

Using The TEOST® MHT-4 To Identify Robust Antioxidant Systems For Modern Engine Oils

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Abstract

A research tool has been developed that utilizes the Thermo-Oxidation Engine Oil Simulation Test (TEOST®) MHT-4 to collect information on engine oil oxidation and deposit formation. The technique capitalizes on the traditional TEOST® features as a deposit formation test, but also generates additional oxidation information by monitoring peak increase in the carbonyl region of the Fourier Transform Infrared Spectrum (FT-IR) of TEOST® used oils and volatiles. The data on overall oxidation and deposit formation is used to generate a “robustness” model for modern engine oil degradation. The tool is used to study low phosphorus Group II passenger car engine oils formulated with different types of antioxidants and a molybdenum dithiocarbamate (MoDTC). The model shows that improved oxidation and deposit control can be achieved by formulating with the molybdenum compound, and that the most effective stabilization system is composed of the organo-molybdenum compound, an alkylated diphenylamine (NDPA), and the hindered phenolic antioxidant 4,4'-methylenebis(2,6-di-tert-butylphenol) (MBDTBP).

Introduction

The cost of commercializing new engine oils has increased significantly in recent years. In addition the greater choice of base stock types, combined with more challenging specifications, and the general trend towards lower phosphorus levels, has made it exceedingly expensive and time consuming to develop new engine oil products. The use of bench tests represents a practical approach to control development costs while at the same time identifying the best candidates for further testing in fired engines. In recent years a number of oxidation and deposit bench tests have been developed as research tools. [1-4] The introduction of the Thermo-Oxidation Engine Oil Simulation Test (TEOST®) MHT-4 for simulating the carbonaceous deposit-forming characteristics of engine oils has reduced the dependence of formulators on the use of engine tests for research purposes. [5] However, traditional use of the TEOST® is strictly for deposit measurements and does not take into account the general oxidation processes that also occur as oil degrades.

Expanding the use of the TEOST® MHT-4 to include general oxidation in low phosphorus (480 ppm) Group II type passenger car engine oils has recently been reported. [6] The work suggests that the proper combination of aminic antioxidant, organo-molybdenum compound and selection of the proper hindered phenolic, can produce a “robust” engine oil providing superior deposit as

well as oxidation control. This paper reviews that work and looks at a more narrow range of additive types. Additional data is also presented in oils containing more typical phosphorus (740 ppm) levels found in today's engine oil products.

Experimental Methods

The antioxidants chosen for this study are shown in Figure 1. The additives HPE and MBDTBP represent two different hindered phenolic antioxidants commonly used in modern engine oils. These hindered phenolics are considered to have low volatility and are therefore suitable antioxidants for high temperature and extended drain use. A nonylated diphenylamine (NDPA) was chosen for this study in an effort to compare an all aminic style of formulating versus the use of a mixed antioxidant system composed of hindered phenolics and aminics. A molybdenum dithiocarbamate (MoDTC) was chosen as the molybdenum source since these materials have beneficial anti-wear properties in addition to their antioxidantcy.

