concept.

To further test the participator/promoter catalyst hypothesis, both ZDTC and ZnAcAc were reevaluated except no copper was present. Viscosity rise curves are given in Figure 19 for 1.0 weight percent ZDTC (Run 28) and 1230 ppm zinc via ZnAcAc (Run 29). Also shown are curves for standard conditions (dashed line) and the no-copper trial (dash-dot). It is seen that ZDTC speeds viscosity rise slightly faster than that of the no-copper case indicating perhaps some zinc catalysis. However, the viscosity rise for the ZnAcAc trial (which contains twice the zinc of Run 28) is clearly slower than that of the no copper case. A plausible explanation is that ZDTC may be interacting with commercial oil additives and hindering their efficacy. In any case, these results lead to the conclusion that zinc requires copper as an adjunct before it displays a catalytic role.

At this point it was suspected that an additional element(s) or compound(s) was involved in the Cu-Zn catalysis. Recall that base stock experiments with zinc compounds did not show any catalytic action. To test this hypotheses, 1230 ppm zinc via ZnAcAc was evaluated in a standard SAE 40 base stock/safflower oil mixture (Run 30).

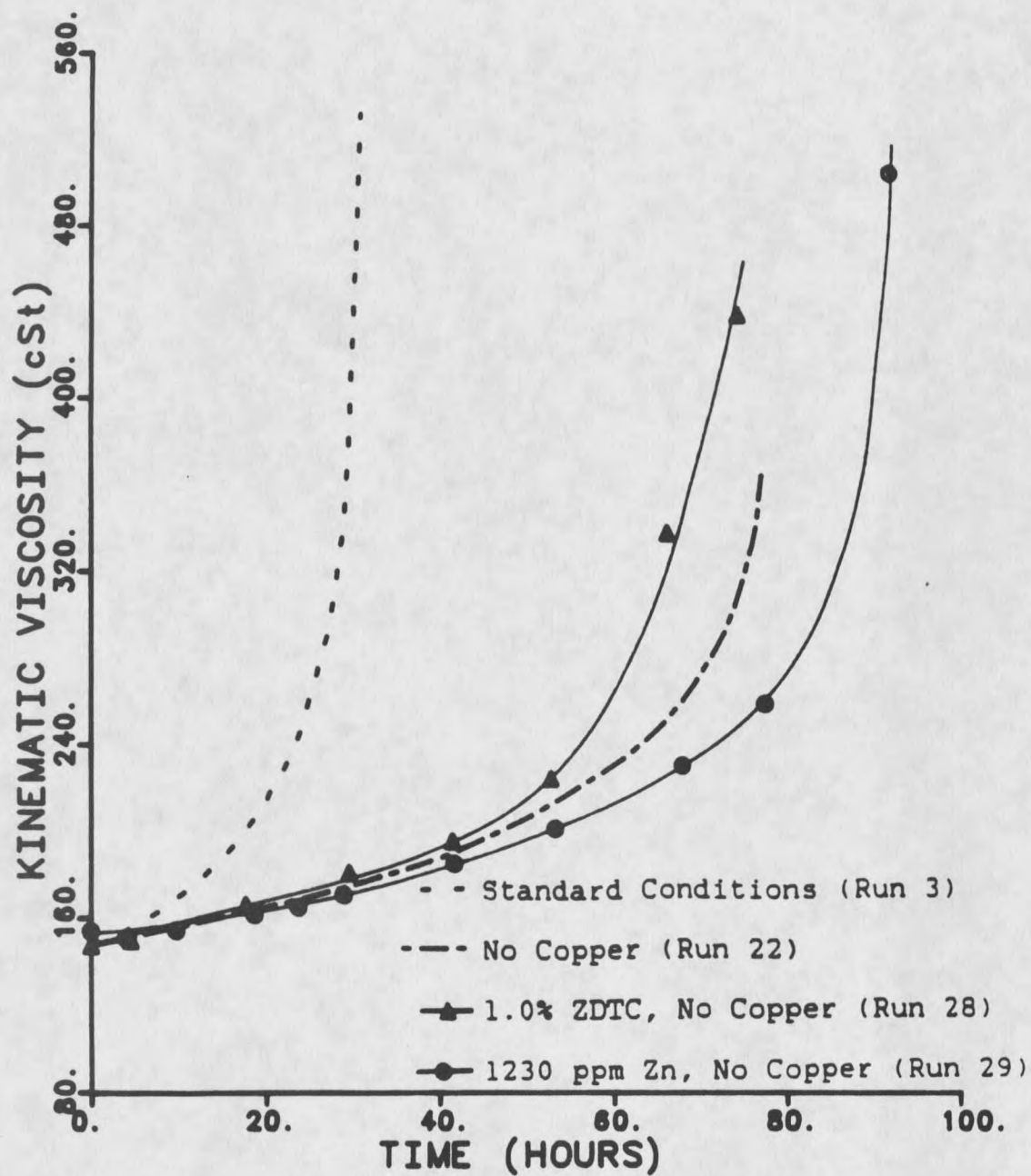
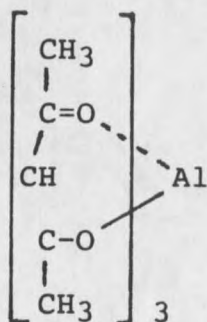


Figure 19. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for 1.0 weight percent ZDTC with no copper, for standard conditions with no copper, and for 1230 ppm zinc from ZnAcAc with no copper.

