한국윤활학회지(1995), 제 11 권 제 5 호
Journal of KSTLE(1995) Vol. 11, No. 5, pp.47~54

Advanced Lubricants for Heat Engines

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Abstract—An advanced liquid lubricants for heat engines has been developed and tested successfully in a prototype engine. The lubricant possesses superior oxidation stability and high temperature stability and is capable of surviving for a minimum of three minutes at 425°C (800°F) at the ring zone and maintains stability at an oil sump temperature of 171°C. The lubricant has been evaluated by the Cummins Engine Co. Out of a field of several dozens of lubricant, six lubricant was selected for a prototype 200 hours endurance testing. The NIST lubricant was one of the two lubricants that successfully finished the endurance testing. This paper describes the key lubricant considerations including oxidation and thermal stability, volatility, deposit control. The engine test conditions and the results will be presented.

Key Words : Lubricants, Heat engine, Oxidation stability, Thermal stability, Volatility

1. Introduction

New lubricant technology is needed for the advanced engine concepts. The proposed low heat rejection (LHR) engine has the advantage of low particulate exhaust emissions, high fuel efficiency, and high power density [1,2]. This design trend will put more stress on the lubricant due to thinner oil films and higher top ring reversal (TRR) temperatures [3]. In the near term, top ring reversial temperatures of the advanced engine may approach 425°C with crankcase temperatures near 200°C. At such temperatures, synthetic lubricants are needed to lubricate such engines.

Key factors that must be considered to design a lubricant for such an engine include oxidative stability, thermal stability, volatility, oxidative volatility, metal cataloysis, and the interplay of these parameters. This paper discusses the research results in developing such a lubricant and the success in the engine test.

The engine test was conducted on a was conducted on a modified Cummins L-10 diesel engine. The modified engine had the following characteristics: 1200 engine rpm, 1814 N.M torque, $23.3\times 10^6/cm^2$ break mean effective pressure, 46 kg/hr fuel flow, oil sump temperature of 171°C, top ring groove temperature of 320°C, top ring reversal liner temperature of 230°C.

Over 70 lubricants were submitted and evaluated by various bench tests at Cummins. Only 8 lubricants were selected for engine tests. The 8 lubricants had 2 mineral oil based, one was a current lubricant used in diesel engines today. This served as a reference.

In designing a lubricant for such an application, concept and test methods were reeded. The concept chosed was a super-stable lubricant based on the kinetics of the oxidation reactions. This means defining stability in terms of temperature and residence time. The lubricant was considered stable if the combination of the time and temperature did not render the lubricant inoperable. This is an important concept. The traditional way of defining stability is too conservative and often leads to the conclusion that no lubricant is available for such an application. A case in point is the fact that mineral oil based lubricants are being used today for diesel engines. The maximum ring zone temperature had been measured at 357°C. According to this temperature, no mineral oil based lubricant should survive. Yet mineral oils have been used satisfactorily. This is because of the short residence time the lubricant undergoes the temperature is short, about 3 minutes. Within the time allowed, the lubricant is functional.

Some of the key consideration for a lubricant used in such an application are shown in Table 1.

Basically, our research during the past four years has been directed towards developing a data base on base fluids, additives and formulations. Con-

Table 1. High temp. liquid lubricants

KEY TECHNICAL ISSUES:
*Base Fluids
*Additives
*Thermal Stability
*Oxidation
*Deposits
*Viscosity
*Friction and Wear

Table 2. Test methods

METHOD	Applications	References
THERMOGRAVIMETRIC ANALYSIS (TGA)		9,13
	Volatility	
	Thermo-oxidative Stability	
DIFFERENTIAL SCANNING CALORIMETRY (DSC)		
ISOTHERMAL	- Oxidation, n Stability	23,24
PROG. TEMP.	- Deposit Formation	17,20,21
THIN FILM MICROOXIDATION TESTS (TFMO)		
	Deposits	11,15,16,22
	High Mol. Wt. Prod.	10-12,15,16
MODIFIED FOUR-BALL TESTS		
	Friction & Wear	13,25,26,27
BULK OXIDATION TEST		
	Oxidation Stability	13
FOURIER TRANSFORM INFRARED (FTIR)		
	Product analysis	18

currently, test method development was pursued to better understand the basic technical issues. This paper discusses the assessment of additives and additive-base oil formulations using a variety of laboratory test methods. Comparisons with benchmark lubricants that have been run in engines are included.

