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(54) Engine oil composition

Motorölsammensetzung
Composition d'huile pour moteur

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DescriptionBackground of the Invention

(1) Field of the Invention

[0001] The present invention relates to an engine oil composition for automobiles. More particularly, the invention relates to the long life and fuel-saving engine oil composition which can suppress the friction loss in the engine to a low level for a long time.

(2) Related Art Statement

[0002] With the progress of the engines, the automobile engine oil compositions (hereinafter referred to briefly as "engine oil compositions") have been required to possess various performances such as wear resistance, oxidation stability, and detergent dispersibility. Recently, in order to suppress the earth from getting warmer due to increase in the content of CO₂ in the atmosphere, how to improve the mileage of the automobiles is an important problem. Accordingly, the fuel saving has been also strongly required with respect to the engine oils.

[0003] Ordinarily, the engine oil composition is composed of a mixture of a base oil purified from petroleum, added with additives such as a detergent, an antioxidant, an anti-wear agent, and a viscosity index improver. In order to increase the fuel efficiency (mileage) of the engine oil, for example, the viscosity of the engine oil is lowered by decreasing the viscosity of the base oil or changing the viscosity index improver. However, friction cannot be reduced in the case of the above ordinary engine oil composition in such an area as a boundary lubricating condition where the viscosity does not contribute to mitigation of the friction. Consequently, a friction modifier (FM) has recently come to be added so as to reduce the wearing in the boundary lubricating area. With respect to the friction modifiers, it is known that organic molybdenum compound such as molybdenum dithiocarbamate (MoDTC) and oxymolybdenum organo phosphodithioate sulfide (MoDTP) are highly effective as described in JP-B 3-23595 (EP-A-113045).

[0004] However, as the time passes, each of the above organic molybdenum compounds used in the engine oil composition is consumed. Therefore, though the fresh engine oil composition gives a low fuel consumption rate, such a low fuel consumption rate of the engine oil composition is deteriorated with the lapse of time. In order to lessen the above drawback, it may be considered that the addition amount of the organic molybdenum compound in a fresh oil is increased. However, if the addition amount of the organic molybdenum compound is merely increased, the cost of the product becomes higher, which is economically unfavorable. Further, among the organic molybdenum compounds, MoDTP contains phosphorus, so that a phosphorus compound may deposit on the surface of an exhaust gas catalyst to deteriorate the catalytic activity. Therefore, the addition amount of the MoDTP cannot be increased beyond a given level.

[0005] On the other hand, since MoDTC contains no phosphorus, increase in its addition amount does not cause decrease in the catalytic activity. However, since MoDTC has a small friction-mitigating effect, it may be considered that MoDTC is used in combination with zinc dithiophosphate (ZnDTP) as an anti-wear agent so as to supplement the wear-mitigating effect of the former. ZnDTP has been frequently used, as antioxidant and anti-wear agent, in the engine oil compositions. However, since ZnDTP contains phosphorus and gives adverse influence upon the exhaust gas catalyst as mentioned above, its addition amount is limited so that good friction-mitigating effect cannot unfavorably be maintained for a long time. Further, it is proposed that MoDTC be used in combination with a sulfur-based extreme pressure additive (See JP-B 5-83599, JP-A-61 127 797). This combination does not afford adverse effect upon the exhaust gas catalyst, but it encounters a practically great problem upon the engine oil composition in that wear largely occurs in the valve train system. WO-A-9 606 904 describes a lubricant composition comprising a major amount of an oil of lubricating viscosity and a minor amount of additives comprising oxymolybdenum dithiocarbamate, zinc dialkyldithiophosphate, one or more additional peroxide decomposing sulfur compounds, an ashless dispersant, and a boron containing additive which may be the ashless dispersant.

Summary of the Invention

[0006] Under the circumstances, it is an object of the present invention to enable the engine oil composition to maintain the friction loss at a low level even when the engine oil composition is used for a long time.

[0007] Furthermore, it is another object of the present invention to enable the engine oil composition to maintain the friction loss at a low level for a long time, while the addition amount of the friction modifier is kept at the same level as formerly employed.

[0008] It is still another object of the present invention to enable the engine oil composition to maintain the friction loss at a low level for a long time without affording adverse influence upon the catalytic activity for exhaust gases.

