Utilizing The TEOST MHT To Evaluate Fundamental Oxidation Processes In Low Phosphorus Engine Oils

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The Thermo-Oxidation Engine Oil Simulation Test (TEOST) MHT protocol was used to generate information on deposits and the formation of polar volatile organic compounds. Fourier Transform IR (FTIR) was then used to analyze the level of oxidation in recovered TEOST used oil as well as in the collected volatiles. Data was generated comparing different antioxidant systems in molybdenum-containing and molybdenum-free low phosphorus engine oil formulations. The results show a surprising difference in deposits, volatiles and carbonyl oxidation based on the presence or absence of molybdenum, and also based on the type of antioxidant system selected. The amount of volatiles produced in the TEOST is related to well-established oxidation mechanisms and also explains specific oxidation processes sometimes seen in Sequence III engines. A mathematical definition of antioxidant effectiveness or "robustness" is proposed that combines TEOST deposits and volatiles measurements with FTIR carbonyl oxidation measurements. These results strongly suggest that analysis of TEOST used oils and volatiles may provide valuable information regarding oxidation in other bench tests as well as potentially in fired engines.

KEY WORDS

Antioxidant Additives, Internal Combustion Engine Oils, Molybdenum, Oxidation, Fourier Transform Infrared Spectroscopy (FTIR)

INTRODUCTION

Recent years have seen the development of more complicated and demanding engine tests for evaluating the oxidative stability and deposit forming tendencies of lubricants. This has been brought on, in part, by changes in engine design and environmental considerations. Confounding these developments are the recent changes in lubricant basestocks and engine oil additives. The introduction of sophisticated after-treatment systems has also placed constraints on the types of additive chemistries that can be utilized in engine oils. Mandated reductions in engine oil phosphorus levels, combined with new engines for evaluating cam wear, have resulted in significant lubricant additive changes. Two of the most important changes, from an oxidation standpoint, have been the use of molybdenum for wear and oxidation control, and the use of higher levels of ashless antioxidants for deposit control (1-2).

The cost of commercializing new engine oils has increased significantly in recent years as engine development and testing costs have increased. With many more basestocks and additive options to

choose from, engine testing has become an exceedingly expensive approach to developing new lubricants. In order to address this problem, a number of oxidation and deposit bench tests have been developed and put into use for engine oil research and product development (3-6). The introduction and industry acceptance of the Thermo-Oxidation Engine Oil Simulation Test (TEOST), protocol MHT-4, for simulating the oxidation and carbonaceous deposit-forming characteristics of engine oils, has reduced the dependence of engine oil formulators on engine tests (7). This bench tool allows for a reasonable level of low cost additive optimization prior to the required engine testing. While the test is known to generate a significant amount of volatile organic compounds, quantifying these materials and understanding their impact on engine oil oxidation has received little attention. This knowledge is even more important today since further reductions in phosphorus are expected in the near future. In addition, modern engines are running hotter, oil drain intervals are getting longer, and engine sumps are getting smaller. All these changes require that effective antioxidant combinations are selected for modern engine oils.

To date, there has not been a comprehensive TEOST MHT-4 study providing a detailed look at rod deposits, recovered oil oxidation, and volatiles formation. The purpose of this paper is to report on such a study. A variety of low phosphorus Group II passenger car engine oils, containing different ashless antioxidant systems, are evaluated in the presence and absence of a sulfur-containing organo-molybdemum additive. The broad set of results is then related to known lubricant oxidation mechanisms and physical degradation processes commonly seen in Sequence Engine tests.

EXPERIMENTAL

Antioxidants

The antioxidants chosen for this study are shown in Fig. 1. The additives HPE, MBBP, and MBDTBP represent three different hindered phenolics commonly used in engine oils. The dimer (MBDTBP) and oligomer (MBBP) are of the same general class of hindered phenolic antioxidants having a CH₂ bridge between the phenolic aromatic rings. The ester (HPE) represents a monocyclic hindered phenolic that is structurally quite different from the previous two. All of these hindered phenolics are of low volatility and considered effective antioxidants in high temperature lubricant applications. A nonylated diphenylamine (NDPA) was chosen for this study because of the known antioxidant synergy when combined with hindered phenolics (8). A molybdenum dithiocarbamate (MoDTC) was chosen as the molybdenum source since these materials have beneficial anti-wear properties in addition to their antioxidancy, and are likely to see more use as engine oil phosphorus levels continue to drop.