2. Test Methods

In this study, a number of different laboratory tests were utilized to develop the information required to select the proper mix of additives and summarized in Table 2. The development of the methodology in some cases was extensive and is described in detail elsewhere, as indicated by the refereces in the table.

The search for superstable lubricants covered a wide range of fluids and additives and the utilization of meaningful bench tests was critical to the development of a data base for selection of high temperaure lubricants. It was essential that the lubricant have an effective survival rate at high temperatures. it was also desirable that the lubricant produces thermal decomposition fragments or reaction products that will degrade under the thermo-oxidative conditions without the formation of detrimental deposits. The TGA and DSC test methods enabled rapid evaluation of the thermal and oxidative stability of research fluids and additives in a rapid and efficient manner.

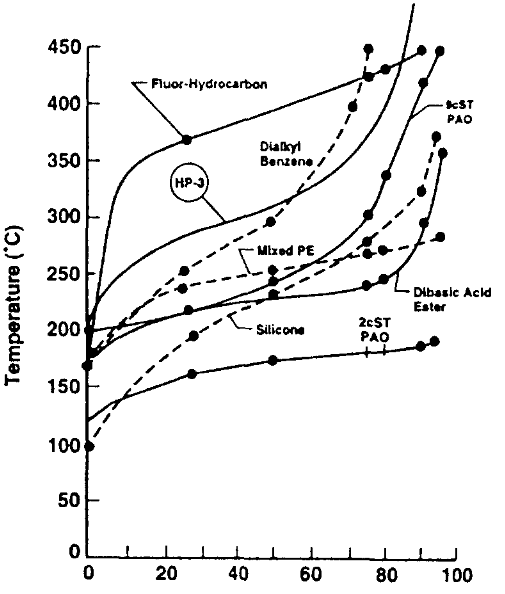

Fig. 1. TGA volatility curves.

TGA was used to give an indication of the volatility at which the formation of volatile reaction products occurred. The volatility of several fluids are shown in Fig. 1. This shows "distillate type" weight loss curves obtained under an inert atmosphere. The results include a unique multicomponent NIST base fluid, designated HP-3. HP-3 was selected to obtain good volatility properties and to solubilize novel high temperature additives.

3. Additives

The availability of additives is a major problem in developing high temperature fluids. The requirements for the additives include good thermal and oxidative stability, solubility and compatability

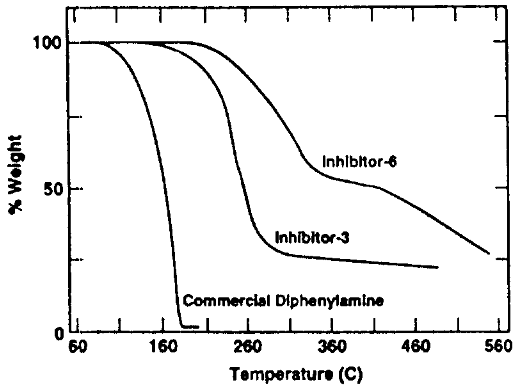

Fig. 2. TGA additive evaluations.

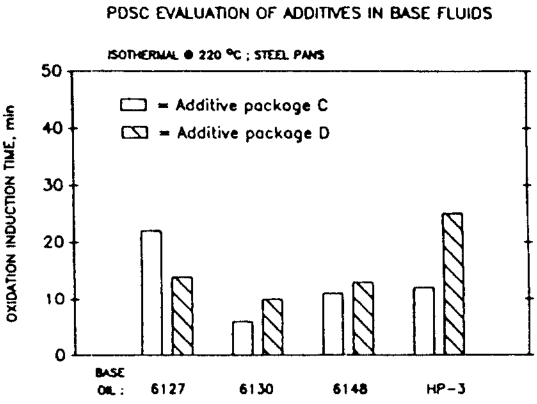

Fig. 3. Isothermal PDSC tests.

with other components in the formulation. The additives must be effective at high temperatures and in the crankcase and preferably be synergistic, or at least not antagonistic, to onther additives in the system. In addition, the additives should not contrbute significantly to deposits in the top ring reversal (TRR) zone. The additives considered included, antioxidants, dispersants, surface active inhibitors and friction and wear additives.

