Vegetable oil dilution of diesel engine lubricating oil
by Chance Rewolinski

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

Abstract:
The lubricating oil environment of a diesel engine operated on vegetable oil fuel was simulated on a laboratory scale to study effects of system parameters on lubricating oil degradation, primarily excessive viscosity increase.

Initial parameters investigated for effect on viscosity increase were temperature, vegetable oil dilution level, catalyst level, and gas flow rate. Viscosity increased more rapidly for higher temperature and higher concentration of vegetable oil. Higher catalyst level accelerated the rate of viscosity increase, with copper showing a much higher catalytic activity than iron. Oxygen was required to obtain a viscosity increase, with higher oxygen flow rates slightly increasing rate of viscosity rise.

Mechanisms of acid and free radical catalysis of polymerization yielding viscosity increase were investigated. Relationship of amount of free acids in the oil to increase in viscosity was investigated by measuring total base number of contaminated lubricating oil. Amount of free acid was varied by addition of phosphoric acid, octadecylamine, and a commercial lubricating oil total base number enhancer. None of these approaches had any significant effect on viscosity increase, indicating that drop in total base number and viscosity increase are not causally related.

Free radical catalysis was investigated by periodic additions of a commercial free radical polymerization initiator to samples of contaminated lubricating oil. Viscosity response from this additive was similar in form and magnitude to that from oxygen, indicating that viscosity increase of contaminated lubricating oil is due to a free radical mechanism.

A single sulfur compound was employed to limit the copper catalyst action by poisoning. A single chelating agent was used to sequester and limit the action of solubilized catalyst. Neither of these approaches reduced the viscosity increase of contaminated lubricating oil.

Degraded lubricating oil samples were tested for lubricity by use of a four-ball wear tester. Lubricity of contaminated, degraded lubricating oil was superior in all eases to uncontaminated, degraded lubricating oil.

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Chance Rewolinski

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

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Initial parameters investigated for effect on viscosity increase were temperature, vegetable oil dilution level, catalyst level, and gas flow rate. Viscosity increased more rapidly for higher temperature and higher concentration of vegetable oil. Higher catalyst level accelerated the rate of viscosity increase, with copper showing a much higher catalytic activity than iron. Oxygen was required to obtain a viscosity increase, with higher oxygen flow rates slightly increasing rate of viscosity rise.

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INTRODUCTION

General Considerations

America has enjoyed easy access to inexpensive, convenient fuels for a number of years. Events of the past decade have upset this pattern by causing uncertainties in the continued steady supply of energy, especially liquid fuels. These uncertainties include foreign control of a large part of current crude oil reserves and the realization that these resources are finite and nonrenewable. These conditions have prompted various researchers and government agencies to look for alternative sources of fuel.

Biomass fuels represent one source of renewable alternate energy. Falling within this broad class are vegetable oils which are candidates for replacing diesel fuel. They were among the first fuels used by Rudolph Diesel in his original engine around the turn of the century, and were later used in a farm demonstration by the Ford Motor Corporation at the 1934 World's Fair in Chicago [1]. Compared with other alternate fuels they are easy to process and handle. Although they may become replacements for diesel fuel if technical and economic obstacles are overcome, vegetable oils cannot now be produced in sufficient quantities to replace all the diesel fuel currently in use. They could, however, be utilized to ease spot shortages which occur [2].

One location where occurrences of spot shortages would be critical is the farming industry where the timeliness of the fuel supply could determine the farm's success or failure. A number of oilseed crops are currently grown on farms. If the seeds are to be processed for oil, an oil extraction plant is often located within a reasonable distance, so the system is already partially in place to guarantee farmers access to the fuel they need. To maintain this supply about 10 to 15 percent of the cultivated farmland would have to be devoted to this use [2]. This may seem excessive, but in 1919 when the agricultural acreage used to produce feed for horses and mules was at its peak, 22 percent of harvested crop land was used for this "fuel source" [3].

The particular oilseed crop chosen would depend on locale but should have a high oil yield per pound of seed and high crop yield per hectare, and have useful side products. Examples of crops suitable for the north central United States and central Canada include sunflower, canola (or rapeseed) and safflower. Sunflower has the advantage that it may be grown on marginal lands with a minimum use of agricultural chemicals although yield may decrease. It is also suitable for most of the continental United States, e.g., Texas, both coasts, and Montana and North Dakota [4]. When grown with normal cultivation practices, sunflower also has a significantly higher energy output/input ratio than other traditional oilseed crops such as soybeans, peanuts and cottonseed [5].

Economic Considerations

Economic situations also influence acceptance of vegetable oil as a diesel fuel substitute. Currently, diesel fuel is readily available at about half the price of vegetable oil, but this price differential has steadily decreased over the past eight years. If vegetable oils increase in price at the same rate as inflation, and petroleum prices increase at 2 to 3 percent over inflation, then it will be about 20 years until the prices are comparable [5]. This is a difficult prediction to make as many factors are involved. Widespread use of vegetable oil will only come about when the price of diesel fuel and vegetable oil more closely approach each other. This could come about either by the steady increase in cost as oil reserves are depleted, or by emergency shortfalls caused by political reasons.

Technical Problems

While economics provides the driving force for adopting a new fuel source, technical problems must also be overcome. Modern high speed diesel engines currently used in agriculture and transportation have been specifically designed to run on commercially available diesel fuel which is in turn refined to close specifications.

When a new fuel is used in place of the one for which the engine is designed, technical problems abound. Two methods of solution present themselves. One is to modify the engine mechanically (i.e., design the engine for the new fuel). The second is to modify the fuel and method of engine operation without making any design changes in the engine. In the United States the emphasis has been on the latter since the strategy of using vegetable oils is to supplement diesel fuel in times and areas of shortage rather than replacing diesel fuel entirely. Countries with less secure energy sources may choose the former approach. Brazil, for instance, has a national goal of replacing 16 percent of its diesel consumption with vegetable oil by 1985 [6]. Caterpillar has extended their warranty on some engines operating on up to 10 percent vegetable oil, but only in Brazil [2].

The technical problems of using vegetable oil fuels in diesel engines have been known for years. Since there was no economic incentive for their solution in the late 1920s, these problems still exist today. Problems include:

1. Difficulty with cold weather fuel handling, starting and operation. Vegetable oil is more viscous than diesel fuel, causing handling problems at low temperatures. For example, the pour point of sunflower oil is about -9 C, while that of diesel fuel is -18 C [7]. Vegetable oil is also less volatile than diesel fuel so it does not vaporize as readily as diesel fuel in a cold engine. The flash point of diesel fuel is typically about 70 C, while the flash point for vegetable oils is typically about 320 C [5].

2. Plugging and gumming of fuel lines, filters and injectors. In their crude state vegetable oils contain phosphatide gums, waxes and solid fines. Removal of these by refining, including dewaxing, degumming and filtering through a 4 micron filter substantially reduces these problems. Oil is often "alkali refined" where the degumming is done with an alkaline wash to neutralize the corrosive free fatty acids. If the oil were subsequently bleached and deodorized it would meet edible oil specifications [5].

3. Coking of injector nozzles, and carbon deposits and varnish on pistons and heads. This is probably also due to the low volatility of the vegetable oil, combined with the polyunsaturated nature of the vegetable oil. Since the oil does not completely vaporize, even in a warm engine, it coats the lining of the combustion chamber where it is able to polymerize, forming varnish and carbon deposits. Although diesel fuel may also cause deposits in the combustion chamber they are easily displaced during normal engine operation [8]. The deposits from vegetable oil fuels are very persistent. They have been shown to cause catastrophic failure of the engine in as little as 87 hours in a direct injection diesel engine operated on pure vegetable oil [9].

When vegetable oil is used in an indirect injection diesel engine, these deposits are almost eliminated. Some indirect injection engines have been successfully operated on pure sunflower oil for over 2300 hours at 70% load [2]. This is still much less than the expected 10,000 hour life of a diesel truck engine before a major overhaul [10].

4. Lubricating oil dilution and failure. This also seems due to the low volatility and polyunsaturated nature of the vegetable oil. Unburned or partially burned liquid fuel blows by the piston rings where it dilutes the lubricating oil. As the concentration builds up, the vegetable oil polymerizes and the lubricating oil thickens. Serious dilution can take place rapidly when the engine is operated at low rpm while under load. This problem is usually reduced when an indirect injection engine is used [2].

5. Excessive engine wear. This is caused by coking and varnish, degraded lubricating oil, and by any free fatty acids which are formed by hydrolysis of the vegetable oil during storage and combustion. Fatty acids are very corrosive at temperatures above 150 C [2].

Some of these problems could be reduced or eliminated by use of indirect injection engines. This is not a viable alternative, at least for the short term strategy in the United States, since most of the engines currently in use in agriculture and transportation are direct injection. Hence, to solve these problems work must be done to either modify the fuel or to make minor mechanical modifications of the direct injection engines currently in place.

Attempts to modify the fuel include transesterification, cracking, and use of fuel additives, with most researchers looking at transesterification. This process replaces the glycerol with three separate molecules of alcohol such as methanol or ethanol. As long as the transesterification yield is greater than 90 percent this process substantially reduces the coking and deposit problem discussed above [11]. Cold weather handling is still a problem as transesterification generally raises the pour point of the fuel. Lubricating oil dilution also continues to occur.

There are two primary criticisms of transesterification. First, it adds cost to a fuel already priced at twice the cost of diesel fuel. Second, the intent of using vegetable oil fuels to fill in during spot shortages and emergency situations will not be met since processing equipment for transesterification would need to be assembled. This applies to both farm scale and larger scale (cooperative and commercial) operations.

A number of commercially available fuel additives have been tested for elimination of the coking problem. Only a few have been found which show promise of reducing the coking problem. These will be subject to further testing [12].

Several minor engine modifications have been tried to reduce the coking problem. Work has focused on the injectors, since that is the location where coking is first noted. Modifications include injector retraction, water cooling of the injectors, and teflon coating of the injectors. None of these modifications had any effect [12].

Of the problems discussed above, lubricating oil thickening by dilution with vegetable oil is particularly suitable to laboratory study by simulation of the crankcase environment. Simulation allows more precise control of individual variables than is possible with actual engine tests. Thus, the particularly serious problem of lubricating oil failure could be at least partially quantified without recourse to expensive engine tests.

PREVIOUS RESEARCH

Lubricating oil dilution by vegetable oil fuel is a commonly reported problem which occurs under a number of different engine test conditions. It occurs most rapidly under low speed and partial load which are the conditions favoring incomplete combustion [2, 13]. It is generally considered to occur more readily in direct injection engines, but is also reported in indirect injection engines which are usually thought to be somewhat immune to the problems caused by use of vegetable oil fuels.

Peterson et al. [2] report 160 percent increase in lubricating oil viscosity over a 100 hour oil change interval when an indirect injection engine is operated with pure linoleic safflower oil. The engines were operated at wide open throttle with the load cycled on and off at 15 minute intervals. The Engine Manufacturers Association [14] considers that a 50 percent increase in lubricating oil viscosity over the length of an oil change is an indication of test failure. The Engine Manufacturers Association standardized test for alternate fuels is shown in Appendix A.

Yarbrough et al. [15] report a rapid buildup of total solids in the lubricating oil of an indirect injection engine operated on pure degummed, dewaxed sunflower oil under full rated load at constant rpm. Lubricating oil would need to be changed two to three times more frequently than recommended by the engine manufacturer to maintain suitable lubricating oil quality.

Work has been done by several researchers in simulating the lubricating oil environment within the engine. Unless otherwise noted, lubricating oil tested by cited researchers is API CD SAE 30. Bauer et al. [16] used ASTM D 943, "Oxidation Characteristics of

Inhibited Steam Turbine Oils," as the basis for test development. Lubricating oil was intentionally contaminated with soybean oil and then exposed to heat, air, agitation, and various metals of engine construction. Samples were heated in a constant temperature oil bath. Sample containers were glass test tubes. Air was supplied through 2 mm I.D. glass tubes from high pressure cylinders. Flow rates of 1 l/hr gave sufficient agitation.

Oil viscosity was measured to determine thickening. Copper and iron together, molybdenum, manganese, chromium, and nickel were tested to determine effect on rate of viscosity increase of 10 percent soybean oil in lubricating oil. The rate of viscosity increase with copper and iron was an order of magnitude greater than the other catalysts. The range of soybean oil dilution levels tested was 0% to 10%. There was little difference in the rate of viscosity increase through 1.0%, with the rate at 3.0% slightly higher, and 10.0% significantly higher. Tests were run at 100 C and 120 C. The rate of viscosity increase was significantly higher at the higher temperature.

Adams et al. [17] tested a range of soybean oil dilution levels from 0% to 50%. Water levels from 1% to 9% were tested to simulate condensation in the crankcase. Test samples were held at 85 to 95 C, and agitated by aeration. Catalytic amounts of cobalt and manganese were tested. Viscosity increase was independent of amount of water present. No significant viscosity increase occurred in 240 hours without the added metal, but samples containing 10.0% or more soybean oil became highly viscous in 94 hours with addition of manganese and cobalt.

Engine tests with a direct injection engine were also performed by Adams and coworkers. The test schedule was based on the EMA's recommended test method. Lubricating oil viscosity measured at 75 C increased 385% after 200 hours engine operation on a 1:1 blend of soybean oil and diesel fuel. Even though lubricating oil viscosity increased only 3.2% at 100 hours of engine operation, the level of lubricating oil dilution was judged as unacceptable by the authors due to the potential for catastrophic thickening of the lubricating oil.

Lubricating oil deterioration when contaminated with methyl esters of soybean and babassu oils was tested in a MacCoull apparatus by Siekman et al. [18]. A MacCoull apparatus, which is used to determine the corrosional effect of a test fluid on a bearing material, consists of a rotating conical shaft submerged in the oil sample to be tested. A stationary shaft supports the rotating cone with a test bearing. Catalyst is added in the form of copper baffles. Oil is sprayed off the conical shaft and runs down the side of the glass beaker containing the test apparatus and oil sample. The sample is aerated by diffusion through holes in the cover of the beaker.

Soybean oil is polyunsaturated, with an iodine number of 128 and babassu oil is essentially saturated, with an iodine number of 17. Iodine number is a measure of vegetable oil or fatty acid unsaturation, and is directly proportional to the degree of unsaturation. Dilution levels were 5.0%, 10.0%, and 20.0%. Test duration was 8 hours in all cases, and also 24 hours with 10.0% soybean oil ester. Temperatures tested were 150 C and 170 C. Kinematic viscosity at 40 C and total base number (TBN) by ASTM D 2896, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titrations," were evaluated as test parameters. Reduction in TBN, which indicates a drop in alkaline reserve and a rise in amount of free acids, rose with increasing contamination with ester. The effect is more pronounced with the soybean ester than with babassu ester, especially at higher dilution rates and higher temperature.

By assuming an iodine number of zero for the lubricating oil, and calculating the iodine number of the contaminated lubricating oil sample, a straight-line relationship is shown between the reduction in TBN and the amount of double bonds introduced. This indicates that acid-forming oxidation is taking place largely at points of unsaturation.

The viscosity, TBN, and percent ester (analyzed by infrared spectroscopy) were evaluated during the 24 hour test. The viscosity increased fairly quickly, doubling in 16 hours, and leveling off at 24 hours with total increase of 156%. The reduction in TBN was fairly constant with a slight leveling off at 24 hours, with a total drop of 44%. The drop of 16% in ester concentration during this time period was attributed to evaporation and reaction of the ester. The flash point of soybean oil methyl ester (methyl soyate) is 178 C [19].

Bench and vehicle testing were also done by the Siekman group using indirect injection engines fueled with pure methyl soyate. In both cases, the lubricating oil was intentionally contaminated with 5% methyl soyate. In a bench test of 100 hours, the viscosity increased to 5 times the initial value, while the TBN dropped only slightly. The soot content of the oil increased to 4.0%. The increase in viscosity was attributed to this, rather than breakdown in the antioxidant capacity of the oil. The ester content of the lubricating oil dropped from 5.2% initially to 3.2% after 75 hours. In a reference test using methyl soyate as fuel, but with uncontaminated lubricating oil, the ester content never exceeded 1.0%.

Vehicle testing was done under actual driving conditions of a light duty delivery van, with oil change intervals of 7500 km. Viscosity and TBN stayed essentially normal, with soot increasing only one tenth as much as in the bench tests.

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

Bench testing was done with a direct injection engine run 10 hours per day at full rated load and speed using ethyl soyate fuel. Six different lubricating oils, all SAE 30, five API CD, one API CC were tested. Samples of lubricants were subjected to conventional used oil analyses, including TBN, viscosity and loss of dispersancy by blotter spot test. Concentration of ester was determined by infrared analysis. Tests were terminated when lubricant breakdown based on loss of dispersancy occurred. In all cases, lubricating oil viscosity decreased to a minimum of about 50 percent of initial viscosity at 40 hours followed by rapid viscosity increases at 60 to 70 hours. Tests were terminated at 60 to 75 hours. Ester content of the lubricating oil increased to about 20% at 60 hours. At this time, the concentration of ethyl linolate and ethyl linolenate dropped markedly, indicating depletion of the antioxidant additives in the oil. The TBN also fell to unacceptable limits indicating increasing acid content of the oil, while insolubles and wear metals (copper, lead, and iron) in the oil increased to unacceptably high values.

Korus et al. [21] examined the effect of three commercial antioxidant diesel fuel additives on oxidative polymerization of pure, high erucic rapeseed oil. Samples were heated to 240 C in open glass beakers in a forced air convection oven. Viscosities increased more rapidly with the additive in all three cases.

Romano [22] used 25 ppm butylated hydroxytoluene (BHT), a commercial food antioxidant, in a 1:1 mixture of lubricating oil and methyl soyate. Samples were degraded by heating to 140 C and aeration with 30 l/hr air. At 100 hours the viscosity of the sample without BHT had risen one and one half times as much as the samples with BHT, while TBN in both samples was below acceptable limits. At 200 hours viscosity of the sample with BHT had risen above that of the sample without BHT. The author concluded that BHT is not a suitable antioxidant for this system.