Passenger Car Engine Oil Formulations

An engine oil preblend was prepared by mixing additives and base oil so that the finished engine oil contained 4.80 wt. % succinimide dispersant, 1.80 wt. % overbased calcium detergent, 0.5 wt. % neutral calcium detergent, and 0.60 wt. % secondary zinc dialkyldithiophosphate, with the balance composed of Group II base oil. The Group II base oil had a kinematic viscosity @ 100°C of 6.1 cSt, a viscosity index of 114, and a Noack volatility of 8 wt. %. The organo-molybdenum compound, alkylated diphenylamine and hindered phenolics were added to the preblend as shown in Table 1. The Group II base oil was used as the diluent to complete the blend. In all cases organo-molybdenum compound MoDTC was added to deliver 360 ppm molybdenum ion to the finished

engine oil. The specific additive combinations in Table 1 were selected in order to detect synergies that might be apparent in the TEOST. For example, there are reports in the literature of alkylated diphenylamine/molybdenum combinations, and alkylated diphenylamine/hindered phenolic combinations, showing enhanced deposit control in certain bench and engine tests (9-10). All the finished engine oil blends contained 470 ppm of phosphorus, 520 ppm of zinc, and 2400 ppm of calcium.

The preblend was kept constant in all the test samples in order to minimize deposit formation or volatility effects caused by changes in additives and base oils. This insured that observed changes would correlate exclusively to changes in antioxidant systems or the presence of molybdenum.

TEOST MHT-4

The TEOST MHT-4 was run according to the ASTM method and manufacturer specifications (11). Test conditions and a diagram of the depositor rod assembly are shown in Fig. 2. Oil is introduced to the heated wire-wound depositor rod through the oil feed tube. A thin film of oil moves evenly down the rod and is collected at the oil flow out point. Recovered oil is circulated back to the depositor rod via a precision pump. During the 24 h test period volatiles (actually, aerosol particles) are produced that flash off the hot rod surface and coalesce on the glass mantle. These volatiles run down the inside of the mantle skirt and are collected in a trough from which they are directed to the 'condensed volatiles out' tube and recovered in a glass vial. At the end of the test, deposits are determined by the increase in depositor rod weight and reported in milligrams (mg). The collected volatiles are accurately weighed and reported in grams (g). Accurate weight of the recovered oil was not possible due to losses in the pump and feed system. The weight of the recovered oil, however, can be estimated as the original sample weight minus the amount of volatiles collected. The TEOST ASTM method reports the expected test repeatability using the same operator/instrument and reproducibility between different test labs. In order to minimize variability, all tests were performed on the same instrument (by the same operator) using the same batch number of depositor rods. Nine engine oils were selected for duplicate testing.

Fourier Transform Infrared (FTIR) Spectroscopy measurements on the recovered oil and volatiles were performed using a modification of the method reported by Obiols (12). A KBr cell path length of 0.037 mm was used. Oxidation was measured by calculating the carbonyl area (C=O) between 1650 cm⁻¹ and 1820 cm⁻¹ in the FTIR spectra. The carbonyl area is representative of the quantity of all products containing a carbonyl function that are formed during the oxidation process (aldehydes, ketones, carboxylic acids, esters, or anhydrides). Therefore, an increase in area represents an increase in oxidation. These carbonyl areas are slightly different from the Peak Area Increase (PAI) values reported by Obiols. It was felt that PAI values of TEOST recovered oil and volatiles might be somewhat misleading. Subtracting TEOST fresh oil peak areas from recovered oil or volatiles peak areas would not take into account the total lubricant since oil sample is fractionated during the test. The carbonyl contribution from the HPE ester group was viewed as insignificant compared to oxidation taking place in the lubricants. Therefore, a correction for the presence of HPE carbonyls was not performed.