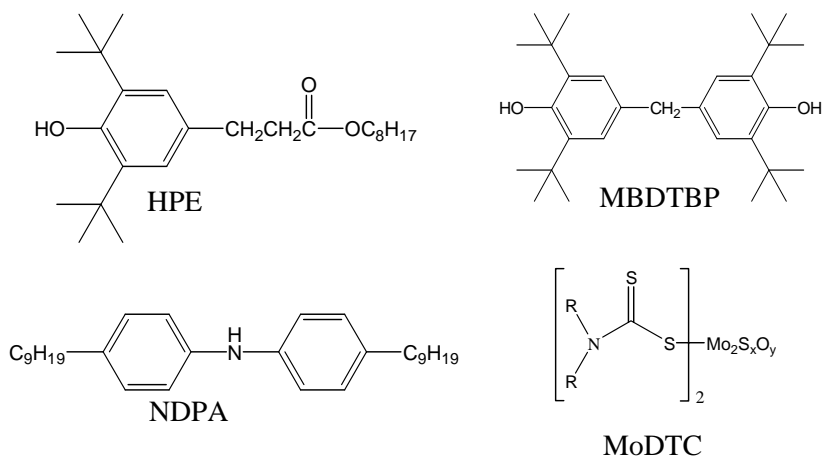


Figure 1. Antioxidants used in study

Engine oil formulations contained 4.8 wt. % dispersant, 2.3 wt. % detergents and the desired amount of ZDDP to produce the targeted level of phosphorus. All base oils were of the Group II type and had a kinematic viscosity @ 100°C of 6.1 cSt, a viscosity index of 114, and a Noack volatility of 8 wt. %. The various antioxidants and molybdenum compounds were added to the engine oil as described in Table 1, which clearly illustrates the four different formulation approaches under evaluation. Oils 1 through 4 are representative of an approach that utilizes only aminic (NDPA) antioxidant. Oils 5 through 8, and 10 through 13, are representative of an approach that utilizes a mixture of hindered phenolics and aminics. Finally, oils 9 and 14 are representative of an all hindered phenolic formulation approach. Note also that some formulations contain molybdenum (Oils 3 through 9) while others are molybdenum-free (Oils 1 through 2 and 10 through 14).

TABLE 1 - COMPOSITION OF TESTED ENGINE OILS							
Oil #	Engine Oil Preblend (wt. %)	MoDTC (wt. %)	Mo (ppm)	NDPA (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		1.50		1.70
10	96.00			0.75	0.40		2.85
11	96.00			0.75	0.75		2.50
12	96.00			0.75		0.40	2.85
13	96.00			0.75		0.75	2.50
14	96.00				1.50		2.50

The TEOST® MHT-4 was run according to ASTM test method D 7097. [7] A cross-section of the test assembly is shown in Figure 2. In this test an oil sample of 8.5 grams (containing Fe/Pb/Sn catalyst) is introduced onto a heated wire-wound depositor rod via the oil feed tube at a rate of 0.25 g/min. The depositor rod is maintained at 285°C. A thin film of oil moves evenly down the heated rod while air passes through the system at a rate of 10 cc/min. Recovered oil is collected at the oil flow out point and re-circulated back to the depositor rod with a precision pump. During the test, volatile components present in the oil, or generated during oil aging, flash off the hot rod and are collected on the trough of the glass mantle. These accumulated volatiles are directed out of the system via the condensed volatiles out tube, and are finally collected in a glass vial. At the end of the 24 h test deposits are determined by the increase in rod weight and reported in milligrams (mg). The collected volatiles are weighed and reported in grams (g). The weight of the recovered oil was estimated from the difference between original fresh oil weight and the amount of volatiles collected.

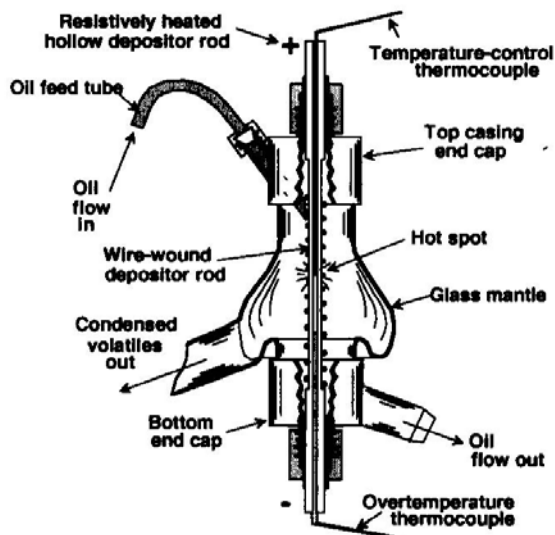


Figure 2. TEOST® MHT-4 Assembly

Fourier Transform Infrared (FT-IR) Spectroscopy measurements on the recovered oil and volatiles were performed using a modification of the method reported by Obiols. [8] 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 FT-IR spectra. An increase in carbonyl area corresponds to an increase in numerous oxidation products (aldehydes, ketones, carboxylic acids, esters, or anhydrides) generated during oil degradation.