Rate of solids formation was slower than that of the standard control trial and heavy solids formation was noted at 7.5 hours exposure time. The results clearly indicate lack of any catalytic activity and, in fact, were just the opposite. Perhaps as suggested by Howard et al, zinc may provide a metal center at which some type of antioxidation is taking place [38]. Whether this is the case or not, the results seem to confirm that Cu-Zn catalysis requires an additional component(s).

At this point in the research it was desirable to show that the acetylacetonate of ZnAcAc and the carbamate of ZDTC were not antagonistically interacting with mixture components. Therefore, similar compounds with different cations were acquired to check for interaction.

First, the compound aluminum acetylacetonate (AlAcAc) was evaluated at 1230 ppm aluminum in an otherwise standard commercial SAE 40/safflower oil mixture (Run 31). This compound, similar to CuAcAc and ZnAcAc, has the following structure:



Acetylacetonates with alkaline earth/alkali cations were sought but not readily available. This is unfortunate as

aluminum has been known to act as a promoter catalyst [22]. Figure 20 gives the viscosity rise curve for AlAcAc as well as that for the standard control (dotted line) and that for 1230 ppm ZnAcAc (dash-dot). It is seen that AlAcAc speeds viscosity rise yielding a curve that is very similar to that of ZnAcAc. Whether this is due to aluminum or the acetylacetonate is not known. However, because of valence as well as molecular weight differences between the two compounds, more than three times as much acetylacetonate was introduced via AlAcAc than by ZnAcAc. If the acetylacetonate were to show any catalysis, one might expect the AlAcAc viscosity curve to rise faster.

The results of this experiment alone are not conclusive. However, Burn found that while ferric acetylacetonate was pro-oxidant in effect in indene, it had a negligible effect on the rate of oxidation of cumene [37]. Furthermore, when one considers in addition the fact that cupric acetylacetonate reacts much like metallic copper, then it seems reasonable to conclude that little if any additive interaction, or catalysis for that matter, was exhibited from the acetylacetonates of CuAcAc, ZnAcAc, and AlAcAc. In addition, the results of this run indicate that soluble aluminum has a significant catalytic impact on polymerization in this system.

Having concluded that the acetylacetonate functionalities were most likely not involved in catalysis, several

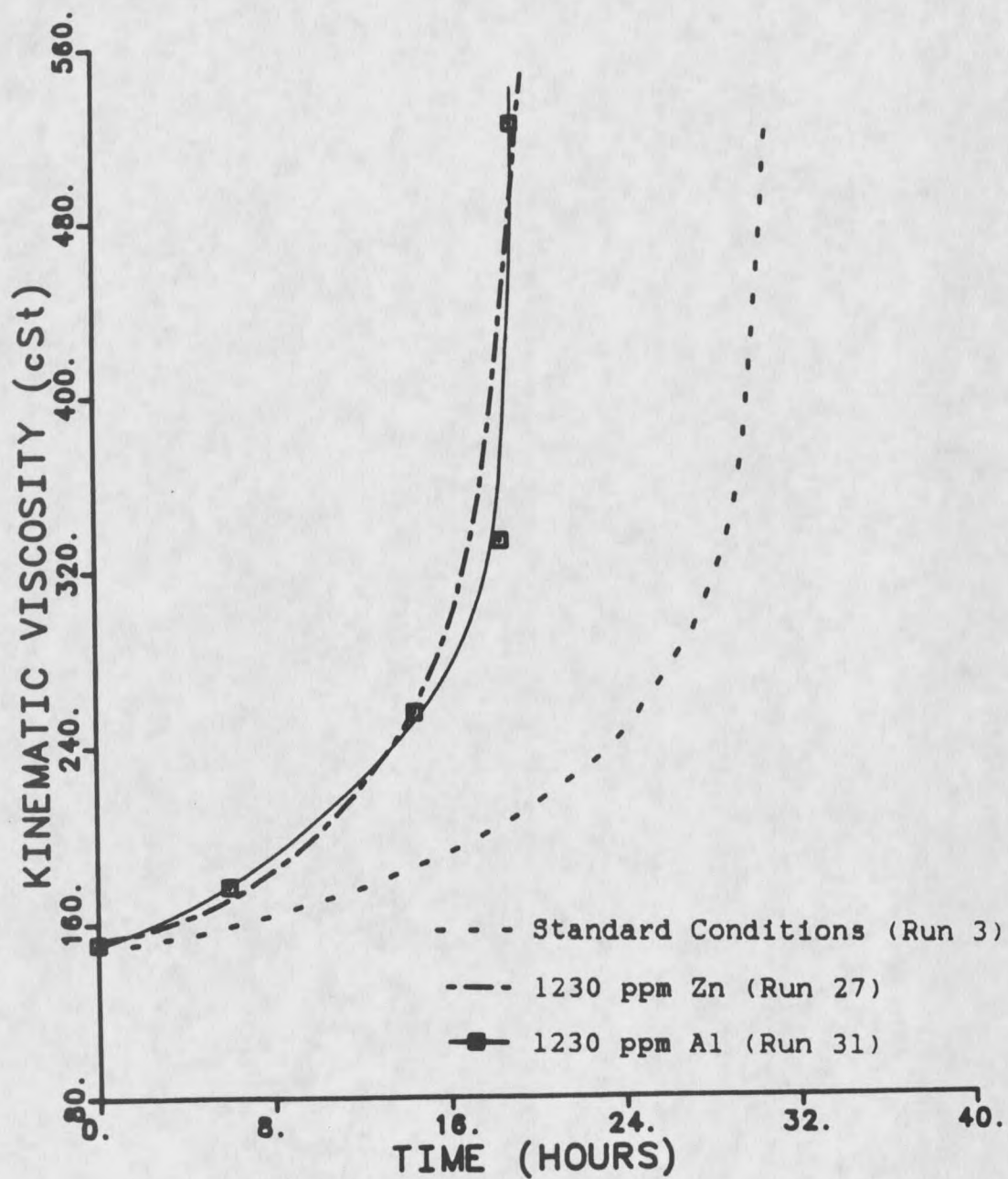
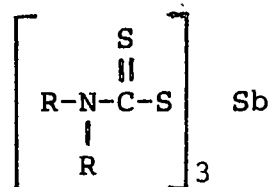


