Final Report Submitted to DOE/OTM Tribology Program

September 1992 - September 1993

Project Title:

The Effect of Alternative Fuels on the Stability and Lubricity of
Crankcase Lubricants

Submitted By

E. E. Klaus, J. L. Duda, and R. J. Shah

Department of Chemical Engineering
The Pennsylvania State University
University Park, PA 16802

MASTER

ds
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Table of Contents

Summary Statement	1
Introduction	4
Test Development	6
Experimental Studies	
Experimental Procedure Designed To Simulate the Condition in a Fuel Injector System ...	7
Experimental Procedure Designed To Simulate the Condition in the Crankcase	9
Study Conducted on Two Diesel Crankcase Lubricants Designed for Use With Methanol Fuel	9
Solubility	10
Study of Stability and Wear Properties After 20% Methanol Contamination	10
Stability and Wear Properties of Raffinate and Extract Phases	11
Development of Bulk Oxidation Test To Simulate Methanol Fueled Engines	12
Studies of M-85 Alternative Fuel	14
Tables	16
Figures	21
Appendix A: Timetable for Proposed Work	32

Summary Statement

Energy and environmental concerns have created a major thrust in the U.S. towards alternative fuels for internal combustion engines. One of the main problems associated with the utilization of alternative fuels is the effect of these fuels on the performance of the engine and its lubrication systems. The potential lubrication problems can be severe and quite diverse, depending upon the specific characteristics of the alternative fuel chemistry, the composition of the base lubricant and its additives and the characteristics of the bearing materials in the engine. For example, in the case of alcohol fuels (methanol or ethanol), small amounts of the alcohol in the crankcase can cause phase separation of components of the lubricant base stock and additive package, leading to excessive wear and/or lubricant degradation. In contrast, in the fuel injection system, small quantities of the lubricant are exposed to large quantities of the alcohol fuel which can lead to extract (fuel soluble) and raffinate (fuel insoluble) phases which can cause injector plugging and/or excessive injector wear.

The purpose of this research is to study the effect of alternative fuels on the functioning of crankcase lubricants with these three main goals:

1. Develop simple, rapid test protocols to evaluate the influence of alternative fuels on the stability and lubricity of lubricants under conditions simulating engine operation. The objective is to have these test protocols serve industry as a precursor evaluation procedure before expensive engine tests are conducted. The reliability of these test procedures to predict the influence of additives on lubricant performance under actual operating conditions will be determined by comparison of these test results with available engine and fleet tests.
2. Use the developed test procedures to evaluate commercially available lubricants for applications with alternative fuels and determine the influence of various bearing materials, including conventional steel as well as advanced ceramic materials.
3. Use the test procedures to evaluate classes of lubricants and lubricant additives as well as fuel additives, and develop lubricants and additives for compatibility with specific alternative fuels.

The work required to obtain these goals was broken down into a series of tasks and a timetable for these tasks was developed. The description of the individual tasks and timetable is presented in Appendix A. This information was taken directly from the original proposal for this work. The work was conducted following this timetable with the exception that an additional task of developing a bulk oxidation technique was introduced. Because of the paucity of available used lubricants from engines fueled with alternative fuels, it was necessary to develop a bulk oxidation test which would simulate lubricant degradation occurring in engines using alternative fuels. Progress on development of the desired bulk oxidation tests are presented at the end of this report. Following the original plan, work was initiated on the use of methanol as an alternative fuel, and then was extended to M-85 fuel.

As planned, an extraction protocol was developed in the first six months of the project for two distinct cases. These cases are the phase stability problems associated with crankcase oil contacting a small amount of methanol, and the extraction of methanol-soluble components from the lubricant by large quantities of methanol to simulate conditions that exist in the area of the fuel injector. This work is identified as Task IA in the project plan (see Appendix A).

After the extraction protocol was developed, the procedure was used to determine the composition of the extract and raffinate phases as described in Task IB. Concurrently, a technique was developed utilizing the Penn State microoxidation test to evaluate the oxidative stability of the various fractions of the lubricant which are distributed by the extraction protocol (Task IIA). Concurrently with this work, work was initiated on Tasks IIB and IIC.

The study of two diesel lubricants designed for methanol-fueled engines were used with the stability and wear test to quantify problems in this area. The resulting data show that contamination with small amounts of methanol in the crankcase can preferentially precipitate additives and reduce the stability and lubricity of the remaining lubricant. In the fuel injection system where large amounts of fuel are involved, the effects of the fuel can significantly reduce the stability and increase the wear.