Key features of the FT-IR analysis for oil # 2 are shown in Figure 3. The illustrated overlays are composed of the recovered used oil, the volatiles, and the deposits. Note the very strong carbonyl absorbance in all three spectra. The deposits show substantial absorbance associated with the presence of hydroxy, carboxylic acid and carbonyl oxidation, which is expected since polar organic compounds are surface active and adhere to the depositor rod. Of importance in the development of the robustness model is the carbonyl region for the recovered used oil and volatiles. The peak areas associated with this region are used to generate the total carbonyl oxidation data used in the model.

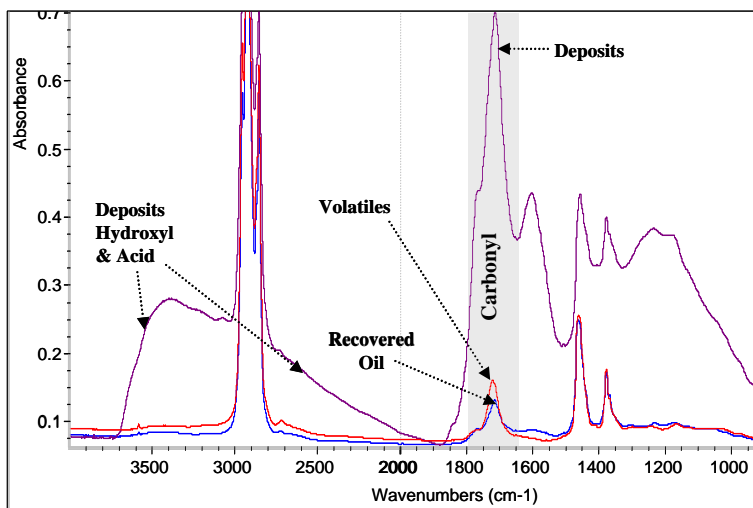


Figure 3. FT-IR Spectra of TEOST® MHT-4 Recovered Used Oil, Volatiles, and Deposits

Results and Discussion

Mechanism of Lubricant Degradation

Figure 4 illustrates the chemical relationship between TEOST® MHT-4 volatiles formation and conventional oxidation processes. Note that the chain scission step converts radical intermediates into lower molecular weight fragments composed of aldehydes and ketones plus alkyl radicals ($R\cdot$). These represent the volatile products produced during typical lubricant degradation as well as the volatile oxidation fractions produced in the TEOST® test. The aldehydes and ketones can react further to produce low molecular weight carboxylic acids, which lead to an increase in acidity of the lubricant. The aldehydes and ketones can also undergo an Aldol type condensation, which leads to higher molecular weight polar products. Eventually the polarity and molecular weight of degradation products increase to the point where solubility in

the lubricant is impacted. At that point these degradation products adhere to the metal surfaces of the engine or the TEOST® wound rod and result in deposit formation. Note in this entire process there are many opportunities to form carbonyl (C=O) oxidation products. These carbonyl species are what's detected in the FT-IR analysis.

