(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 161 325 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.03.2010 Bulletin 2010/10

(51) Int Cl.:
C10M 137/10 *(2006.01)*

(21) Application number: **09168516.4**

(22) Date of filing: **24.08.2009**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR
Designated Extension States:
AL BA RS

(30) Priority: **28.08.2008 US 199968**

(71) Applicant: **Afton Chemical Corporation**
Richmond, VA 23219 (US)

(72) Inventors:
- **Sheets, Roger M.**
  Glen Allen, VA 23060 (US)
- **Guinther, Gregory H.**
  Richmond, VA 23233 (US)
- **Loper, John T.**
  Richmond, VA 23238 (US)

(74) Representative: **Dunleavy, Kevin James**
Knoble & Yoshida LLC
p/o De Vries & Metman
Overschiestraat 180
1062 XK Amsterdam (NL)

(54) Lubricant formulations and methods of lubricating a combustion system to achieve improved emissions catalyst durability

(57) Different zinc dialkyldithiophosphate (ZDDPs) exhibit different volatilities and have different effects on automotive emissions control catalysts. The ZDDPs and their respective decomposition fragments that have low volatility will have a correspondingly lower detrimental effect on combustion emissions control systems, because there are simply fewer phosphorous atoms that will pass through the combustion system to reach the emissions control system. Specifically, it has been discovered that ZDDPs that contain a significant fraction of MIBC ZDDP exhibit significantly lower volatility than other ZDDPs.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention is directed to a lubricant formulation and to methods of lubricating a combustion system in order to achieve improved emissions catalyst durability in an emissions control system associated with the combustion system. Specifically, the method is directed to using a relatively low amount of a predetermined phosphorous-containing additive in a lubricant in order to minimize emissions control catalyst poisoning. The invention is also directed to the examination of TEOST MHT trapped volatiles to select a specific phosphorous-containing additive that produces the least amount of emissions control catalyst poisoning.

BACKGROUND

[0002] Phosphorous is a known element found and incorporated in lubricant compositions for combustion systems. Unfortunately, emissions from combustion systems that include phosphorous can poison the catalyst components of emissions control systems. Specifically, phosphorous emissions from lubricants can poison these catalysts as a result of either blow-by volatiles or by combustion, thereby reducing an emissions catalyst's efficiency or ability to otherwise reduce or convert harmful combustion system emissions. For instance, there has been concern for many years that phosphorous from engine oils is volatilized, passes through a combustion chamber, and is subsequently deposited on a catalyst system in a passenger car, thereby causing the automobile emission control system to lose efficiency. Therefore, as new engine oil specifications have been introduced, there has been a trend to require a reduction in the amount of phosphorous in fresh engine oils.

SUMMARY

[0003] Accordingly, it is an object of the present invention to help solve the problem of catalyst poisoning as a result of the combustion of phosphorous in a combustion system. Further, it is an object of the present invention to give special attention to the specific types of ZDDP that may be used as an additive in a lubricant composition. Additionally, the method of the selection of a specific ZDDP composition may be used in conjunction with industry limitations regarding phosphorous content in a lubricant composition to help control and minimize phosphorous poisoning of catalyst in an emissions control system.

DETAILED DESCRIPTION

[0004] It has been discovered that different zinc dialkyldithiophosphates (ZDDPs) exhibit different volatilities and have different effects on automotive emissions control catalysts. In other words, ZDDPs will decompose as a result of normal wear and use in an engine crankcase. Different ZDDP molecules will therefore decompose into different fragment molecules. The decomposition fragments can have substantially different levels of volatility. The ZDDPs and their respective decomposition fragments that have low volatility will have a correspondingly lower detrimental effect on combustion emissions control systems, because there are simply fewer phosphorous atoms that will pass through the combustion system and reach the emissions control system. In other words, the less volatile the deleterious molecules are, the fewer molecules there are to pass through combustion by way of engine blow-by or simple combustion. Conversely, if a ZDDP and its respective decomposition fragments have a high volatility, then there is an increased number of these molecules that pass through the combustion system, thereby resulting in increased poisoning of the emissions control catalyst.

[0005] ZDDP is a well-known lubricant additive for use with all types of internal combustion engines. ZDDP is included in additive packages for the purposes of at least improved anti-wear and anti-oxidation properties. However, the term "ZDDP" refers, in fact, to many different alternative molecules. The difference between the molecules is mostly in the different alkyl components and in the relative spatial relationship of the alkyl components around the phosphorous molecule. Different ZDDPs can have different performance properties in a lubricant.