Figure 20. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with AlAcAc and for standard conditions with ZnAcAc.

compounds with carbamate functionalities were sought to test for its (carbamate) role in polymerization. Actually, reasons for seeking these compounds were two-fold. These compounds were also sought to test for their efficacy as antioxidants.

The first of these additives to be tested was antimony dialkyldithiocarbamate (SbDTC). Chemically this compound has the following structure [48]:



This compound, soluble in petroleum and synthetic lubricant bases is reported by the manufacturer as one of the most versatile of the dithiocarbamate additives. It is generally used as an antioxidant, antiwear agent, and extreme pressure additive. Recommended concentration levels are 0.1 to 1.0 weight percent [48].

Figure 21 gives viscosity rise against time for a standard 5.0% safflower exposure where 1.0 weight percent SbDTC was added at the onset of the trial (Run 32). Also shown are curves for the standard case exposure (dotted line) and that for 1.0% ZDTC (dash-dot line). The viscosity rise curve for SbDTC is seen to fall directly between that of the standard case and that for ZDTC. It may be that antimony, like zinc and perhaps aluminum, may be some type

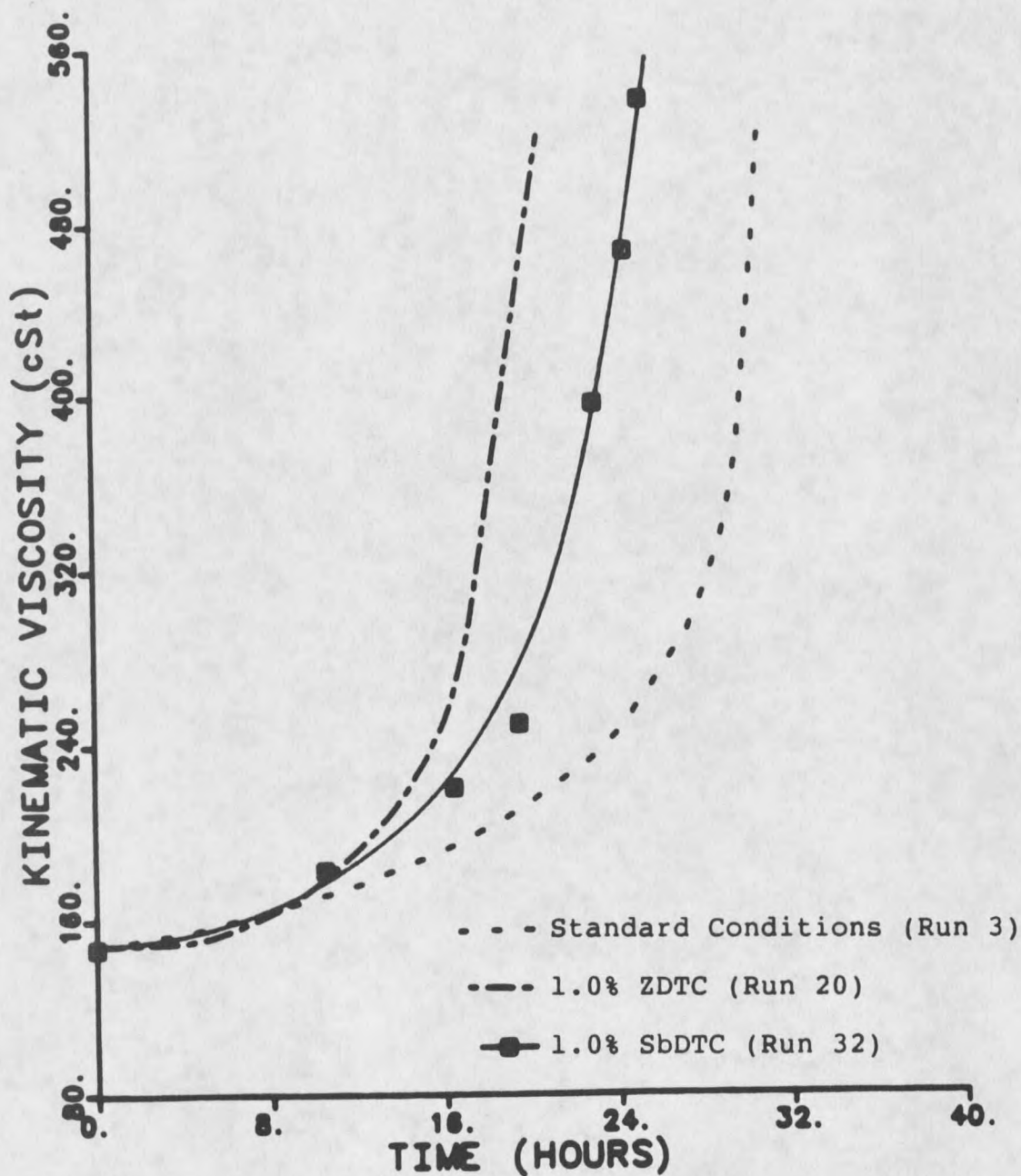
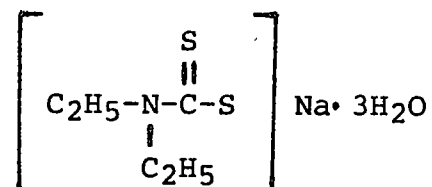


Figure 21. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 1.0 weight percent SbDTC and for standard conditions with 1.0 weight percent ZDTC.

of catalyst. On the other hand, it may be that interaction between the carbamate and other additives may be taking place.