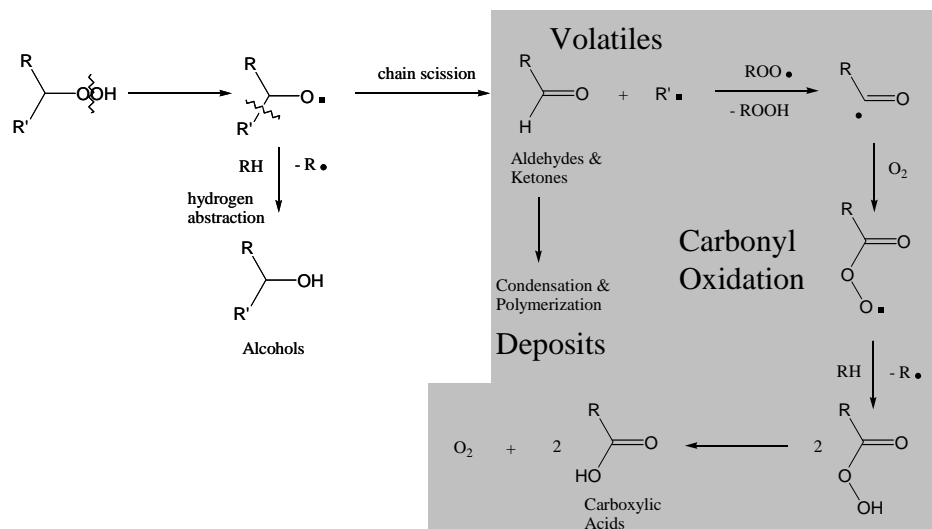


Figure 4. Mechanism of lubricant Oxidation and Deposit Formation

This scheme suggests that the amount of volatiles produced in the TEOST® MHT-4 may be representative of polymer precursor formation. These volatiles are not directly detrimental in the test since they are stripped from the re-circulated oil sample and effectively removed. However, their presence should be detrimental in most oxidation bench tests and certain types of fired engines.

It becomes apparent from Figure 4 that the deposits, volatiles and carbonyl oxidation products are all relevant for getting a complete picture of lubricant degradation. The TEOST® MHT-4 apparatus is uniquely designed for measuring all these parameters in one bench test.

TEOST® MHT Results

A complete listing of the TEOST® MHT-4 results for total rod deposits, collected volatiles weight, and carbonyl oxidation of recovered used oil and collected volatiles by FT-IR, is provided in Table 2.

Deposit results are shown graphically in Figure 5. Note that the zero point of the horizontal axis represents engine oil already formulated with 0.75 wt. % of NDPA. Therefore the total antioxidant used is determined by the sum of the value on the horizontal axis plus 0.75 wt. %. In general the addition of molybdenum improves deposit control. This has been well documented in the literature. [9] Also, a greater spread in the deposit results is seen at the higher antioxidant levels, and this spread becomes greater in the molybdenum-free systems. In general, the antioxidant combination of hindered phenolic and NDPA (diamond, triangle) out performs the use of NDPA alone (circle). Finally, the use of MBDTBP in combination with NDPA (triangle)

appears to be the most effective with and without molybdenum. This is especially the case at the higher treat rate of MBDTBP (Oils 6 and 11) where low deposit values of 9.9, 12.2 and 13.6 are observed.

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	31.7	2.24	19.5	27.9
6	9.9	1.87	14.0	22.9
	12.2	2.24	18.8	24.6
7	28.8	2.54	29.1	37.5
	28.3	2.44	27.9	35.2
8	26.2	2.23	22.4	32.2
	27.9	2.58	24.6	32.2
9	32.6	2.18	28.0	45.5
10	43.7	3.16	44.4	45.5
11	13.6	2.32	26.6	31.8
12	40.6	2.69	42.0	52.5
	39.3	2.49	41.3	55.6
13	41.0	3.00	46.3	50.6
14	26.0	2.35	33.4	45.1