The additive candidates were obtained from several participating companies. Initially, the additives were screened, neat, using the TGA to establish their volatility over the desired temperature range. Some typical additives are shown on Fig. 2. Following the TGA evaluation, selected additives were blended into a candidate base fluid, such as HP-3, and evaluated in the pressurized DSC (PDSC).

The PDSC tests involved isothermal studies to evaluate oxidation stability and programmed temperature studies to determine deposit forming characteristics of the fluids and additives. The isothermal PDSC results obtained with several formulations are found in Fig. 3. The additives were effective in improving the oxidation stability of the base oil as measured by the oxidation induction time in the isothermal PDSC test.

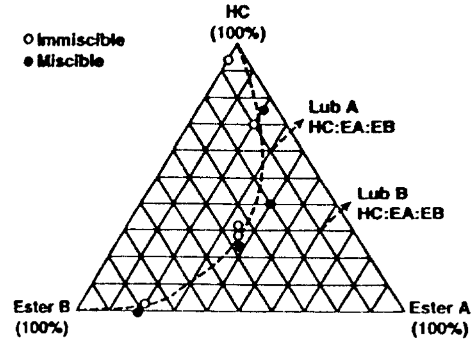

Fig. 4. Base stock solubilities.

Table 3. Additive solubility test

Antioxidant "AOP" Solubility:				
Base Fluid	--Wt % Additive--			
	0.1	1.0	2.0	5.0
PAO	N	N	N	N
Mineral Oil	Y	N	N	N
H-3 Fluid	Y	Y	Y	Y

N=not soluble Y=soluble

Selected combinations of additives are bein evaluated to determine synergistic or antagonistic effects in various base stocks. Concentration effects were also considered and investigated to determine the most effective antioxidant concentration level.

Some additives selected were unusual in that they are not normally uses with lubricants. One reason they are not being used in lubricant formulations is that they are relatively insoluble in hydrocarbon type base fluids. In the present work, solubility studies were performed to evaluate the concentration limitations on selected additives alone and in combination with other components. A schematic illustration of mixed base stock solubilities is shown in Fig. 4. HP-3 was selected to enhance additive solubility. An example of additive solubility studies is shown in Table 3. Once the fluids were formulated, periodic visual checks of the compatability of the additives and base flouids were made over about a 1-

year period. Cursory observations were made for particulates, phase separation or sediment.

4. Deposits

The deposit forming characteristics of the .fluids and additives have been a major concern. It has been shown that top land carbon deposits can result in loss of oil control [19]. Loss of oil control can also result in increased engine emissions. To evaluate deposit forming tendencies of lubricants, a "two-peak" method using a proessurized modification of the DSC was developed [17,21]. The incentive for the method was the need for improved repeatability due to the low levels of deposits produced by the candidate high temperature formulations. Basically, a thin film of lubricant is oxidized under oxygen at 690 kPa (100 psig) over a temperature range from room temperature to 550°C.

A simple reactor to meet our requirements was designed and fabricated, Fig. 5 [17]. A sample of 0.7 mg produces a thin film of 100 um or less in the pan. "olatility and evaporative losses are controlled through the use of holes drilled in the cover of the pan. Normally, one hole is adequate although 0-3 have been used as required. The result is a thermogram similar to the one on Fig. 6 where the first peak is the primary oxidation peak and the second is related to deposit forming tendencies of the fluid. The peaks reflect the net heat of the endothermic and exothermic reactions occurring in the reactor.

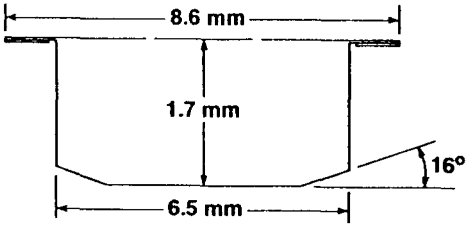

Fig. 5. NIST steel PDSC sample pan (reference 17).

