

LONG-LIFE ENGINE OIL COMPOSITION WITH LOW
OR NO ZINC CONTENT

FIELD OF THE INVENTION

[001] The present invention relates to lubricating compositions for use in natural gas fired internal combustion engines.

BACKGROUND OF THE INVENTION

[002] Internal combustion engines fueled with natural gas are typically used to drive compressors used in the oil and gas industry to compress natural gas at well heads and along pipelines. These engines typically have up to 16 cylinders and often generate between 500 to 3,000 HP. Because of how they are used, they need to be able to run continuously near full load conditions, with shut downs only for periodic maintenance such as oil changes. Under these operating conditions, the engine lubricant is subjected to high temperatures promoting oxidation and nitration processes that can limit lubricant life. Therefore, oil formulators and gas engine operators are continually seeking engine oils that have improved resistance to oxidation and nitration.

[003] In addition to controlling oxidation and nitration susceptibility of gas engine oils, the oil must also be formulated to have an ash content appropriate for correct operation of a given engine because the ash acts as a solid lubricant, protecting the valve-seat interface of the engine. For this reason, gas engine oils are classified according to their ash content. The classifications are:

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<u>Ash Designation</u>	<u>Ash level, mass% (ASTM D874)</u>
Ashless	Ash < 0.1%
Low Ash	0.1% < Ash < 0.6%
Medium Ash	0.6% < Ash < 1.5%
High Ash	Ash > 1.5%

[004] A gas engine oil having a low sulfated ash content is the subject of US 5,726,135. The oil contains a mixture of detergents, one of which has a total base number (TBN) of 250 or less and a second having a TBN of about half or less than the first.

[005] US 6,191,081 discloses a gas engine oil having a medium or high sulfated ash content. The oil contains three groups of metal detergents. The first group is selected from metal salicylates, sulfonates, phenates and other metal salts having a TBN of 150 or higher. The second group is selected from similar groups as the first but having a TBN of 50 to 150. The third group is selected from metal sulfonates and salicylates having a TBN of about 10 to 50. Also, one of the low or medium TBN detergents is a metal salicylate.

[006] In US 6,140,281 there is disclosed a gas engine oil in which the detergent is a mixture of one or more metal sulfonates and/or one or more metal phenates combined with one or more metal salicylates in which each metal salt has substantially the same TBN.

[007] In patent publication US 2005/0153851 A1, a long life lubricating oil for gas fired engines is disclosed. The oil contains a mixture of neutral and overbased metallic detergents and at least one trinuclear molybdenum compound.

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[008] The foregoing references illustrate what is well known in the art, namely, that the proper combination of additives is necessary to assure that an oil formulation will possess the requisite effectiveness. For example, some friction modifiers affect metal surfaces differently than do antiwear agents. When both are present, the friction reducing and antiwear agents may compete for the surface of the metal parts subject to lubrication. This competition can produce a lubricant that is less effective than is suggested by the individual properties of the additive components.

[009] Accordingly, the components of a gas engine lubricant need to be selected to meet the specified ash level and to provide, among other functions, a high level of oxidation and nitration resistance. Whether selected components and their amounts can be balanced to meet desired specifications is not a priori predictable.

SUMMARY OF THE INVENTION

[010] The present invention relates to a lubricating oil of extended life as evidenced by reductions in viscosity increase oxidation and nitration relative to current commercial and reference oils. The oil, especially useful as a natural gas engine lubricating oil, comprises a major amount of a base oil of lubricating viscosity and a mixture of certain metallic detergents in an amount sufficient to provide a sulfated ash in the range of about 0.3 mass % to about 2.2 mass % based on the total mass of the composition, the ash level being determined by ASTM D874. The oil of the invention is further characterized as having less than about 0.1 mass %, based on the total mass of the composition, of a zinc dialkyldithiophosphate.

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[011] The lubricating composition of the invention may also include other standard additives used in formulating commercial lubricating compositions other than trinuclear molybdenum friction reducing additives.

DETAILED DESCRIPTION OF THE INVENTION

[012] The lubricating compositions of the present invention include a major amount of a base oil of lubricating viscosity. No particular limitation is placed on the base oil. In general, the base may be any oil used in ordinary lubricating compositions. Suitable base oils include natural and synthetic oils and mixtures thereof in API categories I, II and III. Typically, the base oil will have a kinematic viscosity in the range of about 9 to about 16 cSt at 100°C, and preferably from about 10 to about 13 cSt at 100°C. As used herein, the kinematic viscosity is determined by method ASTM D445.