[0006] In simplistic terms, ZDDPs are formed by combining alcohols with thiophosphates. ZDDPs are generally described by the alcohol that is used in the synthesis process to donate the alkyl groups to the ZDDP molecule. So for instance, "primary" ZDDPs are formed from primary alcohols including, but not limited to, n-decanol, n-octanol, 2-ethyl-1-hexanol, 1-hexanol, 4-methyl-1-pentanol, 2-methyl-1-propanol , 1-pentanol, 1-butanol, 1-propanol and mixtures thereof. Similarly, "secondary" ZDDPs are formed from secondary alcohols including, but not limited to, 2-propanol, 2-butanol, 2-pentanol, 4-methyl-2-pentanol, 2-hexanol, 2-octanol and 2-decanol and mixtures thereof. "Aryl" ZDDPs include those formed from phenol, butylated phenol, 4-dodecyl phenol and 4-nonyl phenol and mixtures thereof. In lubricant formulations, different ZDDPs are often mixed to obtain the different benefits of the different types of ZDDP.

[0007] It has been surprisingly discovered that a ZDDP formed with a significant fraction of or all methylisobutylcarbonol (MIBC or 4-methyl-2-pentanol) exhibits significantly lower volatility than other ZDDPs. In general, ZDDP compounds when heated are known to undergo rearrangement reactions which include esterification and beta scission. Esterification generates a new neutral or non metal containing phosphate triester. It is envisioned that neutral phosphate compounds are more volatile than phosphate metal salts. It is thought that steric bulk around the oxygen moiety of the ZDDP can reduce the rate of ester formation. It is hypothesized that the MIBC ZDDP exhibits low volatility due to the steric bulk present in the MIBC alcohol moiety.

[0008] It is an important discovery that an all MIBC ZDDP or mixture of ZDDPs including a significant fraction of MIBC ZDDP exhibits a relative low volatility as compared with other ZDDPs. As a result, an all MIBC ZDDP will have a less detrimental effect on an emissions catalyst than other ZDDPs. This means that the relative assessment of the negative effects on emissions is not a direct correlation with respect to the phosphorous content as is the present convention. Therefore, it is necessary to assess the real effects of ZDDP in performance tests before determining any need for lower phosphorous content in a lubricant.

[0009] In addition to MIBC ZDDPs, it is believed that there could possibly be other ZDDPs that have relatively lower volatility than conventional ZDDPs. Other low volatile ZDDP's can include those prepared with higher molecular weight secondary alcohols such as 2-ethylhexyl alcohol or with mixtures of MIBC alcohol and other higher molecular weight secondary alcohols.

[0010] Other lubricant additive components may likewise affect the volatility of phosphorous-containing compounds in a lubricant composition. In one example, detergents including calcium sulfonate can reduce the deleterious phosphorous poisoning of emissions control system catalysts when these detergents are used together in a lubricant composition with a ZDDP additive. While recognizing these benefits, it is not believed that the use of a detergent will have any differential effects with respect to phosphorous poisoning. Therefore, identifying a less volatile ZDDP will have beneficial effects in addition to or regardless of the use of a detergent. It is possible that other additive chemistries may likewise reduce the deleterious effects of phosphorous poisoning generally, but it is not believed that any of those effects differentially treats the various ZDDPs that may be used. Therefore, it is believed that the analysis of ZDDPs of lubricant formulations that are free of, for instance, detergent additive components are the most accurate analysis of the beneficial effects of selecting a low volatile ZDDP component.

[0011] The physical results that demonstrate the low volatility of MIBC ZDDP are shown in multiple tests including phosphorous retention tests and TEOST MHT-4 tests.

<u>Phosphorous Retention Test</u>

[0012] The Phosphorous Retention Test measures the concentration of phosphorous remaining in a used lubricant after 100 hours of Sequence III G testing. The test compares the concentration of phosphorous in the used oil with the concentration of phosphorous in the fresh oil. The formula for calculation of phosphorous retention is as follows: PR100 = ([calcium new]/[calcium @ 100h] X ([phosphorous @ 100h]/[phosphorous new]) X (phosphorous @ 100 hrs./phosphorous new). This equation adjusts the phosphorous concentration for volatile base stock losses as measured by calcium concentration increase. This phosphorous retention analysis is important for lubricant testing, because all oils will be discriminated on the basis of the amount of phosphorous they release. As noted, the phosphorous that the oils release is eventually combusted and goes down stream to the catalyst in the emissions control system.