The key to this bench test is in controlling the competing thermo-oxidation reactions and the evaporative and volatility losses. If too much material is lost as a result of volatility, there is and insufficient amount left to evaluate the deposit formation tendencies properly. If insufficient oxygen is allowed into the system, then oxygen diffusion limitations result and a mixture of products or peaks occurs. Catalytic activity of the iron surfaces also play a role and tends to acdelerate the oxidation reactions. This "Two-Peak Method" has been correlated with engine test data obtained from four companies. The data included tests conducted with reference oils, engine oils and LHRE oils [17,20,21]. The "Two-peak Method" also was correlated with the thin film micro-oxidation (TFMO) deposit test method used by one of the participating laboratories to evaluate engine deposit formation tendencies of oils [16,21,22].

The "2-Peak method" was used to evaluate a series of advanced diesel engine oils including NIST formulations. The 2-peak results are shown on Fig. 7. The performance of three industry HTLL reported in the literature [23], and a current diesel oil are shown for comparison. The four NIST fluids, designated HTLL 1 through 4, are formulation modifications using the base fluid designated HP-3. Most of the deposit results obtained on HTLL fluids

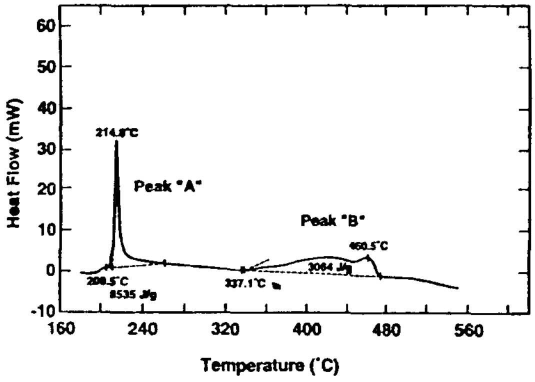

Fig. 6. Typical 2-peak thermogram (reference 21).

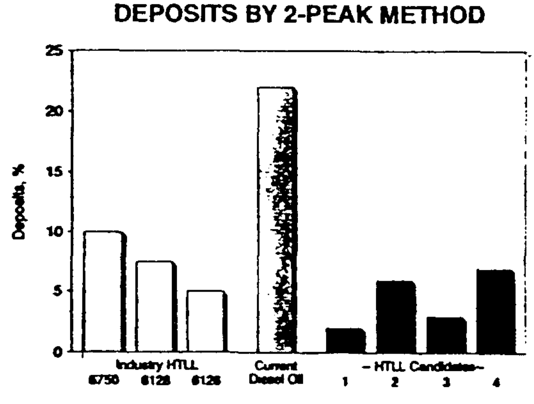

Fig. 7. Deposit formation tests.

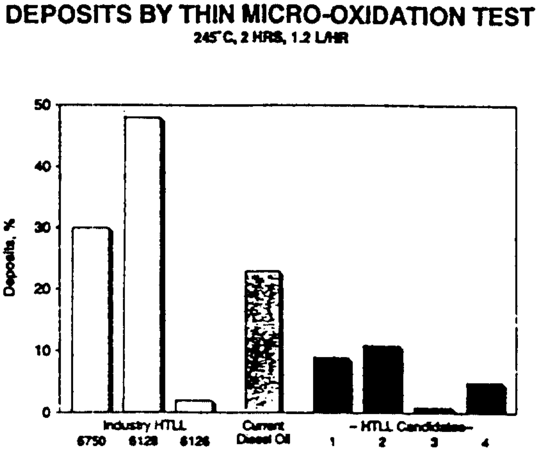

Fig. 8. Deposit formation test.

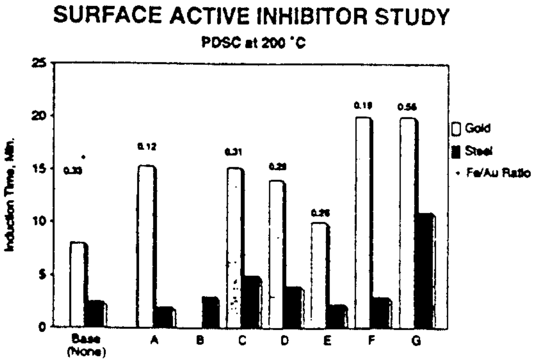

Fig. 9. Isothermal PDSC.