In a survey article, Wexler [23] reviews the polymerization of drying oils or polyunsaturated vegetable oils. Primary reactions are formation of unsaturated ester hydroperoxides by reaction of the oil with oxygen, the decomposition of these materials to free radicals, and the subsequent crosslinking of the free radicals with other olefins resulting in a chain reaction or polymerization. The oxidative chain reaction is preceded by an induction period when nothing seems to occur. This is often attributed to naturally occurring antioxidants such as tocopherols. Induction periods are still observed in certain cases with material that has been rigorously purified. Hence, induction periods may be an inherent property of the material itself.

Based on radioisotope studies, the initial attack by the oxygen takes place at the double bond during the induction period. This is followed by a steady state period during which the oxygen becomes a hydroperoxide by abstracting a hydrogen from the methylenic carbon. This causes a rearrangement of the double bond to a conjugated system and places the hydroperoxide on a newly formed methylenic carbon. The double bonds are generally unconjugated prior to this reaction. Subsequent polymerization takes place by radical attack at an ethylenic carbon. Chain termination takes place when two radicals react with each other [24].

Although polymerization of neat drying oils proceeds via free radical mechanisms, presence of free acids in the lubricating oil system allows the possibility of cationic or acid catalysis, where an acid attacks the double bond directly, forming a carbonium ion with a single bond. The carbonium ion continues the chain by attacking another double bond. Chain termination can occur by ejection of a proton forming an alkene, or by reaction with an anion [24].

Wexler also discusses metal catalysis of the drying of vegetable oils. There are two groups of metals which increase the drying rate of oils. First are the participating driers which show a definite effect on the drying rate, including cobalt, lead, and manganese which are the most active, and also cerium, copper, chromium, iron, tin, vanadium, and zirconium. Generally, these metals occur in at least two valences with the higher being less stable. They are susceptible to oxidation from the lower to the higher valence by the hydroperoxides. The second group, which enhances the activity of the members of the first group, is called the promoter catalysts. It includes calcium, zinc, and lead.

The action of the metal is not clear. They may act as oxygen carriers, stabilizing the diradical form of the oxygen. The metal may also attack the double bond directly forming a positively charged radical which would then initiate more conventional products of autooxidation. Lastly, the higher valence metal may directly attack a saturated portion of the oil molecule, abstracting a positively charged hydrogen and leaving a radical.

The valence of the metal affects its catalytic activity. For example, while metallic copper lowered the reaction rate and yield of peroxides of soybean fatty acids, cupric stearate was one of the most effective catalysts for the oxidation of linoleic acid.

Other materials, such as free radical initiators show catalytic activity toward drying oils. Examples of these are organic peroxides such as benzoyl peroxide and azo compounds such as azo-bis-isobutyronitrile. The use of 0.02% of triphenylmethoxy radical reduced the drying time of tung oil from 40 hours to 5 to 10 minutes.

Aldehydes are formed by the decomposition of hydroperoxides. Subsequent oxidation of aldehydes may account for formation of the mono- and dibasic acids reported [23].

RESEARCH OBJECTIVE

The purpose of this investigation is to examine some of the parameters which affect degradation of lubricating oil contaminated with vegetable oil by use of an apparatus simulating a diesel engine crankcase, and to attempt to elucidate the mechanism(s) of degradation. Parameters to be studied are presence and amount of selected metal catalysts and oxygen, temperature, and level of lubricating oil dilution by vegetable oils. Total base number as it relates to the mechanism of oil degradation will also be studied.

Mechanisms to be studied are acid and free radical catalysis of polymerization of vegetable oil in lubricating oil. Acid catalysis will be studied by altering the total base number. Free radical catalysis will be examined by use of a commercial free radical initiator.

Attempts will be made to limit the action of metal catalysts by poisoning with a sulfur compound and by use of a chelating agent. Wear properties of degraded oil mixtures will also be examined by standard lubricity testing.

MATERIALS AND METHODS

Materials

All vegetable oils used were edible grade obtained from Agricom in Berkeley, California. Oils used were sunflower, high oleic safflower, and high linoleic safflower. Lubricating oil was Super HD II low ash MIL-L-2104C API CD SAE 30 manufactured by Amoco Oil Company, obtained under Phillips 66 Oil Company label. All chemicals were reagent grade.

Equipment

Equipment consisted of the reactor system and analytic apparatus. The reactor system (Figure 1) was contained in a steel tank 11" high by 8" wide by 13" long, insulated with 2½" fiberglass insulation on the sides and ½" fiberboard on the bottom. The tank was filled with paraffin oil to a depth sufficient to immerse the test cells to within one inch of their tops. Bath oil was heated with a Polyscience Model 73 immersion circulating heater. Maximum temperature of the controller was 150 C, precision was 0.02 C, power output was variable from 10 to 1000 watts, and pumping rate was 13 liters per minute. A mercury thermometer accurate to 0.1 C was used to monitor temperature. This thermometer was calibrated to the ice point and boiling point of distilled water.

Gas was delivered from a high pressure cylinder through a single stage regulator to a gas header attached to the side of the oil bath. Attached to the header were 6 needle valves for flow control to the test cells and a pressure gauge to monitor gas pressure in the header. Gas was preheated before being delivered to the header by being passed through a loop of ¼" O.D. copper tubing which was immersed in the oil bath. The header was also insulated.

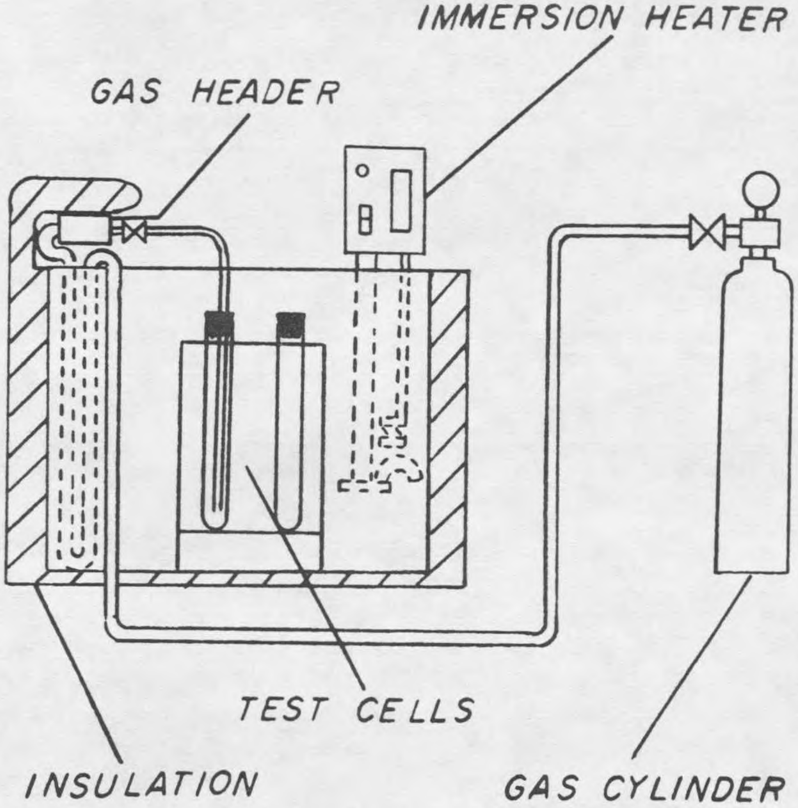


Figure 1. Experimental apparatus for oil degradation.

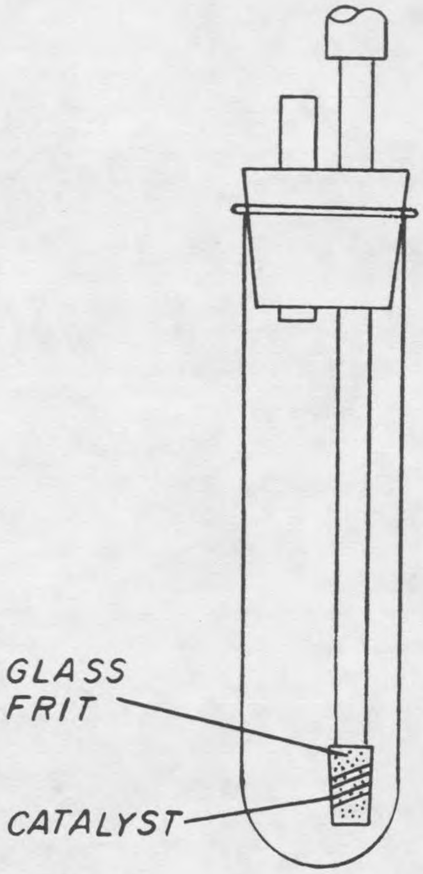


Figure 2. Individual test cell.

A temporary header with two valves was used on several runs. This header was also insulated, and the gas was preheated in a method similar to the permanent header described above.

Test cells (Figure 2) were 1" by 8" pyrex test tubes which held 50 ml sample per cell. The oil bath would accommodate 6 test cells during one run. Gas was delivered to the test cells through ¼" I.D. silicon rubber tubing. Gas was sparged into the sample through 7 mm glass tubes with fritted glass heads. The glass tubes were held in place with two-hole rubber stoppers so the frit was within 5 mm of the bottom of the test cells. Short pieces of 7 mm glass tubing were inserted in the second hold in the stoppers so a soap bubble flow meter could be attached to the test cells to measure flow rates.

Catalyst was introduced in the form of wire wrapped around the fritted portion of the gas inlet tube. Copper and iron wire were chosen on the basis of ASTM D 943, "Oxidation Characteristics of Inhibited Steam-Turbine Oils" [25], and the work by Bauer et al. [16]. The iron wire was 0.0090" in diameter, with a variation of 1.1% based on four measurements. The copper wire was rectangular in cross section and had an average width of 0.0112" and average thickness of 0.0024", with variations of 28.7% and 3.6%, respectively, based on ten measurements. The ratio of iron to copper surface areas per unit lengths was 1.04. When used together, equal lengths of copper and iron were used. Equal lengths of the two were used in accord with ASTD D 943, even though wear metal analysis of actual used lubricating oil shows a higher level of iron than copper. Prior to use the copper and iron wire were sanded to remove oxide coatings. They were then loosely wound together and cleaned with heptane to remove oil and grease. From this point they were handled with gloves. Runs were made with 0, 20, and 100 cm catalyst.

Two parameters were chosen as measures of oil degradation. Viscosity was chosen since elevated viscosity is the most commonly reported problem with lubricating oil used in this service. It is relatively easy to measure and is nondestructive. It provides fairly reliable information about the degree of degradation of the oil.

Viscosity analysis was done with three Cannon-Fenske type viscometers, with a range of 100 to 500 centistokes (cSt). One was factory calibrated; the other two were calibrated using the first as a standard. Temperature was maintained at 40.0 C during viscosity measurements by immersion in a constant temperature water bath using a heater identical to the one used in the oil bath.

Total base number (TBN) was chosen since it provides a measure of the alkaline reserve [18] of the oil. As it falls to lower levels, free acids which could influence the rate of degradation of oil begin to accumulate. Total base number measurements is destructive so multiple test cells were required to determine the TBN history of a single sample. It is also a more involved procedure than viscosity measurements. Because of these considerations TBN was not measured every time a viscosity measurement was made.

Total base number was measured in accord with ASTM D 2986, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration" [26]. The back titration method was chosen as it gives sharper endpoints with some used oils, including the materials generated in these experiments. A 25 ml glass buret was used for titrant delivery, and a Beckman model SS-3 Zeromatic pH meter was used for endpoint detection.

Analysis for wear preventative properties was done according to ASTM D 4172, "Wear Preventative Characteristics of Lubricating Fluid (Four-Ball Method)" [27], by Phoenix Chemical Laboratories in Chicago, Illinois. In this test three ½" diameter steel balls are clamped together and covered by the fluid to be tested. A fourth ball of the same size is pressed with a force of 392 N into the cavity formed by the three stationary balls causing three point contact (Figure 3). The top ball is rotated for 60 minutes at 1200 rpm. Temperature is constant at 75 C. At the end of the test, the scars generated on the lower balls are

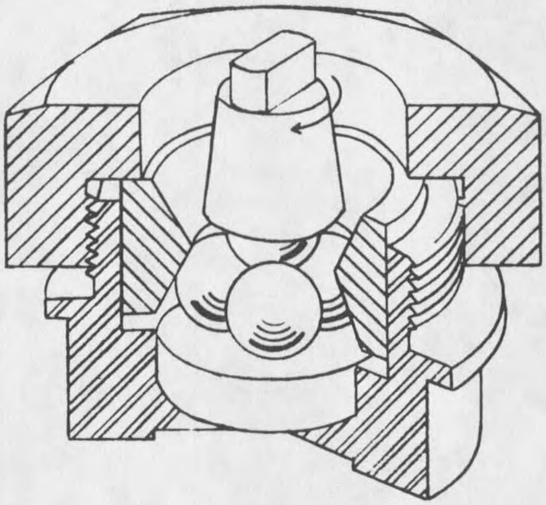


Figure 3. Detail of four-ball wear tester.

measured perpendicular and parallel to the striations. These values are averaged to give the test result.

Experimental Procedure

To begin an experimental run about 50 gm of lubricating oil per test cell were weighed to the nearest 0.01 gm. Vegetable oil was then added to the desired concentration based on weight percent. After being mixed for a minimum of 2 minutes, 50 ml was added to each test cell. Required analysis (viscosity and/or TBN) was performed on this starting material. The fritted glass tube, with or without catalyst as desired, was inserted in the test cell and the stopper was firmly seated. The cells were then submerged to within one inch of the top of the cells.

Gas flow was started about an hour before insertion of the samples to obtain stable flows of preheated gas. Flow was adjusted to the proper rates before being attacned to the test cells. After a few minutes, outlet flows of the test cells were monitored. Whenever a flow rate was used for the first time, the temperature of the test sample was monitored with a Cole-Parmer Instrument Company Model 8530-05 digital thermometer accurate to 1 C and a chromel-alumel thermocouple. These temperatures were always the same as the observed temperatures of the oil bath. Flow rates were measured every 8 to 12 hours with a 10 ml soap bubble flow meter. Flows were adjusted to within 5%, and occasionally varied by 10% from one measurement to the next. Generally, however, they were stable to within 5%. Flow rates of 2000 ml/hr and 4000 ml/hr were used.

To make measurements of viscosity or TBN all six cells were disconnected from the gas flow and removed from the bath. Ten ml samples were pipetted into the viscometer and were allowed to equilibrate for at least 10 minutes. The oil was raised above the upper mark of the viscometer by suctioning with a clean pipette bulb. Time for flow through the viscometer was measured to the nearest 0.01 second. The sample was then returned to the test cell.

For TBN a 5 ml sample was weighed to the nearest 0.1 mg and then titrated according to ASTM D 2896 [26]. In the back titration method 120 ml of 2:1 chlorobenzene:glacial acetic acid titration solvent was added to the sample followed by addition of 10.00 ml of 0.1 N perchloric acid in glacial acetic acid. Electrodes were inserted into this solution, which was titrated potentiometrically with 0.1 N sodium acetate in glacial acetic acid. Uniform additions of 1.00 ml and 0.50 ml were made, the smaller addition size being used near the equivalence point.

When an experimental run was complete, test cells and miscellaneous glassware were cleaned with Phillips 66 nonflammable mechanics solvent, acetone, and soap and water, rinsed with water and distilled water, and air dried. Fritted glass tubes were cleaned in a similar manner followed by a 10 to 20 minute soak in hot chromic acid and rinsing with water and distilled water. They were then rinsed with acetone and suctioned to assure dryness. Viscometers were cleaned with Phillips 66 solvent, rinsed several times with acetone and suctioned. They were also cleaned with chromic acid as required.

RESULTS AND DISCUSSION

Effect of System Variables on Viscosity

Since the oil bath held 6 test cells per run, not all of the test cells from each run were necessarily devoted to examining the same parameter. Also, data from more than one run may be used to examine each parameter. Generally, the parameters examined were viscosity versus time for differing conditions of gas flow rate and catalyst level, total base number (TBN) versus time for differing conditions, and the effect of various additives on viscosity and TBN. Unless otherwise noted, the temperature of the oil bath was 150 C, the vegetable oil used was sunflower oil, and the dilution level was 5.0% by weight. This concentration was chosen because it is an intermediate value of lubricating oil dilution in an actual engine, where the range is from 0% to 15%. It is in the range of many other researchers' work because of this consideration.

Initially, several screening runs were performed to determine a standard set of conditions against which later runs could be interpreted. Flow rates and catalyst levels were selected such that viscosity increases took place in a reasonable length of time and gas flows gave good mixing without causing a foaming problem. A temperature of 150 C was chosen as a compromise between the crankcase temperature and the temperature encountered in the combustion areas of the engine.

Effect of catalyst level is seen in run 1, shown in Figure 4, where 0, 20, and 100 cm of copper-iron combination were used as catalyst. Flow rate of oxygen was 2000 ml/hr. Additional data for 20 cm catalyst is included from run 6, and for 100 cm catalyst from runs 5 and 11. From this data, it can be seen that rate of viscosity increase is strongly affected by catalyst level, with the rate increasing as catalyst level goes up.