[0009] Having made strenuous investigation to accomplish the above-mentioned objects, the present inventors discovered that the combination of MoDTC and ZnDTP with a polysulfide compound can remarkably prolong the performance of the low fuel consumption rate, that is, can maintain the friction-mitigating effect of the engine oil for a long time without affording adverse influence upon the exhaust gas catalyst. Based on this discovery, the inventors have accomplished the present invention.

[0010] That is, the present invention relates to the engine oil composition comprising (1) at least one oil selected from the group consisting of a mineral oil and a synthetic lubricant as a base oil; (2) a molybdenum dithiocarbamate in an amount of 50 to 2000 ppm by weight when calculated as molybdenum (Mo), relative to the total weight of the engine oil composition; (3) zinc dithiophosphate in an amount of 0.01 to 0.2 wt% when calculated as phosphorus (P), relative to the total amount of the engine oil composition; and (4) an ashless organic polysulfide compound in an amount of 0.01 to 0.4 wt% when calculated as sulfur (S), relative to the total amount of the engine oil composition. This engine oil composition is a long life and low fuel consumption engine oil composition which can maintain the friction loss at a low level for a long time.

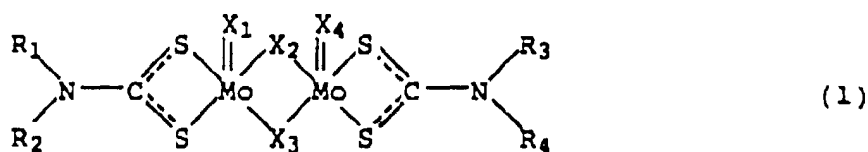
[0011] These and other objects, features and advantages of the invention will be apparent from the following description of the invention with the understanding that some modifications, variations and changes of the same could easily be made by the skilled person in the art.

Detailed description of the invention

[0012] The base oil to be used in the engine oil composition according to the present invention is a mineral oil and/or a synthetic oil. As the base oil, which is used, in the engine oil composition, as a base component occupying a great part of the engine oil composition, any base oil may be used. Specifically, as the mineral oil, use may be made of a lubricant base oil which is producing by obtaining a cut through distilling an ordinary pressure distillation residue of such as a paraffinic crude oil under reduced pressure, treating the resulting cut through extraction with a solvent such as furfural, purification by hydrogenation and dewaxing with a solvent such as MEK/toluene, a lubricant base oil produced by obtaining a deasphalted oil by deasphalting the above pressure-reduced distillation residue and treating it by any of the above appropriate processes, a highly purified base oil obtained through isomerization of slack wax and dewaxing an appropriate cut of the isomerized oil with a solvent of MEK/toluene, or an appropriate mixture thereof.

[0013] As the synthetic oil, use may be made of an α -olefin oligomer, a diester synthesized from a dibasic acid such as an adipic acid and a primary alcohol, a polyol ester synthesized from a higher alcohol such as neopentyl glycol, trimethylol propane or pentaerithritol and a monobasic acid, an alkyl benzene or a polyoxyalkylene glycol or an appropriate mixture thereof. Further, needless to say, a mixed oil obtained by appropriately combining the mineral oil with the synthetic oil may be used as a base oil for the engine oil composition according to the present invention.

[0014] The molybdenum dithiocarbamate (MoDTC) to be used as an additive in the present invention is a compound expressed by the following formula (1)



[0015] In the formula (1), R_1 through R_4 independently denote a straight-chain or branched-chain alkyl group or a straight-chain or branched-chain alkenyl group having four to eighteen carbons; and X_1 through X_4 independently denote an oxygen atom or a sulfur atom, the ratio between the number of the oxygen atom or atoms and that of the sulfur atom or atoms with respect to X_1 through X_4 being 1/3 to 3/1. As R_1 through R_4 , the alkyl group is preferred. More specifically, butyl group, 2-ethylhexyl group, isotridecyl group or stearyl group may be recited. These four R_1 through R_4 existing in one molecule may be identical with or different from each other. Further, two or more MoDTCs differing in terms of R_1 through R_4 may be used in a mixed state.

[0016] MoDTC is used in the addition amount of 50 to 2000 ppm by weight, preferably 300 to 1000 ppm by weight, when calculated as molybdenum (Mo), relative to the total weight of the engine oil composition. If the addition amount is less than 50 ppm by weight, the friction-reducing effect is small, whereas if it is more than 2000 ppm by weight, the friction-reducing effect is saturated and the cost increases.