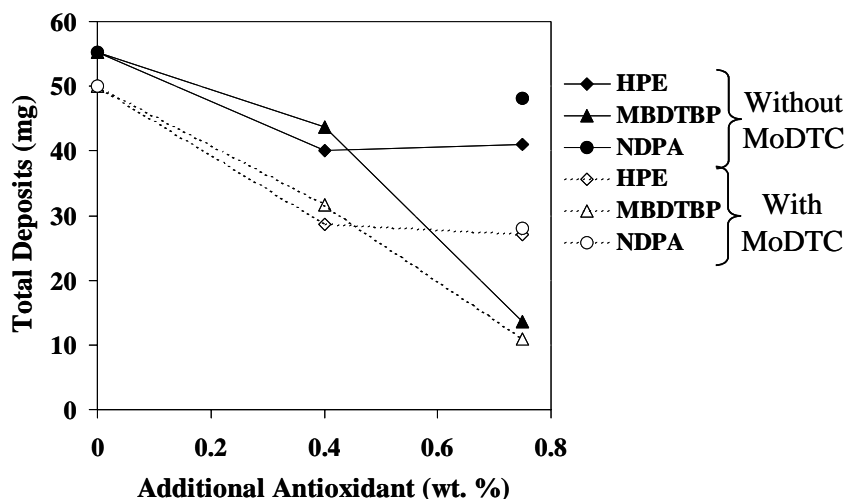


Figure 5. TEOST® MHT-4 Deposits in Engine Oils Containing 0.75 wt. % NDPA

The weight of volatiles produced in the TEOST® MHT-4 is shown graphically in Figure 6. Here it is observed that the molybdenum-containing oils generally produce less volatiles compared to the molybdenum-free oils. Also, at the higher treat level the combined system of MBDTBP and NDPA (triangle) produces less volatiles compared to the combined system of HPE and NDPA (diamond) or NDPA alone (circle). As mentioned above the volatiles are not directly detrimental in the TEOST® since they are effectively removed from the test. However,

the formation of high volatiles results in less used oil re-circulating over the depositor rod during the course of the test. This means the remaining used oil undergoes more passes over the heated rod. This process can potentially lead to greater used oil oxidation and a higher end of test deposit level on the rod.

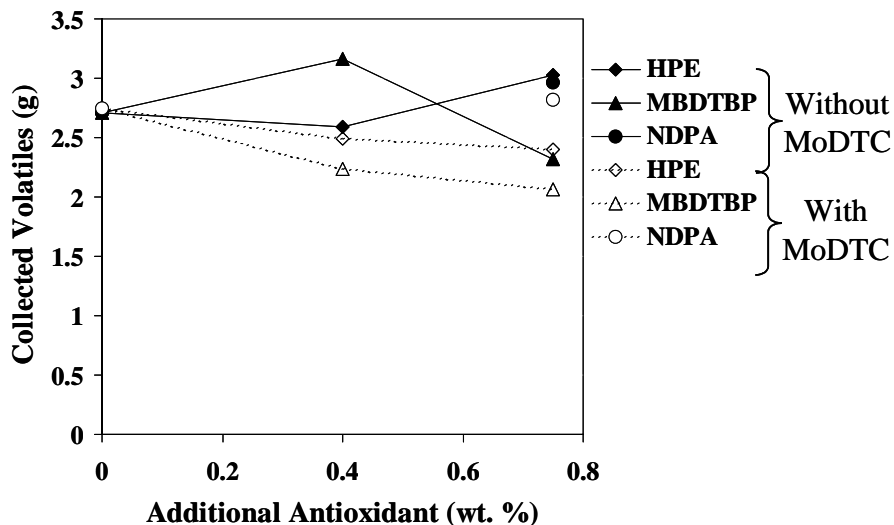


Figure 6. TEOST® MHT-4 Volatiles Formation in Engine Oils Containing 0.75 wt. % NDPA

Carbonyl oxidation for the recovered used oils and volatiles are provided in Figure 7 and 8. These results are similar to those seen for the deposit measurements, although some of the rankings are slightly varied and the differentiation between the various additive types appears to be more pronounced. From this data it's much more apparent that the mixed antioxidant system composed of MBDTBP and NDPA (triangle) is preferred over the HPE/NDPA equivalent (diamond). The differentiation between the molybdenum-containing and molybdenum-free systems also appears to be greater.