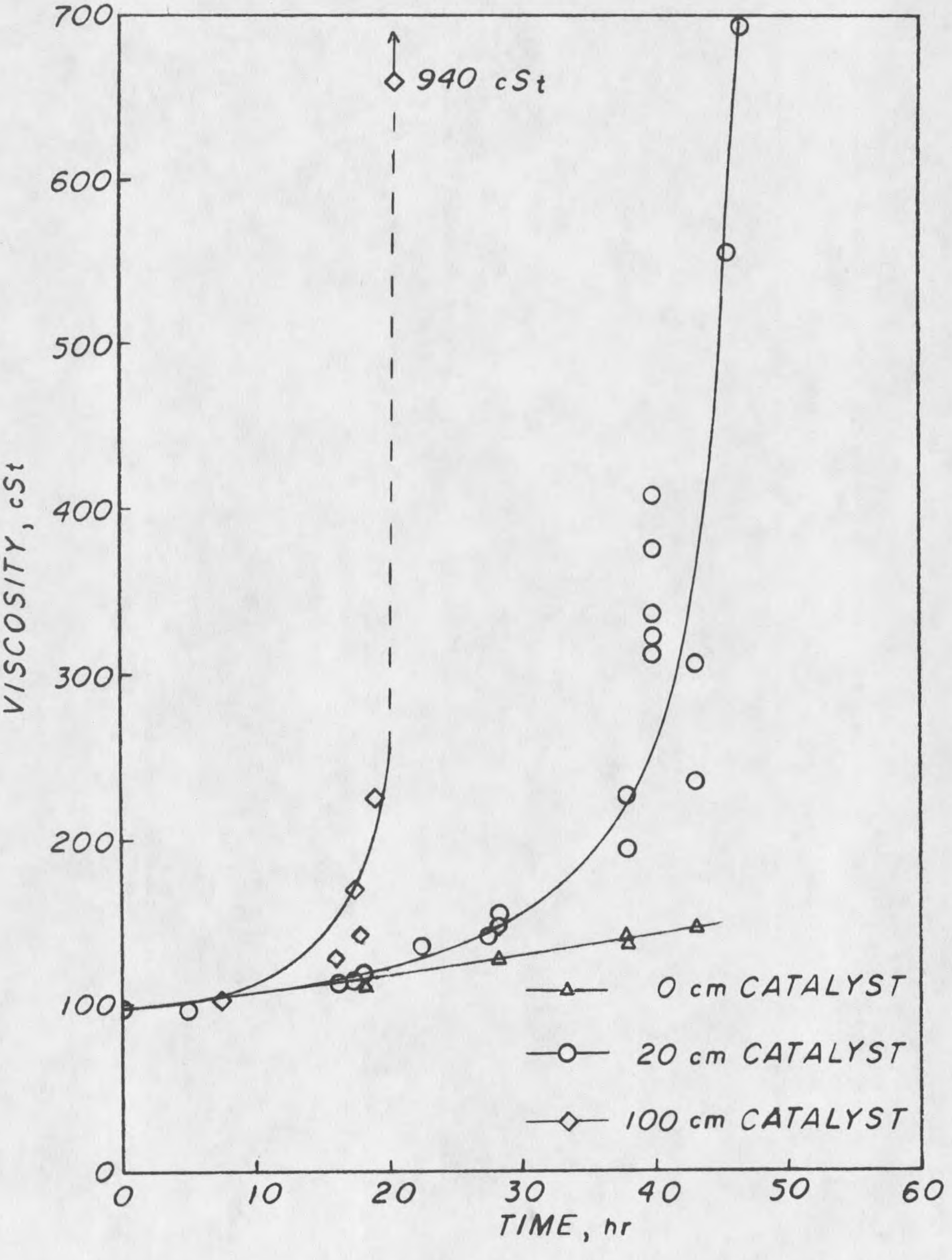


Figure 4. Viscosity vs. time for 0, 20, and 100 cm copper-iron catalyst and 2000 ml/hr oxygen.

As the work progressed, the conditions of 20 cm copper-iron catalyst, 2000 ml/hr oxygen, and a vegetable oil concentration of 5.0% by weight evolved as the standard set of conditions. The results of these conditions are shown in the center curve on Figure 4. For ease in comparison, this curve is reproduced in all the following graphs whenever appropriate. It is shown as an unlabeled dotted line.

The shape of these curves is consistent with the concept of lubricating oil thickening due to polymerization of the vegetable oil diluent. As polymerization proceeds, molecular weight, and hence viscosity, builds exponentially as progressively larger oligomers combine by addition.

Effect of copper versus effect of iron was examined in run 12, where 20 cm of copper wire was used in one cell, and 20 cm of iron wire was used in a second cell. When these results are compared with results from the standard set of conditions (shown as the solid and dotted line, respectively), it can be seen that iron has little catalytic activity, while copper has a slightly greater catalytic effect than using copper and iron together.

Copper and iron were not tested separately for catalytic activity before run 12 because other work [16,23,25] implied that both metals play a role in catalysis. Separate tests were performed to determine how much each contributed to viscosity buildup. Iron was included in the final run after this result was obtained for the sake of consistency, and because the combined presence of both metals may have subtle effects.

Effect of oxygen flow rate is seen in Figure 6, which compares the results of run 2 with the standard set of conditions. In run 2, flows of 4000 ml/hr of oxygen were used with 0 and 20 cm of copper-iron catalyst, while the standard set of conditions uses 2000 ml/hr oxygen and 20 cm copper-iron catalyst. Additional data for 20 cm catalyst is shown from run 7. Rate of viscosity increase is only slightly affected by oxygen flow rate. This is useful to note when considering the imprecision of the control of the flow rate.

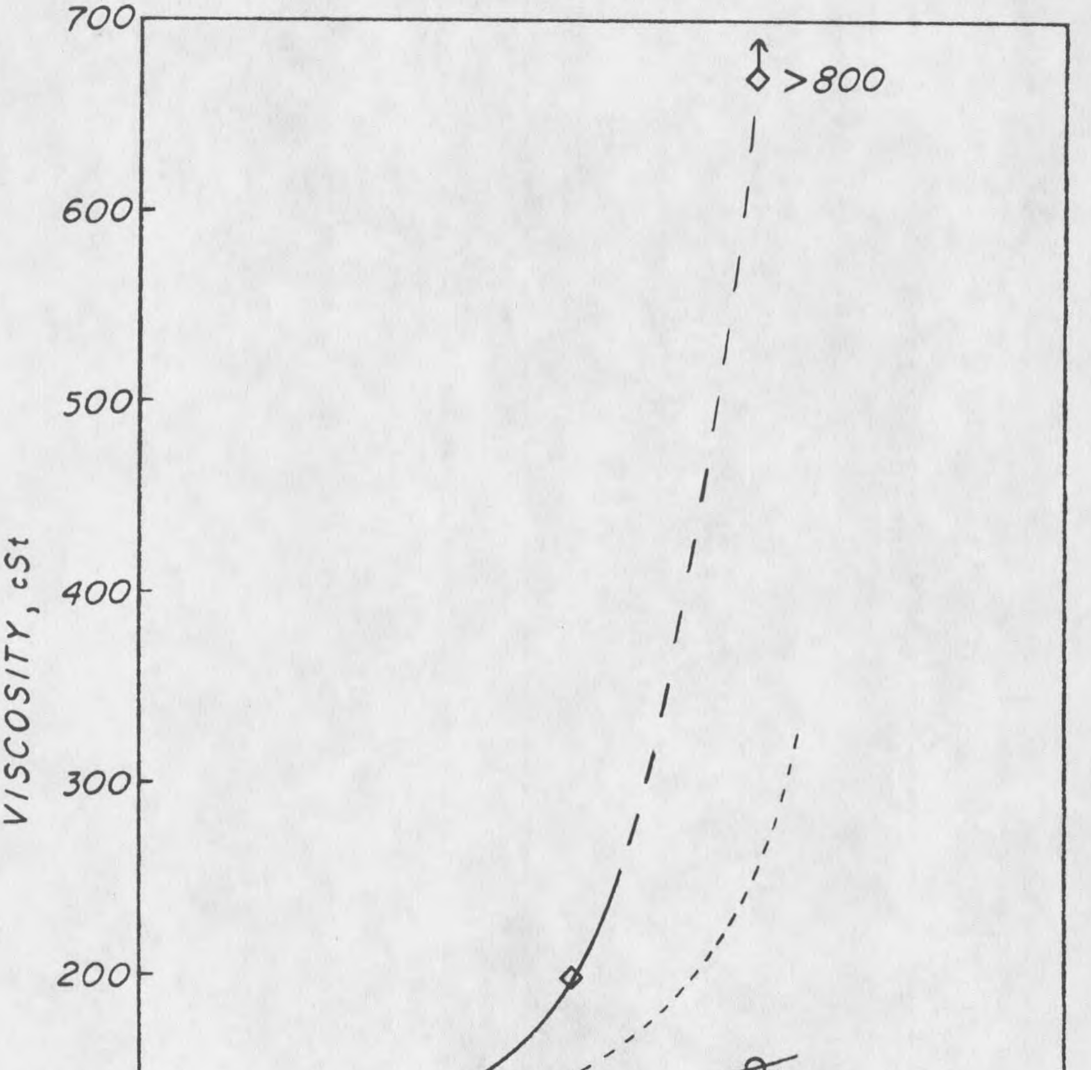


Figure 5. Viscosity vs. time for 20 cm copper and iron catalysts and 2000 ml/hr oxygen.

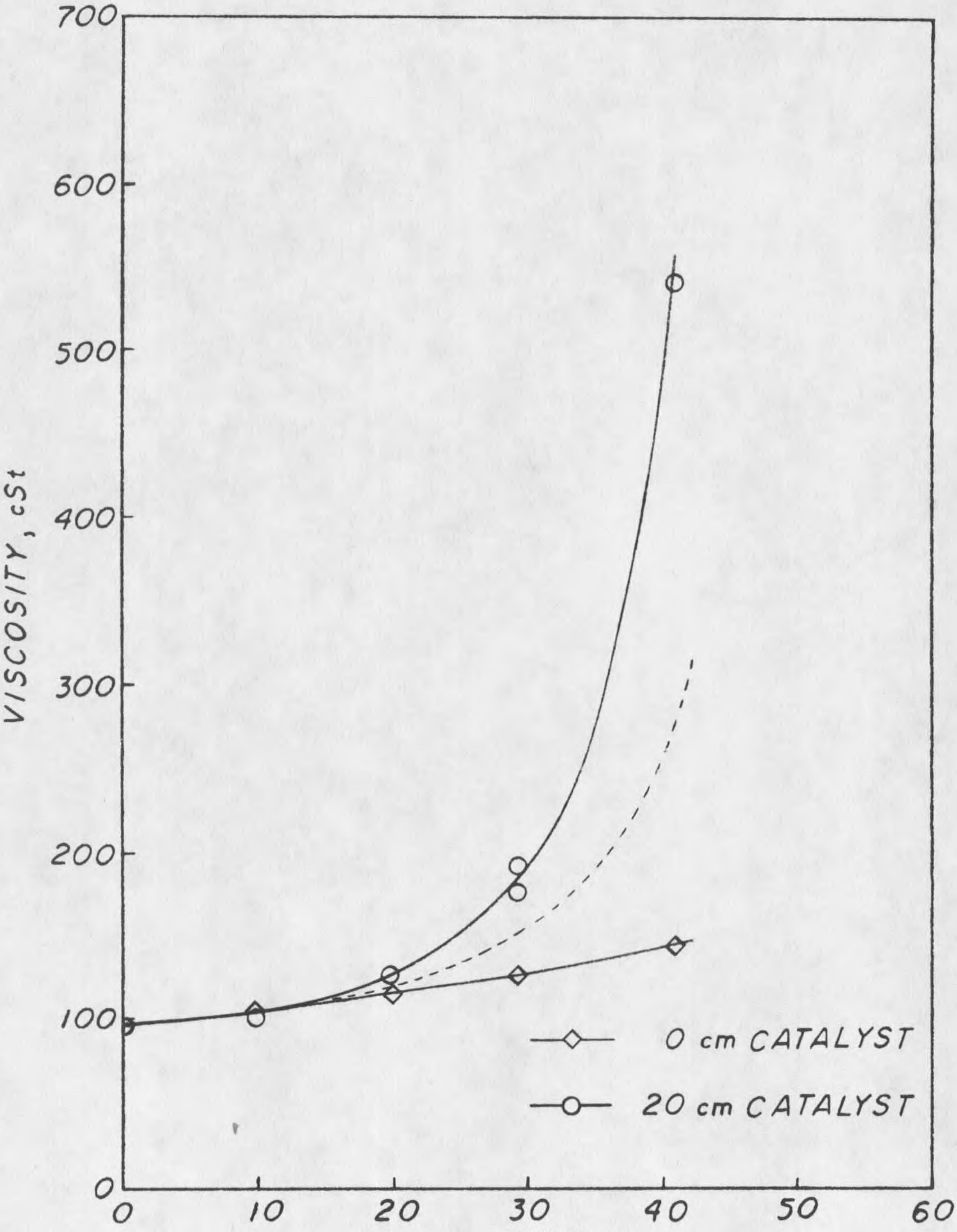


Figure 6. Viscosity vs. time for 0 and 20 cm copper-iron catalyst and 4000 ml/hr oxygen.

The curve obtained for an oxygen flow of 2000 ml/hr and no catalyst is the same as the curve obtained with an oxygen flow of 4000 ml/hr and no catalyst. For 20 cm catalyst, the curve for the higher flow rate is somewhat higher. This may indicate that chemical reaction is rate controlling when catalyst is not present, while mass transfer is rate controlling when catalyst is present. However, the two curves for no catalyst may diverge at a longer elapsed experimental time.

Rate of viscosity increase is strongly influenced by substitution of nitrogen for oxygen. When nitrogen was used at a flow rate of 4000 ml/hr with 20 cm copper-iron catalyst in run 2, viscosity stayed constant throughout the run.

This dependency on presence of oxygen allows the possibility of two mechanisms of viscosity increase, both due to oxidation of polyunsaturated vegetable oils. As previously discussed, free radical catalysis of drying oils occurs when they are exposed to oxygen. Such a mechanism may predominate here. As discussed below, formation of acids is seen to be dependent on the presence of oxygen, so acid catalysis of vegetable oil polymerization is a second possibility for the mechanism of viscosity increase.

Increasing the concentration of vegetable oil is clearly seen to raise the rate of viscosity increase in Figure 7, showing data from runs 3, 5, and 13. Again, the standard set of conditions of 5.0% sunflower oil, 2000 ml/hr copper and 20 cm copper-iron catalyst is shown as a dotted line. The main effect of varying the concentration of vegetable oil is to set the number of double bonds that are added to the system. Figure 8 compares the viscosity increase for 5% linoleic safflower oil from run 5 and 5% oleic safflower oil from run 6 with the standard condition of 5.0% sunflower oil. Iodine numbers are 140 and 89, respectively [28], where iodine number is directly proportional to the extent of unsaturation. The main difference between the two oils is the degree of unsaturation, so it is clear that a higher level of added double bonds increases the rate of viscosity rise.

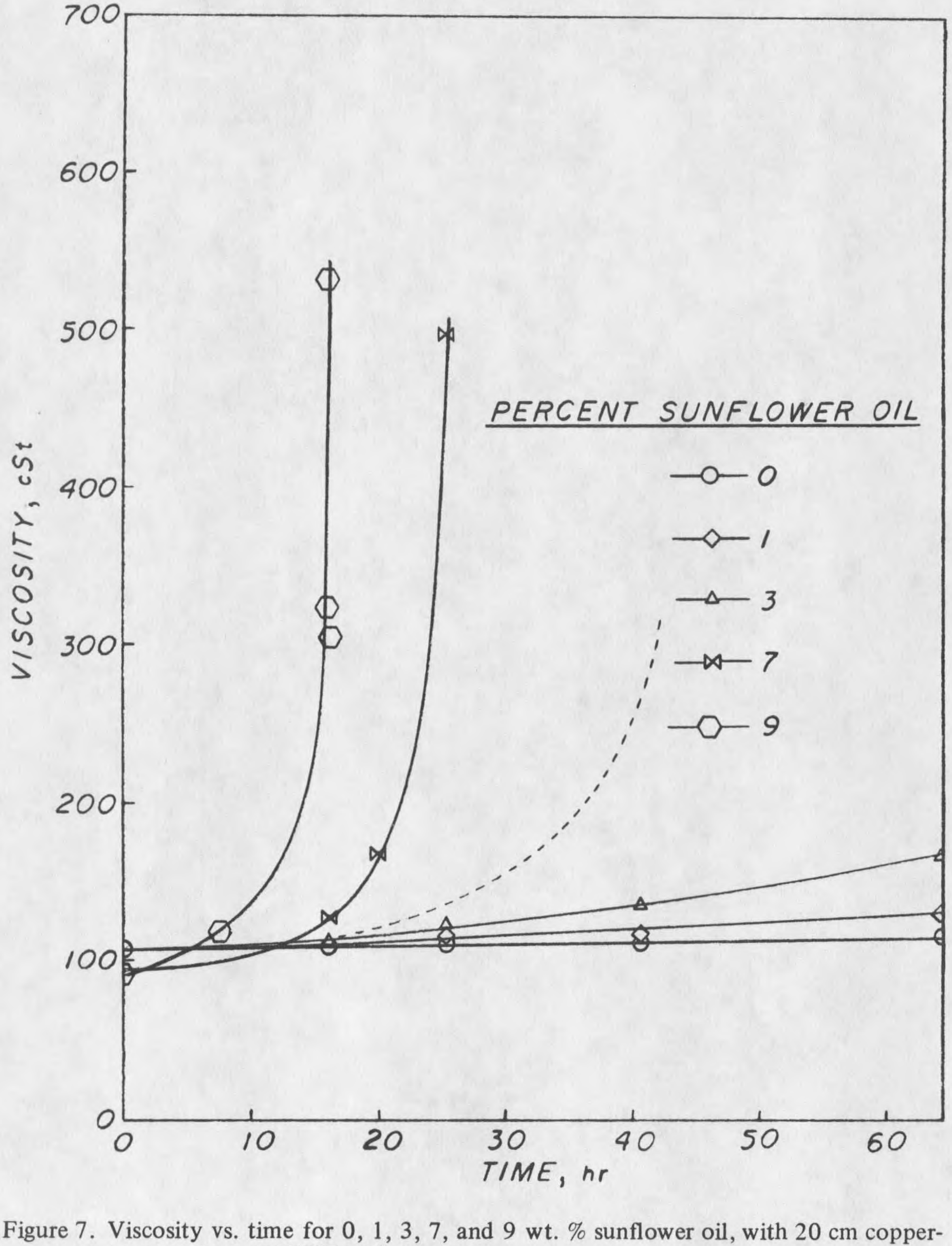


Figure 7. Viscosity vs. time for 0, 1, 3, 7, and 9 wt. % sunflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