The second carbamate trial involved the compound sodium diethyldithiocarbamate (NaDTC).



This compound, structurally similar to the other carbamates, exists as a trihydrate. Whether or not it is used commercially in the lubricant industry is unknown. The literature does indicate, however, that NaDTC has been known to deactivate copper [16].

Figure 22 presents viscosity rise data for a standard case exposure where 615 ppm sodium via NaDTC was added at the trial onset (Run 33). It is seen that this curve is similar to the standard control case (dotted line) with perhaps slightly better performance. This result indicates that 1) the carbamate, and mostly likely the phosphate, functionality does not seem to be an antagonist and 2) antioxidants of the ZDTC and ZDTP type based on other cations may have potential as effective antioxidants. Also, this run tends to confirm that the antimony of Run 32 had a catalytic impact on polymerization of the commercial oil mixture.

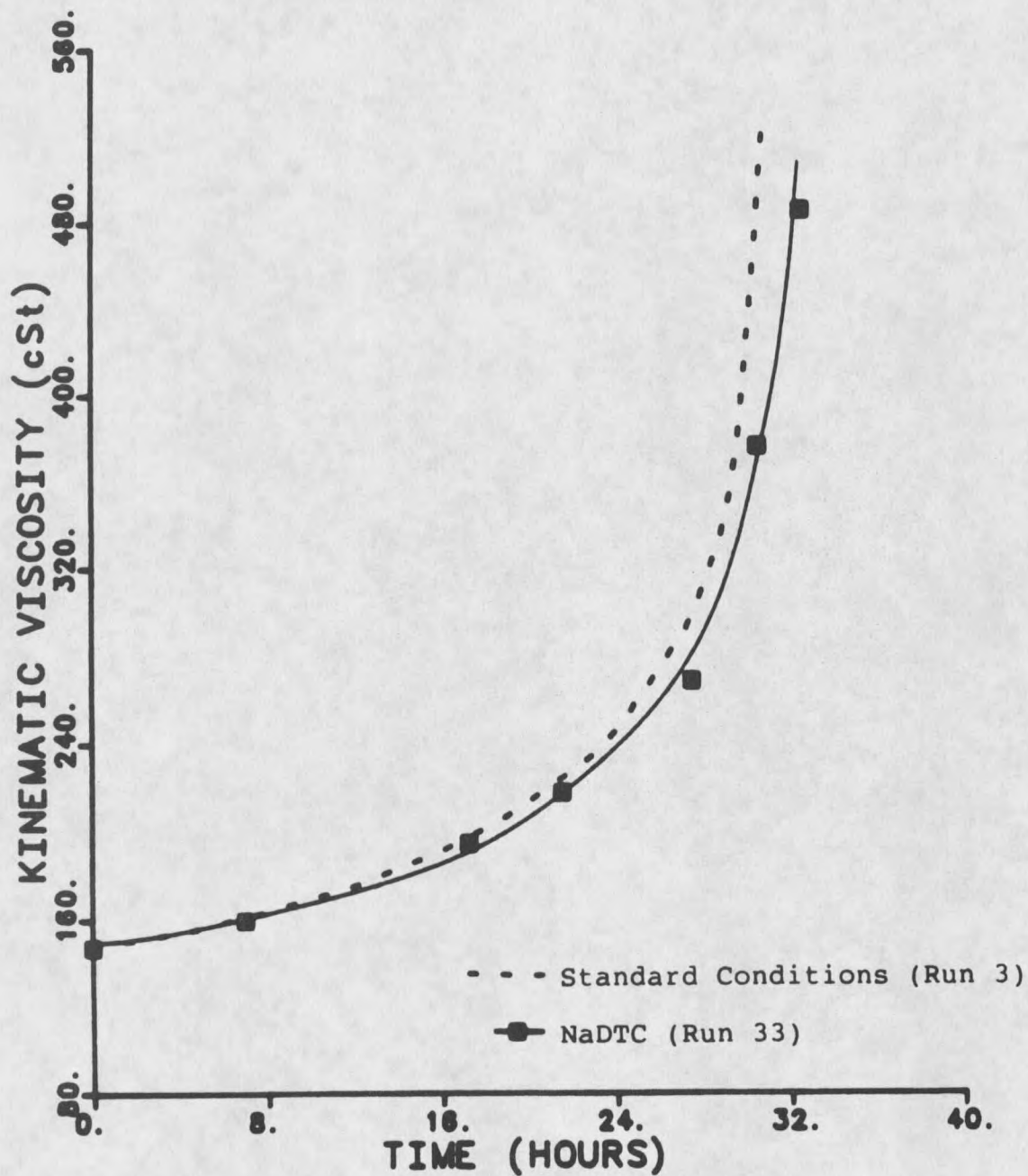


Figure 22. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with NaDTC.