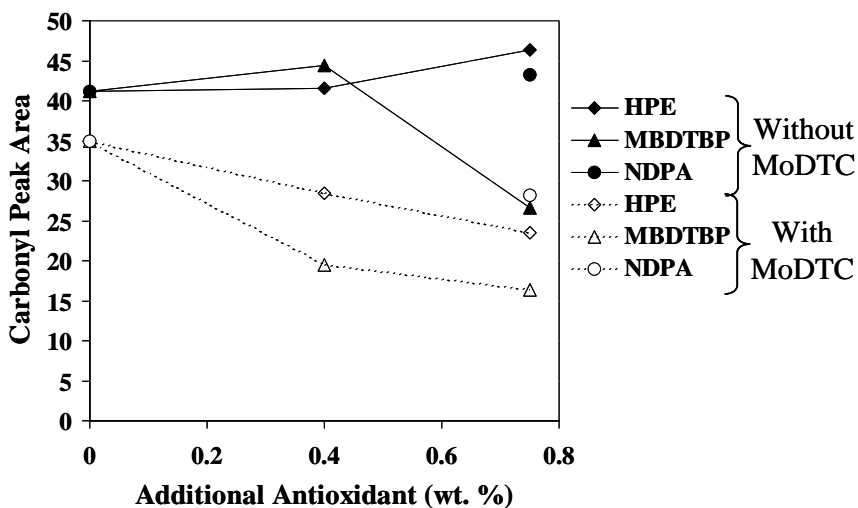


Figure 7. TEOST® MHT-4 Used Oil Oxidation in Engine Oils Containing 0.75 wt. % NDPA

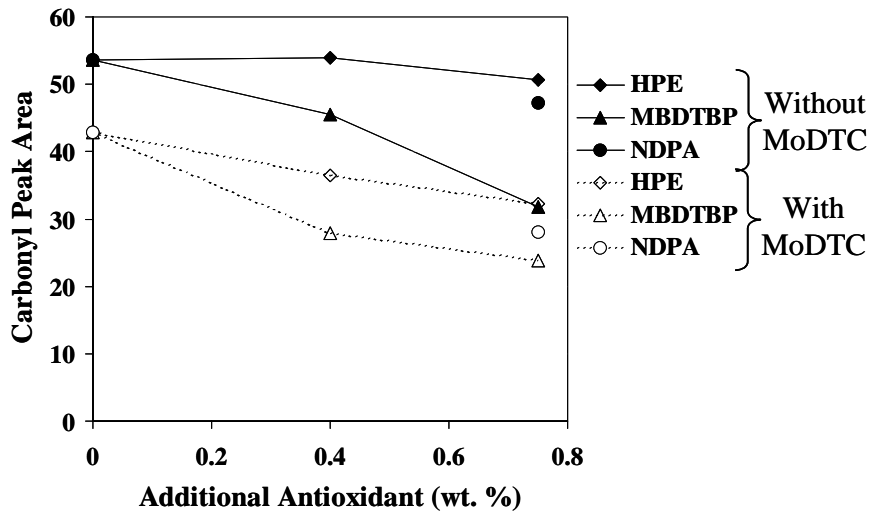


Figure 8. TEOST® MHT-4 Volatiles Oxidation in Engine Oils Containing 0.75 wt. % NDPA

Definition Of A Robust Antioxidant System

Webster defines robust as “capable of performing without failure under a wide range of conditions.” For engine oil stressed in the TEOST® MHT-4, robustness can be represented by the data-free graph illustrated in Figure 9, where y-axis incorporates “total carbonyl oxidation” and x-axis incorporates “total deposits.” Total carbonyl oxidation may be calculated from the carbonyl peak areas and weight data by using the following equation:

$$\text{Total C=O Oxidation} = [\text{Volatiles C=O Peak Area} \times \text{wt.}] + [\text{Rec. Oil C=O Peak Area} \times \text{Wt.}]$$

