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54 **Engine oil composition.**

57 The invention provides an engine oil composition characterized by containing a major amount of lubricating base oil and

(a) about 0.01 to 30 % by weight of an overbasic oil-soluble metal salt prepared by use of an alkaline-earth metal borate,

(b) about 0.01 to 5 % by weight of a friction modifier,

(c) about 0.01 to 5 % weight of an antioxidant as essential components, on the basis of the total amount of the composition.

## 2. Background of the Invention

### (1) Field of the Invention

5 This invention relates to an engine oil composition, and more particularly to an engine oil composition useful as a lubricating oil for gasoline engine, diesel engine, and the like.

### (2) Description of the Prior Art

10 Because of increased concern regarding the energy-saving measures to counter oil shocks, the research for a fuel-saving internal combustion engine lubricating oil has been recently intensified. As measures for fuel-saving by use of lubricating oil to meet such situation, the following measures are now under review among business circles: (a) Lowering viscosity of lubricating oil with the intension of reducing engine friction loss under hydrodynamic lubricating conditions, and (b) Addition of friction reducers with the  
15 intension of reducing engine friction loss under mixed and boundary lubrication.

Addition of friction modifiers to lubricating oil is indispensable especially in latest fuel-saving lubricating oil, and many compounds have been heretofore been found to be useful. However, it has been observed that even though these compounds possess a high fuel-saving effect on the fresh lubricating oil, they gradually lose said effect in the aged lubricating oil due to degradation during engine operation. While many  
20 antioxidants have widely been used heretofore and proved to be effective to some extent for preventing the degradation, they could not necessarily provide satisfactory results in view of their lubricating performance.

The present invention is based on a discovery whereby excellent fuel-saving effect can be attained employing an overbasic metallic detergent prepared by use of an alkaline-earth metal borate as an additional component of an engine oil composition containing a friction modifier and an antioxidant.

25 The present invention provides an engine oil composition having a specific combination of lubricating additives and excellent fuel-saving effect over a long period of time.

## 3. Summary of the Invention

30 It is an object of the subject invention to provide a fuel-saving engine oil composition comprising a lubricating base oil and

(a) about 0.01 to 30 % by weight of an overbasic oil-soluble metal salt,

(b) about 0.01 to 5 % by weight of a friction modifier,

(c) about 0.01 to 5 % weight of an antioxidant as essential components, on the basis of the total amount  
35 of the composition.

## 4. Detailed Description of the Invention

40 Either mineral oils or synthetic oils may be used as the lubricating base oils of the instant invention. Any paraffinic or naphthenic lubricating base oils may be acceptable wherein said base oils are manufactured by a process consisting mainly of topping crude oil followed by vacuum distillation to give a lubricating oil fraction, and refining said lubricating fraction by a process selected from the group consisting of solvent deasphalting, solvent extraction, hydro-cracking, solvent dewaxing, catalytic dewaxing, hydro-refining, sulfuric acid treating, and clay treating.

45 The synthetic oils of the present invention include,  $\alpha$ -olefin polymers (polybutenes, octene-1 oligomers, decene-1 oligomers, and the like), alkylbenzenes, alkylnaphthalenes, diesters (ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, di-3-ethylhexyl sebacate, and the like), polyol esters (trimethylolpropane caprilate, trimethylolpropane pelargonate, pentaerythritol- 2-ethyl hexanoate, pentaerythritol pelargonate, and the like), polyoxyalkylene glycol, polyphenyl ether, silicon oils, perfluoroalkyl ethers, and mixtures thereof.

Preferred kinematic viscosity of these lubricating base oils is in a range of about 3 to 20 cSt at 100 ° C.

55 The overbasic oil-soluble metal salts (a) of the present invention are prepared by a reaction of an oil-soluble metal salt such as an oil-soluble alkaline-earth metal sulfonate, alkaline-earth metal saricylate, alkaline-earth metal pheneate, alkaline-earth metal phosphonate with an oxide or hydroxide of an alkaline-metal in the presence of boric acid or boric acid anhydride. Among oil-soluble metal salts, alkaline-earth metal saricylates are most appropriate. Generally, the overbaic oil-soluble metal salts (a) of the present invention have a total base number of about 100 or more, and preferably 170 or more, and a particle size of less than about 0.1  $\mu$ m, and preferably less than about 0.05  $\mu$ m.