In addition to the stability studies on the samples resulting from the extraction protocol, a sequential four-ball wear test was developed and utilized with small lubricant samples to elucidate the wear characteristics resulting from the extraction protocol. This effort is described in Tasks IIIA and IIIB.

Finally, some preliminary studies were conducted with M-85 alternative fuel. These preliminary studies indicate that M-85 may cause more lubrication problems in engines than was realized with methanol fuel. The base oils in the lubricant are often more soluble in M-85 than methanol, but the additive package solubility has not changed significantly. Consequently, the raffinate phase can be comprised of a small amount of the higher molecular weight base oil and additives that are not completely soluble in this residual base oil.

In conclusion, test procedures have been developed to produce lubricant fractions which can be caused by contact with alternative fuels in the crankcase and the area of the fuel injector. Associated test procedures have also been developed so that the oxidative stability and the wear characteristics of the lubricant fractions from the extraction protocol can be evaluated. Although these test procedures have been used to evaluate some lubricants, the significant impact of these tests on the development and evaluation of lubricants for alternatively fueled engines has only been initiated, and these tests should be the basis for extensive future studies.

There was strong interaction between this project and industry. The most significant interaction occurred with the Detroit Diesel Corporation, which supplied lubricants developed for alternative fuel usage, as well as used lubricants. Throughout the project, a continuing dialog was maintained between Detroit Diesel to compare their experiences with fleet operations and the experimental work of this project. The project also resulted in interactions with Mobil Oil and Texaco.

Introduction:

In methanol-fueled spark ignition and diesel engines, the crankcase lubricant is used to lubricate the bearings, valves, piston ring-cylinder wall area, and the fuel injector. In essentially all current commercial crankcase lubricants, the base oils are not completely soluble in methanol. In general, the additive packages may even be less soluble than the base oils. This produces an extract phase (methanol soluble) which contains the less viscous portion of the base oil, as well as the methanol soluble additives.

The raffinate phase (methanol insoluble) contains the viscous portion of the base oils along with the methanol insoluble portion of the additive package. In some cases, the raffinate phase on a methanol-free basis may consist of two phases because the additives in the phase may not be soluble in the portion of the base oil contained in this phase. This problem is more serious in the higher SAE grades of crankcase oil and more particularly, in those viscosity grades that contain more heavy-duty additive packages. The fuel injector is lubricated with a small amount of crankcase lubricant in the presence of a large amount of methanol fuel.

The oil in the crankcase also presents a methanol compatibility problem. A small amount of methanol added to the oil in the crankcase produces an insoluble or precipitate phase. During the start-up of an engine, "blow by" from the combustion chamber provides unburned and partially burned fuel as a contaminant in the lubricant. This crankcase dilution consists of small quantities of methanol and water which are not compatible with the lubricant and results in the formation of a second phase, or precipitate. "Blow by" contamination of a gasoline engine at start-up may result in the build up of 3-5% crankcase contamination. It may take 20 miles of normal driving to remove this "blow by" contamination. To represent many engine starts, a single contamination of 20 % methanol in the crankcase was used. This single contamination is based on the notion that some of the lubricant components that are precipitated in each engine start-up are not completely redissolved in the crankcase oil.

The Penn State microoxidation test was used to show changes in the lubricant stability due to changes in the lubricant additive package after methanol - lubricant contact. The Penn State microoxidation test conducted at 225°C has been shown to be useful for correlating results of lubricant stability in III series automotive engine tests. Microoxidation tests at 245°C have been shown to correlate well with Caterpillar heavy duty diesel engine data bases. A 30-minute test at 225°C can show evidence of stability loss under mild operating conditions, while a 120-minute test is considered a severe test of lubricant stability.

A sequential four-ball wear test and a scuffing load test have been developed to show the effectiveness of anti-wear behavior in lubricants which have been used to predict wear in heavy duty hydraulic equipment and automotive engines. The test condition in the previous correlation studies included 52-100 steel balls and a 10 kg load [1.43 GPa (208,000 psi) initial Hertz bearing loading]. The limited sample size after methanol extractions requires that this 10 ml oil charge test in the four-ball wear tester be modified to run on much smaller samples. The development and use of small volume four ball wear tests is described in this report.

The general test protocol described in this report has been used to evaluate a series of new and used lubricants used in urban buses powered by Detroit Diesel engines fueled with methanol. The resulting stability and lubricity tests on the extract and raffinate fractions as well as the sample from each lubricant after contamination with 20 % methanol were compared with performance data for the same lubricants in the bus fleet. These comparisons show strong correlative trends between these laboratory tests and the performance of the lubricants in the bus fleet. This report deals with the improvement of the tests involved in this study and includes additional details on the various tests used in the protocol.