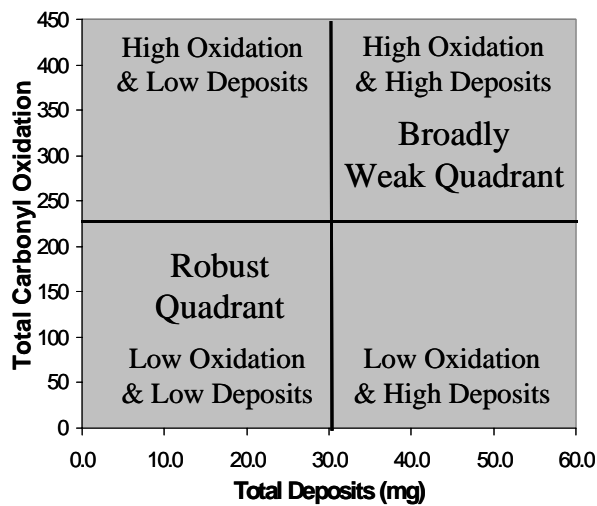


Figure 9. Defining a Robust Antioxidant System For Engine Oils

This approach allows analysis of data by combining conventional oxidation, normally associated with FT-IR carbonyl peak increase, with traditional use of the TEOST® MHT-4 as a deposit formation tool. Note that such a graph can be divided into four quadrants. The top right quadrant represents the region where high deposits and high oxidation occur. Engine oils residing in this area are said to exist in a broadly weak stabilization quadrant and thus contain a weak antioxidant system. Alternatively, the bottom left quadrant represents the region where low deposits and low oxidation occur. Engine oils residing in this area 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 performance as a function of engine oil formulation type.

Analysis of the data in Table 2 using the above equation produces the graph shown in Figure 10. Regression analysis shows the presence of two separate linear equations, one corresponding to molybdenum-free engine oils, and one corresponding to molybdenum-containing engine oils. The shift in intercept is clearly a function of formulation type (presence or absence of molybdenum). Of special importance is the shift of data point groups from the broadly weak region (top right), associated with molybdenum-free formulations, to the robust region (bottom left), associated with molybdenum-containing formulations. The magnitude of this shift is a measure of overall antioxidant system effectiveness or robustness.

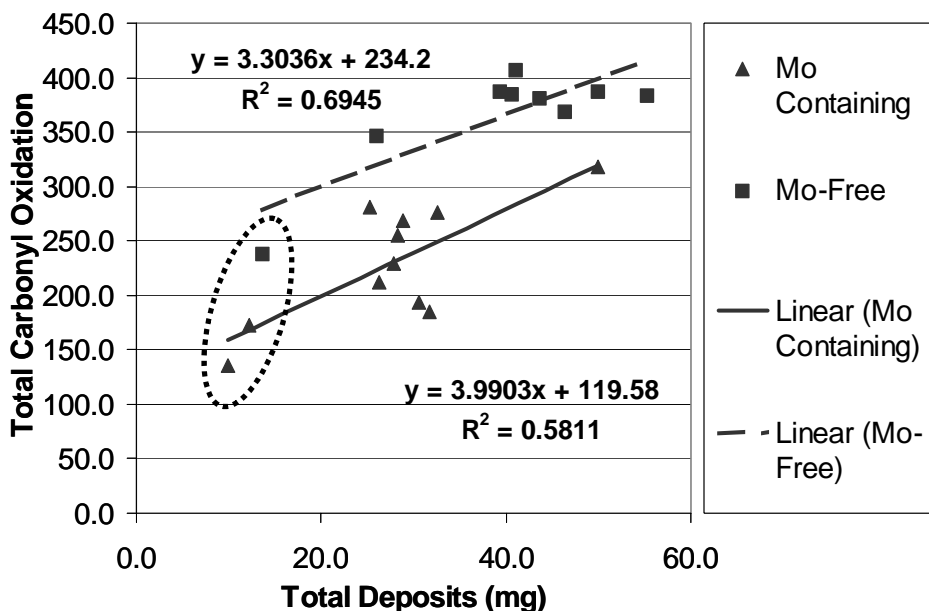


Figure 10. Correlation Between Total Oxidation and Deposits in the TEOST® MHT-4

Note that certain MBDTBP containing oils are strongly shifted to the robust quadrant. These engine oils are circled in Figure 10. In addition to MBDTBP they all contain NDPA and represent both molybdenum-containing and molybdenum-free systems. Thus formulations containing combinations of NDPA and MBDTBP appear to provide excellent oxidation and deposit control and are considered highly robust or effective.