Any methods for preparing the overbasic metal salts may be acceptable. For example, a method has been known which comprises reacting an oil-soluble metal salt aforesaid, a hydroxide or an oxide of alkaline-earth metal, and boric acid or boric acid anhydride in the presence of water, an alcohol such as methanol, ethanol, propanol, or butanol, and a diluent such as benzene, toluene or xylene at a temperature of about 20 to 200 °C for about 2 to 8 hours, heating the mixture at about 100 to 200 °C to remove water, followed by removing the alcohol and the diluent if necessary, to give a overbasic metal salt. The reaction conditions may be employed suitably depending on raw material type, the amount of reactants and the like. Typical of such prior art practices are those disclosed in Japanese patent Publication Nos. 116688 /60 and 204298 /61 and the disclosures of which are incorporated by reference.

A content of the overbasic metal salt prepared by use of an alkaline-earth metal borate of the present invention is in an amount of about 0.01 to 30 % by weight, and preferably about 0.05 to 5 % by weight, on the basis of the total amount of the composition.

The content of less than about 0.01 % by weight is not preferable because of the insufficient display of the fuel-saving effect of the overbasic metal salt wherein the effect can not be maintained over a long period of time. Inversely, when it is in excess of about 30 % by weight, there is no additional merits due to the excessive addition. Other overbasic oil-soluble metal salts, such as those prepared by use of alkaline-earth-metal carbonates can not provide an engine oil composition which can persistently maintain the fuel-saving effect throughout the engine operation.

Any friction modifiers (b) which have been used in conventional engine oils may be employed in the present invention. Such modifiers, for example, include molybdenum dithiophosphates, molybdenum dithiocarbamates, molybdenum disulfides, fluorocarbons, boric acid esters, alkylamines, higher alcohols, higher fatty acids, fatty acid esters, fatty acid amides and the like.

Typical friction modifiers include molybdenum sulfide diethyldithiophosphate, molybdenum sulfide dipropyldithiophosphate, molybdenum sulfide dibutyldithiophosphate, molybdenum sulfide dipentyl-dithiophosphate, molybdenum sulfide dihexyldithiophosphate, molybdenum sulfide dioctyldithiophosphate, molybdenum sulfide didecyldithiophosphate, molybdenum sulfide didodecyldithiophosphate, molybdenum sulfide di(butylphenyl) dithiophosphate, Molybdenum sulfide di(nonylphenyl) dithiophosphate, oxymolybdenum sulfide diethyldithiophosphate, oxymolybdenum sulfide dipropyldithiophosphate, oxymolybdenum sulfide dibutyldithiophosphate, oxymolybdenum sulfide dipentyl-dithiophosphate, oxymolybdenum sulfide dihexyldithiophosphate, oxymolybdenum sulfide dioctyldithiophosphate, oxymolybdenum sulfide didecyl-dithiophosphate, oxymolybdenum sulfide didodecyldithiophosphate, oxymolybdenum sulfide di(butylphenyl) dithiophosphate, oxymolybdenum sulfidedi(nonylphenyl) dithiophosphate, molybdenum sulfide diethyl-dithiocarbamate, molybdenum sulfide diethyldithiocarbamate, molybdenum sulfide dipropyldithiocarbamate, molybdenum sulfide dibutyldithiocarbamate, molybdenum sulfide dipentyl-dithiocarbamate, molybdenum sulfide dihexyldithiocarbamate, molybdenum sulfide dioctyldithiocarbamate, molybdenum sulfide didecyl-dithiocarbamate, molybdenum sulfide didodecyl-dithiocarbamate, molybdenum sulfide di(butylphenyl) dithiocarbamate, molybdenum sulfide di(nonylphenyl) dithiocarbamate, oxymolybdenum sulfide diethyl-dithiocarbamate, oxymolybdenum sulfide diethyldithiocarbamate, oxymolybdenum sulfide dipropyldithiocarbamate, oxymolybdenum sulfide dibutyldithiocarbamate, oxymolybdenum sulfide dipentyl-dithiocarbamate, oxymolybdenum sulfide dihexyldithiocarbamate, oxymolybdenum sulfide dioctyldithiocarbamate, oxymolybdenum sulfide didecyl-dithiocarbamate, molybdenum sulfide didodecyl-dithiocarbamate, oxymolybdenum sulfide di(butylphenyl) dithiocarbamate, oxymolybdenum sulfide di(nonylphenyl) dithiocarbamate, lauryl amine, myristyl amine, palmitic amine, stearyl amine, oleyl amine, lauryl alcohol, myristyl alcohol, palmitic alcohol, stearyl alcohol, oleyl alcohol, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, lauryl amide, myristyl amide, palmitic amide, stearyl amide, oleyl amide.