Test Development:

Penn State Microoxidation Test has been developed for the purpose of quantitative evaluation of lubricant degradation at high temperature and combines a thin film oxidation test with Gel Permeation Chromatography (Size Exclusion Chromatography). The analysis from this test procedure is designed to show evaporation, oxidation product, and remaining oil fractions as a function of molecular weight and also the deposit forming tendency of the lubricant. In this study, tests are performed using a 20 μ l sample, test temperature is controlled at 225°C, air flow rate controlled at 20 cc / minute and the test durations are 30 and 120 minute respectively, for the original lubricant and the extract and raffinate fractions of the lubricant. The percentage of the deposit formed is the only property measured in this study. It is necessary to reduce the lubricant sample size in the four- ball wear tests to accommodate the small test samples available. Hence, to accommodate the small samples, the four ball wear tester has been modified to enable the wear test to be performed with sample volumes as low as 0.2 cc. In this new design, three stationary balls are placed in a carefully machined steel insert that takes up 99.8 per cent of the volume normally occupied by the lubricant. This insert is the only modification or addition to the assembly and use of the four ball wear tester in these studies. To evaluate the influence of sample size on wear characteristics, a second insert was made to replace only 80 per cent of the lubricant normally used in the four ball wear test. A series of sequential four- ball wear tests have been conducted to demonstrate the effects of sample size. Tests using 10 ml, 2 ml, and 0.2 ml samples have been studied for the base oil, base oil - tricresyl phosphate (TCP) blends, and blends of base oil-zinc dithiophosphates (ZDP). The results of this studies are shown in Figures 1, 2, and 3.

Table 1 contains the data for the "run in" and "steady state" wear for the oil tested. The Hertz elastic deformation is considered to represent zero wear. During the first 30 minutes wear in the four-ball tester at 600 rpm, 75°C and 10 kg load, the "run in" portion of the wear has occurred. Tests conducted for several additional 30-minute increments demonstrate a different but constant rate of wear which is considered to be a "steady-state" wear rate. It can be seen from Figure 1 that the "run in" wear rate does

change for a base oil as the sample volume changes. The "steady state" rate of wear, however, does not change for the base oil as the sample size changes.

Figure 2 indicates that for base oil containing 1%TCP, the smaller sample shows a lower "run in" wear than the larger sample. The differences in "run in" wear rates for the blend are less than the base oil alone. Again, the "steady state" wear rates for the samples containing TCP are the same for both sample sizes. Figure 3 contains wear rate data for the "run in" and "steady state" at two sample sizes for a lubricant containing 1% ZDP. In this case, the wear rates are the same for both sample sizes.

Almost all current conventional crankcase lubricants contain zinc dithiophosphate (ZDP), some special lubricants compounded with ashless additive packages may more closely resemble the wear values obtained with TCP. The steady state rate of wear is the more important value in this study since the additional package in commercial lubricants are not generally disclosed. However, an increase in either "run in" or "steady state" wear of the extract over the original lubricant would indicate a loss of effectiveness of the anti-wear additive. Scuffing in the four-ball wear tester can be described as the case where the incremental wear for any 30-minute increment exceeds 0.2 mm in wear scar diameter. In many cases, the change in this scuffing criteria is more prominent than the change in "run in" or "steady state" wear. The scuffing load test used started at 40 kg and was increased in 20 kg increments until scuffing occurred. Again, a drop in scuffing load of the extract fraction below that of the original would indicate a loss of effectiveness of the additive package.

Experimental Procedure Designed To Simulate the Condition in a Fuel Injector System:

The volume ratio of the methanol fuel to the lubricant is almost infinite in the fuel injector. Based on solubility tests (Section 3) an extraction ratio of methanol to oil of 1000:1 was chosen to simulate the extraction occurring in the fuel injector. A detailed description of the test procedure is described below:

1. Eight 500 milliliter flasks are used in this extraction procedure. 500 milliliter of methanol is added to each flask, and then 0.5 cc of the lubricant is added. The system is sealed against spills and then well shaken.
2. All eight flasks are then kept for 24 hours in a water bath at 25°C.
3. To separate the extract and the raffinate phases, the flasks are removed from the water bath and the extract phase is decanted carefully into a 5 liter distillation flask.
4. Most of the methanol in the 5-liter flask can be separated by distillation controlled at 65°C.
5. The raffinate remaining in the 500 milliliter flasks is collected by diluting with hexane and collecting the solution in a 125 milliliter filtration flask. Vacuum distillation at 25 mm of Hg pressure is used to strip the solvent out of the system. The sample collected is the raffinate phase.
6. To collect the extract phase the distillation at atmospheric pressure is stopped when approximately 50 milliliters of the mixture remains in the 5-liter flask. The solution is then transferred to a 125-milliliter flask for final methanol recovery by vacuum distillation at 25 mm Hg pressure.
7. Penn State microoxidation tests are conducted with both the extract and raffinate phases. Test conditions include 20 μ l of sample, 225°C, and test times of 30 and 120 minutes.
8. Sequential four-ball wear tests are conducted with both phases. The test conditions include 40-kilogram loading, 600 rpm, test times of 30 and 60 minutes and the volume of the lubricant is 0.2 milliliter.
9. Scuffing tests are conducted with the samples collected. This test consists of a 0.2 milliliter sample running for 30 minutes in the four ball wear tester at 40-, 60-, 80-, and 100 kilogram loads until scuffing is detected. Scuffing in this type of test is defined as an increase in wear scar of 0.2 mm diameter or more (Δ wear) in a 30 minute "run in" or "steady state" sequence.

Experimental Procedure Designed to Simulate the Condition in the Crankcase:

During the cold start of an engine, the lubricant in the crankcase is diluted with some unburned methanol fuel. The fuel evaporates from the system when the crankcase gets hot which may take from 30 to 60 minutes depending on engine operating conditions. This process is repeated every time the engine is started after a long shut down. To simulate this process in the laboratory on the bench scale, the lubricant is contaminated with a one time charge of 20% methanol. The clear lubricant layer of the mixture is removed, and the methanol removed by vacuum distillation. This lubricant sample experimental procedure is described below :

1. The lubricant is mixed with 20% methanol in a screw top test tube and then shaken for two hours using a mechanical shaker.
2. The mixture is allowed to settle for 3 hours where there is a clear separation between the phases.
3. Ten milliliters of the clear lubricant phase is removed using a syringe.
4. This lubricant sample is then vacuum stripped to remove the methanol.
5. Penn State microoxidation tests are conducted with the vacuum-stripped sample. Test conditions include 20 μ l of sample, 225°C, and test times of 30 and 120 minutes.
6. Sequential four-ball wear tests are conducted with the sample. The test conditions include 40-kilogram loading, 600 r.p.m., test times of 30 and 60 minutes, and the volume of the lubricant used is 0.2 milliliter.
7. Scuffing four-ball wear tests are also conducted with the sample. The test conditions start at 40 Kg and proceed in 20 Kg increments until scuffing (Δ wear of 0.2 mm or higher) occurs.

Study Conducted on Two Diesel Crankcase Lubricants Designed for Use With Methanol Fuel

Two diesel lubricants designed for use with methanol-fueled engines were used in this study. These lubricants A and B were run in methanol-fueled diesel engines by the Detroit Diesel Corporation.

Samples of both the new and used lubricants were available for study with the Penn State procedure described in this report. A limited amount of data were also obtained with lubricants A and B using methanol containing fuel additives L and M. These fuel additives were used to improve injector wear and plugging.

Solubility:

The experimental procedure to determine lubricant solubility at various volume ratios of methanol has been described in the test procedure designed to simulate the condition in the fuel injector.

Extractions with methanol were carried out using new lubricants A & B and crankcase draining from lubricants A & B after approximately 5,000 and 10,000 miles in a methanol-fueled diesel engine, respectively. The result of one of the extractions is shown on Figure 4. These data show that at dilutions of 1000:1 solvent:oil ratio, the used oil increases in solubility with use in the engine. These extraction studies are the basis of the 1000:1 solvent:oil ratio used to evaluate behavior of the lubricant in the fuel injector system. The GPC curves for the same lubricants are shown in Figures 5 and 6 and indicate the relative distribution of the extract and raffinate phases. The extract phase shows that the methanol soluble material has a lower molecular weight than the original. The extract phase also has a lower refractive index than the raffinate. It is not clear that this difference in refractive index is due to the separation of the additive package or the types of hydrocarbon structures in the two fractions.

Study of Stability and Wear properties after 20% Methanol contamination:

Both lubricants A and B were treated with 20% methanol to simulate crankcase dilution. In both cases, the formation of a precipitate was observed. The clear methanol-free lubricant fractions were evaluated for oxidative stability as shown in Table 2. These data show a decrease in stability due to the crankcase dilution effect. The samples generated in these crankcase dilution studies were also evaluated

in the small volume sequential four-ball test as shown in Table 3. These data show no decrease in anti-wear effectiveness for lubricant A. There was, however, an increase in wear noted for lubricant B.