[013] The metallic detergents included in the lubricating compositions of the invention are: (i) a first neutral calcium alkylsalicylate detergent, and (ii) a second neutral or overbased metallic detergent or mixture of detergents other than neutral calcium alkylsalicylate, selected from the group consisting of calcium and barium sulfonates, phenates, and alkylsalicylates. Typically, the alkylsalicylates will have from about 4 to about 30 carbon atoms in the alkyl group, which may be linear or branched.

[014] Also, the mass ratio of (i):(ii) will be from about 0.1:1.0 to about 3:1, preferably from 0.2:1 to 2:1, and more preferably from 0.3:1 to 1:1.

[015] The neutral calcium alkylsalicylate (i) typically has a TBN in the range of about 150 or less. If metal detergent (ii) includes a neutral metallic detergent, such neutral metallic detergent will also typically have a TBN in the range of

about 150 or less. If metal detergent (ii) includes an overbased metallic detergent, such overbased metallic detergent will typically have a TBN of about 160 to about 400. As used herein, TBN is determined by the method ASTM 2896-98. If both neutral and overbased metallic detergents are present, the ratio of neutral to overbased metallic detergent is in the range of about 10:1 to about 0.1 to 1.

[016] The total amount of metallic detergents (i) and (ii) is in an amount sufficient to provide the complete lubricant composition with a sulfated ash, as determined by ASTM method D874 in the range of about 0.3 mass % to about 2.2 mass %. The person skilled in the art will appreciate that the amounts of metallic detergents suitable to achieve this property may vary depending on the type of metallic detergents (i) and (ii) used. Conveniently, the neutral calcium alkylsalicylate (i) is present in the range of about 0.1 mass% to about 2.1 mass%, based on the mass of the total composition. In a separate embodiment, metallic detergent (ii) is conveniently present in the range of from about 0.5 mass% to about 10 mass %, preferably in the range of from about 0.6 mass % to about 8 mass%, more preferably in the range of from about 0.7 mass % to about 7 mass%.

[017] The composition of the invention may include a zinc dialkyldithiophosphate in an amount of about 0.1 mass % and less, for example, between about 0.1 mass % and 0.0 mass %, and preferably 0.0 mass %, based on the mass of the total composition.

[018] Desirably, the compositions of the invention also include one or more additives typically used in standard additive packages such as ashless dispersants (about 0.5 to 8 vol%), ashless antioxidants (about 0.05 to 15 vol%), metal passivators (about 0.01 to 0.2 vol%), pour point depressants (about 0.05 to 0.6

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vol%), viscosity index improvers, dyes, and antifoamants (about 0.001 to 0.2 vol%) with the proviso that such additives will not include a trinuclear molybdenum compound.

[019] Thus, the fully formulated oil may contain ashless dispersants such as succinimide dispersants, ester dispersants, ester-amide dispersants and the like. Preferably, the dispersant is a succinimide dispersant, especially a polybutenyl succinimide. The molecular weight of the polybutenyl group may range from about 800 to about 4,000 and preferably from about 1,300 to about 2,500. The dispersant may be head capped or borated or both.

[020] Examples of suitable antioxidants include aminic antioxidants and phenolic antioxidants. Typical aminic antioxidants include alkylated aromatic amines, especially those in which the alkyl group contains no more than 14 carbon atoms. Typical phenolic antioxidants include derivatives of dialkylhydroxy aryl compounds in which the alkyl groups are in the o- and/or p-position. Such additives may be used in an amount of about 0.02 to 5 mass % based on the total mass of the composition.

[021] Examples of metal deactivators include arylthiazole, triazoles or alkyl substituted dimercaptothiadiazoles.

[022] Pour point depressants that may be included are exemplified by poly (meth) acrylates, dialkylfumarates and alkylaromatic polymers.

[023] Silicon antifoaming agents and polysiloxane oils are illustrative of suitable antifoamants.

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[024] Viscosity index improvers (VII's) may be any polymer which imparts multiviscosity properties to the finished oil such as olefin copolymers, styrene-diene block copolymers, star copolymers and the like used in amounts up to about 15 vol%.

[025] Lubricating oil additives are described generally in "Lubricants and Related Products" by Dieter Klamann, Verlag Chemie, Deerfield, Fla., 1984, and also in "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith, 1967, pages 1 to 11, the disclosures of which are incorporated herein by reference.

[026] The present invention is further described in the following non-limiting examples and comparative examples.