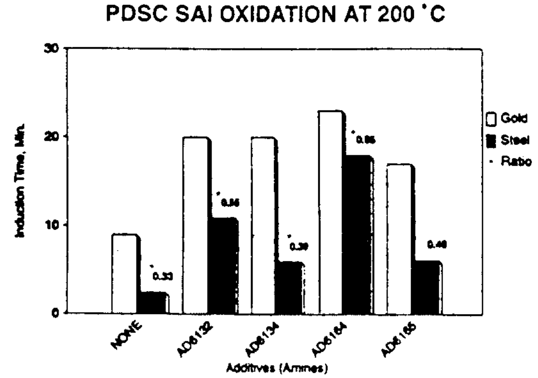

Fig. 10. Amine type SAI.

are below the 10% deposit level in the two peak method. This is below the level of current conventional diesel oils which normally fall between 10 and 35% in the "Two-Peak" test. Several dozen current diesel engine oils and high temperature liquid lubricant candidates were evaluated in the deposit studies using both the "Two-Peak" and thin film micro-oxidation mathods [21].

The thin film micro-oxidation (TFMO) test is being utilized by some companies to evaluate deposit forming tendencies of lubricants [16, 22]. Correlation between the TFMO test and the PDSC tests has been reported [21]. The results obtained by us on the TFMO test on our fluids are summarized on Fig. 8. Both the TFMO and "Two-Peak" methods when used in conjunction with other techniques, such as fourier transform infrared (FTIR) and gel permeation chromatography (GPC), can be used to obtain additional information on the reaction products.

We have initiated a cooperative study with an industry participant to conduct a feasibility study of the role of these fluids play in particulate formation. The study will use both methods and will try to determine if the higher molecular weight reaction products contribute significantly to the organic fraction of the particulates generated by the engine.

5. Catalytic Effects

The presence of metals have been shown to be catalytic in lubricant oxidation reactions. To evaluate the effect of metals and surface active inhibitors (SAI), we have utilized an isothermal PDSC method in which the sample is evaluated in an essentially inert pan (gold) and then in a steel pan. The oxidation induction pariods obtained in both tests are compared to get an SAT indes. The SAI index simply refers to the oxidation induction time obtained on the steel surface divided by the induction time for the same fluid on a gold surface. Some two dozen additives have been screened using this procedure to see if they can reduce the effect of the metal on oxidation induction time. The results for several of the additives are shown on Fig. 9. Once an additive was found to be effective, it was included in the base formulation and evaluated for any antagontistic or synergistic effects with the other additives. Most of the two-dozen SAI's evaluated were effective at low temperatures (185°C) but were ineffective above 200°C in these tests. One compound in a series of amine compounds obtained because of their high temperature

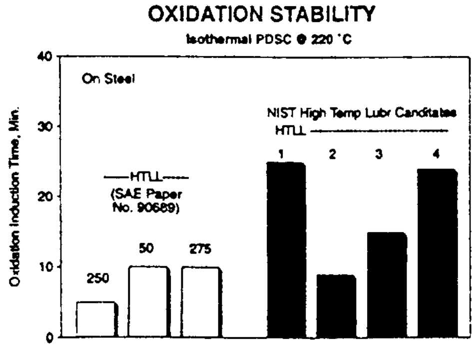

Fig 11. Fourmulated HTLL tests.

stability in the TGA was effective in eliminating the catalytic activity when used alone. It was 85% effective in the formulated fluid, Fig. 10.

5. Oxidation Stability

The isothermal DSC method is one oxidation stability test used to evaluate the candidate high temperature liquid lubricants. The induction period at selected temperatures is evaluated. The paper by Marolewski discusses three fluids that have undergone low heat rejection engine tests. One passed a 250 hour test with no problems in an engine with TRR temperatures of 340°C. The second failed at about 50 hours in an engine with TRR temperatures of about 400°C. The third and best of the three fluids passed a 275 hour test in an engine with a TRR temperature of 450°C. These three oils were used as baseline fluids in the DSC oxidation studies and are compared with four research formulations on Fig. 11. The results show significant improvement of the oxidation stability of the research fluids. Combining these results with the TGA and deposit studies of the research formulations, the fluids are excellant candidates for evaluation in an advanced engine. Since preliminary screening will probably involv more conventional engines, the low temperature oxidation properties of the fluids are being evaluated.