Stability and Wear properties of Raffinate and Extract phases:

Previous extraction studies are the basis of the 1000:1 solvent:oil ratio used in these studies to evaluate behavior of the lubricant in the fuel injector system. Tables 4, 5, and 6 show the behavior of oils A and B with methanol, methanol+L, methanol+M, and methanol+M+2 %H₂O.

In Table 4, microoxidation tests are used to compare the stabilities of the extract and raffinate fractions with that of the original lubricant. It is believed that fuel additives L and M in this study contain both dispersants and anti-wear additives to improve the problems of plugging and cylinder-piston wear in the injector. These oxidation stability data show some interesting trends. In the case of lubricant A, the extract phase shows much better deposit values than the raffinate phase. In all cases, the extract phase of lubricant A shows some corrosion rather than a deposit under the 30-minute test. Only in the case of extraction with methanol-containing fuel additive L is there evidence of greater deposits for the extract phases after 120 minutes test than for the original oil. These data suggest that the additive package is very sensitive to the effects of methanol extraction. Lubricant B produces fractions from the methanol extraction that appear to be less stable than those of lubricant B. The effects of methanol on lubricant stability with and without additives and contaminants appear to be very complex.

The extract phase is methanol with a small quantity of base oil and additives. The physical properties as well as the oxidative stability of the extract phase should have little or no effect on plugging the injector. On the other hand, the raffinate phase, which contains high molecular weight (more viscous) portion of the lubricant as well as fractions of the additive package which may not be as soluble in the base oil in the raffinate, does represent a potential problem for injector plugging.

The data in Table 5 show the lubricity of the same fractions that were measured for stability and shown in Table 4. In general, the wear properties of the raffinates are better than those of the extracts.

It is clear from the data that only in the case of extraction with pure methanol, without additives is the wear of the raffinate close to that of the original lubricant. In general, the wear properties of the fractions from these extractions are significantly increased. These increases appear to be due to the separation of the total additive package in the extraction. Differences in the wear properties between new and used lubricants are shown in Table 7. The used oil has significantly higher wear rate and confirms the depletion or change in the antiwear additive package in the oil after it has been in the engine. The scuffing loads for the extract fractions of A and B are shown in Table 6. It can be seen that in all of the cases shown, the extract phases show higher "run in" wear than the original. In all cases except the extract phase of lubricant A using methanol with fuel additive L, the scuffing loads of the extract phases are significantly lower than those of the original lubricants.

Development of Bulk Oxidation Test To Simulate Methanol Fueled Engines:

Experiments have been conducted to develop a bulk oxidation test to produce lubricant degradation equivalent to that in a methanol fueled bus engine after 10,000 miles of operation. This oxidized oil sample and a crankcase drain sample from an actual engine that has run 10,000 miles on methanol can be compared using analytical techniques to verify the severity of the bulk oxidation procedure. Drain samples of lubricant B represent 10,000 miles of use in an urban bus while drain sample A represents about 7,000 miles. Both lubricants have been included in this study of bulk oxidation. The bulk oxidation test was designed to use the same test cell as the microoxidation test. A test temperature of 225°C was chosen to simulate the temperature typically found in the hot zone of an engine. Iron powder (1 gram) was used to provide a large catalytic surface area. The air inlet tube in the current microoxidation reactor was extended to within 0.6 cm of the bottom of the reactor. An air flow of 5 liters of air per hour was injected through the air inlet tube to disperse the air and iron powder catalyst throughout the 10 ml oil sample.

Tests of 8 and 10 hours were run on new oils A and B in the 10 ml bulk oxidation test using one gram of iron powder. Two additional 8 hour, 10 ml tests were run on oil using no catalyst and a single piece of low-carbon steel sheet. These test results are compared with the oil drain samples and 30-minute microoxidation samples on Table 8. The oxidized products in these test samples were measured by a combination of clay percolation and GPC analysis. These tests show the 8-hour bulk test with iron powder to be about the same severity as the 30-minute microoxidation test at 225°C and somewhat more severe than the engines after 7,000 to 10,000 miles. The 10-hour bulk tests are almost twice as severe as the engines in producing oil degradation.

The 30-minute microoxidation deposit test on the drain samples and 8-hour bulk oxidized samples of oil B are shown in Table 9. These data show the degree of oxidation of these two samples to be about the same. The extract and raffinate samples from the drain and the 8-hour bulk microoxidation test also show good agreement.

Some additional data are available for the drain samples of oils A and B. The pick up of iron in these two samples with use is shown in Table 10. The oil solubility in methanol for the new oil samples, the oil drain samples, and 30-minute microoxidation samples are shown in Table 11. With both lubricants, the used and oxidized samples show a substantial increase in methanol solubility. These data suggest that the raffinate phase will contain less base oil. The base oil in the raffinate phase of most oils studied did not provide an adequate solvent for the additive package found in the raffinate. These data suggest that further studies of the additive split between the extract and raffinate should be studied on oil drain, bulk oxidized, and microoxidized samples. The metals in the additive package can easily be measured in these fractions by atomic absorption spectroscopy. The metals of most interest in most packages are Ca, Mg, and Zn.