Commercial Oil: Additive
Interaction Study

Recall that the effectiveness of ZDTC was reportedly due to its decomposition products rather than the zinc salt itself [47]. Perhaps ZDTC would be effective if the zinc could be tied up, allowing decomposition products to inhibit oxidation. To test this theory, 1.0 weight percent ZDTC was combined with 1.0 weight percent NNPD, in an otherwise standard case exposure (Run 34). This same combination in base stock gave performance slightly worse than that of NNPD alone. However, base stock lacks the additives of commercial oil, e.g. detergents and dispersants, which may mix synergistically with the ZDTC/NNPD combination in the commercial oil mixture. The viscosity rise curve for the present run as well as those for the standard case (dotted line) and 1.0 weight percent NNPD (dash-dot) are given in Figure 23. The curve for the combined additives is seen to fall between the control and NNPD curves. Whether the components of ZDTC are complexing with NNPD or simply hindering its ability to sequester copper is unknown. In any case, the NNPD does not appear to be able to completely overcome the catalytic impact of zinc.

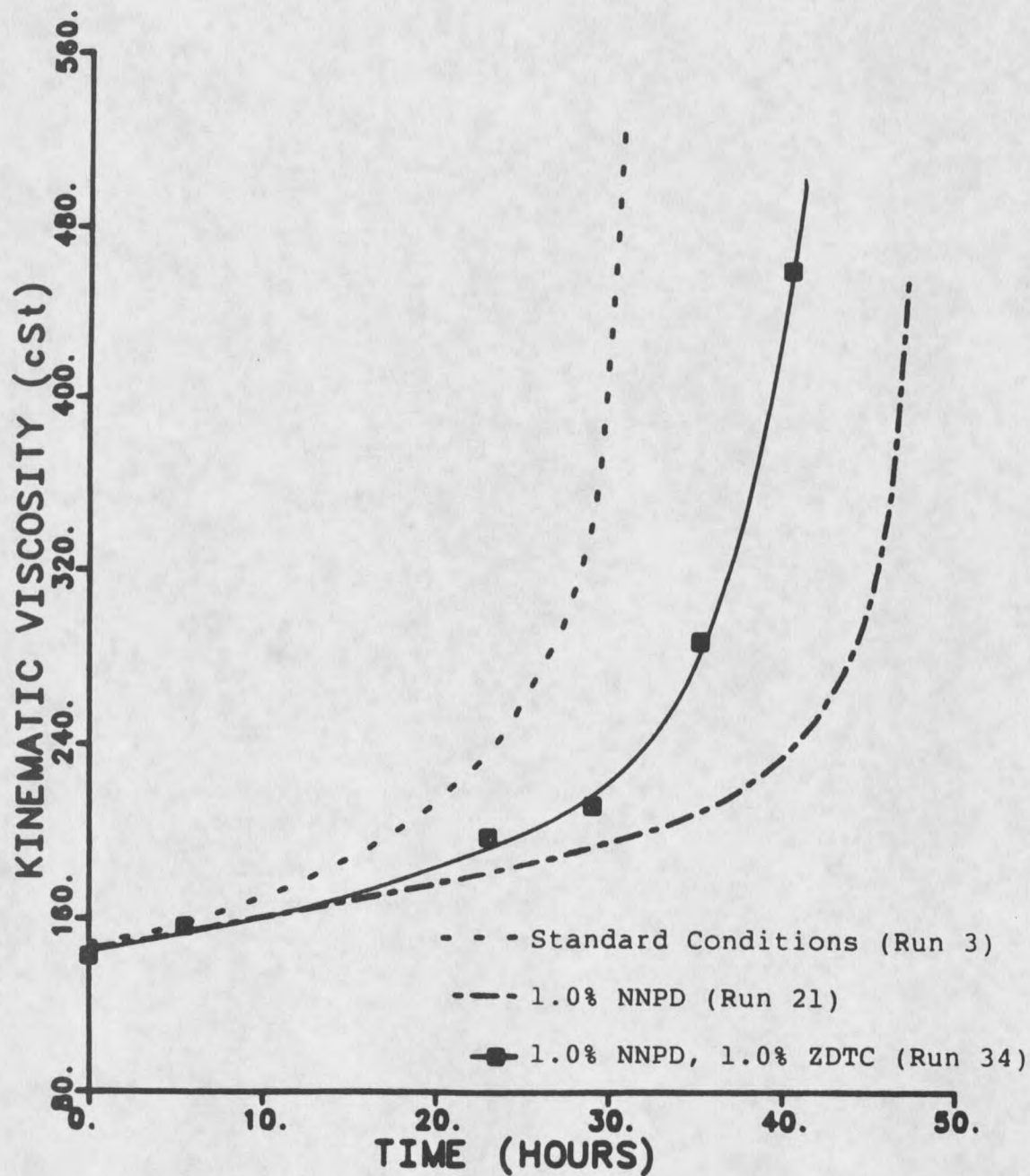


Figure 23. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with 1.0 weight percent ZDTC and 1.0 weight percent NNPD and for standard conditions with 1.0 weight percent NNPD.

Commercial Oil: Final Formulation

Of the variety of additives analyzed for alkalinity maintenance and antioxidant efficacy, two compounds appear to be likely candidates for any final additive formulation. These compounds are the overbased calcium phenate (OCP), for alkalinity maintenance, and the antioxidant NNPD. Not mentioned previously is that OCP may yield an added benefit. Figure 24 presents the viscosity rise curve for the OCP trial reported earlier (Run 17). Again, the dotted line is a standard run result. As shown, there appears to be a retarding effect on polymerization just as that seen with ODA (Run 16).