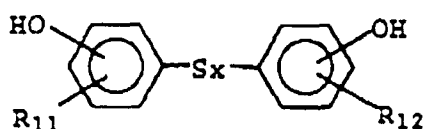
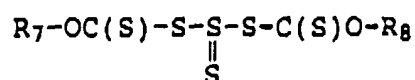
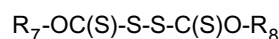
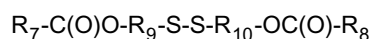
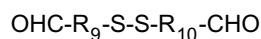
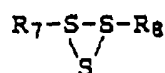
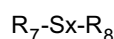
[0017] The zinc dithiophosphate (ZnDTP) to be used as an additive in the present invention is a compound expressed by the formula (2):

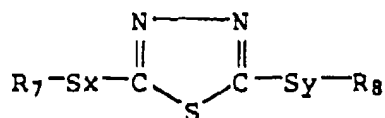


[0018] In the formula (2), R_5 and R_6 independently denote a straight-chain or branched chain alkyl group or a straight-chain or branched chain aryl group having three to eighteen carbon atoms. As R_5 and R_6 , an alkyl group, particularly, a primary alkyl group is preferred from the standpoint that the friction-mitigating performance must be maintained for a long time. More specifically, for example, propyl group, butyl group, pentyl group, hexyl group, octyl group and lauryl group may be recited. These two R_5 and R_6 existing in one molecule may be identical with or different from each other. Further, two or more kinds of ZnDTPs differing in terms of R_5 and R_6 may be used in a mixed state.

[0019] ZnDTP is added in an amount of 0.01 to 0.2 wt%, preferably 0.04 to 0.2 wt%, more preferably 0.04 to 0.1 wt% when calculated as phosphorus (P), relative to the total amount of the engine oil composition. If the addition amount is less than 0.01 wt%, the wear-preventing performance of the engine oil composition for the valve train system is deteriorated. On the other hand, if it is more than 0.2 wt%, influence of the phosphorus component upon the catalytic activity for the exhaust gas becomes greater.

[0020] The ashless organic polysulfide compound to be used in the present invention includes organic compounds expressed by the following formulae, such as sulfides of oils or fats or polyolefins, in which a sulfur atom group having two or more sulfur atoms adjoining and bonded together is present in a molecular structure.





[0021] In the above formulae, R_7 and R_8 independently denote a straight-chain, branched-chain, alicyclic or aromatic hydrocarbon group in which a straight chain, a branched chain, an alicyclic unit and an aromatic unit may be selectively contained in any combined manner. An unsaturated bond may be contained, but a saturated hydrocarbon group is preferred. Among them, alkyl group, aryl group, alkylaryl group, benzyl group, and alkylbenzyl group are preferred. R_9 and R_{10} independently denote a straight-chain, branched-chain alicyclic or aromatic hydrocarbon group which has two bonding sites and in which a straight chain, a branched chain, an alicyclic unit and an aromatic unit may be selectively contained in any combined manner. An unsaturated bond may be contained, but a saturated hydrocarbon group is preferred. Among them, alkylene group is preferred. R_{11} and R_{12} independently denote a straight-chain or branched-chain hydrocarbon group. "x" and "y" denote independently an integer of two or more.

[0022] Specifically, for example, mention may be made of sulfurized sperm oil, sulfurized pinene oil, sulfurized soybean oil, sulfurized polyolefin, dialkyl disulfide, dialkyl polysulfide, dibenzyl disulfide, di-tertiary butyl disulfide, polyolefin polysulfide, thiadiazol type compound such as bis-alkyl polysulfanyl thiadiazole, and sulfurized phenol. Among these compounds, dialkyl polysulfide, dibenzyl disulfide, and thiadiazol type compound are preferred. Particularly, bis-alkyl polysulfanyl thiadiazole is preferred.

[0023] As the lubricant additive, a metal-containing compound such as Ca phenate having a polysulfide bond is used. However, since this compound has a large coefficient of friction, it is not suitable. To the contrary, the above organic polysulfide compound is an ashless compound containing no metal, and exhibits excellent performance in maintaining a low coefficient of friction for a long time when used in combination with MoDTC and ZnDTP.