The total amount of oxidation in the oil drain, 30-minute microoxidation test, and 8-hour bulk oxidation tests are determined by comparing the GPC curves of a clay percolated sample from a given test with an equal volume of oxidized lubricant before the clay percolation. The amount of polymerized and

oxidized lubricant can be shown directly by superimposing the GPC curve of the original sample with that of the oxidized sample. The oxidized and polymerized oil will be defined by the portion of the GPC curve that has a higher molecular weight than the original sample. The oxidized and polymerized material in the samples already discussed for total oxidation are shown graphically in Figures 7 through 10.

In Figure 7, the amounts of oxidized and polymerized product in the drain sample and the 30-minute microoxidation test of oil are essentially the same. This product is a relatively small fraction of the total oxidized product as shown in Table 8. The case of the 120-minute microoxidation test illustrates a large amount of oxidized and polymerized product by comparison.

Figure 8 shows comparable oxidation polymer products for oil A. In this case, the 30-minute microoxidation is measurably more severe in producing oxidation polymer than the drawn sample. The 120-minute microoxidation test produces a much higher molecular weight oxidation polymer in oil A than the comparable test with oil B.

A comparison of the oxidation polymer production for both oils A and B by engine use and bulk oxidation are shown in Figures 9 and 10. In both cases, the total oxidized product shown in Table 8 is noticeably higher for the bulk oxidation than from the engine drain samples. This same trend is shown in both oils for the amount of oxidized polymer as well. It does appear that the bulk oxidation procedure described in this report is capable of simulating the damage done by the engine to oil in the crankcase. More drain samples will be sought to improve the correlation between time in various engines and time in this newly developed bulk test.

Studies of M85 Alternate Fuel:

Alternative fuel M85 (85% methanol and 15% hydrocarbons) has also been tested in this program. The first milestone was achieved in the second quarter where test methods were established to simulate engine conditions with methanol fuels. The extraction procedure developed for the methanol fuel and the logic behind its implementation have been dealt with in previous reports. A 1000:1 extraction of M85

to oil was performed using the same lubricants A and B. Modification of the extraction procedure was required in the final stages to get a solvent-free extract since gasoline has a higher boiling point than methanol. In the vacuum stripping step, the extract phase which was heated to a temperature of around 150°C and nitrogen was used as a stripping aid to remove all the gasoline. A comparison of the GPC curves of the extract phases after methanol extraction and M85 extraction are shown in Figures 11 and 12. The extract phase with M85 seems to have a slightly higher molecular weight distribution than that of the extract phase with methanol. Further analysis (microoxidation, wear tests, and atomic absorption) of the fractions generated from the M85 extraction have to be performed. Preliminary studies show that M85 may provide more problems than methanol. The base oils appear to be more soluble in M85 than methanol, but the additive package solubility has not changed significantly. This predicts that the raffinate phase may be comprised of a small amount of higher molecular weight base oil and additives that may not be completely soluble in this residual base oil.

Table 1. Wear Values vs. Samples Size in the Four-Ball Tester

Lubricant	Volume	Δ Wear (mm)	
		Run-In	Steady State
Base Oil	10 ml	0.24	0.09
	0.2 ml	0.12	0.08
Base Oil + 1% TCP	10 ml	0.18	0.07
	0.2ml	0.14	0.07
Base Oil + 1% ZDP	10 ml	0.07	0.03
	0.2 ml	0.07	0.03

Table 2. Microoxidation Tests; 20 μ l Samples; 225°C; In Air

Lube	Time, Min	Original wt. % Deposit	20% MeOH wt. % Deposit Contamination
A	30	0.0	0.9
A	120	9.3	12.6
B	30	0.5	1.4
B	120	5.4	6.6

Table 3. Wear Tests; 0.2 ml; 40 kg; 75°C; 52100 Steel; 30 Minutes

Cond.	Lube	Original wt. % Deposit	20% MeOH wt % Deposit Contamination
R-I	A	0.02	0.02
S-S	A	0.01	0.01
R-I	B	0.04	0.05
S-S	B	0.00	0.02