A final experiment was conducted to test a final formulation of OCP and NNPD. Since antioxidants are consumed over the life of an experiment, additions of 0.25 weight percent NNPD were added to an otherwise standard commercial/safflower oil mixture approximately every five hours beginning at zero exposure time. Additions of OCP were also made every five hours beginning at five hours exposure time. Figure 25 gives viscosity rise curves for Run 35 along with the standard control (dotted line) and that for 1.0 weight percent NNPD (dash-dot line). There are several key points of interest in Figure 25. First, although the combined trial of Run 35 appears to rise faster at first, it eventually intersects that of NNPD alone.

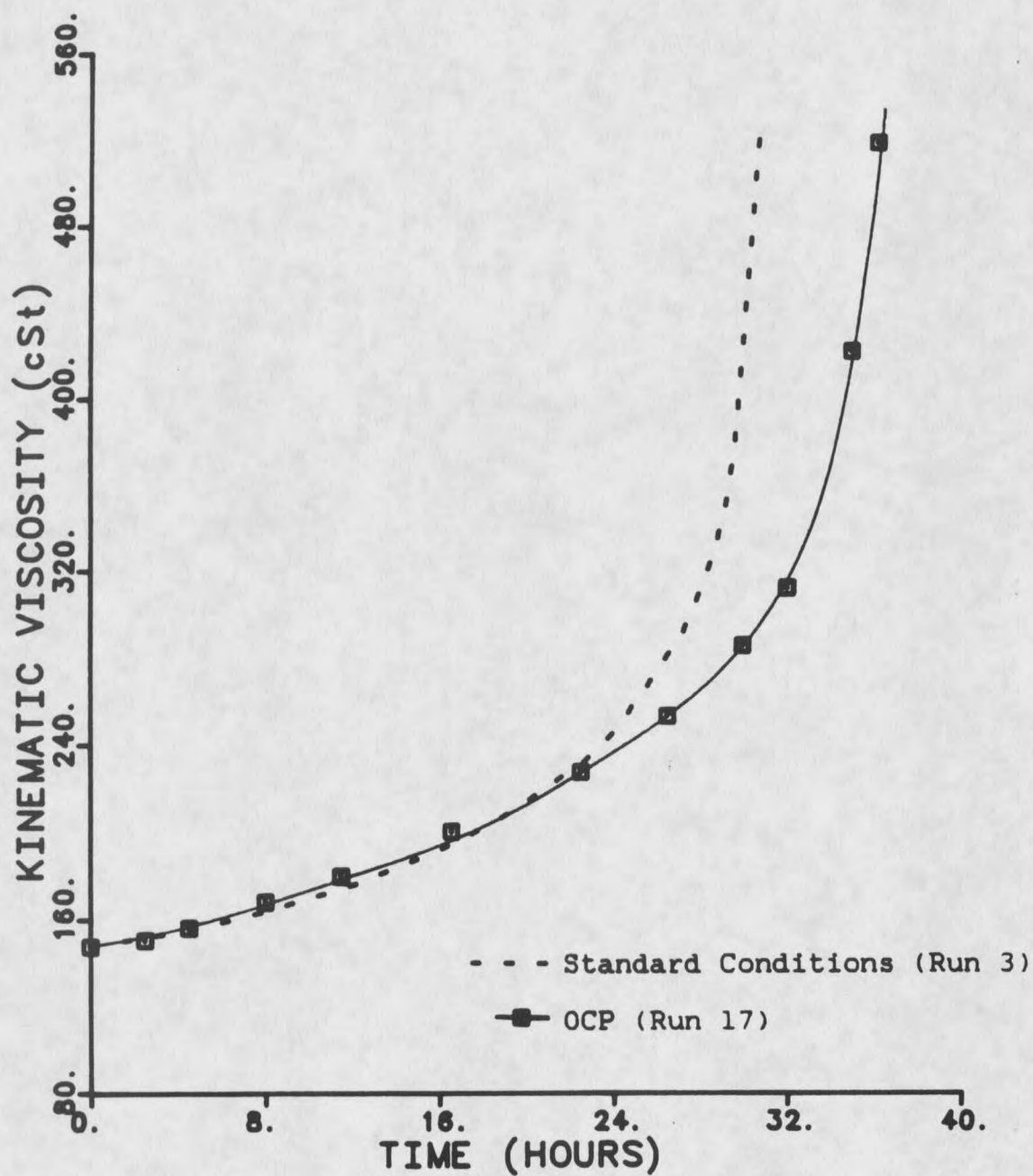


Figure 24. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with periodic additions of OCP.