[0013] An all MIBC ZDDP exhibits a phosphorous retention average of about 87%. The phosphorous retention for mixed ZDDPs averages 81%. The phosphorous retention for a secondary ZDDP averages 78%. As is evident from these results, the amount of phosphorous that is retained in the lubricant is significantly higher when an all MIBC ZDDP is used. In one example, the range for phosphorous retention is greater than about 85%.

<u>TEOST MHT-4</u>

[0014] The TEOST MHT-4 test is a standard lubricant industry test that evaluates the oxidation and carbonaceous deposit-forming characteristics of engine oils. The test is designed to simulate high temperature (285°C) deposits in the piston ring belt area of engines. The focus of the test is to obtain the weight of the deposit formed on a resistively-heated depositor rod held within a casing as bulk oil is flowed past it at a rate of 0.25g/minute. The temperature of the rod is controlled by a thermocouple. The use of a catalyst consisting of 3/2/1 ratio of iron, lead, and tin is used to increase oxidation stress on the oil. The oxidation in the test is measured in terms of the mass of the deposits that are formed on the rod.

[0015] It has been determined that an all MIBC ZDDP yields results around 25 mg. It is desirable to have test yields of less than about 30 mg. Other ZDDP types consisting of primary, secondary, mixed, and aryl zincs yielded 35-70 mg. in the TEOST MHT-4 test.

During the standard operation of the TEOST MHT-4 test a volatile fraction is collected. This fraction was analyzed below by ICP for phosphorous content.

TEOST MHT-4 Volatiles ICP Analysis

[0016] The selection of ZDDP chemistry that produces the least or reduced amount of volatile phosphorous could be accomplished by examination of the TEOST MHT-4 trapped volatiles. The volatiles trapped in the TEOST test are subjected to Inductively Coupled Plasma (ICP) analysis to determine the amount of volatile phosphorous compounds representing the ZDDP decomposition products. The ICP test is described by test protocol ASTM D5185. Briefly a sample is dissolved in an appropriate solvent matrix and is pumped peristaltically through a nebulizer such that a fine spray is introduced into a plasma of highly charged Argon. The energy of the plasma desolvates, atomizes and ionizes the elements in the sample. The atomic and ionic transitions occur due to the elements' excited states and subsequent decay to lower energy states are observable in the ultraviolet and visible spectra. Each element present in the sample emits light at discrete wavelengths which are separated by an Echelle grating and focused upon the solid-state CID detector. The intensities of each element's emission for the sample can be compared against the emissions of standards containing the element at a known concentration to provide a quantitative determination.

[0017] A test was performed on similar lubricant formulations. The volatiles from the TEOST test were analyzed by ICP analysis and the results were found as follows for fully formulated oils containing 500 ppm of phosphorous from ZDDP.

TEOST MHT-4 Volatiles Analysis

ICP Analysis concentration in ppm

[0018]

ZDDP type	**Alcohol types**	Volatile Phosphorus	MHT-4 Deposit
Secondary ZDDP	C3/C6	153	36
Primary ZDDP	C4/C5/C8	256	71
Mixed ZDDP	C3/C4/C8	200	71
Secondary ZDDP	C8 high overbase	86	63
Secondary ZDDP	All MIBC C6	33	27
Aryl ZDDP	Aromatic	6	76

C4 indicates butyl carbon chain

[0019] As is evident from the foregoing test results, the volatile phosphorous order of reduction for the crankcase ZDDPs is as follows: Aryl ZDDP > All MIBC C6 ZDDP> C8 Primary High Overbase ZDDP > Secondary ZDDP > Mixed ZDDP > Primary C4/C5/C8 ZDDP. While the Aryl ZDDP displayed a lower volatile phosphorous fraction, its MHT-4 deposit value was relatively high. The best results have both a low volatile phosphorous fraction and a low deposit value. Preferably, a ZDDP should have a volatile fraction with a phosphorous content less than about 100 ppm and a low MHT-4 test yield of less than about 30 mg. of deposit. Accordingly, it is apparent that the test of the TEOST volatiles using an ICP analysis can be a qualitative gauge with respect to the selection of ZDDPs that have an improved or lessened effect on emissions catalysts.