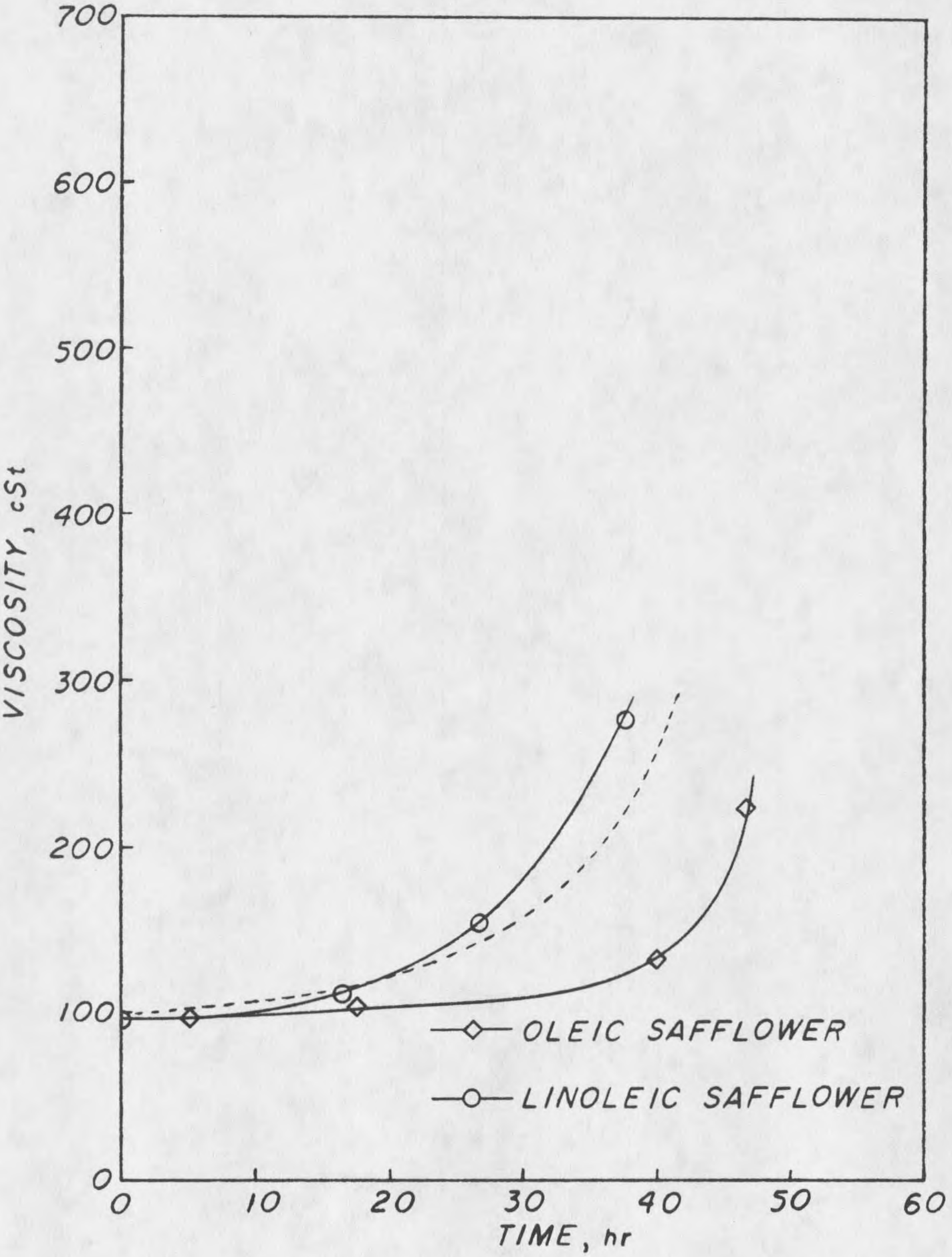


Figure 8. Viscosity vs. time for 5 wt. % linoleic and oleic safflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

This is also consistent with the concept of lubricating oil thickening due to polymerization of vegetable oil diluent, since a higher concentration of double bonds should increase the rate of polymerization.

Temperature has a pronounced effect on rate of viscosity increase as seen in Figure 9 which compares the results of run 4 with the standard set of conditions. A temperature of 120 C was chosen, since this corresponds to a temperature that might be found in the engine crankcase itself. Samples were run at an oxygen flow rate of 2000 ml/hr with 0 and 20 cm catalyst, and 4000 ml/hr with 20 cm catalyst. At an elapsed experimental time of 150 hours, viscosity increased only 17.3% and 29.1%, respectively, for the lower flow rate, and 28.0% for the higher flow rate.

Effect of System Variables on Total Base Number

From the first four runs, a standard set of experimental conditions was chosen for use in the subsequent experiments. These conditions were an oxygen flow rate of 2000 ml/hr, 20 cm copper-iron catalyst, and a temperature of 150 C. As previously mentioned, the results from this set of conditions is plotted on the figures as a dotted line whenever appropriate. Using these conditions, TBN versus time was determined in run 6. In run 7 an oxygen flow rate of 4000 ml/hr gave similar results, with only a slightly sharper fall-off in TBN than the lower flow rate. The resulting S-shaped curves are shown in Figures 10 and 11. Additional data from other runs is also shown, although these data points are at the upper end of the time scale since TBN was determined at the ends of some of the other runs.

The shape of these curves may be due to a changing rate of acid formation, with an increasing rate during the first half of the elapsed time and a decreasing rate during the second half. As discussed above, acids could be formed by oxidation of aldehydes which are formed by decomposition of hydroperoxides [23]. As more hydroperoxides are formed by oxygen attack of double bonds, the rate of their decomposition would increase.

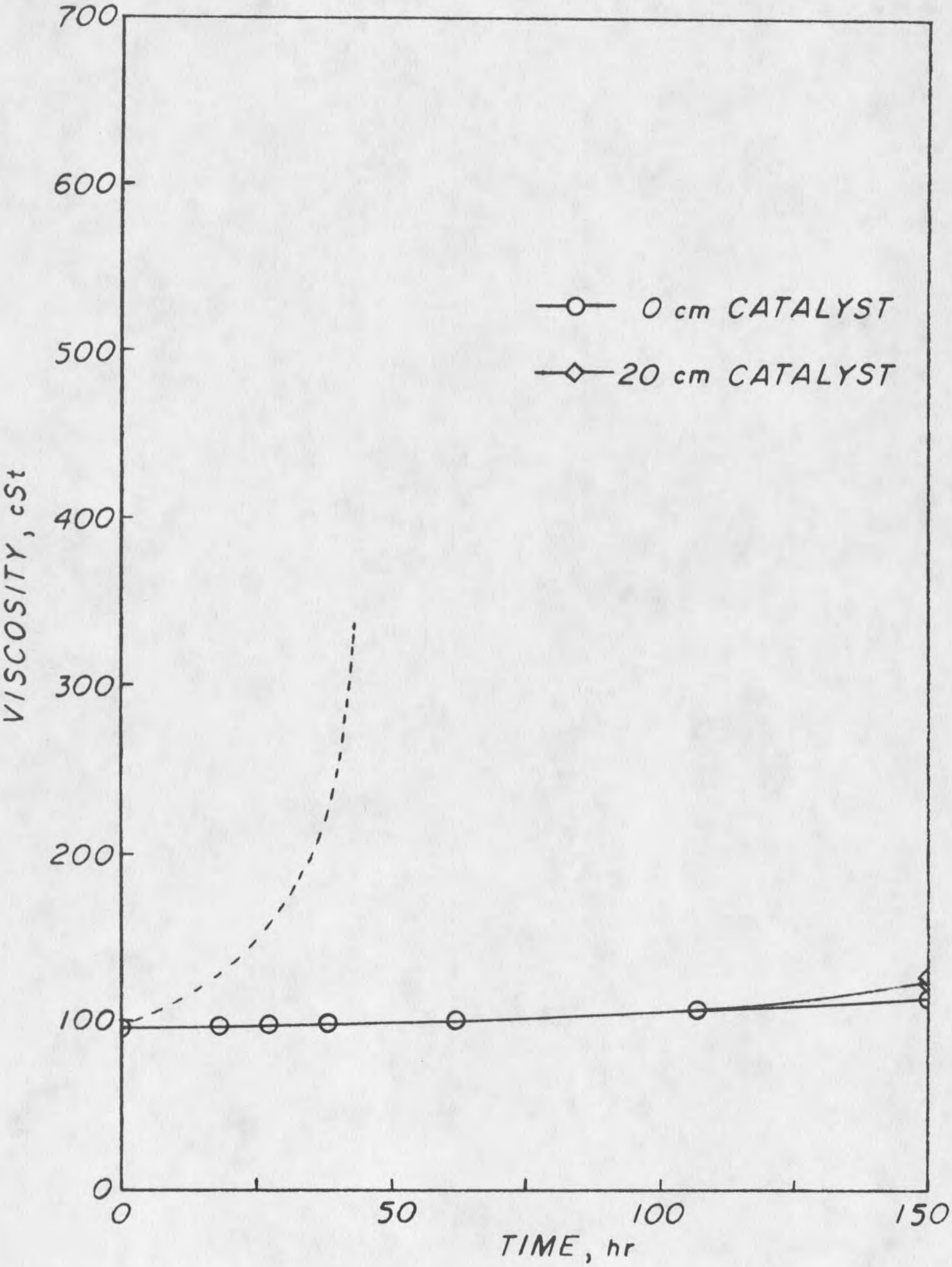


Figure 9. Viscosity vs. time for 120 C, with 0 and 20 cm copper-iron catalyst, and 2000 and 4000 ml/hr oxygen.

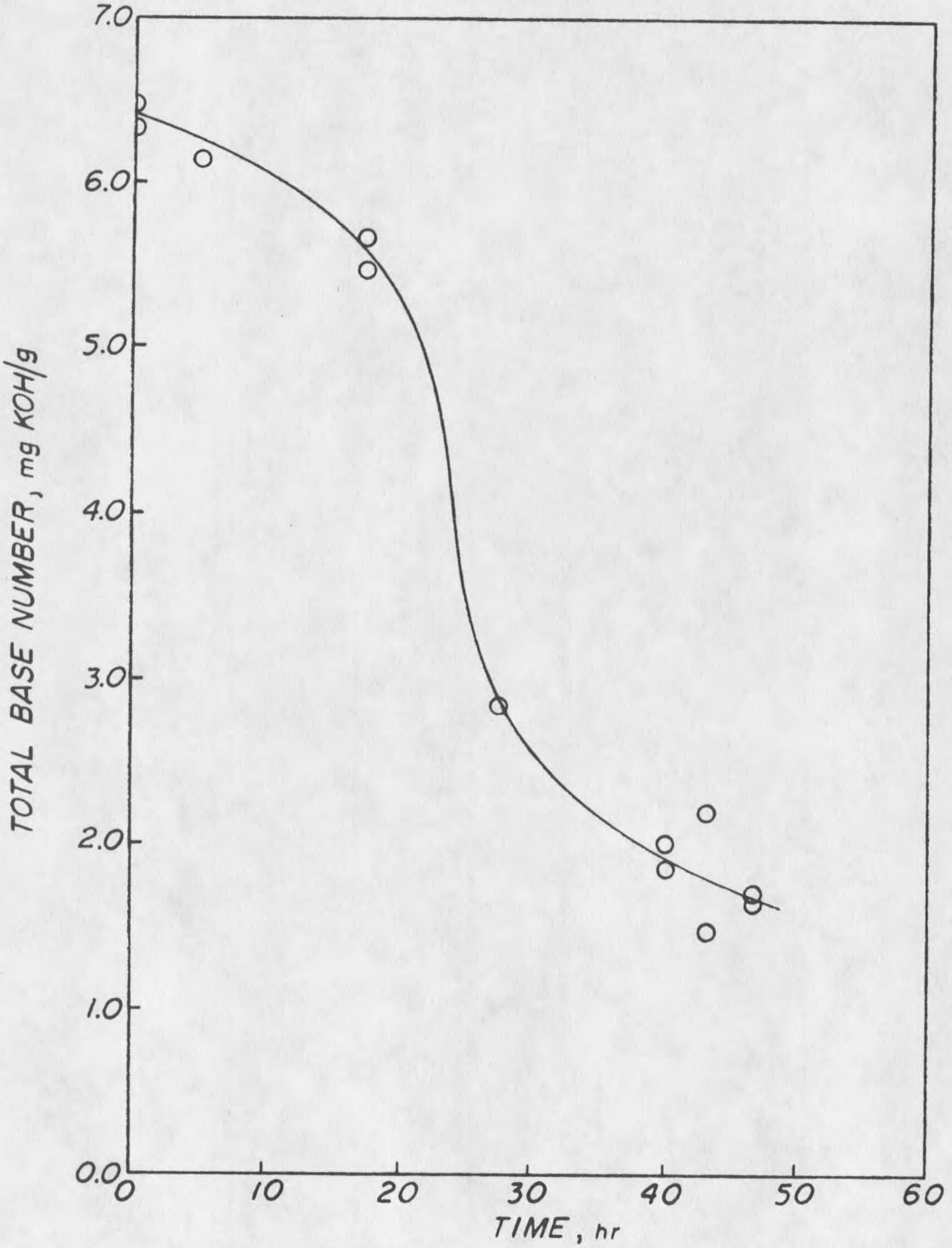


Figure 10. Total base number vs. time for 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

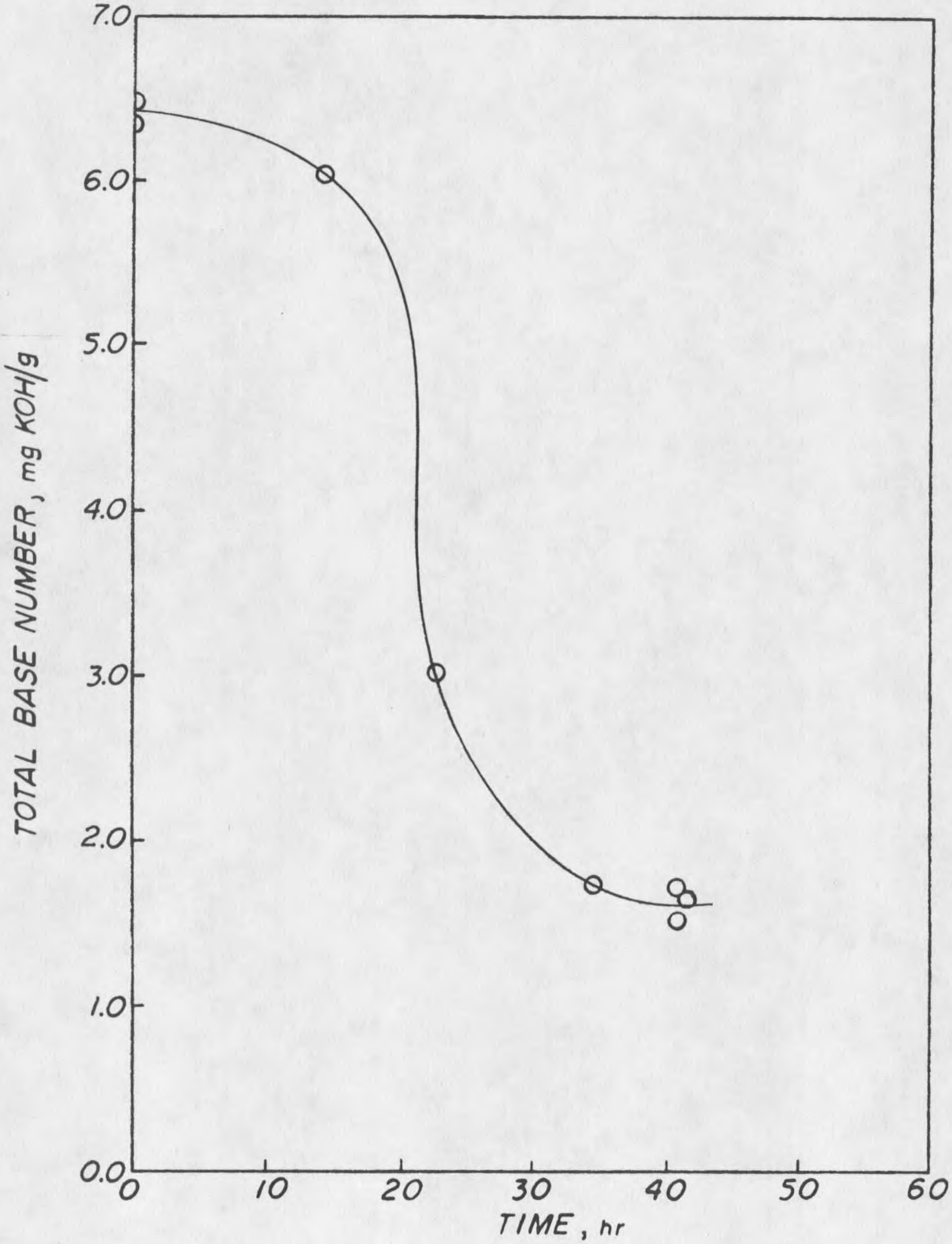


Figure 11. Total base number vs. time for 20 cm copper-iron catalyst and 4000 ml/hr oxygen.

As the concentration of double bonds decreased due to their polymerization and oxidation, the rate of formation of hydroperoxides would decrease after passing through a maximum, and so rate of acid formation would also decrease.

The effect of metal catalysis on the formation of acids was examined in run 13 (shown in Figure 12). Standard conditions were used except no catalyst was added. Although TBN still drops off in an S-shaped curve, the rate is somewhat less than with catalyst. This shows the metals may have a catalytic effect on the formation of acids, but the effect appears to be mild.

These results can be compared with results of TBN decay for pure lubricating oil from run 3. Standard conditions were used, except no sunflower oil was added to the lubricating oil. After 65.25 hours, the TBN was 4.27 mh KOH/g, which is significantly higher than the results discussed above. This increase in formation of acids due to the presence of vegetable oil is probably caused by the reactivity of the double bonds, which may be oxidized to acids via formation of hydroperoxides as discussed above.