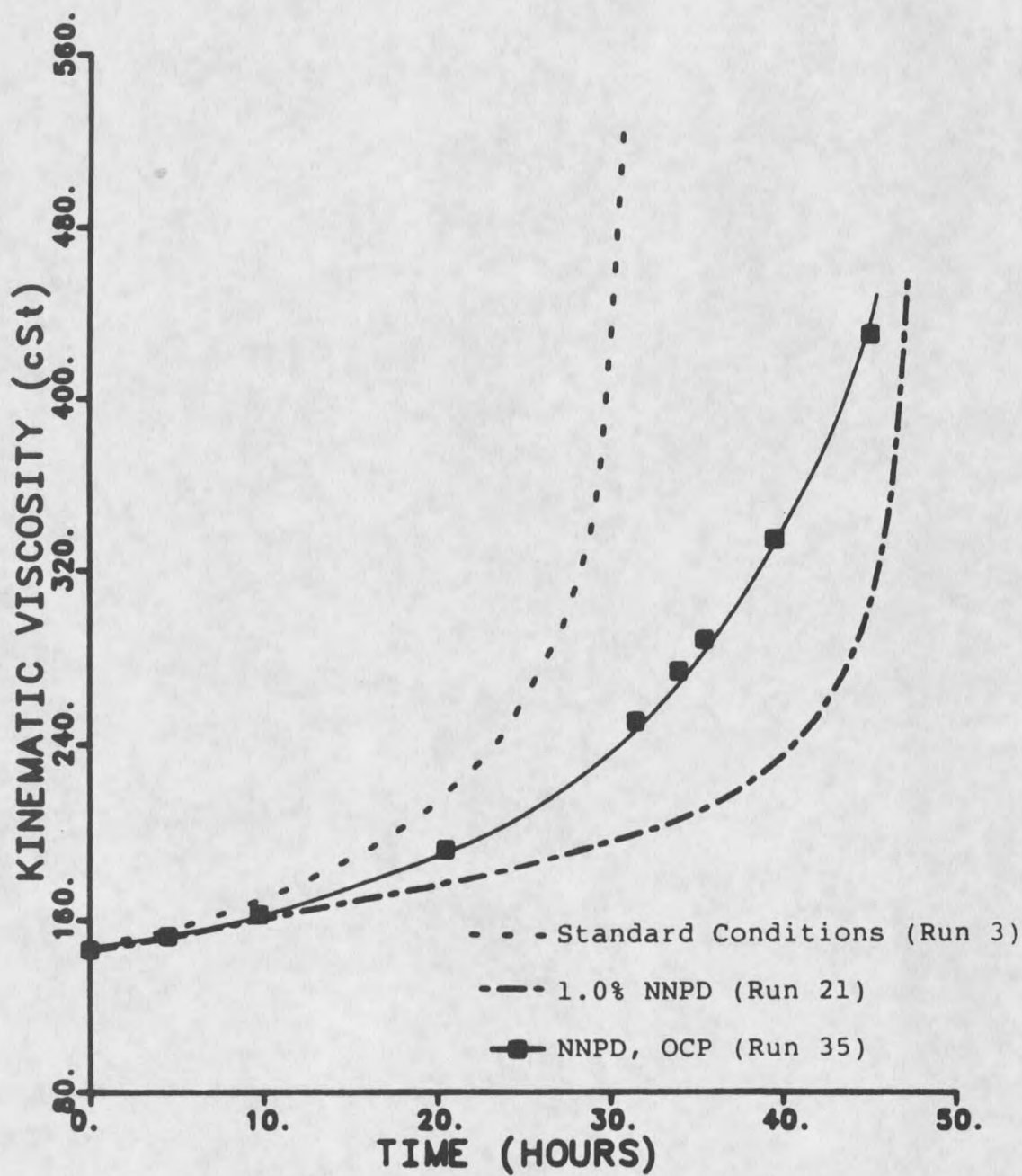


Figure 25. Kinematic viscosity of commercial/safflower oil mixture versus exposure time for standard conditions with periodic additions of NNPD and OCP and for standard conditions with 1.0 weight percent NNPD.

This result tends to indicate that antagonistic interaction between NNPD and OCP does not exist. Second, and more significant, the trial with 1.0% NNPD added initially appears to perform better than frequent additions of small percentages of NNPD. This indicates that the beneficial action of NNPD occurs early on in the experiment, apparently when NNPD is chelating metals important in the initiation of addition polymerization.

Figure 26 gives the TBN decline curve for Run 35 as well as that of the standard case exposure (dotted line). As shown TBN was easily maintained and in fact, remained high after OCP additions ceased. Of primary significance is that OCP appears to work effectively in the presence of NNPD and vice versa. The final formulation, while effective, requires fine tuning in order to achieve an optimum package. However, this work is left to future research.