RESULTS AND DISCUSSION

Mechanism of Lubricant Degradation

In order to relate TEOST volatiles formation to conventional oxidation processes, it is important to understand the chemical mechanism of lubricant oxidation (13). Fig. 3 provides a mechanistic interpretation on how an organic hydroperoxide, formed in the early stages of lubricant oxidation, transforms to polar volatile organic compounds and polymers. At high temperatures the hydroperoxide (-OOH) cleaves to form an alkoxy radical (-O•). Two degradation pathways are available for the alkoxy radical. It can abstract a hydrogen radical from an oil molecule to form an alcohol (-OH), or it can undergo chain scission to form lower molecular weight aldehydes, ketones, and alkyl radicals (R'•). The later path produces volatile polar organic compounds. These lower molecular weight aldehydes and ketones are precursors to carboxylic acids and polymers. At high temperatures, polymerization of these carbonyl compounds results in viscosity increase and the formation of sludge precursors. Eventually these degradation products produce deposits.

This scheme suggests that the amount of volatiles produced in the TEOST may be representative of polymer precursor formation. These volatiles are not detrimental in the TEOST since they are stripped from the re-circulated oil sample and effectively removed from the test. However, their presence should be detrimental in bulk oil oxidation tests, pressurized oxidation tests, or any oxidation test where volatiles are allowed to accumulate in the oil. Such a condition may also exist in certain types of fired engines.

The mechanism depicted in Fig. 3 also suggests that a significant amount of volatiles may form before polymerization and oil thickening. Physically this might be detected as a drop in engine oil viscosity caused by the lower molecular weight volatiles. This would likely occur immediately before polymerization and viscosity increase since the concentration of volatiles would be high. Such an effect is sometimes seen in high temperature oxidation engine tests. An example of this is illustrated by the Sequence IIIE results in Fig. 4 (14). Three examples of engine oil viscosity drop prior to oil thickening are shown. It's proposed that this drop in viscosity is the result of volatiles formation in the Sequence IIIE test. Once a critical concentration of volatiles is reached, however, condensation reactions begin to predominate leading to polymerization and rapid viscosity increase.

It becomes apparent from Fig. 3 that the formation of deposits, volatiles, and carbonyl oxidation products are all relevant parameters for understanding overall lubricant oxidation. The unique design of the TEOST provides a means of measuring all these parameters in one bench test.

TEOST MHT-4 RESULTS

A complete listing of the TEOST results for deposits, collected volatiles, carbonyl oxidation of the recovered used oil, and carbonyl oxidation of the collected volatiles, is provided in Table 2.

Deposit Formation

Deposit results for the molybdenum-free and molybdenum containing engine oils is shown graphically in Fig. 5. Note that the zero point on the horizontal axis represents engine oil already formulated with 0.75 wt. % of the nonylated diphenylamine (NDPA) antioxidant. Thus the

additional antioxidant represents additive top treated to the NDPA containing engine oil. Four observations can be made by analysis of this data.

- (1) The addition of molybdenum to the engine oil generally improves deposit control,
- (2) Greater antioxidant system differentiation is seen at the higher antioxidant levels and in the molybdenum-free engine oils,
- (3) In general, antioxidant combinations of hindered phenolic and NDPA ($\blacksquare, \blacktriangle, \blacklozenge$) out perform the use of NDPA alone (\circ), and
- (4) Ability to reduce deposit formation in the molybdenum-free engine oils ranks as follows: MBDTBP/NDPA > MBBP/NDPA > HPE/NDPA > all NDPA.
- (5) Some systems show a fairly flat response curve for deposits versus top treated antioxidant concentrations. Such formulations may be difficult to improve in the event they give a marginal failure in specific engine tests.

The benefits of the combined hindered phenolic/NDPA antioxidant systems suggest a synergy for deposit control. This is an especially strong synergy for the MBDTBP/NDPA system and is observed in both the molybdenum-free and molybdenum-containing engine oils (as indicated by the respective total deposit values of 13 and 11 mg).