6. Friction and Wear

The high temperature liquid lubricant candidates must have good tribological properties to lubricate and control friction in both metallic and ceramic systerms. The tribological aspects of several of the fluids were evluated on 52-100 steel, Si_3N_4 and SiC using modifications of the four-ball test. The lubricants were evaluated in a steel-on-steel time to failure test in which the lubricant sample size used was 6 ul [25]. The results for the steel on steel tests are found on Fig. 12. A conventional diesel engine oil would last about 15-30 minutes in this test. Some of the better candidates lasted for 6-7 hours, significantly better than anything in the data base.

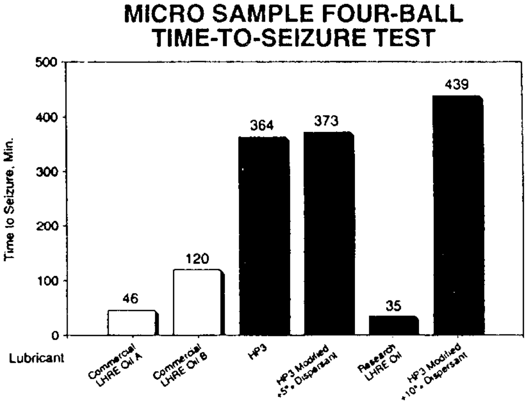

Fig. 12. Micro sample steel-on-steel four ball tests.

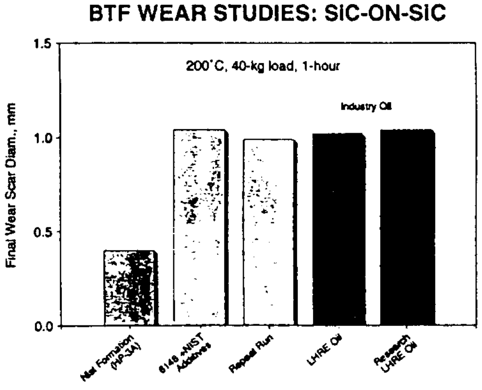

Fig. 13. Ball-on-three flats.

Several tests were conducted on SiC at 200°C using a ball-on-three flats (BTF) version of the four-ball test [25]. The results are found on Fig. 13. Since the additive packages in some of the fluids were similar, the differences in these tests are attributed to the HP-3 base fluid. Candidates containing HP-3 performed better than the candidates with other base fluids. A limited number of BTF tests have been conducted with Si_3N_4. All fluids perfomed well.

Table 4. Properties of lubricants tested in the high temperature L-10 engine

Lubricant	Viscosity (cSt)		VI	TBN	Description
	40°C	100°C			
A-2	90.4	14.1	154	5.9	15W-40, Mineral oil
A-3	61.4	9.5	135	6.2	30 Grade, Synthetic
A-8	65.9	13.6	211	2.4	10W-40, Synthetic
A-9	98.9	14.2	155	4.2	10W-40, Mineral Oil
A-16	108.9	14.7	149	3.5	15W-40, Synthetic
A-58	102.5	15.1	154	9.6	15W-40, Synthetic
A-59	101.8	12.9	122	9.3	15W-40, Synthetic
A-62	89.0	12.2	132	4.2	15W-40, Synthetic

Table 5. Comparisons of the test results for the lubricants tested in the high temperature L-10 engin program

Lubricant	L-10 Engine Test Duration (hr)	Crownland Carbon, %	Top Groove Fill, %
A-3	142	0.0	28.2
A-8	200	4.5	25.0
A-9	96		
A-16	53		
A-58	158	0.0	29.8
A-59	200	0.8	19.8
A-62	53		

7. Engine Test Results

Based on all these bench tests screening, a candidate was selected and submitted to Cummins. A-total of 8 lubricants were selected by Cummins for engine tests.

The physical properties of the lubricants tested are shown in Table 4. A-59 is the lubricant developed at NIST as described in this paper. Of the eight lubricants tested, only two were able to finish the 200 hours endurance. Others either failed due to oil consumption, deposite, or turbocharger rotor breakage. The resluts are shown in Table 5. Only four deposit results are available from the engine tests, in reality, only A-8 and A-59 results are from the 200 hours duration. The engine test results tend to validate our approach.

8. Conclusion

A super-stable liquid lubricant has been successfully developed and demonstrated in an experimental prototype engine.

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