TEOST® MHT-4 Deposit Results in Conventional Engine Oils

The work discussed thus far was performed in low phosphorus engine oils. It was of interest to evaluate the antioxidant systems used in this study in a formulation more representative of current engine oil technology. As a result, TEOST® MHT-4 evaluations were performed on engine oils similar to those described above but containing a higher level of phosphorus (740 ppm) derived from ZDDP and a lower level of molybdenum (90 ppm) derived from MoDTC. This formulation style is more representative of GF-5 type technology. The deposit results from this evaluation are shown in Figure 11. As with the previous testing, the baseline formulations were already formulated with 0.75 wt. % of aminic antioxidant NDPA.

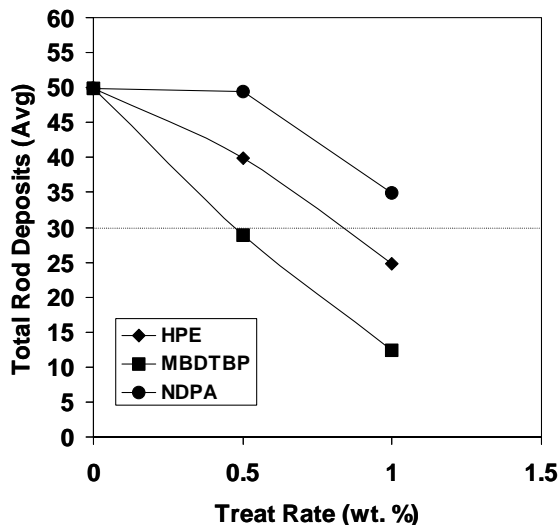


Figure 11. TEOST® MHT-4 Deposits in Engine Oils Containing Higher Phosphorus Levels

The performance ranking for deposit control is similar to that seen in the low phosphorus formulations. Again the mixed MBDTBP/NDPA system (square) performs the best, followed by the mixed HPE/NDPA system (diamond), with the all NDPA system (circle) showing the weakest performance. These results confirm that the ranking of antioxidant effectiveness for deposit control is not significantly affected by phosphorus or molybdenum levels in the oil, although it may be argued that more consistent differentiation is observed in these re-balanced formulations.

Conclusions

This study demonstrates that the TEOST® MHT-4 can be used to evaluate engine oil oxidation as well as its traditional use as a deposit formation test. By combining carbonyl oxidation and deposit data one can develop a model for engine oil stabilization. This model is useful in identifying robust engine oils that are resistant to deposit formation as well as conventional oxidation processes. Such a tool has immense value in reducing costs associated with additive and engine oil development.

The above study clearly demonstrates that use of the phenolic MBDTBP, combined with aminic NDPA, provides excellent stabilization against traditional oxidation as well as deposit formation.

Additional performance improvements can be achieved by adding organo-molybdenum compound MoDTC to the engine oil. Thus the three-way combination of MBDTBP, NDPA and MoDTC represents a highly robust stabilization system for modern engine oils having potential compatibility with a wide range of additive and basestock types.

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Author Biography

Vincent Gatto has worked for 22 years as an applications and product development scientist in the area of antioxidants. He is currently a Senior Advisor for Albemarle Corporation and manages a technical service and applications team. Prior to Albemarle he worked 16 years for Ethyl Corporation as an additive scientist. Vince received his Ph.D. in chemistry from the University of Maryland, and held a postdoctoral position at the University of Miami prior to working for Ethyl. Vince holds approximately 70 U. S. patents and technical publications in the areas of chelation, additives, and antioxidants for polymers, lubricants and fuels.