Volatiles Formation

Figure 6 provides results for the amount of volatiles collected at the end of the TEOST experiment. Clear trends are difficult to detect from this data. The difficulty in interpretation may be due to the poor repeatability of the volatiles measurement. Of the nine samples run in duplicate, only five gave a standard deviation of less than 0.20 grams. Statistical analysis of the replicated data using the least significant differences method confirms that Oil # 8 produces significantly lower volatiles compared to Oils # 2 and 3. These data points are highlighted in the Fig. 6 charts. This analysis further highlights the performance benefits seen when combining MBDTBP with NDPA. The combined antioxidant system in Oil # 8 produces significantly lower volatiles compared to the use of NDPA alone in Oil # 3.

It is important to point out that volatiles have no impact on the formation of deposits in the TEOST, since they are effectively removed from the test. However, they may have a negative impact on other oxidation processes and tests. As Fig. 3 indicates, the volatile products resulting from chain scission are precursors to a variety of detrimental materials. The resulting aldehydes and ketones produced from chain scission can take part in condensation reactions to produce oligomers and polymers that result in viscosity increase and engine oil thickening. The aldehydes and ketones can also undergo radical reactions to produce carboxylic acids that further catalyze degradation of the engine oil. So overall, it's desirable to have robust engine oil that produces low deposits and minimal volatiles. This insures optimum oxidation control under a variety of environments and test conditions.

FT-IR Peak Area Increase

An overlay of the FTIR spectra generated from oil sample #2 is shown in Fig. 7. The overlay is composed of three spectra, the recovered used oil, the volatiles, and the deposits. The spectrum of the deposits was collected using FTIR microscopy techniques by measuring reflectance off deposit solids carefully removed from the depositor rod. The recovered used oil and volatiles spectra were

collected using KBr cells. Note the very strong carbonyl absorbance in all three spectra. The large intensity in the deposits spectrum is an artifact of the surface analysis technique, and should not be compared quantitatively with the other spectra. The deposits, however, do show substantial absorbance associated with the presence of hydroxy, carboxylic acid and carbonyl oxidation. This is expected since polar organic compounds are surface active and would adhere more strongly to the depositor rods. The presence of carbonyl oxidation in the volatiles is a strong indication that they have oxidized and are not simply un-oxidized oil fractions that have volatilized under the conditions of the test.

Carbonyl oxidation for the recovered used engine oils is provided in Fig. 8. Carbonyl oxidation for the collected engine oil volatiles is provided in Fig. 9. These results are similar to those seen for the deposit measurements, although some of the rankings are slightly different. Again, the addition of molybdenum is found to be beneficial as indicated by the reduction in carbonyl oxidation. The MBDTBP/NDPA antioxidant system is clearly more effective for controlling carbonyl oxidation in both the recovered oil and volatiles. Also, the observation of antioxidant system differentiation is apparent when comparing the molybdenum-free and molybdenum-containing engine oils. As with the deposit results, greater antioxidant system differentiation is seen at the higher antioxidant concentrations and in the molybdenum-free engine oils.

Practical Antioxidant Synergy In All Aspects Of TEOST Lubricant Oxidation

Figures 10 (molybdenum-free) and 11 (molybdenum-containing) compare all measured TEOST parameters for three different antioxidant systems: the use of MBDTBP alone, the use of NDPA alone, and the combination of MBDTBP and NDPA. Note the considerable benefits associated with the use of a mixed antioxidant system composed of MBDTBP and NDPA. For both molybdenum-free and molybdenum-containing engine oils the combined antioxidant system provides the best deposit control, control of recovered oil oxidation, control of volatiles formation and control of carbonyl oxidation of the volatiles. These two graphs clearly display the comprehensive antioxidant synergy that is gained by combining a hindered phenolic antioxidant with an alkylated diphenylamine antioxidant. One interesting observation is that MBDTBP appears to be more effective than NDPA in the molybdenum-free engine oils, while NDPA is generally more effective than MBDTBP in the molybdenum-containing engine oils.

Comparing Fig. 10 and 11 also shows the robust nature of the combined MBDTBP/NDPA antioxidant system. Note the effectiveness of this combination in the presence or absence of molybdenum. Also note the effectiveness of this combination towards controlling oxidation under a variety of test parameters. This level of effectiveness in two different formulation types and for all measured parameters is not observed when the other hindered phenolic types are used in combination with NDPA. Thus the MBDTBP/NDPA combination represents a versatile antioxidant system.