EXPERIMENTAL

Lab Nitration Screener Test

[027] A lab nitration screener test was used to assess the oil life performance of various oil compositions. The test results identify a number of parameters, including oil viscosity increase, oxidation, and nitration. Basically, the oils are evaluated by maintaining them at a fixed elevated temperature while subjecting them to oxidizing conditions. The oil performance is evaluated by measuring the viscosity increase, oxidation and nitration throughout the test. In each test, a Reference Oil is always tested, and all results are reported as a ratio of the result for the test oil divided by the result for the Reference Oil so that large values represent greater levels of lubricant degradation and lower values represent a measure of longer oil life. For example, if the test oil has an oxidation result less than 1, then the test oil demonstrates performance superior to that of the Reference Oil.

EXAMPLES AND COMPARATIVE EXAMPLES

[028] The accompanying Table sets forth the composition and test results for a series of gas engine oil lubricating compositions. All the oils use an API Group I base oil. Example 3 and Comparative Oil 5 are low ash oils; all others are nominally high ash. All are SAE 30 Grade except Comparative Oil 1, which is SAE 40 grade. In the Table, Additive Package 1 and Additive Package 2 are typical high ash natural gas engine oil additive combinations.

[029] Reference Oil 1 is a premium, zinc-free, commercial gas engine oil, and Comparative Oils 1 and 2 are commercial zinc-free oils.

[030] In Example Oils 1, 2 and 3 and Comparative Oils 3, 4 and 5, the balance of the additive system was the same for each and was kept constant. This additive system included an ashless dispersant, ashless antioxidant, pour point depressant, metal passivator and antifoamant. As shown in the Table, Comparative Oils 3, 4 and 5 were identical to Example Oils 1, 2 and 3, respectively, but with inclusion of 0.29 vol % (0.36 mass %) of zinc dialkyldithiophosphate, ZDDP, an amount used in most modern commercial gas engine oils.

[031] The results in the Table demonstrate the wide performance range of the current commercial oils, viz., Reference Oil 1 and Comparative Oils 1 and 2. As can be seen, the formulations of Examples 1, 2 and 3 have superior oil life (as reflected in oxidation, nitration and/or oil thickening control) compared to the zinc-free formulations of Reference Oil 1 and Comparative Oils 1 and 2.

TABLE 1 - Test Oils and Screener Test Results

Formulation Description		Reference Oil 1	Comparative Oil 1	Comparative Oil 2	Invention Example 1	Invention Example 2	Comparative Oil 3	Comparative Oil 4	Invention Example 3	Comparative Oil 5
Component (vol%)	Description	Group I Basestocks	Group I Basestocks	Group I Basestocks	Group I Basestocks	Group I Basestocks	Group I Basestocks	Group I Basestocks	Group I Basestocks	Group I Basestocks
	Competitive Commercial Sample	-----	100.00	-----	-----	-----	-----	-----	-----	-----
	150 SN Basestock	1.70	-----	2.93	12.55	13.50	12.55	12.54	15.00	15.00
	600 SN Basestock	89.30	-----	89.629	73.84	74.69	73.55	75.36	77.19	76.90
	Additive Package 1	8.70	-----	-----	-----	-----	-----	-----	-----	-----
	Additive Package 2	-----	-----	6.33	-----	-----	-----	-----	-----	-----
	Zinc Dialkyl Dithiophosphate	-----	-----	-----	-----	-----	0.29	0.29	-----	0.29
	Neutral barium sulphamate	-----	-----	-----	5.80	-----	5.80	-----	-----	-----
	Neutral calcium alkylsalicylate	-----	-----	-----	2.00	2.00	2.00	2.00	2.00	2.00
	Overbased calcium sulphamate	-----	-----	-----	-----	4.00	-----	4.00	-----	-----
	Balance of Additive System	-----	-----	-----	5.0	5.0	5.0	5.0	5.0	5.00
	Pour point depressant	0.30	-----	0.30	-----	-----	-----	-----	-----	-----
	Antifoamant	0.001	-----	0.001	-----	-----	-----	-----	-----	-----
	Neutral calcium sulfonate	-----	-----	0.81	0.81	0.81	0.81	0.81	0.81	0.81
Kinematic Viscosity, cSt	Measured kv@100°C	11.91	14.09	11.99	11.98	11.75	12.18	12.05	11.25	11.30
Sulfated Ash, Mass %		2.2	1.5	2.0	2.0	2.0	2.0	2.0	0.25	0.3
Nitration Screener Test	Oxidation (relative to Reference Oil 1)	1.00	1.51	1.04	0.44	0.72	0.63	0.89	0.74	1.36
	Nitration (relative to Reference Oil 1)	1.00	1.29	1.44	0.62	0.96	0.63	1.35	0.55	1.04
	Viscosity increase (relative to Reference Oil 1)	1.00	2.82	1.01	0.45	0.62	0.74	0.96	0.51	0.90