[0024] The above ashless organic polysulfide compound (hereinafter referred to briefly as "polysulfide compound") is added in an amount of 0.01 to 0.4 wt%, preferably 0.1-0.3 wt%, more preferably 0.2-0.3 wt%, when calculated as sulfur (S), relative to the total amount of the engine oil composition. If the addition amount is less than 0.01 wt%, it is difficult to attain the intended effect, whereas if it is more than 0.4 wt%, there is a danger that corrosive wear increase. Needless to say, only one kind of the above polysulfide compound may be used, and two kinds of such polysulfide compounds may also be used in combination.

[0025] In order to ensure the performance suitable for the intended use, engine oil additives other than the above may be appropriately added to the engine oil composition according to the present invention so as to improve the total performance. As such engine oil additives, mention may be made of so-called metallic detergents such as sulfonate, phenate and salicylate of alkaline earth metals such as Ca, Mg and Ba and alkali metals such as Na, ashless dispersants such as alkenyl succinic acid imide, succinic acid esters and benzylamine, phenolic anti-oxidant such as bisphenol, amine-based anti-oxidant such as diphenylamine, and viscosity index improvers such as olefin copolymer or polymetacrylate. Further, other engine oil additives such as a pour point depressant, anti-corrosion agent and antifoaming agent may be appropriately added, provided that the engine oil composition does not contain a boron containing additive in the case that the ashless organic polysulfide compound is not a thiadiazol type compound.

(Experiments)

[0026] The present invention will be explained in more detail with reference to Examples and Comparative Examples.

[0027] A lubricant in each of Examples and Comparative Examples was prepared by using Mineral Oils 1 or 2 having the following properties as a base oil.

Table 1

	Mineral oil 1	Mineral oil 2
Density (15°C)g/cm ³	0.862	0.821
Dynamic viscosity (40°C)mm ² /s	17.7	19.7
Dynamic viscosity (100°C)mm ² /s	3.78	4.51
Viscosity index	99	147
Flow point (°C)	-15.0	-15.0

Table 1 (continued)

	Mineral oil 1	Mineral oil 2
Content of saturated component (%)	76.5	98.8

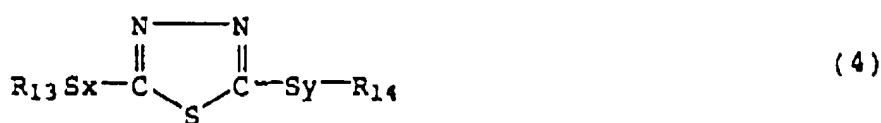
[0028] As additives, the following were used.

(1) MoDTC:

[0029] Compound having the above-mentioned formula (1) in which R_1 through R_4 are all 2-ethylhexyl groups.

(2-1) Sulfur-based additive 1

[0030] Sulfur-based additive 1 means an additive containing the polysulfide compound used in the present invention, and includes a thiadiazole type polysulfide compound having the following formula. The content of sulfur in the sulfur-based additive is 36 wt%.



[0031] In the formula R_{13} and R_{14} independently denote the same meanings as R_7 and R_8 do, respectively.

(2-2) Sulfur-based additive 2

[0032] Sulfur-based additive 2 means an additives containing a sulfurized oil and fat type polysulfide compounds, and the content of sulfur in the sulfur-based additive 2 is 10.5 wt%.

(2-3) Sulfur-based additive 3:

[0033] Sulfur-based additive 3 means an additives containing a dibenzyl disulfide, and the content of sulfur in the sulfur-based additive 3 is 25.5 wt%.

(3-1) ZnDTP1

[0034] ZnDTP1 is a primary alkyl compound of the above formula (2) in which R_5 and R_6 are 2-ethylhexyl groups.

(3-2) ZnDTP2

[0035] ZnDTP2 means secondary alkyl compounds of the above formula (2) in which R_5 and R_6 are isopropyl groups or isohexyl groups or a mixture of these compounds each having the respective two above alkyl groups.

(4) Additive package

[0036] Additive package includes metallic detergent, ashless dispersant, phenolic anti-oxidant, amine-based anti-oxidant, viscosity index improver, anti-corrosion agent and antifoaming agent.

[0037] The above mentioned base oils and additives were selectively mixed at recipes shown in Table 3, thereby preparing long life and low fuel consumption engine oil compositions according to the present invention as Examples 1 through 5. In the same manner, base oils and additives were selectively mixed at recipes shown in Table 5, thereby preparing engine oil composition as Comparative Examples 1 through 8. In Tables 3 and 5, figures for the ingredients are compounding rates based on the unit "wt %" except that the foaming agent is based on the unit "wt ppm".