A content of the friction reducer (b) of the present invention is in an amount of about 0.01 to 5 % by weight, and preferably about 0.05 to 2 % by weight, on the basis of the total amount of the composition.

The content of less than about 0.01 % by weight is not preferable because of the insufficient display of the friction reducing effect. Inversely, when it is in excess of about 5 % by weight, there is no additional merits due to the excessive addition.

Any antioxidants (c) may be employed which have been used in conventional engine oils. Such antioxidants, for example, include phenol type, amine type, sulfur type, zinc thiophosphate type, phenothiazine type antioxidants, and the like. Typically, they include diphenylamine, p,p'-dioctyl diphenylamine, p,p'-dinonyl diphenylamine, p,p'-didodecyl diphenylamine, phenyl- $\alpha$ -naphthylamine, p-octylphenyl- $\alpha$ -naphthylamine, p-nonylphenyl- $\alpha$ -naphthylamine, p-dodecylphenyl- $\alpha$ -naphthylamine, 2,6-di-tert.-butylphenol, 2,6-di-tert.-butyl-p-cresol, 2,6-di-tert.-butyl-4-ethylphenol, 2,2'-methylenebis (4-methyl-6-tert.-butylphenol), 2,2'-methylenebis (4-ethyl-6-tert.-butylphenol), 4,4'-methylenebis (2,6-di-tert.-butylphenol),

4,4'-bis (2,6-di-tert.-butylphenol), 4,4'-thiobis (6-tert.-butyl-o-dresol, zinc dialkyl dithiophosphate, phenothiazine, and mixtures thereof.

A content of the antioxidant (c) of the present invention is in an amount of about 0.01 to 5 % by weight, and preferably about 0.1 to 2 % by weight, on the basis of the total amount of the composition.

5 The content of less than about 0.01 % by weight is not preferable because of the display of the antioxidation effect for a short period of time. Inversely, when the amount is in an excess of about 5 % by weight, there is no additional merits due to the excessive addition.

In the present invention, the following conventional lubricating oil additives can be additionally used to improve further the performance of the present composition if necessary, in so far as they do not deviate  
 10 from the gist of the present invention. Examples of these additives include extreme pressure additives such as tricresyl phosphate, triphenyl phosphate, zinc dithiophosphates,; rust preventives such as petroleum sulfonates, dinonyl naphthalene sulfonates and the like; metal deactivating agents such as benzotriazole and the like; metal-based detergents such as alkaline-earth metal sulfonates, alkaline-earth metal salicylates, alkaline-earth metal peneates, alkaline-earth metal phosphonates and the like; ashless dispersants such as  
 15 succinimide, succinic esters, benzylamine and the like; deformers such as silicon oils and the like; viscosity index improvers and pour point depressants such as polymethacrylates, polyisobutylenes and polystyrenes and the like; and mixture thereof.

Generally, a content of the viscosity index improver is in an amount of about 1 to 30 % by weight, the deformer is in an amount of about 0.0005 to 1 % by weight, the metal deactivating agent is in an amount of  
 20 about 0.005 to 1 % by weight, and other additives are in amounts of about 0.1 to 15 % by weight respectively on the basis of the total amount of the composition.

The engine oil compositions of the present invention are suitable for two cycle and four cycle gasoline engine oils, diesel engine oil for land use, marine diesel engine oil, and the like.

25 While the advantages of the compositions according to the present invention will be described in detail hereinbelow in conjunction with the following examples, it is to be noted that the scope of the present invention should not be limited to these examples.

Examples and Comparative Examples

30 According to the composition indicated in Table 1, the engine oil compositions of the present invention were prepared. Performance tests were conducted with respect to these compositions by the following method.