CLAIMS:

1. A lubricating composition having long life as evidenced by a reduction in viscosity increase, oxidation and nitration, comprising:
 - (a) a major amount of an oil of lubricating viscosity;
 - (b) a mixture of metallic detergents comprising:
 - (i) a first neutral calcium alkylsalicylate detergent, and
 - (ii) a second neutral or overbased metallic detergent or mixture of metallic detergents selected from the group consisting of calcium and barium sulfonates, phenates, and alkylsalicylates, and excluding neutral calcium alkylsalicylates, and
 - (c) from 0.0 mass % to about 0.1 mass % of a zinc dialkyldithiophosphate based on the total mass of the composition.
2. The composition of Claim 1 wherein the first metallic detergent, (i), is present in the range of about 0.1 mass % to about 2.1 mass %, based on the total mass of the composition.
3. The composition of Claim 1, wherein the second metallic detergent or mixture of detergents (ii) is present in the range of about 0.8 mass % to about 10 mass %, based on the total mass of the composition.
4. The composition of Claim 1 wherein the combined amount of metallic detergents (i) and (ii) is sufficient to provide the total composition with a sulfated ash range of from about 0.3 mass% to about 2.2 mass%.
5. The composition of Claim 4 including 0.0 mass % zinc dialkyldithiophosphate.

6. The composition of Claim 5 wherein the second metallic detergent (ii) is a mixture of neutral barium sulfonate and neutral calcium sulfonate.

7. The composition of Claim 5 wherein the second metallic detergent (ii) is a mixture of overbased calcium sulfonate and neutral calcium sulfonate.

8. The composition of Claim 5 wherein the second metallic detergent (ii) is a neutral calcium sulfonate.

9. A lubricating oil composition having long life as evidenced by a reduction in viscosity increase, oxidation and nitration, comprising:

(a) a major amount of an oil of lubricating viscosity;

(b) a mixture of metallic detergents comprising:

(i) a neutral calcium alkylsalicylate detergent in an amount ranging from about 0.1 mass % to about 2.1 mass %, based on the total mass of the composition, and

(ii) a second neutral or overbased metallic detergent or mixture of detergents other than neutral calcium alkylsalicylate selected from the group consisting of calcium and barium sulfonates, phenates, and alkylsalicylates wherein the amount of metallic detergent is sufficient to provide the total composition with a sulfated ash range of from about 0.3 mass % to about 2.2 mass %, and

(c) from 0.0 mass % to about 0.1 mass % of a zinc dialkyldithiophosphate based on the total mass of the composition.

10. The composition of Claim 9 wherein the mass ratio of (i) to (ii) is in the range of about 0.1:1.0 to about 3:1.9.

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11. A method for extending the life of a lubricating oil as evidenced by a reduction in viscosity increase, oxidation and nitration, the method comprising:

adding to the lubricating oil:

(a) a mixture of metallic detergents, comprising

(i) a neutral calcium salicylate detergent and

(ii) a second neutral or overbased metallic detergent or mixture of detergents other than neutral calcium alkylsalicylate selected from the group consisting of calcium and barium sulfonates, phenates, and alkylsalicylates, wherein the amount of metallic detergent is sufficient to provide the total composition with a sulfated ash range of from about 0.3 mass % to about 2.2 mass %, and

(b) from 0.0 mass % to about 0.1 mass % of a zinc dialkyldithiophosphate based on the total mass of the composition

12. The method of Claim 11 wherein the amount of the neutral calcium salicylate detergent added is in the range of 0.1 to 2.1 mass % based on the total mass of the composition.

13. In a lubricating composition, the use of a mixture of metallic detergents comprising:

(i) a first neutral calcium alkylsalicylate detergent, and

(ii) a second neutral or overbased metallic detergent or mixture of metallic detergents selected from the group consisting of calcium and barium sulfonates, phenates, and alkylsalicylates, excluding neutral calcium alkylsalicylates.

14. The use of Claim 13, wherein the amount of metallic detergents is sufficient to provide a composition with a sulfated ash range of from about 0.3 mass % to about 2.2. mass %.