[0020] The lubricants that benefit the most from the discovery of low volatility ZDDPs are low total phosphorous content lubricants. Using historical concentrations of ZDDP at greater than 1,000 ppm, the issue of relative volatility of the phosphorous component becomes moot, because there is so much phosphorous that any volatility level at all is enough to poison an emissions control catalyst. However, if a lubricant has less than 800 ppm, or in another example, less than 700 ppm, or still further alternatively, less than 600 ppm of phosphorous, the reduced volatility can present significant durability improvement with respect to the preservation of the emissions control catalyst.

[0021] The foregoing examples are directed to all or substantially all MIBC ZDDPs. It is believed that ZDDPs containing a significant fraction or portion of MIBC ZDDPs can benefit from reduced phosphorous volatility. In the foregoing examples, the MIBC ZDDP constitutes 100% or substantially 100% of the ZDDP used. In another example, the ZDDP incorporates at least 90% of MIBC ZDDP. In a still further example, the lubricant may incorporate at least 80%, or still further alternatively, at least 70% of MIBC ZDDP. Still further, it is believed that a lubricant may benefit from the incorporation of at least 50% MIBC ZDDP when seeking to lower phosphorous volatility.

[0022] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

[0023] Patentee does not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part of the invention under the doctrine of equivalents.

Claims

1. A lubricant composition comprising:

(a) a base oil; and
(b) an additive composition comprising a zinc dialkyldithiophosphate component;

wherein the lubricant has a phosphorous content of less than 800 ppm; and either

(a) the trapped volatiles resulting from the TEOST MHT-4 test using ICP analysis results in a phosphorous content of 60 ppm or less or,
(b) the lubricant has a TEOST MHT-4 test yield of less than 30 mg of deposit; and the TEOST MHT-4 volatile fraction has a phosphorous content of less than 100 ppm.

2. The lubricant composition as claimed in claim 1, wherein the trapped volatiles resulting from the TEOST MHT-4 test using ICP analysis results in a phosphorous content of 60 ppm or less.

3. The lubricant composition as claimed in claim 2;
wherein the ICP analysis results in a phosphorous content of 40 ppm or less.

4. The lubricant composition as claimed in claim 1, wherein the TEOST MHT-4 test yield is less than 25 mg.

5. The lubricant composition as claimed in any one of claims 1 and 4, wherein the TEOST MHT-4 volatile fraction has a phosphorous content of less than 65 ppm.

6. The lubricant composition as claimed in any one of claims 1 and 4, wherein the TEOST MHT-4 volatile fraction has a phosphorous content of less than 40 ppm.

7. The lubricant composition as claimed in any one of claims 1-6, wherein substantially all of the phosphorous in the lubricant is originated in the zinc dialkyldithiophosphate additive component.

8. A lubricant composition as claimed in any one of claims 1-7,
wherein a phosphorous retention value of the lubricant composition is greater than 85% after oil aging based on an initial phosphorous amount in the lubricant composition.

9. A lubricant composition as claimed in claim 8, wherein the phosphorous retention value is greater than 87%.

10. The lubricant composition as claimed in any one of claims 1-9, wherein the zinc dialkyldithiophosphate comprises substantially all methylisobutylcarbanol zinc dialkyldithiophosphate.

11. The lubricant composition as claimed in any one of claims 1-9, wherein the zinc dialkyldithiophosphate comprises at least 90% methylisobutylcarbanol zinc dialkyldithiophosphate.

12. The lubricant composition as claimed in any one of claims 1-9, wherein the zinc dialkyldithiophosphate comprises at least 80% methylisobutylcarbanol zinc dialkyldithiophosphate.

13. The lubricant composition as claimed in any one of claims 1-9, wherein the zinc dialkyldithiophosphate comprises at least 50% methylisobutylcarbanol zinc dialkyldithiophosphate.

14. A method of evaluating a zinc dialkyldithiophosphate additive for use in an engine lubricant formulation that has reduced catalyst poisoning effects in a combustion emissions control system, the method comprising the steps of:

performing a TEOST MHT-4 test using a lubricant that comprises a zinc dialkyldithiophosphate additive component;
collecting the trapped volatiles resulting from the TEOST MHT-4 test; and
analyzing the trapped volatiles to determine the amount of phosphorous in the trapped volatiles.

15. The method described in claim 14, wherein the analyzing step comprises analyzing the trapped volatiles using ICP analysis.