(LFW friction test)

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LFW friction test is carried out on both oxidation degraded samples and freshly prepared samples. The test conditions are as follows:

40	<u>Load</u>	<u>Speed</u>	<u>Oil temperature</u>
	30 lb	1500 r.p.m.	80 °C

45 The oxidation degraded sample oils were prepared by oxidizing new sample oils under the following conditions on the basis of " the method for testing oxidaton stability of lubricating oil" prescribed by JIS K 2514 3.1:

Temperature 150 °C  
 Duration 72 hours

50 Table 1 shows the test results.

As is apparent from the results shown in Table 1, the engine oil compositions according to the present invention have excellent performance as an engine oil in which the fuel-saving effect can be maintained persistently throughout the engine operation because of the synergism of each component.

55 On the contrary, when the compositions of Comparative Examples 1 and 2 in which an overbasic oil-soluble metal salt prepared by use of calcium carbonate instead of an overbasic oil-soluble metal salt (a) prepared by use of an alkaline-earth metal borate is used, or an antioxidant of component (c) of the present invention is omitted, are compared with those of Example respectively, the friction coefficient increases after oxidation degradation in both cases, and the time during which the fuel-saving effect may be maintained is

shorter in both cases.

Table 1

Composition	Example	Comparative	Comparative
	Example 1	Example 1	Example 2
	Wt. %		
(a) Calcium borate <sup>1)</sup>	2.1	-	2.1
Calcium carbonate <sup>2)</sup>	-	2.1	-
(b) Organic molybdenum-based compound <sup>3)</sup>	1.1	1.1	1.1
(c) Amine type antioxidant	0.15	0.15	-
Phenol type antioxidant	0.3	0.3	-
Viscosity Index Improver, Ashless dispersant and the like	10.8	10.8	10.8
Refined mineral oil (3.7 cSt @ 100°C)	the balance	the balance	the balance
Lubricating Performance			
Friction coefficient	before degradation	0.040	0.045
	after degradation	0.040	0.065
			0.060

- 1) Overbasic oil-soluble metal salt prepared by use of calcium borate
- 2) Overbasic oil-soluble metal salt prepared by use of calcium carbonate
- 3) Molybdenum content (by Wt.%) in oil was 0.05

Claims

1. An engine oil composition comprising a major amount of lubricating base oil and

(a) about 0.01 to 30 % by weight of an overbasic oil-soluble metal salt prepared by use of an alkaline-earth metal borate,  
(b) about 0.01 to 5 % by weight of a friction modifier,  
(c) about 0.01 to 5 % weight of an antioxidant as essential components, on the basis of the total amount of the composition.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-2 028 703 (ESSO) * Whole document * ---	1	C 10 M 141/00 C 10 M 163/00 //
Y	FR-A-1 526 762 (LUBRIZOL) * Whole document * ---	1	(C 10 M 141/00 C 10 M 125:26 C 10 M 129:00
Y	WO-A-8 807 073 (ELF) * Whole document * ---	1	C 10 M 129:06 C 10 M 129:40 C 10 M 129:70
Y	US-A-4 534 873 (CLARK) * Whole document * ---	1	C 10 M 133:06 C 10 M 133:16 C 10 M 135:18
D,Y	GB-A-2 149 810 (SHELL) * Whole document * ---	1	C 10 M 137:10 ) (C 10 M 163/00 C 10 M 125:26
A	US-A-4 501 678 (KATAYAMA et al.) * Whole document * ---	1	C 10 M 129:00 C 10 M 129:06 C 10 M 129:40
A	US-A-4 358 385 (ZOLESKI et al.) * Whole document * ---	1	-/-
A	EP-A-0 317 354 (EXXON) * Whole document * -----	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-06-1991	Examiner DE LA MORINERIE B.M.S.B.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>.....  &amp; : member of the same patent family, corresponding document</p>			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
			C 10 M 129:70 C 10 M 133:06 C 10 M 133:16 C 10 M 135:18 C 10 M 137:10 )
			<b>TECHNICAL FIELDS SEARCHED (Int. Cl.5)</b>
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28-06-1991</b>	Examiner <b>DE LA MORINERIE B.M.S.E.</b>
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

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