Acid Catalysis

When the curve of TBN versus time is compared with the viscosity versus time curve, it can be seen that TBN falls off sharply before viscosity begins to rise significantly. This is seen clearly in Figures 13 and 14 where TBN is plotted against viscosity for runs 6 and 7. When TBN falls to about 3.0 mg KOH/g the viscosity begins a very rapid increase. As TBN falls, the acidic species increase in concentration, with significant increases beginning to occur shortly after a TBN of 3.0 mg KOH/g is achieved [22]. This increase in free acids before significant rise in viscosity makes acid catalysis of vegetable oil polymerization a possibility. Runs 8, 10, 11, and 12 were performed to see if viscosity increase in the degraded lubricating oil was due to acid catalysis.

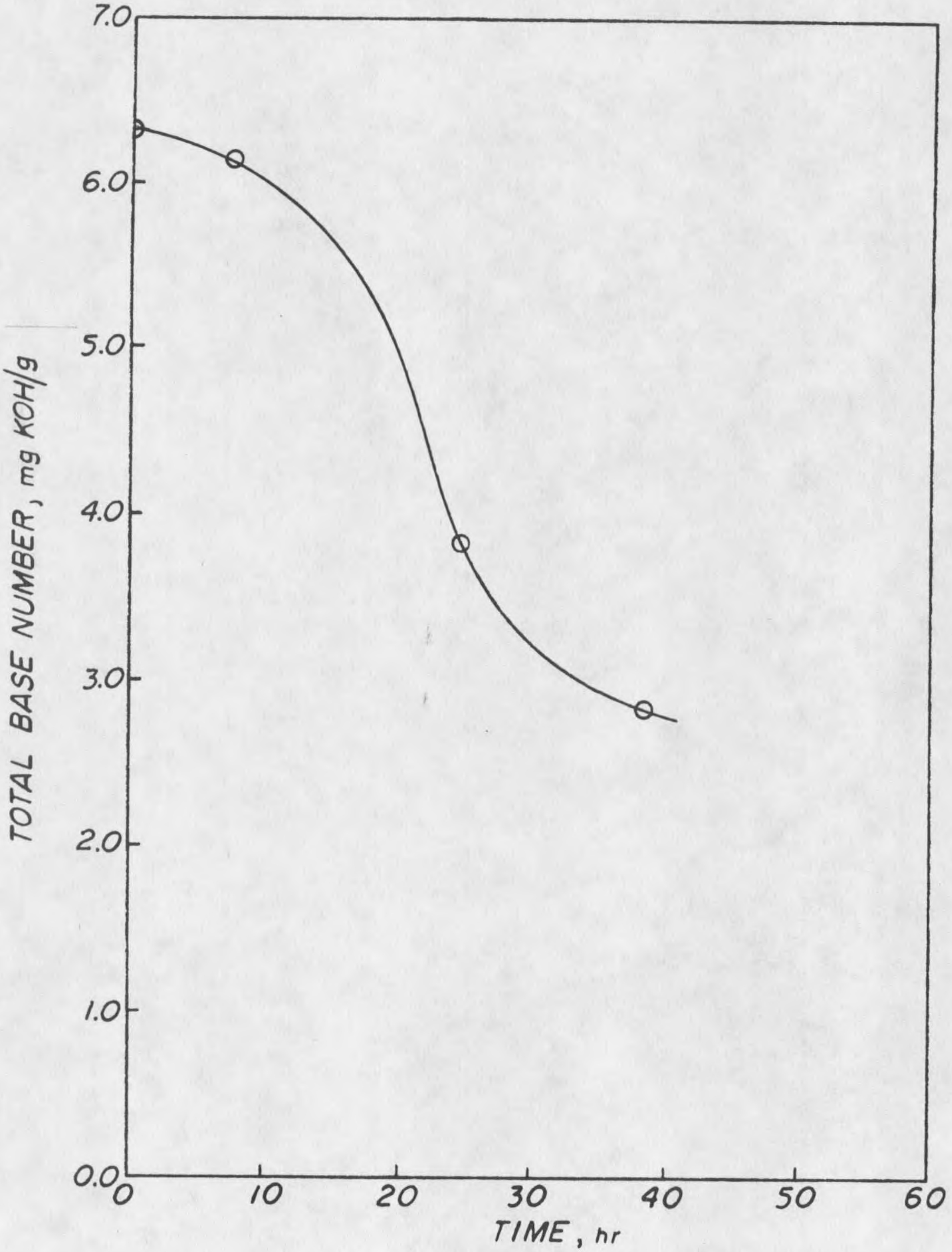


Figure 12. Total base number vs. time for no catalyst and 2000 ml/hr oxygen.

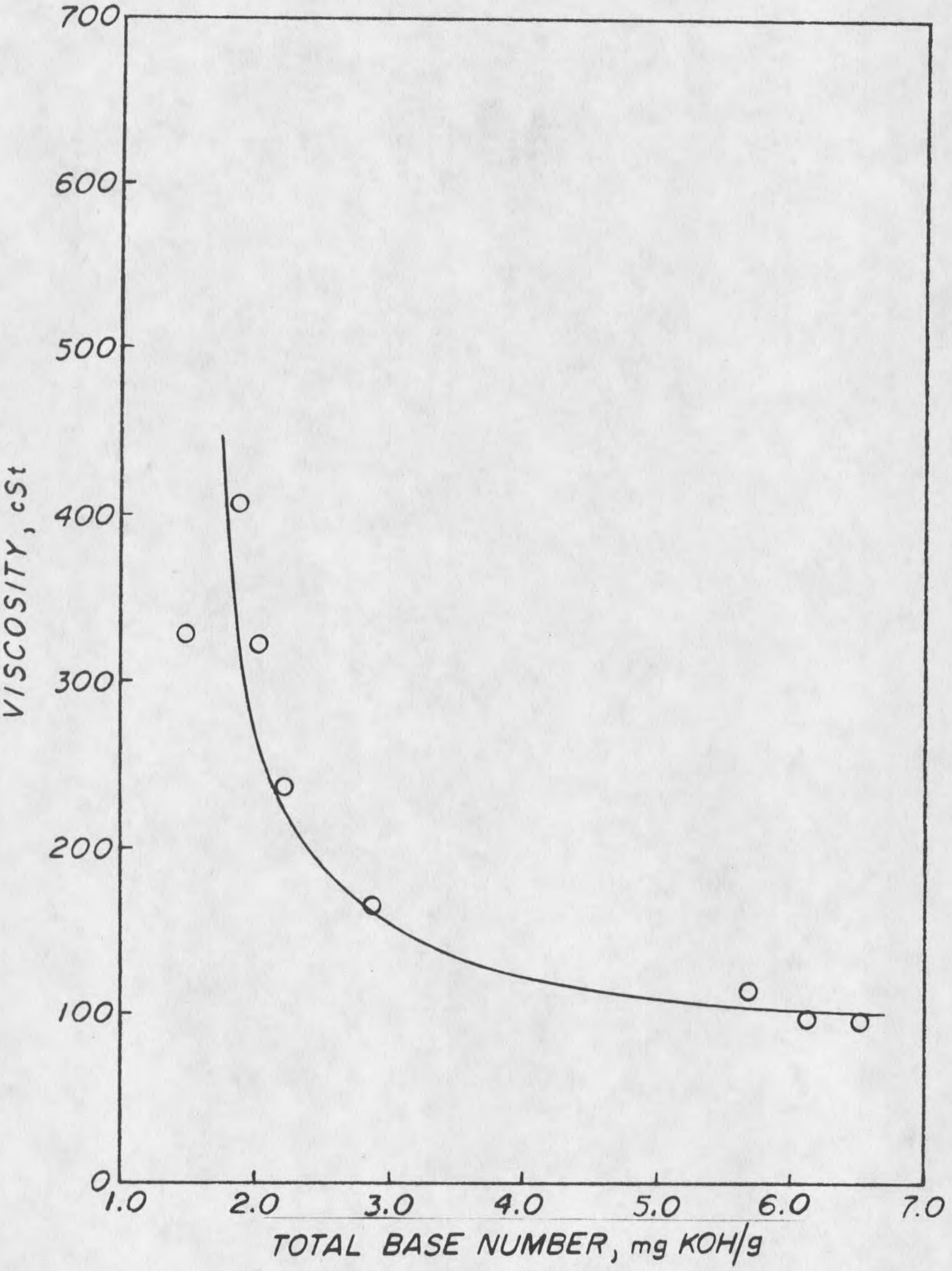


Figure 13. Viscosity vs. total base number for 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

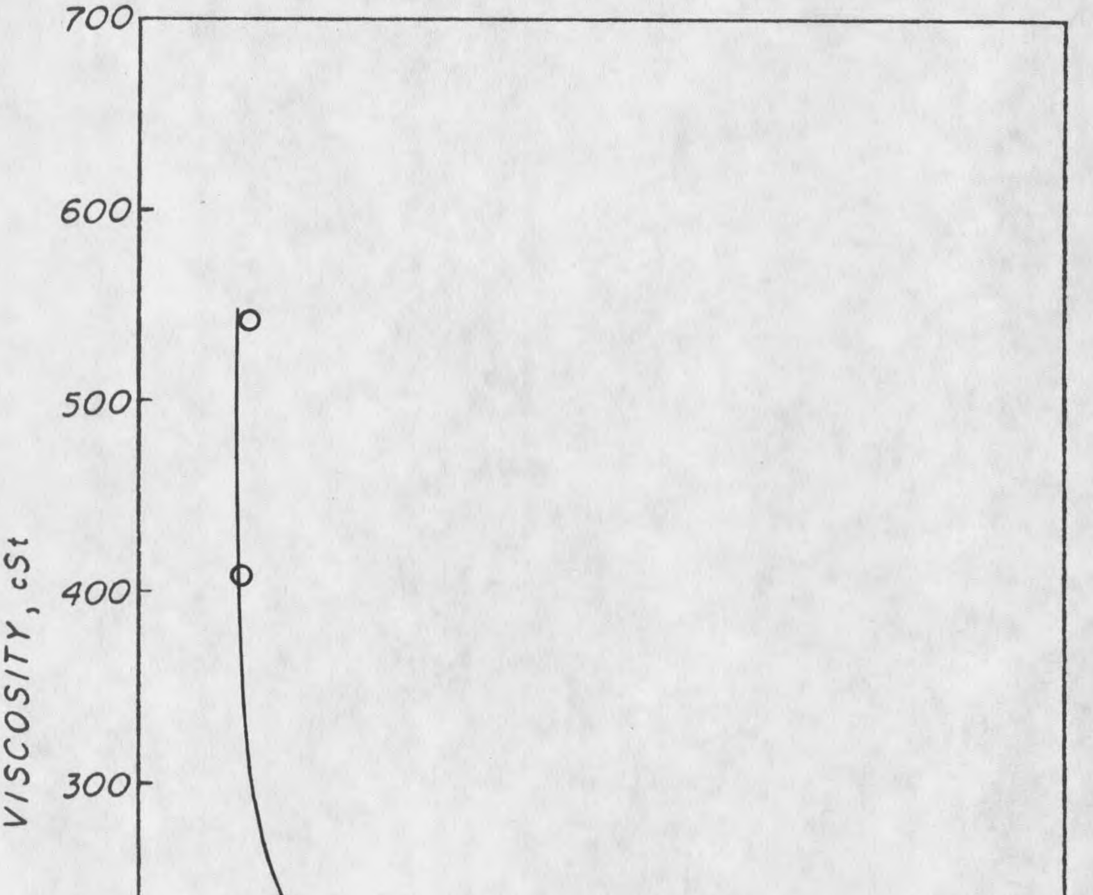
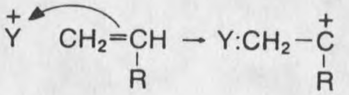


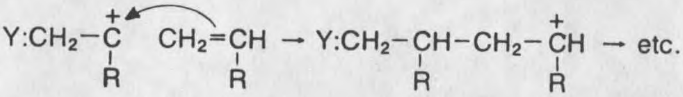
Figure 14. Viscosity vs. total base number for 20 cm copper-iron catalyst and 4000 ml/hr oxygen.

In runs 8, 10 and 12, the intention was to periodically add a compound which could maintain the TBN without having any other significant effect. Maintenance of TBN was desired in order to keep the concentration of free acids reduced. Thus, if acid catalysis of the polymerization is significant, the reduction in free acid concentration should reduce or eliminate viscosity rise in contaminated lubricating oil.

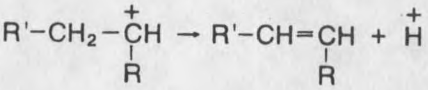
In acid catalysis, the acid attacks the double bond, forming a carbonium ion with a single bond. The carbonium ion continues the chain by attacking another double bond. Chain termination can occur by ejection of a proton forming an alkene, or by reaction with an anion [24]. This process is outlined in Equations 1-3, with Y representing the acid.



$$\overset{+}{Y}\quad CH_2{=}\underset{\underset{R}{|}}{C}H \rightarrow Y{:}CH_2-\underset{\underset{R}{|}}{\overset{+}{C}} \qquad (1)$$



$$Y{:}CH_2-\underset{\underset{R}{|}}{\overset{+}{C}}\quad CH_2{=}\underset{\underset{R}{|}}{C}H \rightarrow Y{:}CH_2-\underset{\underset{R}{|}}{C}H-CH_2-\underset{\underset{R}{|}}{\overset{+}{C}}H \rightarrow \text{etc.} \qquad (2)$$



$$R'-CH_2-\underset{\underset{R}{|}}{\overset{+}{C}}H \rightarrow R'-CH{=}\underset{\underset{R}{|}}{C}H + \overset{+}{H} \qquad (3)$$

The test for TBN is a destructive test, so in order to maintain a fairly constant sample volume three test cells were required for each sample. Cell 1 was first used to measure TBN. Cells 2 and 3 were assumed to have the same TBN, so material was transferred to cell 1 from cells 2 or 3. An addition of the TBN maintenance agent weighed to the nearest 0.1 mg was made, and TBN was checked again. If the desired TBN was achieved, similar additions were made to cells 2 and 3 with subsequent make-up to cell 1.

First, octadecylamine, an eighteen carbon saturated hydrocarbon with an amine functional group on one end, was employed. Octadecylamine was chosen with the intent that it would be soluble in the lubricating oil system and, due to its basic character, would help maintain TBN. Solubility was tested by adding octadecylamine to undegraded, diluted lubricating oil, with solution being achieved by heating the oil mixture. A solution of 52% octadecylamine separated into two phases immediately upon cooling, but a solution of 15% remained one phase for over 8 hours. Since the TBN of pure octadecylamine is 213 mg KOH/g, additions of 3% or less were used to achieve the desired TBN of lubricating oil samples. Hence, solubility was not a problem.

To determine the effect of the presence of octadecylamine on viscosity, additions of 0.67% or 0.30 g per 50 ml, and 2.90% or 1.30 g per 50 ml were made to undegraded, diluted lubricating oil. Viscosity of the two samples was 99 cSt and 91 cSt, respectively, compared to 96 cSt for undegraded, diluted lubricating oil. Hence, significant increases in viscosity cannot be attributed to simple addition of octadecylamine.

For the first addition at 13 hours elapsed time, 0.30 g per 50 ml sample were required to raise the TBN from 5.6 to 6.9 mg KOH/g. At 20.5 hours, the TBN had fallen to 3.1 mg KOH/g, which is somewhat less than would be expected without any addition of alkaline material. Viscosity had risen to 178 cSt which is significantly higher than would be expected without addition of octadecylamine. Addition of 1.01 g was required to raise the TBN to 6.0, making the total octadecylamine 1.31 g per 50 ml sample. After returning the samples to the bath, foaming and carryover occurred immediately, and the run was terminated.

There were two possible explanations for the unexpectedly low values of TBN after addition of octadecylamine. Total base number could be reduced by reaction of octadecylamine with some component of the lubricating oil system, which contains a complex mixture of chemical additives. This reaction would then prevent the octadecylamine from reacting with free acids in the desired manner.

Second, octadecylamine could have been rapidly evaporating from the test cells. Based on the boiling points of octadecylamine at 760 and 10 mm Hg [29], the vapor pressure is approximately 1.3 mm Hg at 150 C as found by a Cox chart. In run 9 an initial addition of 0.41 g octadecylamine per 50 ml was made to raise the TBN of the diluted lubricating oil from 6.25 to 8.29 mg KOH/g. Nitrogen at a flow of 2000 ml/hr was substituted for oxygen and the TBN was periodically monitored. Twenty cm copper-iron catalyst was included. Results in Figure 15 show the TBN was maintained at least 1.0 mg KOH/g above that of the oil without octadecylamine for 10 hours. Thus, the low values of TBN in run 8 must be due to reaction of octadecylamine rather than its rapid evaporation. Results from run 8 also show that this undesired reaction of octadecylamine is dependent on oxygen, since TBN was maintained when nitrogen was substituted for oxygen.

An experimental plan similar to run 8 was used in run 10 in order to see if the foaming problem and unexpected decrease in TBN would occur again. These results are shown in Figure 16, where the vertical dashed line indicates a jump in TBN due to an addition of octadecylamine. Again, the dotted line shows viscosity versus time for the standard set of conditions, which are 2000 ml/hr oxygen, 20 cm copper-iron catalyst and 5% sunflower oil.

Additions of 0.34 g and 0.74 g octadecylamine were made at 16 and 21 hours, respectively, with no foaming problems. At 21 hours the TBN had fallen to 3.5 mg KOH/g, again slightly less than would be expected without any additions. At 36 hours the TBN had fallen to 2.1 mg KOH/g, almost exactly the value expected without any additions. An addition of 1.04 g was required to raise the TBN to 6.3 mg KOH/g. Immediate foaming was noted upon return of the samples to the oil bath, so the run was terminated. As can be seen in Figure 16, viscosity again increased more rapidly than would be expected without addition of octadecylamine.