Mathematical Definition For A Robust Antioxidant System

A proposed definition for a robust antioxidant system is provided in Fig. 12 where a data-free graph is presented. The y-axis incorporates "Total carbonyl oxidation", while the x-axis provides "total deposits". Total carbonyl (C=O) oxidation is calculated using the following formula:

Total C=O Oxidation = [Volatiles C=O Peak Area x Wt.] + [Rec. Oil C=O Peak Area x Wt.]

This method allows for the use of all measured TEOST test parameters in the data analysis. Recovered oil weight is determined by the difference between volatiles collected and the total weight of the fresh oil sample. Note that such a graph can be divided into four quadrants. Of importance for this study is the top right and bottom left quadrants.

The top right quadrant represents a condition where high deposits and high total carbonyl oxidation is seen. Engine oils residing in this region are said to exist in a broadly weak stabilization quadrant and thus contain a weak antioxidant system. Alternatively, the bottom left quadrant represents a condition where low deposits and low total carbonyl oxidation is seen. Engine oils residing in this region are said to exist in a robust stabilization quadrant and thus contain a robust antioxidant system. Plotting data on this type of graph can provide valuable insight regarding antioxidant response as a function of engine oil formulation type.

An example of the use of this quadrant method is shown in Fig. 13 where the individual data points in Table 2 are plotted based on the presence or absence of molybdenum. Linear regression analysis shows the presence of two separate lines, one corresponding to molybdenum-free engine oils, and one corresponding to molybdenum-containing engine oils. Note that the slope for these two lines is similar but the intercepts are significantly different. This shift in intercept is clearly a function of formulation type. In this case the presence or absence of molybdenum. More important, however, is the skewed nature of the individual data points. Note that the molybdenum-free engine oils reside predominantly in the weak quadrant of the graph (top, right), while the molybdenum-containing engine oils are shifted predominantly to the robust quadrant of the graph (bottom, left). The magnitude of this shift is a measure of overall antioxidant effectiveness or robustness.

Further analysis of the data using this quadrant method shows that certain MBDTBP containing oils are very strongly shifted to the robust quadrant. These engine oils are circled in Fig. 13 and represent both molybdenum-containing and molybdenum-free systems. All these oils contain 0.75 wt. % MBDTBP and 0.75 wt. % NDPA. Thus a tool is now available for identifying antioxidant systems that are effective in a variety of formulation types. This implies that other factors such as basestock type, ZDDP chemistry or oxidation test severity can be analyzed for the purposes of optimizing an antioxidant system.

CONCLUSIONS

A number of conclusions can be proposed based on the TEOST MHT results presented in this paper.

- a. 4,4'-methylenebis(2,6-di-tert-butylphenol) (MBDTBP) is synergistic with alkylated diphenylamines for deposit, oxidation, and volatiles control.
- b. Other hindered phenolic types (HPE and MBBP) do not show the same level of synergy.
- c. Molybdenum improves the effectiveness or "robustness" of ashless antioxidant systems.

- d. Differentiation in overall phenolic performance is more evident at higher phenolic concentrations (1:1 by weight of NDPA/phenolic) and in the absence of molybdenum.
- e. Evaluation of TEOST volatiles and recovered oil using Fourier Transform Infrared Spectroscopy techniques combined with traditional TEOST deposit measurements provides valuable information for understanding fundamental oxidation pathways that can impact other bench and possibly engine tests.
- f. These tools can be applied to the study of component variations in engine oils.
- g. Robustness can be used as a broad measure of the ability of a formulation to perform in a wide variety of environments.

It is important to note that the importance of TEOST volatiles data is subject to the use of a consistent base oil type and additive system. Comparison between different viscosity grade oils, or oils containing substantially different additive packages, is not meaningful. However, the technique is of great value when optimizing an engine oil antioxidant system. By minimizing deposits and volatiles, one can improve the robustness of a given additive package/basestock combination. The reporting of volatiles in the TEOST is actually mentioned in the ASTM method (11), and measuring carbonyl oxidation is now a common practice for characterizing used engine oils. Combining these methods with deposit measurements should further reduce the lubricant industries dependence on engine tests for research and development. These tools are also of great value to the additive researcher and lubricant formulator as a means of optimizing antioxidant performance in complex additive systems prior to engine testing.