Table 4. Microoxidation Tests; 20 μ l Samples; 225°C; In Air

Lube	Time Min.	Orig.	MeOH		MeOH + L ⁽¹⁾		MeOH + M ⁽¹⁾		MeOH + M ⁽¹⁾ + 2 % H ₂ O	
			wt % Deposit							
			Raf	Ext	Raf	Ext	Raf	Ext	Raf	Ext
A	30	0.0	5.9	-0.2	1.7	-0.4	1.8	-0.4	3.0	-1.0
A	120	9.3	12.0	0.5	7.7	25.1	8.8	5.4	19.2	2.6
B	30	0.5	0.8	0.1	3.7	4.1	5.8	-0.5	2.6	3.6
B	120	5.4	8.2	12.0	16.1	30.0	26.1	16.1	11.9	7.8

(1) 0.06 % fuel additives L and M are used

Table 5. Wear Tests: 0.2 ml; 40 kg; 75°C; 52100 Steel; 30 Minutes

Cond	Lube	Orig.	MeOH		MeOH + L ⁽¹⁾		MeOH + M ⁽¹⁾		MeOH + M ⁽¹⁾ + 2 % H ₂ O	
			wt % Deposit							
			Raf	Ext	Raf	Ext	Raf	Ext	Raf	Ext
R-I	A	0.02	0.04	0.10	0.16	0.10	0.08	0.13	0.16	0.11
S-S	A	0.01	0.01	0.08	0.15	0.09	0.05	0.08	0.14	0.07
R-I	B	0.04	0.02	0.07	0.12	0.13	0.08	0.12	0.13	0.20
S-S	B	0.00	0.02	0.03	0.11	0.13	0.07	0.09	0.03	0.10

(1) 0.06 % fuel additives L and M are used

Table 6. Scuffing Load: 0.2 ml; 75°C; 52100 Steel; 30 minutes

Lube	Load, Kg	Orig Δw , min	MeOH	MeOH+L ⁽¹⁾	MeOH+M ⁽¹⁾
			Ext Δw , min	Ext Δw , min	Ext Δw , min
A	40	0.02	0.10	0.10	0.13
	60	----	0.10	0.10	0.30
	80	0.05	0.38	0.13	----
	100	0.59	----	0.71	----
B	40	0.04	----	0.13	0.12
	60	0.07	----	0.17	0.33
	80	0.18	----	0.22	----
	100	0.60	----	----	----

(1) 0.06 % fuel additives L and M are used

Table 7. Four-Ball Wear Tests
40 Kg; 75°C Δ Wear

Lubricant	Run-In, Δw min	Steady-State Δw min
A	0.02	0.01
Used A	0.11	0.05
B	0.04	0.00
Used B	0.16	0.08

Hertz area = 0.30 min at 40 Kg load on 52100 steel

Table 8. Comparison of Percentage of Oxidized Products in Oil Drain Samples, Samples from Microoxidation Tests, and Samples from Bulk Oxidation Tests.

% Removed by Clay Percolation ⁽¹⁾		
	A	B
Oil Drain Sample	10	14
30-Minute Microoxidation	17	16
10 cc Oxid. 8-Hour, 1 g Fe Powder	15	17
10 cc Oxid. 10-Hour, 1 g Fe Powder	21	24
10 cc Oxid. 8-Hour, No Fe Powder	--	6
10 cc Oxid. 8-Hour, LCS Sheet	--	11

- (1) Oxidized liquid products are measured by the increased amount of lubricant absorbed on clay due to oxidation.

Table 9. Comparison of the Stability of the Raffinate and Extract Phases from the Oil Drain Sample and the Oxidized Sample.

Deposit values are determined from a 30-minute microoxidation test at 225°C.

Wt. % of Deposit			
	Original	Raffinate	Extract
B, Oil Drain Sample	3.0	6.3	11.0
B, 10 cc. Oxid. 8-Hour	4.2	6.4	8.6

Table 10. Conditions of Oil Drain Samples.

	Description	Fe Content (ppm)
A	New Used, 142 hr.	BDL ¹ 15
B	New Used, 10,800 mi.	BDL 30

¹ Below detection level.

Table 11. Solubility of Original, Oil Drain Samples, and Samples from Microoxidation Tests in Methanol.

Solubilities are expressed as weight percent.

Vol % Soluble in Methanol		
	B	Q
New	34	32
Oil Drain Sample	49	52
30-Minute Microoxidation	53	55

Four-Ball Wear Test
75°C, 40 Kg

21

Figure 1

Four-Ball Wear Test
75°C, 40 Kg

Figure 2

Four-Ball Wear Test
75°C, 40 Kg

Figure 3

Figure 4. Solubility of Lubricant A in methanol

Figure 5. GPC curve for lubricant A extracted at 500:1 fuel to oil.