Although it is clear that octadecylamine is reacting with something other than the desired free acid species, the complexity of the lubricating oil system leaves the nature of this reaction uncertain.

Due to the problems encountered in runs 8 and 10 when adding noncompatible compounds to the lubricating oil system, Amoco 9231, a commercial lubricating oil additive,

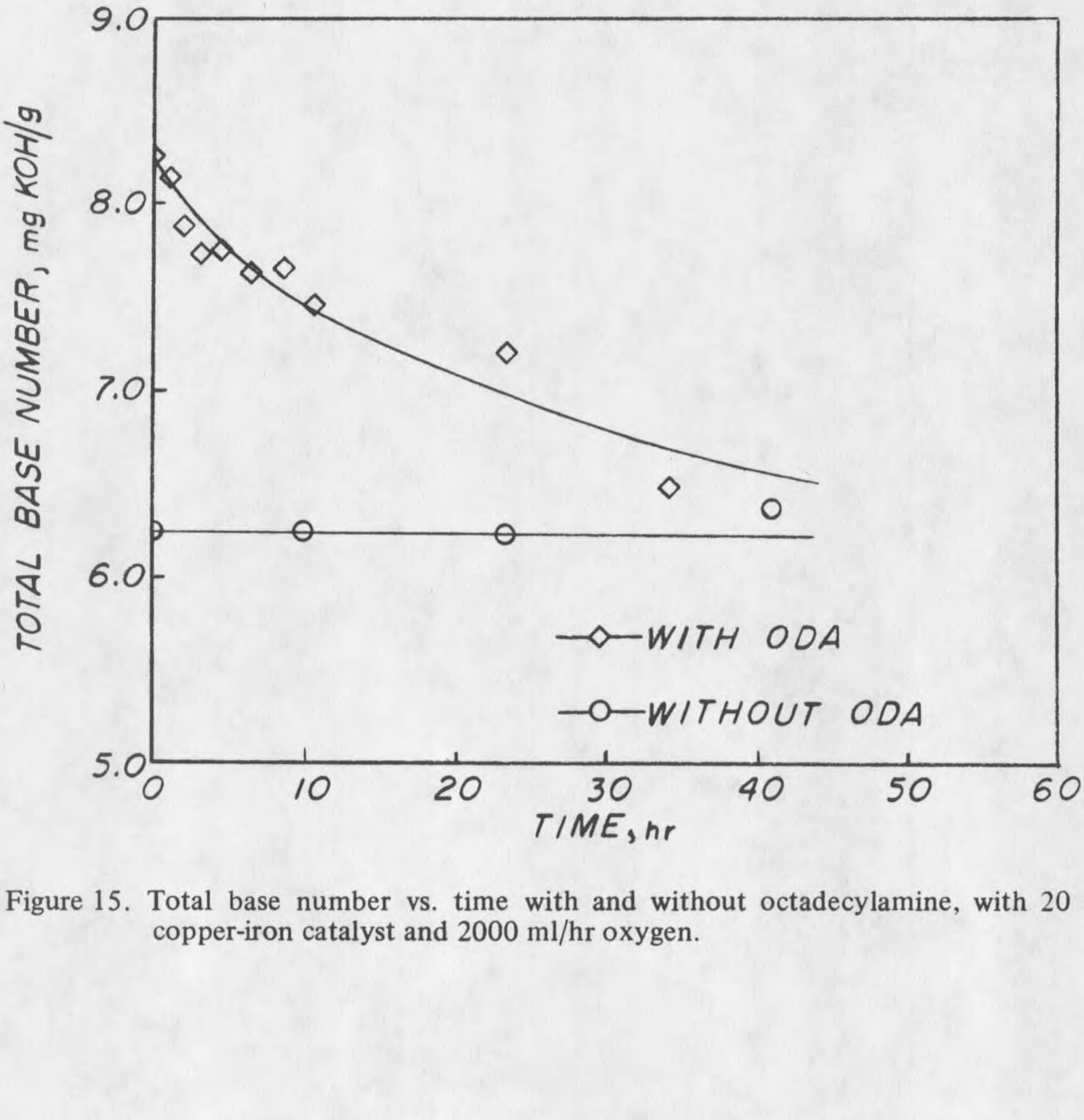


Figure 15. Total base number vs. time with and without octadecylamine, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

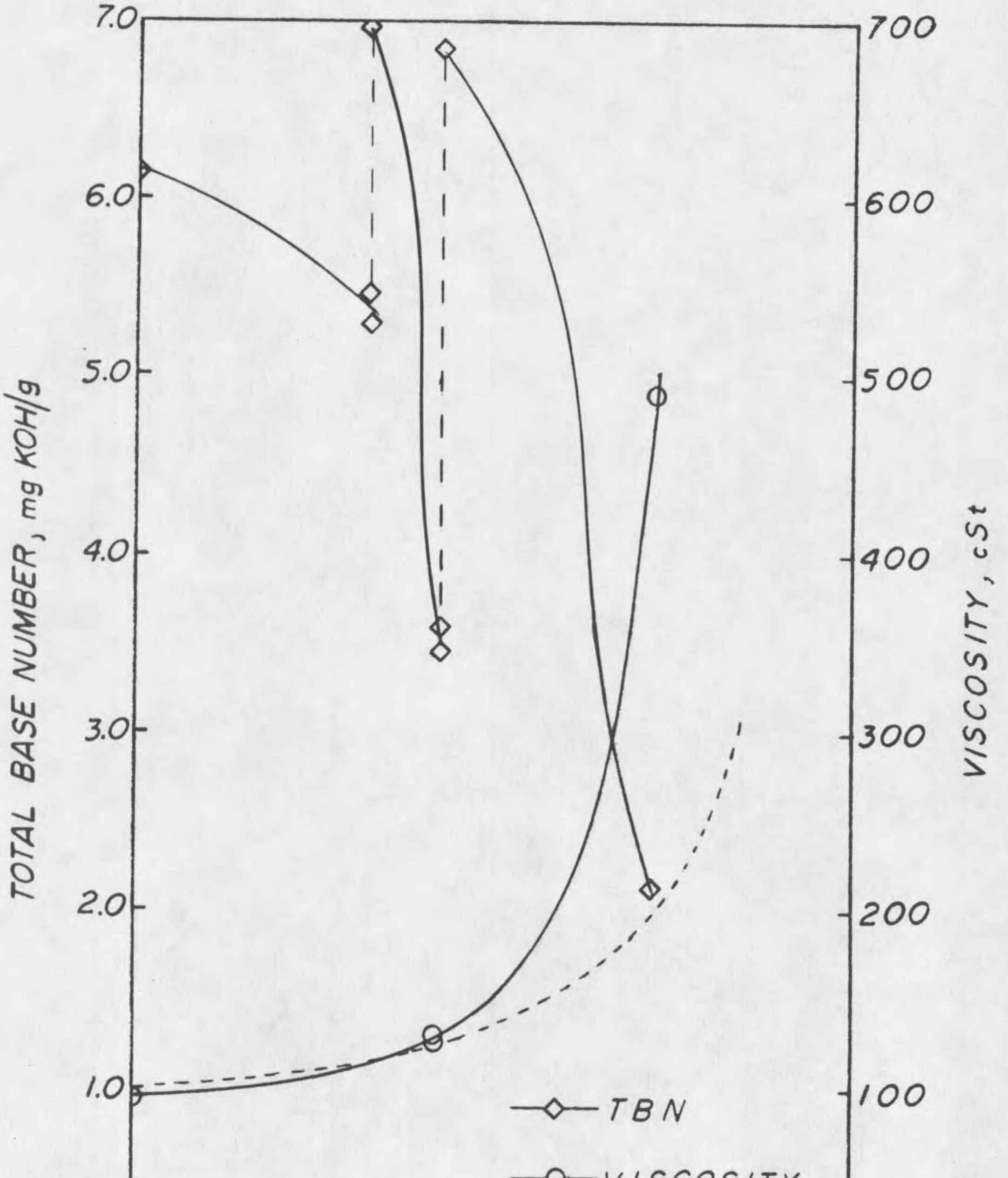


Figure 16. Total base number and viscosity vs. time for periodic additions of octadecylamine, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

was obtained from Amoco Petroleum Additives Corporation. This material is used as an oxidation inhibitor and TBN enhancer in lubricating oils formulated for both diesel and gasoline engines. Since the lubricating oil used in this work was formulated by Amoco Oil Company, it was felt this would be a compatible additive.

Amoco 9231 is an overbased calcium phenate formulation. This is a calcium salt of a substituted phenolate ion which has excess calcium added during the formation of the phenate. The TBN of Amoco 9231 is 252 mg KOH/g, about 18% higher than octadecylamine.

Results of run 12 using Amoco 9231 are shown in Figure 17, with the vertical dashed lines indicating a jump in TBN due to addition of Amoco 9231. Viscosities are slightly higher than would be expected without additives, as can be seen from the dotted line which shows the viscosity versus time for the standard set of conditions. At no point did the TBN fall below 4.3 mg KOH/g; the average value was 5.9 mg KOH/g. Additions were made at three different times. Total amount of Amoco 9231 added was 0.85 g. This amount of Amoco 9231 was also added to undegraded, diluted lubricating oil to determine the effect on viscosity, causing an increase of only 2.95 cSt or 3.05% above the diluted lubricating oil value.

Through the use of Amoco 9231 the TBN was maintained well above 3.0 g KOH/g throughout this experiment. Viscosity still rose at close to the expected rate. This is clear evidence that acid catalysis of polymerization is an unlikely possibility.

In run 11, phosphoric acid was added to diluted lubricating oil to a level of 3.0% with the intention of lowering the TBN. Reaction was not immediate, but when monitored at 12 hours, the TBN had fallen to 0.18 mg KOH/g, indicating the presence of free acid [22]. The color of the sample was black, as opposed to the normal brown found in all other samples. Examination of Figure 18, which shows viscosity versus time for the addition of phosphoric acid and for the standard set of conditions shows viscosities slightly less than expected, but certainly not out of a reasonable range of values. This shows that when TBN

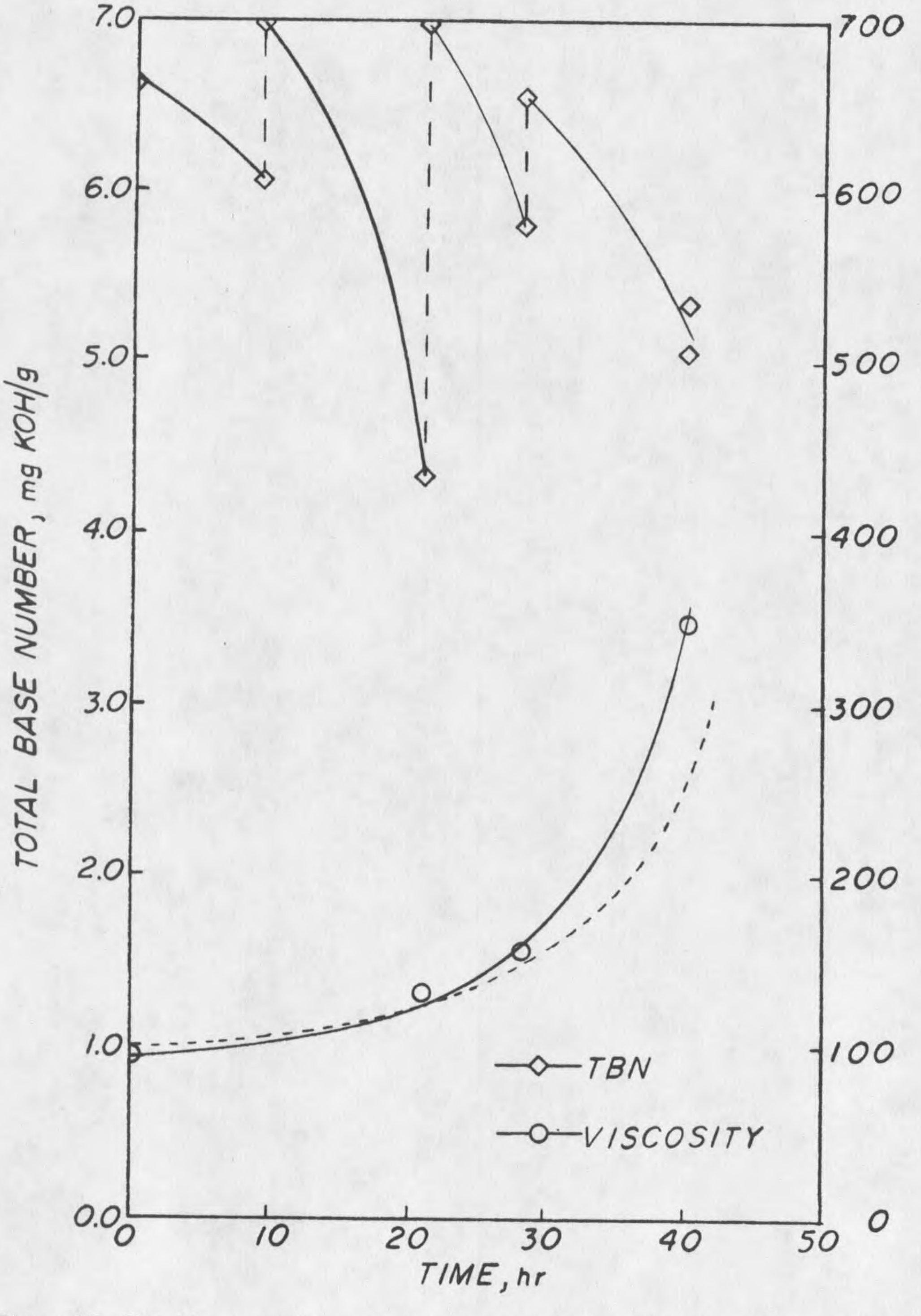


Figure 17. Total base number and viscosity vs. time for periodic additions of Amoco 9231, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

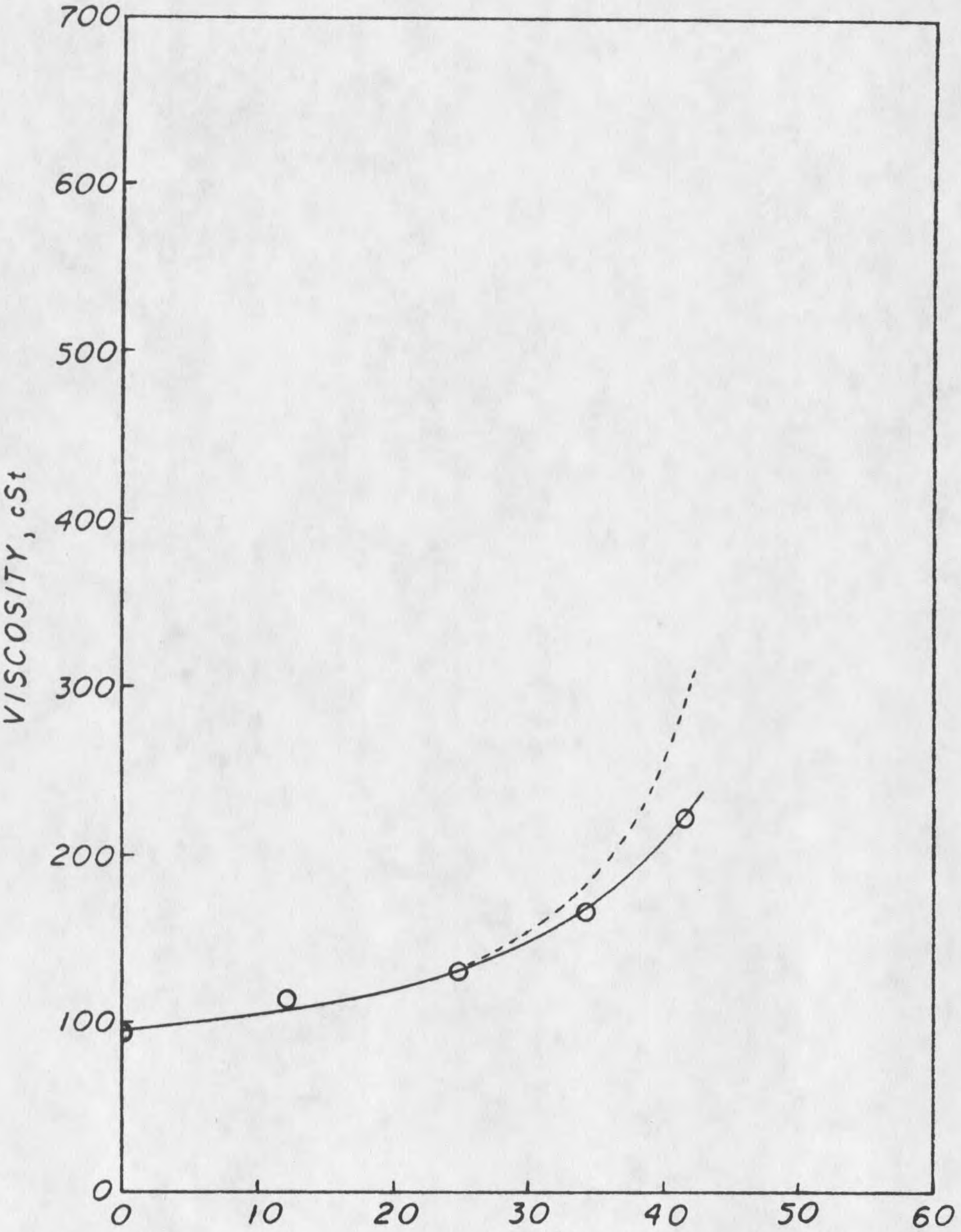


Figure 18. Viscosity vs. time for addition of phosphoric acid, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

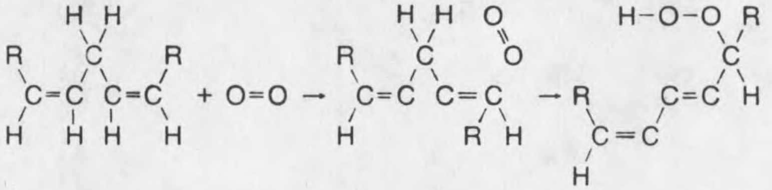
is substantially reduced, viscosity still rises at the expected rate. This is further evidence against the likelihood of an acid catalysis mechanism.