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Fig. 1 – Antioxidants Used In Study.











NDPA





TABLE 1 - COMPOSITION OF TESTED ENGINE OILS										
Oil #	Engine Oil Preblend (wt. %)	MoDTC (wt. %)	Mo (ppm)	NDPA (wt. %)	MBBP (wt. %)	MBDTBP (wt. %)	HPE (wt. %)	Diluent (wt. %)		
1	96.00			0.75				3.25		
2	96.00			1.50				2.50		
3	96.00	0.80	360	1.50				1.70		
4	96.00	0.80	360	0.75				2.45		
5	96.00	0.80	360	0.75	0.40			2.05		
6	96.00	0.80	360	0.75	0.75			1.70		
7	96.00	0.80	360	0.75		0.40		2.05		
8	96.00	0.80	360	0.75		0.75		1.70		
9	96.00	0.80	360	0.75			0.40	2.05		
10	96.00	0.80	360	0.75			0.75	1.70		
11	96.00	0.80	360			1.50		1.70		
12	96.00			0.75	0.40			2.85		
13	96.00			0.75	0.75			2.50		
14	96.00			0.75		0.40		2.85		
15	96.00			0.75		0.75		2.50		
16	96.00			0.75			0.40	2.85		
17	96.00			0.75			0.75	2.50		
18	96.00					1.50		2.50		

Fig. 2 – Thermo-Oxidation Engine Oil Simulation Test (TEOST MHT-4).





Fig. 3 – Mechanism of Oil Oxidation – Formation of Alcohols, Aldehydes, Ketones and Acids.



Fig. 4 – Observed Viscosity Drop Before Oil Thickening In The Sequence IIIE Engine (14).

TABLE 2 - TEOST MHT-4 RESULTS								
Oil #	Total Deposits (mg)	Collected Volatiles (g)	Recovered Oil Carbonyl	Collected Volatiles Carbonyl				
1	55.3	2.71	41.2	53.6				
2	50.0	3.15	46.5	43.9				
	46.3	2.82	39.8	50.4				
3	30.6	2.52	20.9	27.3				
	25.3	3.12	35.5	28.7				
4	50.0	2.75	34.9	42.8				
5	19.8	2.18	25.8	37.9				
	24.2	2.27	22.4	34.8				
6	19.5	2.59	24.8	27.7				
	24.3	2.89	25.5	29.1				
7	31.7	2.24	19.5	27.9				
8	9.9	1.87	14.0	22.9				
	12.2	2.24	18.8	24.6				
9	28.8	2.54	29.1	37.5				
	28.3	2.44	27.9	35.2				
10	26.2	2.23	22.4	32.2				
	27.9	2.58	24.6	32.2				
11	32.6	2.18	28.0	45.5				
12	33.1	2.43	36.7	49.7				
	45.6	2.45	39.4	55.3				
13	29.2	2.72	33.3	37.3				
14	43.7	3.16	44.4	45.5				
15	13.6	2.32	26.6	31.8				
16	40.6	2.69	42.0	52.5				
	39.3	2.49	41.3	55.6				
17	41.0	3.00	46.3	50.6				
18	26.0	2.35	33.4	45.1				





Fig. 6 – TEOST MHT-4 Evaluation of Antioxidant Systems In Low Phosphorus Engine Oils Containing 0.75 Wt. % NDPA – Deposit Formation.





Fig. 7 – TEOST MHT-4 Evaluation of Low Phosphorus Engine Oil Volatiles – Comparison Between MBDTBP and NDPA.

















Fig. 12 – Defining A Robust Antioxidant System For Low Phosphorus Engine Oils



Total CO Oxidation = volatiles CO peak area * wt + rec. oil CO peak area * wt

Fig. 13 – Correlation Between Total Carbonyl Oxidation & Deposit Formation



Total CO Oxidation = volatiles CO peak area * wt + rec. oil CO peak area * wt

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