[0038] The Engine oil compositions thus prepared as Examples and Comparative Examples were evaluated with respect to the friction performance and wear characteristic in the valve train system according to the following methods.

(1) Friction performance

[0039] With respect to fresh lubricants and used ones, the coefficient of friction was measured under the following conditions by using an SRV tester. As test pieces, a ball made of SUJ-2 (bearing steel material, Japanese Industrial Standards), and having 10 mm in diameter and a disc made of SUJ-2 were used.

Table 2

Test conditions		
	Break in conditions	Actual test conditions
Load (N)	10	200
Amplitude (mm)	1.5	1.5
Frequency (Hz)	50	50
Temperature (°C)	40	80
Time (min)	10	30

[0040] The coefficient of friction is the average coefficient of friction determined in the friction test during the final 20 minutes.

[0041] The used oil compositions are oil compositions obtained when the oil was subjected to running in simulation with an actual car driving. The engine was operated under an AMA running mode at an oil temperature of 100°C and a water temperature of 100°C, and the engine oil composition was sampled after the lapse of 160 hours (corresponding to 4000 km) and 400 hours (corresponding to 10000 km). The thus obtained used oil compositions were subjected to the above friction test.

(2) Valve train system wearing test

[0042] Each engine oil composition was subjected to the valve train system wear test according to JASO (Japanese Automobile Standards Organization) M328-91. Then, scuffing of a rocker arm was evaluated, and a worn amount of a cam nose was measured.

[0043] Evaluation results in Examples 1 through 5 are shown in Table 4, and those in Comparative Examples 1 through 8 are shown in Table 6. In Tables 4 and 6, scuffing of the rocker arm was evaluated by using a figure between 1 to 10.0, "1" and "10.0" being the lowest and the highest, respectively.

Table 3

	Example 1	Example 2	Example 3	Example 4	Example 5
Mineral oil 1	84.5	83.1	84.3	-	85.0
Mineral oil 2	-	-	-	84.5	-
MoDTC additive	2.0	2.0	2.0	2.0	2.0
Content of Mo in oil composition	0.08	0.08	0.08	0.08	0.08
Sulfur-based additive 1	0.6	-	-	0.6	0.6
Sulfur-based additive 2	-	2.0	-	-	-
Sulfur-based additive 3	-	-	0.8	-	-
Content of Sulfur in oil composition	0.22	0.21	0.20	0.22	0.22
ZnDTP 1	1.5	1.5	1.5	1.5	-
ZnDTP 2	-	-	-	-	1.0
Content of P in oil composition	0.095	0.095	0.095	0.095	0.090
Metallic detergent	2.0	2.0	2.0	2.0	2.0
Ash-based dispersant	4.0	4.0	4.0	4.0	4.0
Phenolic anti-oxidant	0.8	0.8	0.8	0.8	0.8

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Table 3 (continued)

	Example 1	Example 2	Example 3	Example 4	Example 5
Amine-based anti-oxidant	0.4	0.4	0.4	0.4	0.4
Viscosity index improver	4.0	4.0	4.0	4.0	4.0
Corrosion inhibitor	0.2	0.2	0.2	0.2	0.2
Antifoaming agent (ppm)	5	5	5	5	5

Table 4

		Example 1	Example 2	Example 3	Example 4	Example 5
Dynamic viscosity (40°C)mm ² /sec		53.5	54.5	52.5	51.4	54.3
Dynamic viscosity (100°C)mm ² /sec		9.4	9.5	9.3	9.8	9.5
Viscosity index		160	159	161	180	160
Coefficient of friction	fresh oil composition	0.045	0.043	0.044	0.042	0.040
	used oil composition (160 hrs)	0.044	0.047	0.046	0.041	0.050
	used oil composition (400 hrs)	0.066	0.063	0.067	0.059	0.072
Wear of valve-moving system (rocker arm scuffing): Merit rating		9.0	8.6	8.7	8.6	9.2
Wear of cam nose μm		3	4	5	4	3