Figure 6. GPC curve for lubricant B extracted at 500:1 fuel to oil.

Figure 7. GPC analysis of Lubricant B and its oxidized and oil drain samples.

Figure 8. GPC analysis of Lubricant B and its oxidized and oil drain samples.

Figure 9. GPC analysis of Lubricant A and its oxidized and oil drain samples.

Figure 10. GPC curve for Lubricant A (original/used/bulk oxidized).

Figure 11. GPC curve for Lubricant B (original/extract with methanol and M85).

Figure 12. GPC curve for Lubricant A (original/extract with methanol and M85).

Appendix A

Timetable for Proposed Work

Timetable for Proposed Work

The proposed work can be broken down into the following tasks, and the timetable for these tasks is presented in the following pert chart. All of the tasks for the first 18 months of the proposed study are clearly defined in this pert chart. Since many of the activities in the second half of this proposed three-year study are strongly dependent upon progress and results in the first half of the project, many of the details of the tasks for the latter phases of the program are not clearly delineated on the pert chart prepared at this time. As this pert chart indicates, the initial emphasis of this project will be placed on the utilization of methanol as an alternative fuel since fleet test data are available for methanol to guide this study.

- IA. Development of extraction protocol to break lubricants into extract and raffinate phases after contact with methanol. Procedures will be developed for the two cases: (a) the precipitation of a second phase in crankcase lubricants after contact with a small amount of methanol in order to simulate the conditions existing in the sump of the lubrication system in which a small amount of methanol fuel enters the lubrication system each time the engine is started. (b) The extraction of methanol-soluble components of the lubricant by a large quantity of methanol to simulate the conditions that exist in the area of the fuel injector.
- IB. Analysis of the composition of the extract and raffinate phases resulting from the developed extraction protocol. Of particular interest will be the distribution of components of the additive package between the different extract and raffinate phases.
- IC. Utilize extraction protocol to evaluate the relative compatibilities of various components of lubricants and lubricant additive packages.
- ID. Modification of extraction protocol to accommodate other alternative fuels, starting with ethanol and a methanol fuel blend consisting of 85% methanol and 15% hydrocarbons.
- IIA. Develop technique to evaluate the oxidative stability of the various fractions of the lubricant which are distributed by the extraction protocol developed in Task IA. This test procedure will be based

on utilization of Penn State's microoxidation test, and the main emphasis will be placed on determining the appropriate test conditions such as temperature and time which give the greatest correlation between this test and fleet test results. The work will be initiated on the differences in deposit formation in the early stages of lubricant oxidation which leads to deposits and fuel injector plugging.

- IIB. Utilization of oxidation stability to compare the microoxidation stability of extracted conventional lubricants with extracted lubricants which have been developed for use with methanol fuels.
- IIC. Utilization of the microoxidation test procedure to determine the relationship between the distribution of different components of additives and lubricant on the oxidation process.
- IID. Use microoxidation test procedures to evaluate other alternative fuels starting with ethanol and methanol-hydrocarbon blends.
- IIIA. Miniaturize lubricant volume in the four-ball wear tester to handle the small quantities (approximately 1 ml) of the phases formed in the extraction protocol of Task IA. The volumes of the extract and raffinate fractions (solvent free) of typical lubricants approach an asymptotic value at 1000:1 methanol-to-oil ratio. To obtain at least 1 ml of lubricant in the fraction containing the least lubricant, one gallon of methanol is required. For the four-ball wear tests using conventional lubricant volumes, extractions with as much as 50 gallons of methanol would be required.
- IIIB. Use miniaturized four-ball wear tester to determine best conditions for evaluating the steady-state wear characteristics of the extract and raffinate lubricant fractions produced by the extraction protocol.
- IIIC. Determine operating conditions for the miniaturized four-ball wear tester to determine the scuffing load of the lubricant fraction.

- IIID. Use developed steady-state wear tests and scuffing tests to evaluate conventional commercial lubricants as compared to those specifically developed for use with methanol fuel.
- IIIE. Use wear test procedure to evaluate other alternative fuels starting with ethanol and methanol-hydrocarbon blends.
- IIIF. Utilize scuffing test to evaluate other alternative fuels starting with ethanol and methanol-hydrocarbon blends.
- IV. Evaluate fleet test data as it becomes available and use these results in developing and optimizing the test protocols for the evaluation of lubricant oxidation and wear and scuffing characteristics. This is an ongoing activity in which fleet tests being conducted by the various industries are incorporated into this study to optimize the test procedures and overall data base.
- V Utilize the developed test procedures and results on available lubricants to develop new lubricant formulations.

PERT CHART

DATE

FILMED

6/1/94

END