Article

Phenothiazine Derivatives as Antioxidants for Engine Oils

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(Manuscript received 19 October 2009; accepted 3 September 2010; published 15 October 2010)

(Presented at the mini-Symposium on Additives Technology of Lubricants for the Next Generation in the World Tribology Congress 2009)

Phenothiazine derivatives have been known to function as antioxidants for engine oils, transmission fluids and industrial lubricants. Alkylated phenothiazines are amines which contain sulfur and have lower bond dissociation energy, i.e. a higher rate constant than their “parent” alkylated diphenylamines. They are highly reactive towards radicals and are therefore excellent inhibitors against autoxidation and polymerisation. Since alkylated phenothiazines can provide superior oxidation stability, help to prolong the useful life of lubricants and significantly improve the durability and resistance of lubricants when exposed to high temperatures, they are of increasing importance. Performance requirements have become more stringent in the past 10 to 20 years and the demand for longer drain intervals has grown steadily. Also, the use of Group II, III and IV base oils is becoming more wide spread. Such base oils have very little sulfur content since natural sulfur-containing antioxidants are either absent or removed during the severe refining process. These evolutions in performance and base oil chemistry can be well handled by the use of phenothiazine chemistry.

Keywords: phenothiazine, antioxidants, oxidation stability

1. Introduction

Lubricants, like all organic materials, are prone to thermo-oxidative degradation. Fortunately, this degradation can be minimised or retarded. Primary and secondary antioxidants are used successfully to improve the oxidative stability of oils exposed to high temperatures and to extend their service life.

Types of antioxidants typically used are:

- Radical Scavengers (primary antioxidants)
 - Aromatic amines
 - Hindered phenols
- Peroxides Decomposers (secondary antioxidants)
 - Organophosphorus compounds
 - Organosulfur compounds
- Multifunctional Antioxidants
 - Zinc dithiophosphates
 - Organomolybdenum compounds

Primary antioxidants slow down the thermo-oxidative degradation chain process by trapping radicals.

Table 1 Order of magnitude of the rate constant of the radical (rad^o) trapping reaction by the antioxidant AH¹⁾

Free Radicals	Symbol	Rate Constant, M ⁻¹ s ⁻¹
C- radicals/ alkyl radical	R ^o	10 ⁵
Alkoxy radicals	RO ^o	10 ⁹
Peroxy radicals	ROO ^o	10 ⁶

Secondary antioxidants react with Peroxides (ROOR' / ROOH).

The efficiency of an antioxidant depends upon its structure. For primary antioxidants, such as aminic antioxidants, the dissociation energy of the N-H bond, E_(N-H), is a key parameter. Amines which contain sulfur (e.g. alkylated phenothiazines) have a lower bond dissociation energy i.e. higher rate constant, than their “parent” alkylated diphenylamines (ADPA). A decrease of E_(N-H) by a few kJ/mol can increase the rate constant by a factor of 10.

Table 2 N-H Bond Dissociation Energy of AO

AO structure
$E_{(N-H)}$ in kJ/mol	326	356

A blend of primary and secondary antioxidants provides a higher level of protection to lubricants since it will deactivate the free radicals and also the hydroperoxides. Significant gain in durability and resistance of the lubricant when exposed to high temperature can be achieved.

2. Applications

Certain alkylated phenothiazines show surprisingly high stabilizer activity and very adequate solubility in broad range of mineral and synthetic oils. The term mineral oil includes all mineral oils used for lubricant purposes, such as hydrocarbon mineral oils. The synthetic oil may be, for instance, an aliphatic or aromatic carboxylic ester, a polymeric ester, polyalphaolefin, or a silicone²⁾.

Alkylated phenothiazine additives are known to be particularly effective as antioxidants in esters (i.e. Group V base oil). It has been reported that the most widely used antioxidants in turbine lubricants for aircraft gas turbine are certain secondary amines, including phenothiazines containing aromatic nuclei. These amines have traditionally been used as antioxidants for synthetic ester-based lubricants in gas turbine engines³⁾.