Table 5

	Compara- tive Example 1	Compara- tive Example 2	Compara- tive Example 3	Compara- tive Example 4	Compara- tive Example 5	Compara- tive Example 6	Compara- tive Example 7	Compara- tive Example 8
Mineral oil 1	85.1	83.6	86.0	-	86.5	87.6	86.6	88.0
Mineral oil 2	-	-	-	85.1	-	-	-	-
MoDTC additive	2.0	2.0	2.0	2.0	-	-	2.0	-
Content of Mo in oil composition	0.08	0.08	0.08	0.08	0	0	0.08	0
Sulfur additive 1	-	-	0.6	-	0.6	-	-	0.6
Sulfur additive 2	-	-	-	-	-	-	-	-
Sulfur additive 3	-	-	-	-	-	-	-	-
Content of Sulfur in oil	0	0	0.22	0	0.22	0	0	0.22
ZnDTP 1	1.5	3.0	-	1.5	1.5	-	-	-
ZnDTP 2	-	-	-	-	-	1.0	-	-
Content of P in oil	0.095	0.190	0	0.095	0.095	0.090	0	0
Metallic clearing agent	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Ash-based dispersant	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Phenolic antioxidant	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Amine-based antioxidant	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Viscosity index improver	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Corrosion inhibitor	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Antifoaming agent (ppm)	5	5	5	5	5	5	5	5

Table 6

	Compara- tive Example 1	Compara- tive Example 2	Compara- tive Example 3	Compara- tive Example 4	Compara- tive Example 5	Compara- tive Example 6	Compara- tive Example 7	Compara- tive Example 8
Dynamic viscosity (40°C)mm ² /sec	51.8	55.0	51.6	49.6	52.8	50.1	48.9	48.4
Dynamic viscosity (100°C)mm ² /sec	9.2	9.6	9.2	9.6	9.3	9.0	8.8	8.7
Viscosity index	161	160	162	182	160	162	161	160
Coefficient of friction	0.041	0.041	0.040	0.041	0.103	0.112	0.072	0.109
	0.061	0.040	0.058	0.052	0.113	0.113	0.091	0.109
	0.103	0.090	0.093	0.092	0.114	0.113	0.110	0.111
Wear of valve-moving system (rocker arm scuffing): Merit rating	8.7	8.9	6.6	8.7	8.4	8.6	6.3	0
Wear of cam nose μm	5	4	19	6	7	5	22	84

[0044] Examples 1 through 3 in Table 3 are engine oil compositions which all used Mineral Oil 1 and also employed a thiadiazole compound, a sulfurized oil and fat type compound and dibenzyl disulfide as the polysulfide compound, respectively. Example 4 is the same engine oil composition as in Example 1 except that Mineral Oil 1 was replaced by more highly purified Mineral Oil 2. In Example 5, a secondary alkyl type was used as ZnDTP.

[0045] In Table 5, Comparative Example 1 is an engine oil composition containing no polysulfide compound, and Comparative Example 2 is an engine oil composition containing much ZnDTP. Comparative Example 3 is an engine oil composition containing no MoDTC, and Comparative Example 4 is the same engine oil composition as Comparative Example 1 except that the base oil was replaced by highly purified Mineral Oil 2. Comparative Example 5 is an engine oil composition containing no MoDTC, and Comparative Example 6 is an engine oil composition containing neither MoDTC nor polysulfide compound, and Comparative Example 7 is an engine oil composition containing neither ZnDTP nor polysulfide compound. Comparative Example 8 is an engine oil composition containing neither MoDTC nor ZnDTP.

[0046] Comparison between Examples and Comparative Examples in Table 4 and Table 6 reveals that particularly the coefficients of friction of the engine oil compositions in Examples are clearly smaller as compared with those in Comparative Examples after deterioration for 400 hours, though the former do not almost differ from the latter with respect to the fresh engine oil compositions, i.e., changes in the coefficient of friction of the engine oil compositions in Examples are smaller than those in Comparative Examples even after long-term use.

[0047] For example, Comparison between Example 1 and Comparative Example 1, between Example 2 and Comparative Example 2 and between Example 4 and Comparative Example 4 reveals that when the polysulfide compound was used in combination, the coefficient of friction particularly after the passage of 400 hours remarkably decreased. Comparison between Example 3 and Comparative Example 3 reveals that in Comparative Example 3, since no ZnDTP was used in combination, the coefficient of friction after the passage of 400 hours was not only high, but also the worn amount of the cam nose conspicuously increased. Comparison between Example 5 and Comparative Examples 5 and 6 reveals that in Comparative Examples 5 and 6, since no MoDTC was used in combination, the coefficient of friction was high from the beginning. In Comparative Example 7, since neither ZnDTP nor polysulfide compound were used in combination, the coefficient of friction with the passage of 400 hours was not only high, but also the worn amount of the cam nose conspicuously increased. In Comparative Example 8, since neither MoDTC nor ZnDTP were used in combination, the coefficient of friction was not only high from the beginning, but also the worn amount of the cam nose was extremely high.