Runs 8, 10, 11, and 12 clearly indicate acid catalysis is not the mechanism for viscosity increase in lubricating oil diluted with vegetable oils. Neither raising nor lowering the free acid concentration by altering the TBN had any substantial effect on viscosity increase. These runs also show the complex nature of the lubricating oil system, which makes exact explanation of some observed phenomena difficult.

Free Radical Catalysis

Since acid catalysis did not explain the polymerization of the vegetable oil, run 13 was performed to examine a free radical polymerization mechanism.

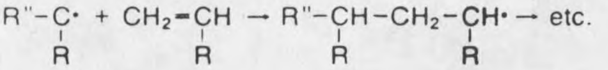
In this model, oxygen begins the polymerization by attacking the double bond. The oxygen abstracts a hydrogen from the methylenic carbon, causing a rearrangement of the double bond to a conjugated system and formation of a hydroperoxide. This is diagrammed in Equation 4.



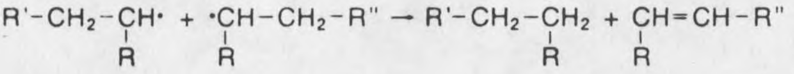
(4)

The relatively unstable hydroperoxide decomposes at the oxygen-oxygen bond to form a radical, which then initiates polymerization by attacking ethylenic carbons. Chain termination can occur by combination of two radicals, or by disproportionation where an alkane and an alkene are formed by reaction of two radicals [24]. These steps are shown in Equations 5-7. Addition of a peroxide initiates the polymerization as shown in Equation 5.

$$R-O\cdot + CH_2=\underset{R}{CH} \rightarrow R-O-CH_2-\underset{R}{CH}\cdot \qquad (5)$$

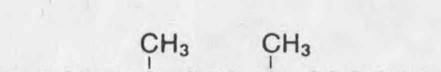


$$R''-\underset{R}{C}\cdot + CH_2=\underset{R}{CH} \rightarrow R''-\underset{R}{CH}-CH_2-\underset{R}{CH}\cdot \rightarrow \text{etc.} \qquad (6)$$



$$R'-CH_2-\underset{R}{CH}\cdot + \cdot\underset{R}{CH}-CH_2-R'' \rightarrow R'-CH_2-\underset{R}{CH_2} + \underset{R}{CH}=CH-R'' \qquad (7)$$

Standard conditions of 150 C, 20 cm copper-iron catalyst, and 2000 ml/hr gas flow were used. Nitrogen was substituted for oxygen. An organic peroxide, obtained from Lucidol Pennwalt Corporation in Buffalo, New York, was then periodically added to generate free radicals. The peroxide, whose trade name is Lupersol 130, is shown below.



$$(CH_3)_3COO-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{C}}-OOC(CH_3)_3$$

Lupersol 130 is 90.0 to 95.0% pure, has a vapor pressure of 55 mm Hg at 151 C, and a half life of 57 minutes at 150 C. Its typical decomposition products in inert media are methane, ethane, carbon monoxide, carbon dioxide, acetone and t-butyl alcohol, all of which have high vapor pressures at 150 C. None of these decomposition products were expected to react significantly with any system components. Lupersol 130 is used commercially as a crosslinking agent for polyolefins and a free radical initiator in vinyl polymerizations [30].

Periodic additions of 0.1% and 0.5% were made to two different cells every 2.5 hours for 27.5 hours. Additions were then made at 38.5, 42.5, and 47.5 hours. Viscosity measurements and times of peroxide additions are shown in Figure 19.

The viscosity at 40 C of Lupersol 130 is 4.0 cSt, and both it and its decomposition products have high vapor pressures at the experimental temperature. Thus, viscosity increase cannot be attributed to simple physical presence of the peroxide.

The rate of viscosity increase for the same experimental conditions with oxygen and without peroxide (which is the standard set of conditions) is also shown in Figure 19 as a

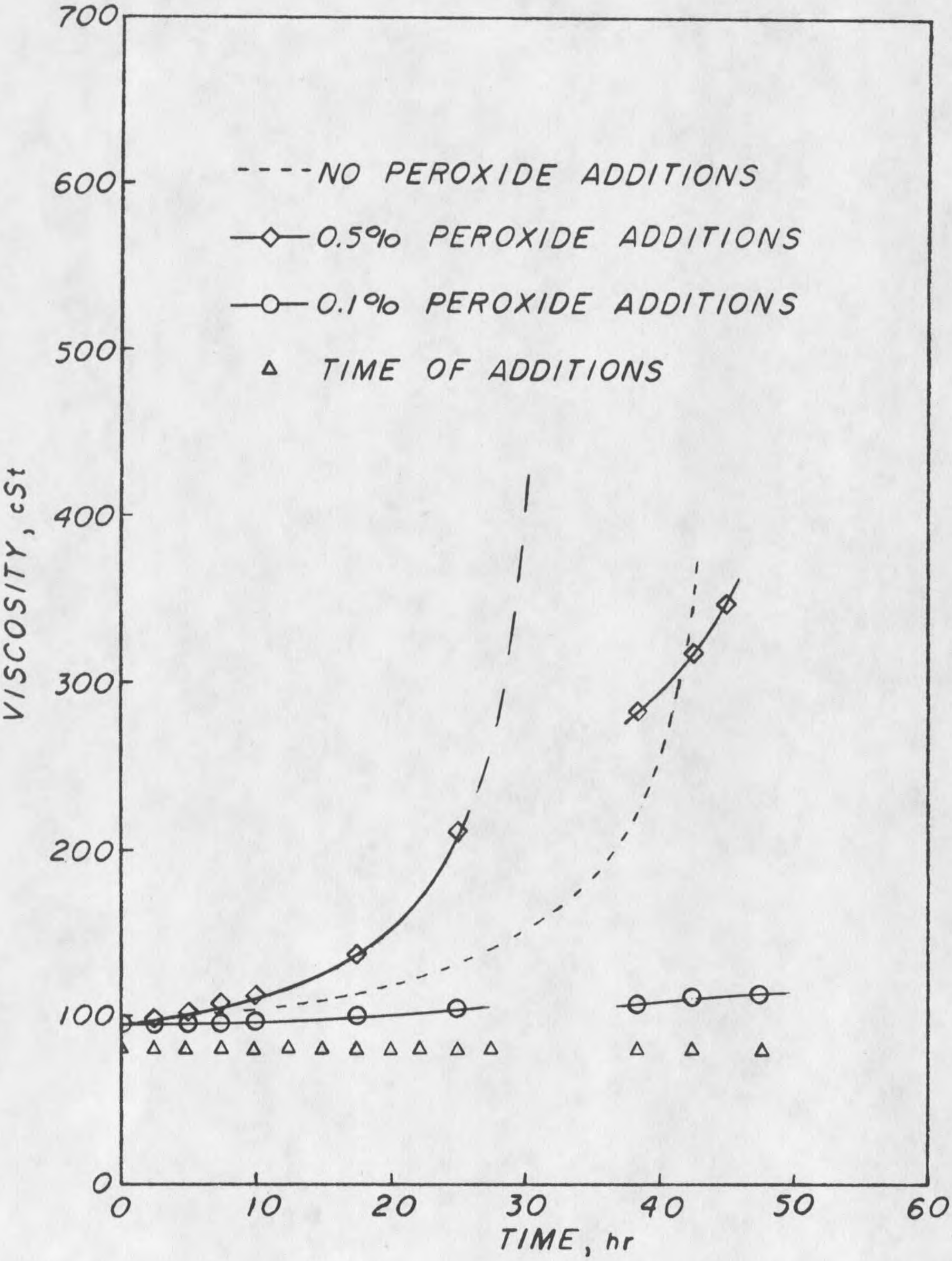


Figure 19. Viscosity vs. time for periodic additions of Lupersol 130, with 20 cm copper-iron catalyst and 2000 ml/hr nitrogen.

dotted line. The curve for the higher addition rate of Lupersol 130 is extrapolated in the figure as a dotted line. This extrapolation implies what would happen if regular additions of peroxide would have been continued.

The curves in Figure 19 are broken to indicate the lapse in addition of Lupersol 130. When additions were resumed at 38.5 hours, they were more widely spaced than in the first 27.5 hours of the experiment. This caused the difference in slopes that is clearly seen for the two sections of the curve for the higher addition rate. These more widely spaced additions lengthen the time between introduction of free radicals and so the second section of the curve is somewhat flatter than the first.

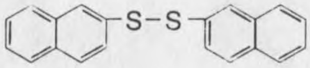
Clearly, the higher and lower addition rates of Lupersol 130, both of which are in the range of commercial dosage rates, bracket the curve where oxygen is used to induce viscosity increase. The shape of the curves is also similar to that obtained with oxygen. This similarity in both shape and magnitude among the curves generated by oxygen and Lupersol 130 indicates the strong likelihood of a free radical mechanism for viscosity increase in lubricating oil contaminated with vegetable oil.

At the end of the run, the TBN for the sample with the higher addition rate of peroxide was 6.30 mg KOH/g, indicating that few free acids were formed by the action of the peroxide. Thus, oxygen, not just free radicals, is required for acid formation. This is as expected, since free radicals would not oxidize double bonds to acids.

Sulfur Compounds

In run 12 an attempt was also made to decrease the catalyst activity by poisoning it with a sulfur compound. If this approach were successful, an addition of sulfur to the engine lubricating oil might limit the action of catalysts present in the oil as wear metals.

The material chosen was 2,2′-dinaphthyl disulfide, shown below.



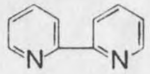
Basis for the choice of this sulfur compound was its melting point of 140 C and its high molecular weight, insuring fairly low volatility and thermal stability at 150 C, and its probable chemical compatibility with the system. A single addition of 0.52 g or 1.18% of 2,2′-dinaphthyl disulfide, representing an addition of 0.24% sulfur was made at the beginning of the run. Viscosity increased more rapidly than would be expected without any additive present, rising to 257 cSt in 28 hours. Since the viscosity at 9 hours was only slightly above the expected value, this increase was not due solely to the physical presence of the sulfur compound.

Amoco 9231 has 3.0% sulfur in it. At the end of run 12, a total of 0.025 g or 0.058% sulfur had been added to the cells investigating Amoco 9231 as a TBN maintenance agent. Although the nature of the sulfur compound in Amoco 9231 is unknown, it had no apparent effect on viscosity increase, and thus did not appreciably poison the copper catalyst.

Although sulfur compounds can be free radical inhibitors [31] and catalyst poisons, it appears that the 2,2′-dinaphthyl disulfide enhanced the polymerization reaction. Certain antioxidants can show a pro-oxidant effect in some cases. Phenolic types of antioxidants, such as hydroquinone may react with organic acids to form a radical species of antioxidant, which subsequently abstracts a hydrogen from a hydrocarbon, thus regenerating the antioxidant and forming a free radical hydrocarbon. Although it was not noted in the literature review until after run 12, diphenyl disulfide, which is very similar to 2,2′-dinaphthyl disulfide, also shows this pro-oxidant behavior [23]. This result from run 12 strengthens the likelihood of a free radical mechanism for the polymerization of vegetable oil in lubricating oil.

Chelating Agent

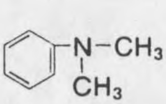
In run 13, an attempt was made to remove the solubilized copper, which may be the active form of the catalyst, from the system by use of a chelating agent. A single addition of 0.19 g per 50 ml of sample or 0.37% of 2,2′-dipyridyl was made. The structure of 2,2′-dipyridyl is shown below.



This material generally shows strong chelating activity with copper in both its valence states and iron in its lower valence state [32].

Under standard test conditions the viscosity increased to over 800 cSt in 17.5 hours. Since this is much faster than the rate of viscosity increase without the chelating agent it is clear that there is some interaction between it and the lubricating oil system.

Although the nature of this interaction is not clear, the 2,2′-dipyridyl may act as an activator, which reduces the activation energy of the peroxide decomposition reaction. Certain amines, such as N,N-dimethylaniline, shown below, fall into this class of compounds.



The 2,2′-dipyridyl may show similar activity as its structure is somewhat related to N,N′-dimethylaniline.

Wear Preventative Properties

As previously discussed, samples from a number of runs were sent to Phoenix Chemical Laboratories for wear analysis. To determine the precision of the analysis, one individual sample was divided into two samples. The variation between the average scar diameter of the two samples was 0.03 mm, well within the repeatability limits of 0.12 mm given in ASTM D 4172 [27].

Average scar diameter did not seem to be related to length of time of degradation for lubricating oils containing vegetable oil, but showed a definite relation to time for oils containing no vegetable oil. These results are shown in Figure 20.

Results indicate a weak relationship between average scar diameter and viscosity, as shown in Figure 21. Scar diameter does not begin to rise until oil viscosity rises well above the point of oil failure. All samples with viscosity below 400 cSt show an average scar diameter less than or equal to the value for undegraded pure lubricating oil. Even at a viscosity of 693 cSt, the average scar diameter for lubricating oil diluted with sunflower oil is less than the value for pure lubricating oil degraded under the same conditions and for the same length of time. Failure of this oil in an engine would be due to poor fluid handling characteristics rather than poor wear preventative properties.

Improvement of lubrication due to contamination with vegetable oil is probably due to physical adsorption of vegetable oil on the metal surfaces caused by the polar nature of vegetable oil [33]. A solid film is formed on the metal surface by closely packed molecules of vegetable oil. This film resists metal penetration and forms a zone of low shear stress at the outer surfaces of the adsorbed monolayers. Coefficient of friction between metals lubricated with fatty acids decreases with increasing chain length up to 14 carbons for fatty acids, after which it becomes constant [33].

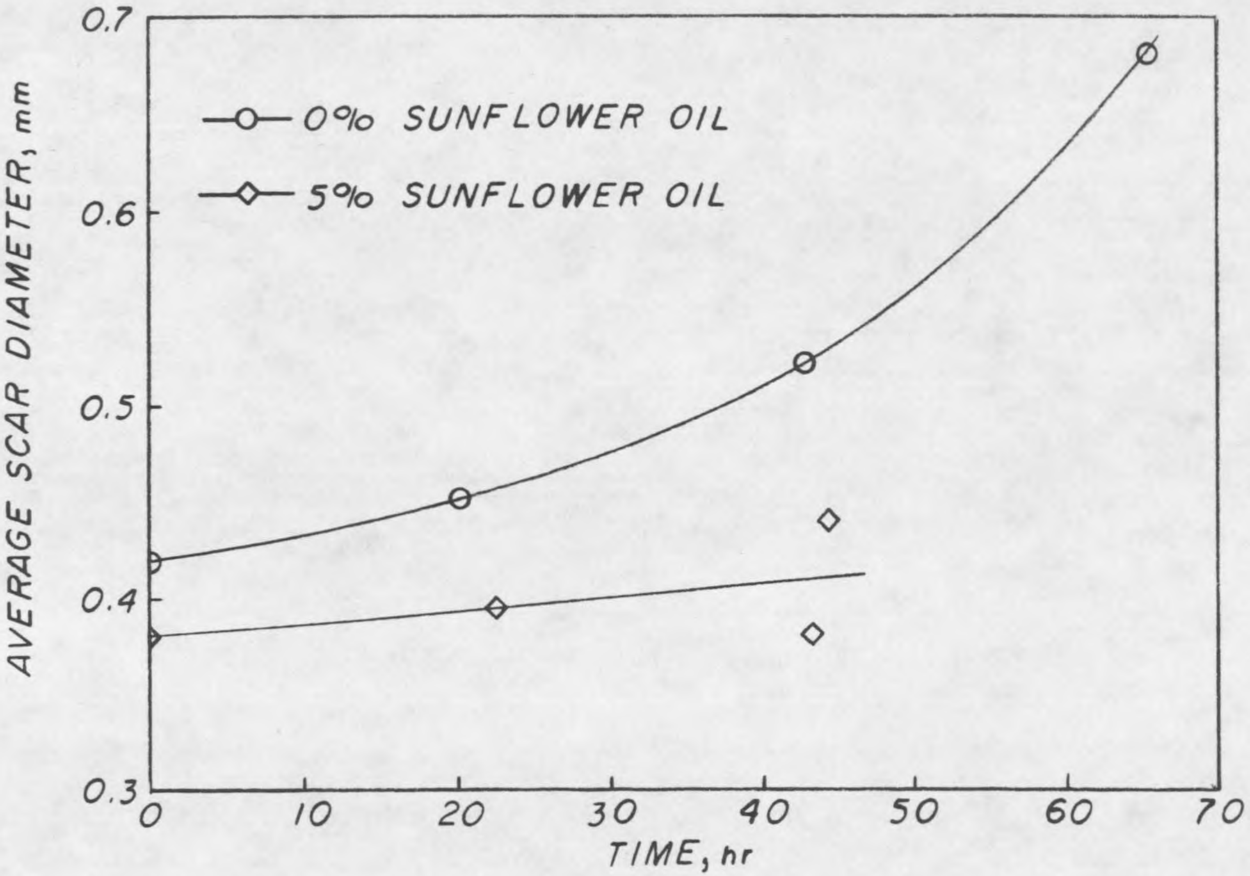


Figure 20. Average scar diameter vs. time for 0 and 5 wt. % sunflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