It is a known fact that lubricating oils used in internal combustion engines and transmissions of automobiles or trucks are subjected to demanding environments during use. These environments result in the lubricant suffering oxidation catalyzed by the presence of impurities in the oil, such as iron (wear) compounds and elevated temperatures. The oxidation manifests itself by increases in acid or viscosity and deposit formation or any combination of these symptoms. These are controlled to some extent by the use of antioxidants which can extend the useful life of the lubricating oil, particularly by reducing or preventing unacceptable viscosity increases. In this regard, studies have shown that the combination of an alkylated diphenylamine, a sulfurized olefin/fatty oil and/or an ashless dialkyldithiocarbamate, and an alkylated phenothiazine, is highly effective at controlling crankcase lubricant oxidation and deposit formation⁴⁾.

Besides oxidation inhibition, other parameters such as rust and wear control are also important. It has been found that a lubricant composition comprising an effective combination of alkylated phenothiazines plus alkylated diphenylamines along with an ashless

antiwear additive and ashless rust inhibitor, is particularly effective in enhancing oxidation inhibition, as well as rust and wear control⁵⁾.

In light of the volatility of crude oil supply and demand, fuel economy and lowering friction is becoming increasingly important to regulatory bodies, car manufactures, oil companies, additive suppliers and end-consumers. Accordingly, it has been demonstrated that a lubricating oil composition containing a molybdenum compound, augmented with an alkylated phenothiazine and a secondary diarylamine, can provide improved friction modifier performance as well as improved oxidation control. The combination is particularly suited for use as a crankcase lubricant or transmission fluid, including those with low or zero levels of phosphorus⁶⁾.

Additive and oil companies are constantly faced with pressure from rising raw material prices and the need for product differentiation. It has been reported that a reduction in cost and improved performance can be achieved by using a multifunctional VI improver which improves not only the viscosity index, but is also active as a dispersant and antioxidant. Such an additive can be prepared by incorporating a dispersant unit and antioxidants – aromatic amines and phenothiazines onto the polymer chain. The engine test performance of motor oils containing such multifunctional VI improvers is superior to that of oils containing conventional or dispersant OCP VI improvers. It allows a significant reduction in the amount of classical antioxidant and dispersant used in the dispersant inhibitor package⁷⁾.

Furthermore, reports have also claimed that alkylated phenothiazine additives possess multi-functional properties, which include high temperature oxidation resistance, rust inhibition and wear control⁸⁾.

Piston cleanliness is a critical part of engine oil performance evaluation. There are several factors affecting piston cleanliness including the following:

- Base stock type
- Thermo-oxidative stability of the engine oil
 - The proper selection of AO, aminic, phenolic and ZnDTP
 - Provide the required stability of the oil at both:
 - Bulk oil temp. (120 to 170 °C)
 - Thin film temp. (high oil temp. > 240 °C)
- Dispersant and detergent to handle soot and sludge
 - Dispersant: Soot / sludge (part. size < 0.03 µm)
 - Detergent: Soot / sludge (part. size ≈ 1.0 µm)
- Lubricants capacity to neutralise acids (combustion residues)

- Overbased detergents

Among the factors mentioned above, thermo-oxidative stability is probably the most important of all. If thermo-oxidation is not controlled, engine oil decomposition will lead to oil thickening, sludge formation and the formation of varnish, resin and corrosive acids. These effects are detrimental to the engine components and are likely to eventually result in engine failure. In this regard, antioxidants are effective in tackling sludge problems at a much earlier stage of the ageing process compared to dispersants. They do so by eliminating sludge pre-cursors.

3. Test methods

The following tests were conducted to evaluate the effects of phenothiazines, ADPA and hindered phenols on the performance of engine oils.

TEOST MHT-4

The thermo-oxidation engine oil simulation test, TEOST MHT-4, (ASTM D 7097) is a bench test developed to correlate with piston deposit control when engines are run under high power and high temperature conditions. At the end of the test, the weight of deposits on a heated metal rod is measured. The test conditions are shown in Table 3.