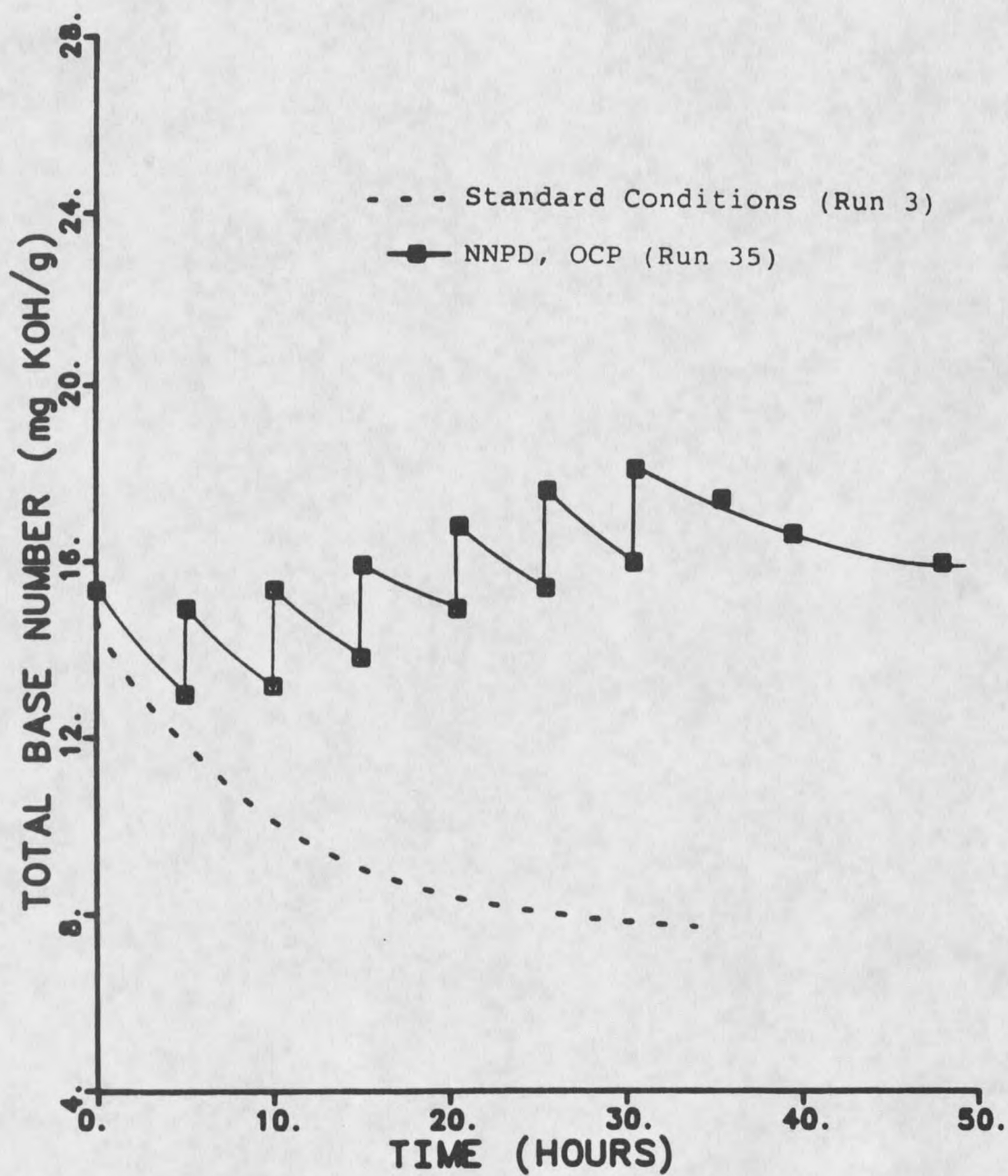


Figure 26. Total base number of commercial/safflower oil mixture versus exposure time for standard conditions with periodic additions of NNPD and OCP.

CONCLUSIONS

1. Research demonstrated that a commercially available metal deactivator and an alkalinity maintenance additive can be combined to effectively delay viscosity rise and suppress alkalinity decline. These compounds, NNPD and OCP, are strong candidates for inclusion in any commercial lube oil to be used with plant oil fuel.
2. Carbamate and phosphate salts of dithio acids based on zinc, antimony, and aluminum cations appear to be incompatible with SAE 40 commercial/safflower oil mixtures due to promotion catalysis by these cations. Other carbamates and phosphates based upon alkali/alkaline earth cations remain as potential antioxidant candidates.
3. Promotion catalysis involving copper and one or more other wear metals poses a major obstacle to inhibition additive development for lubrication/plant oil mixtures. Catalysis at trace metal concentrations poses a special obstacle.

4. The metal deactivator NNPD appears to retard viscosity rise by chelating wear metal catalysts. This beneficial inhibition by NNPD seems to be prominent during the initiation phase of the free radical addition polymerization mechanism.
5. Amines, even as high molecular weight species, have little or no potential as longer term alkalinity maintenance additives for lubrication/plant oil mixtures.
6. Viscosity and alkalinity responses of SAE 40/safflower oil mixtures are generally similar to SAE 30/sunflower oil results of prior research. Thus, prior research results are a useful guide for continuing studies.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Carbamate and phosphate salts of dithio acids based on alkaline earth/alkali cations should be sought and tested for antioxidant efficacy. Future work should avoid transition metal cations which seem to have significant catalytic activity in this system.
2. All metals known to exist at even trace levels in used locomotive lube oil should be screened for catalytic impact on polymerization of lubrication/vegetable oil components. Those found to be catalytically active should be dealt with in the final additive formulation.
3. Dissolution of soluble metal species from metallic foils may be rate limiting. Metals being screened for catalysis should be introduced in a soluble form such as acetylacetonates or naphthenates.
4. Amine/phenol antioxidant combinations should be tested for efficacy. These types of combinations have at times been not only effective but also synergistic [51].

5. The relationship between antioxidant efficacy and alkalinity should be studied. Future work may show that the beneficial action of some antioxidants is nullified in the presence of alkaline compounds.
6. Additive packages should be developed using an optimization technique such as a sequential simplex method [52]. Numerous variables will need to be examined including additive concentrations as well as economic feasibility.

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APPENDIX

TABLE 4. Metal Content Analysis of Used Locomotive Oil [8]
and Burlington Northern's Limits for Trace Metal
Concentrations (parts per million) [46].

<u>Metal</u>	<u>EMD Model</u>	<u>G.E. Model</u>	<u>Maximum Concentration</u>
Aluminum	2.1	----	20
Chromium	5.8	----	80
Copper	17.	17.7	150
Iron	14.6	17.4	60
Lead	7.6	5.6	125
Silver	0.5	----	4
Zinc	3.	----	25

$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$

[illegible][illegible][illegible]
$$\frac{1}{2} \left(\frac{1}{2} \right)^n = \frac{1}{2^{n+1}} = \frac{1}{2^{n+1}} \cdot \frac{1}{2^{n+1}} = \frac{1}{2^{2n+2}} = \frac{1}{2^{2(n+1)}} = \frac{1}{2^{2n+2}}$$

$\frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}{4}$

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1994 1995 1996 1997 1998

[illegible]

Figure 1. The effect of the concentration of the *Agrobacterium* suspension on the transformation efficiency of *Agrobacterium* strains.

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