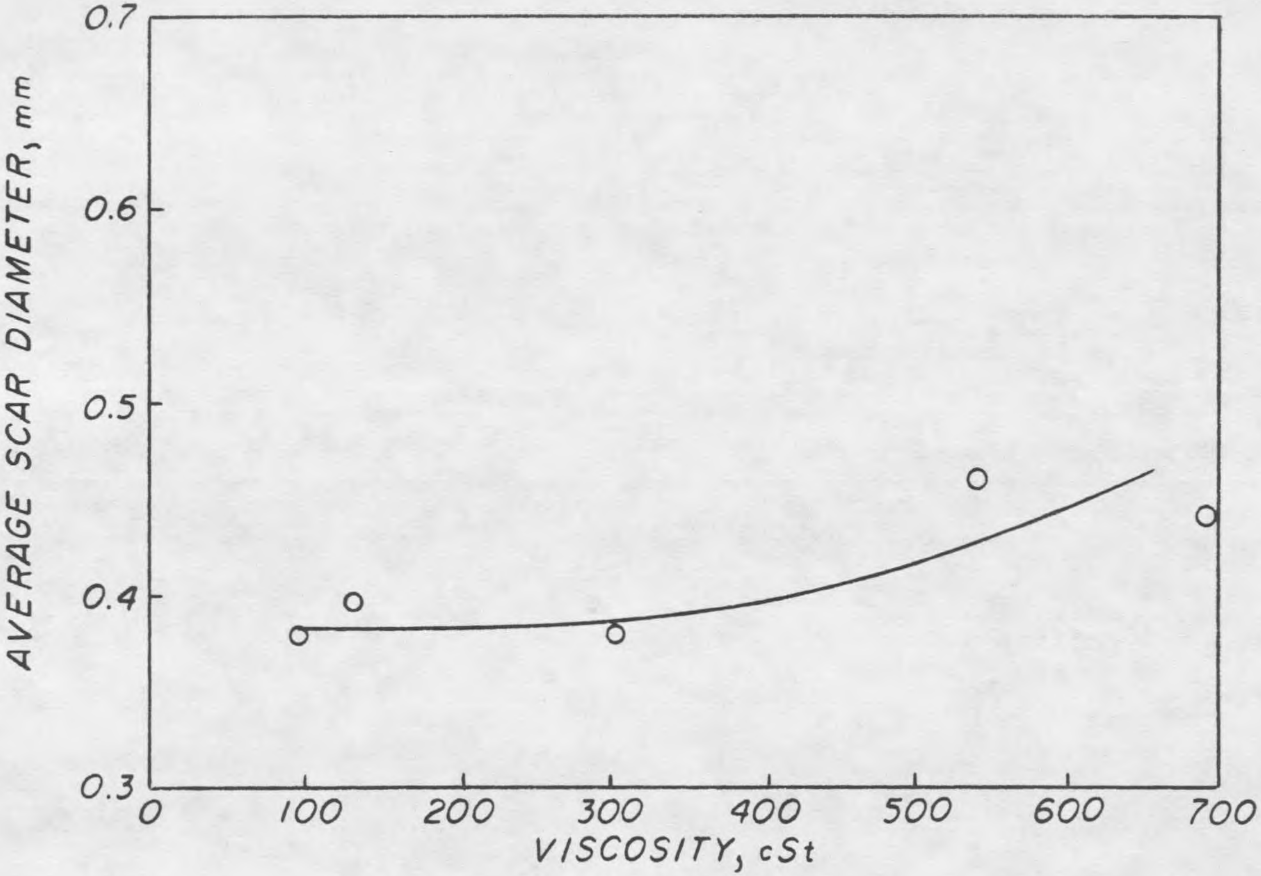


Figure 21. Average scar diameter vs. viscosity for 5 wt. % sunflower oil, with 20 cm copper-iron catalyst.

CONCLUSIONS

This investigation of polymerization of lubricating oil contaminated with vegetable oil has produced the following conclusions:

1. Factors accelerating the rate of viscosity increase in lubricating oil contaminated with vegetable oil are increasing flow rate of oxygen, increasing catalyst level, increasing temperature, and increasing the number of double bonds added by either a higher concentration of vegetable oil or a more unsaturated vegetable oil.

2. Decrease in total base number and increase in viscosity in contaminated lubricating oil are not causally related, demonstrating that free acids play no significant role in the mechanism of viscosity increase.

3. Increase in viscosity of lubricating oil contaminated with vegetable oil is most likely due to an oxygen-induced free radical mechanism.

4. Presence of free radicals or peroxides causes an increase in viscosity, but does not cause a decrease in total base number.

5. Substitution of nitrogen for oxygen eliminates both the increase in viscosity and the decrease in total base number associated with the presence of oxygen.

6. Copper is important in catalyzing viscosity increase in contaminated lubricating oil while iron is not.

7. Combined copper-iron catalyst is important in catalyzing reduction in total base number in contaminated lubricating oil.

8. The chelating agent 2,2′-dipyridyl does not reduce rate of viscosity increase by removing solubilized copper.

9. Sulfur did not seem to have any effect on reducing the rate of viscosity increase by poisoning the copper catalyst.

10. Wear preventative characteristics of contaminated lubricating oil are only weakly related to viscosity. Failure of contaminated lubricating oil in an engine would be due to poor fluid handling characteristics rather than poor wear preventative properties.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Since increase in viscosity of lubricating oil contaminated with vegetable oil is most likely due to a free radical mechanism, effects of system additives which act as free radical inhibitors should be examined as a means of limiting viscosity increase.

2. The specific mechanism of metal catalysis of viscosity increase is not clear. Experimental runs using peroxides, but without metal catalyst(s) present should be performed to elucidate whether the metal is needed only to aid in generating peroxides, or whether it also plays a role in peroxide degradation.

3. Since increase in viscosity of lubricating oil contaminated with vegetable oil is dependent on the presence of double bonds, effects of system additives which react with double bonds in a nonpolymerizing manner should be examined as a means of limiting viscosity increase.

4. Analyze oil mixture samples using infrared and atomic absorption spectroscopy to study concentrations of retained vegetable oils and additives and presence of solubilized metal catalysts. This is desirable to verify the presence of species thought to be affecting the viscosity increase in lubricating oil contaminated with vegetable oil.

5. Additional experiments using metal chelating agents would be warranted if atomic absorption analysis indicates the presence of solubilized copper catalyst.

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APPENDICES

APPENDIX A

ENGINE MANUFACTURERS ASSOCIATION SCREENING TEST

The Engine Manufacturers Association, a trade association of 21 international engine manufacturers, has at the request of the United States Department of Agriculture proposed a 200 hour preliminary durability screening test for alternate diesel fuels [14]. Each test, which is cyclic in nature, begins with a new or rebuilt engine which has been fully blueprinted in terms of weights and measurements of all wear surfaces (e.g., cylinder liners, rings, valves, valve seats, bearings, etc.).

After being broken in for 90 minutes with diesel fuel, the following test schedule is used:

Step	Speed	Torque	Power	Duration-min
1	Rated	–	Rated	60
2	85%	Max	~95%	60
3	95%	28%	25%	30
4	Low Idle	0	0	30

Five consecutive 180 minute tests are to be run, followed by a 9 hour (or longer) shutdown. Test duration is 200 hours of cyclic operation.

Failure of the test is based on several different criteria, any of which constitute failure:

1. Drop in power of 5% or more which cannot be corrected with minor adjustments.

2. Failure to complete the 200 hour test for any reason related to the test fuel.

3. A change in oil viscosity of 50% from the new oil value. Oil may be changed at no less than 100 hours.

4. Failure of oil dispersancy.

5. Wear of engine which would extrapolate to a 50% or greater reduction in engine life.

Tests may be terminated prior to "total engine disaster," but this would constitute test failure.

APPENDIX B

TABLES OF RESULTS AND RUN CONDITIONS

Table 1. Run 1 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	0	0	20	20	100	100
Iron	0	0	20	20	100	100
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 2. Run 1 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	93.6	93.6	93.6	93.6	93.6	93.6
7.5	101.5	100.6	102.2	107.9	102.4	101.7
18.0	112.1	112.8	116.8	119.0	142.5	141.7
28.25	126.7	125.4	147.1	155.2	>800	>800
38.0	139.8	136.6	193.2	226.5		
43.25	147.2	146.2	235.1	326.8		

Table 3. Run 2 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	0	0	20	20
Iron	20	20	0	0	20	20
Flow rate, ml/hr	4000	4000	4000	4000	4000	4000
Gas used	O_2	O_2	O_2	O_2	N_2	N_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 4. Run 2 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	100.8	100.8	100.8	100.8	100.8	100.8
9.75	102.1	104.0	103.0	104.5	96.3	96.5
19.75	129.1	129.5	115.0	115.1	98.1	96.9
29.0	178.6	192.4	127.1	128.5	97.8	99.2
40.75	541.2	>800	145.0	144.9	99.6	99.3

Table 5. Run 3 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	20	20	20	20
Iron	20	20	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*		sun	sun	sun	sun	sun
Oil concentration, wt%	0	1	3	7	9	9

*sun = sunflower.

Table 6. Run 3 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	107.9	106.0	101.6	93.5	90.0	90.0
16.0	107.1	110.0	109.4	129.3	320.6	530.1
18.5					>800	
25.25	108.2	113.7	121.8	494.8		
40.75	110.7	115.8	134.7			
65.25	113.0	128.1	163.2			

Table 7. Run 4 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	0	0	20	20	20	20
Iron	0	0	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	4000	4000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	120	120	120	120	120	120
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 8. Run 4 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	96.0	96.0	96.0	96.0	96.0	96.0
18.75	96.4	96.1	96.6	96.6	96.9	96.7
27.75	96.4	97.2	97.0	96.8	97.5	97.6
38.75	98.0	98.4	98.1	97.7	98.3	98.5
62.25	100.9	100.0	100.0	99.4	100.2	100.4
108.0	106.3	106.3	105.4	105.4	105.9	105.5
154.0	112.5	112.7	124.8	123.0	120.0	125.8

Table 9. Run 5 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	100	100	100	20	20	20
Iron	100	100	100	20	20	20
Flow rate, ml/hr	4000	4000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	lsa
Oil concentration, wt%	5	5	5	5	9	5

*sun = sunflower.
lsa = linoleic safflower.

Table 10. Run 5 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	98.0	98.0	98.0	98.0	89.9	96.3
16.25	125.0	122.4	124.2	111.0	304.2	112.4
20.25	458.8	423.9				
22.5				134.4		
26.5			>800			153.3
37.5						279.1

Table 11. Run 6 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	20	20	20	20
Iron	20	20	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	osa
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.
osa = oleic safflower.

Table 12. Run 6 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	94.5	94.5	94.5	94.5	94.5	98.0
5.0	97.2					97.5
17.5	114.6					101.8
27.5		160.9				
40.0	336.6	373.8	408.9	320.6	312.2	131.8
46.75	>800				>800	222.1

Table 13. Run 6 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	6.50	6.50	6.50	6.50	6.50	
5.0	6.16					
17.5	5.69					
27.5		2.84				
40.0			1.89	2.01		
46.75	1.70				1.65	

Table 14. Run 7 Conditions.

	Cell Number					
	1	2	3	4[+]	5[+]	6[+]
Cm catalyst						
Copper	20	20	20			
Iron	20	20	20			
Flow rate, ml/hr	4000	4000	4000			
Gas used	O_2	O_2	O_2			
Temperature, °C	150	150	150			
Oil type*	sun	sun	sun			
Oil concentration, wt%	5	5	5			

*sun = sunflower.

[+] Terminated due to experimental problems.

Table 15. Run 7 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	97.2	97.2	97.2			
14.0	110.5					
22.75	154.1					
34.5	296.5	228.8	271.2			
41.75	>800	408.1				

Table 16. Run 7 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	6.36	6.36	6.36			
14.0	6.06					
27.75	3.01					
34.5		1.74				
41.75		1.67				

Table 17. Run 8 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	20	20	20	20
Iron	20	20	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 18. Run 8 Additive Amounts.

	Type of Additive – Octadecylamine					
	Additive Used, g, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
13.0	0.2956	0.2956	0.2956	0.2949	0.2956	0.2948
20.5	1.0093	1.0085	0	1.1065	1.0085	1.0083

Table 19. Run 8 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	96.8	96.8	96.8	96.8	96.8	96.8
20.5	179.8	177.0				

Table 20. Run 8 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	6.20	6.20	6.20	6.20	6.20	6.20
13.0†	5.28	5.85				
13.0‡	6.73	6.97				
20.5†	3.26	2.96				
20.5‡	5.98	5.95				

† Before addition of octadecylamine.
‡ After addition of octadecylamine.

Table 21. Run 9 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	20	20	20	20
Iron	20	20	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	N_2	N_2	N_2	N_2	N_2	N_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 22. Run 9 Additive Amounts.

	Type of Additive – Octadecylamine					
	Additive Used, g, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	0.4268	0.4268	0.4268	0.4268	0.4268	0

Table 23. Run 9 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	8.29					
1.0	8.12					
2.0	7.87					
3.0		7.72				
4.0			7.75			
6.5			7.61			
8.5				7.65		
9.75						6.26
10.5				7.46		
23.25						6.24
23.5					7.20	
34.25					6.49	

Table 24. Run 10 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	20	20	20	20
Iron	20	20	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 25. Run 10 Additive Amounts.

	Type of Additive – Octadecylamine					
	Additive Used, g, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
16.0	0.3435	0.3435	0.3444	0.3431	0.3435	0.3433
21.0	1.4814	0.7404	0.5180	0.5084	0.7400	0.7400
36.0	0	1.0374	0	0	1.0365	1.0373

Table 26. Run 10 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	96.8	96.8	96.8	96.8	96.8	96.8
21.0	129.2	126.4				

Table 27. Run 10 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	6.16	6.16	6.16	6.16	6.16	6.16
16.0[†]	5.45	5.30				
16.0[‡]	6.98	6.82				
21.0[†]	3.59	3.43				
21.0[‡]	6.83	6.81				
36.0[†]		2.11				
36.0[‡]		6.27				

[†] Before addition of octadecylamine.

[‡] After addition of octadecylamine.

Table 28. Run 11 Conditions.

	Cell Number					
	1	2	3	4[†]	5[†]	6[‡]
Cm catalyst						
Copper	20	20	100	20	20	20
Iron	20	20	100	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun			sun
Oil concentration, wt%	7	5	5	0	0	5

*sun = sunflower.

[†] Samples for wear analysis only.

[‡] 3.0 wt% H_3PO_4 added at beginning of run.

Table 29. Run 11 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0						97.2
12.0						115.8
16.25			127.2			
17.5			169.6			
19.0			223.5			
20.5			>800			
22.0	>800					
22.25						131.2
34.0						167.7
41.25						224.1
43.5		573.6				
44.5		693.0				

Table 30. Run 12 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	20	20	20	20		20
Iron	20	20	20	20	20	
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	O_2	O_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	5	5	5

*sun = sunflower.

Table 31. Run 12 Additive Amounts.

	Additive Used, g, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
Type of Additive	9231*	9231*	9231*	DD[†]	none	none
0				0.5204		
9.0	0.1605	0.1645	0.1732			
21.0	0.4606	0.3800	0.4636			
28.0	0.2020		0.2815			

*9231 = Amoco 9231.

[†] DD = Dinaphthyl disulfide.

Table 32. Run 12 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	95.3	95.3	95.3	95.3	95.3	95.3
9.0				113.7		
21.0	131.2			174.5	118.3	139.8
28.0	174.5			257.3	129.2	195.9
40.0	>800		346.1	>800	149.5	>800

Table 33. Run 12 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	6.64	6.64	6.64			
13.0†	6.08					
13.0‡	7.00					
21.0†	4.33					
21.0‡	6.99					
28.0†	5.80					
28.0‡	6.55					
40.0	5.05		5.34			

† Before addition of Amoco 9231.
‡ After addition of Amoco 9231.

Table 34. Run 13 Conditions.

	Cell Number					
	1	2	3	4	5	6
Cm catalyst						
Copper	0	0	20	20	20	20
Iron	0	0	20	20	20	20
Flow rate, ml/hr	2000	2000	2000	2000	2000	2000
Gas used	O_2	O_2	O_2	O_2	N_2	N_2
Temperature, °C	150	150	150	150	150	150
Oil type*	sun	sun	sun	sun	sun	sun
Oil concentration, wt%	5	5	5	7	5	5

*sun = sunflower.

Table 35. Run 13 Additive Amounts.

	Additive Used, g, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
Type of Additive	none	none	DP*	none	LU†	LU†
0			0.1862		50	250
2.5					50	250
5.0					50	250
7.5					50	250
10.0					50	250
12.5					50	250
15.0					50	250
17.5					50	250
20.0					50	250
22.5					50	250
25.0					50	250
27.5					50	250
38.5					50	250
42.5					50	250

*2,2' – dipyridyl.

† Lupersol 130, amount shown in μl.

Table 36. Run 13 Results.

	Viscosity, cSt, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0						
2.5					96.4	98.5
5.0					96.8	102.2
7.5	100.4		104.9		97.2	106.1
10.0					98.6	113.4
17.5	110.4		>800		100.6	138.3
20.0				166.3		
25.0	124.9				105.6	212.0
38.5		140.7			109.0	281.3
42.5					110.6	318.8
47.5					112.8	368.4

Table 37. Run 13 Results.

	Total Base Number, mg KOH/gm, versus Time for Different Cells					
	Cell Number					
Time, hrs	1	2	3	4	5	6
0	6.31					
12.5	6.14					
25.0	4.01					
38.5		2.83				
27.5						6.30

Table 38. Additional Total Base Number Results.

Run Number	Cell Number	Time, hrs	Total Base Number, mg KOH/g
1	1	43.25	2.67
1	3	43.25	2.20
1	4	43.25	1.48
1	5	28.25	1.45
2	1	40.75	1.72
2	2	40.75	1.52
2	5	40.75	6.39
3	1	65.25	4.27
3	3	65.25	1.80
3	4	25.25	2.16
3	6	16.0	2.34

Table 39. Wear Test Results.

Run Number	Cell Number	Time, hrs	Average Scar Diameter, mm
1	4	43.25	0.38
2	1	40.75	0.46
3	1	65.25	0.68
4	3	154.0	0.36
5	4	22.50	0.40
5	5	16.25	0.37
5	6	37.5	0.42
†		0	0.42
‡		0	0.38

† Pure lubricating oil.

‡ Lubricating oil with 5% sunflower oil.

Rewolinski, Chance
Vegetable oil dilution of diesel engine..

DATE	ISSUED TO
Ⓕ BW	[redacted]
	[redacted]