Table 3 TEOST MHT-4 test conditions

Equipment	SAVANT TEOST
Test length, hrs	24
Oil sample size, g	8.5
Rod temperature, °C	285
Air flow, ml/min	10
Oil sample flow, g/min	0.25
Catalyst	Liquid naphthenates (Pb/Fe/Sn)

Cat 1 N

The objective of the diesel engine test, Cat 1 N, (ASTM D 6750) is to evaluate the performance of crankcase lubricants with respect to piston deposits, ring sticking, piston, ring and liner scuffing, in conjunction with lower sulfur fuel. The test fixture is a Caterpillar single-cylinder direct-injection diesel test engine with a four-valve arrangement. The test simulates on-highway heavy-duty diesel engine service with low sulfur fuel. At the end of the 252-hour test, the piston, rings and liner are evaluated.

PDSC

The Pressure Differential Scanning Calorimeter, PDSC, test (ASTM D 6186) is a bench test designed to give an indication of the propensity of a formulated lubricant to oxidize. A small quantity of oil is weighed into a sample steel pan and placed in a test cell. The cell is heated to 200 °C and then pressurized with oxygen. It is held at a 200 °C and 3.5 MPa until an exothermic

reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time for the lubricating oil.

Test Samples

The engine oils used as follows:

- Base GF-3 (i.e. fully-formulated gasoline engine oil that meets ILSAC GF-3 requirements)
- Base GF-4 (i.e. fully-formulated gasoline engine oil that meets ILSAC GF-4 requirements).
- Base CG-4 (i.e. heavy-duty diesel engine oil that meets API CG-4 requirements with its AO content removed)

The additives used to top-treat the engine oils were as follows:

- ADPA
- Additive A (i.e. blend of alkylated phenothiazines and ADPA)
- Additive B (i.e. blend of alkylated phenothiazines, ADPA and hindered phenols).

4. Performance test data

The TEOST MHT-4 test was conducted on the following formulations.

- Base GF-3
- Base GF-3 + 0.5% ADPA
- Base GF-3 + 1.0% ADPA
- Base GF-3 + 1.0% Additive A

It can be seen from Figure 1 that the base formulation with 1% of Additive A gave the best result, meeting GF-4 and proposed GF-5 TEOST specifications. This shows that a blend of alkylated phenothiazines and ADPA provides excellent deposit control in high temperature conditions.

The TEOST MHT-4 test was also conducted on the following formulations.

- Base GF-4

Figure 1 TEOST MHT-4 test results (Base GF-3)

- Base GF-4 + 1% ADPA
- Base GF-4 + 1% Additive A
- Base GF-4 + 2% Additive A
- Base GF-4 + 2% Additive B

It can be seen from Figure 2 that the base formulation with 2% of Additive B produced the best result. It meets GF-4 and proposed GF-5 specifications. This shows that a blend of alkylated phenothiazines, ADPA and hindered phenols effectively controls high-temperature deposit formation.

Figure 2 TEOST MHT-4 test results (Base GF-4)

Note: Cat 1N (same limits) also required for API CJ-4

Figure 3 Cat 1N test results

The Cat 1 N engine test was run with the following formulations:

- Base CG-4
- Base CG-4 + 0.55% Additive A
- Base CG-4 + 0.55% ADPA

It can be seen from Figure 3 that the values of the WDN (Weighted Demerits) and TGF (Top Groove Fill) were the lowest for the base formulation with 0.55% of Additive A. It shows that a blend of alkylated phenothiazines and ADPA gave significantly superior performance in Cat 1 N as compared to ADPA alone⁹.

The PDSC test was conducted on the Cat 1 N engine tested oils. It can be seen from Figure 4 that Additive A (i.e. blend of alkylated phenothiazines and ADPA) maintains oxidative stability better than ADPA alone, throughout the entire test.

Figure 4 PDSC evaluation of Cat 1N engine oils

5. Conclusion

A combination of alkylated phenothiazines and ADPA is more effective than ADPA alone in inhibiting oxidation in lubricants. Alkylated phenothiazines are sufficiently soluble in a wide range of base oils and they work synergistically with other additives in improving oxidation stability, rust inhibition, wear control and friction properties of lubricating oils. They can also be incorporated into a VII to make it dual- or multi-functional. The presence of alkylated phenothiazines in addition to ADPA significantly improves the performance in controlling high temperature deposit formation and overall piston cleanliness. This credential makes them ideal antioxidant candidates for modern-day engine oil formulations.

6. References

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