[0048] The engine oil composition of the present invention is characterized in that MoDTC and ZnDTP are combined with the ashless organic polysulfide compound in the respectively specified addition amounts, and that a low coefficient of friction can be maintained in a long-term use even without addition of a large amount of particularly MoDTP or ZnDTP. Therefore, when the engine oil composition according to the present invention is charged into and used in the automobile, splendid effects can be exhibited with respect to fuel consumption saving and environmental maintenance.

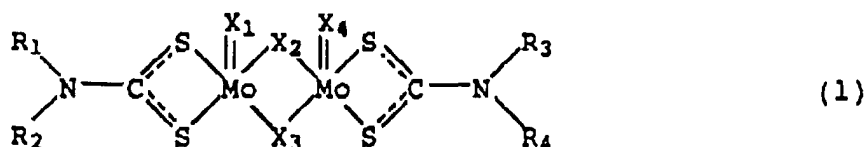
Claims

1. An engine oil composition comprising:

- (1) at least one oil selected from the group consisting of a mineral oil and a synthetic lubricant as a base oil;
- (2) a molybdenum dithiocarbamate (MoDTC) in an amount of 50 to 2000 ppm by weight when calculated as molybdenum (Mo), relative to the total weight of the engine oil composition;
- (3) zinc dithiophosphate (ZnDTP) in an amount of 0.01 to 0.2 wt% when calculated as phosphorus (P), relative to the total amount of the engine oil composition; and
- (4) an ashless organic polysulfide compound in an amount of 0.01 to 0.4 wt% when calculated as sulfur (S), relative to the total amount of the engine oil composition;

provided that the engine oil composition does not contain a boron containing additive in the case that the ashless organic polysulfide compound is not a thiadiazol type compound.

2. The engine oil composition claimed in claim 1, wherein said molybdenum dithiocarbamate (MoDTC) is a compound expressed by the following formula (1)



in which R_1 through R_4 independently denote a straight-chain or branched-chain alkyl group or a straight-chain or branched-chain alkenyl group having four to eighteen carbons; and X_1 through X_4 independently denote an oxygen atom or a sulfur atom, the ratio between the number of the oxygen atom or atoms and that of the sulfur atom or atoms with respect to X_1 through X_4 being 1/3 to 3/1.

3. The engine oil composition claimed in claim 2, wherein said R_1 through R_4 independently denote the alkyl group.

4. The engine oil composition claimed in claim 2, wherein said R_1 through R_4 independently denote butyl group, 2-ethylhexyl group, isotridecyl group or stearyl group.

5. The engine oil composition claimed in any one of claims 1 to 4, wherein said MoDTC is used in the addition amount of 300 to 1000 ppm by weight, when calculated as molybdenum (Mo), relative to the total weight of the engine oil composition.

6. The engine oil composition claimed in any one of claims 1 to 5, wherein said zinc dithiophosphate (ZnDTP) is a compound expressed by the formula (2):



in which R_5 and R_6 independently denote a straight-chain or branched chain alkyl group or a straight-chain or branched chain aryl group having three to eighteen carbon atoms.

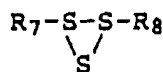
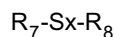
7. The engine oil composition claimed in claim 6, wherein said R_5 and R_6 independently denote an alkyl group.

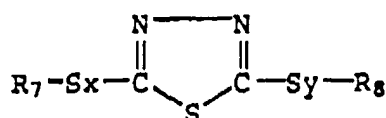
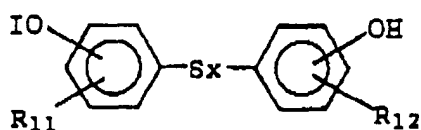
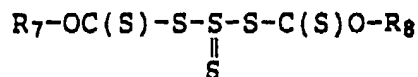
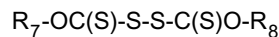
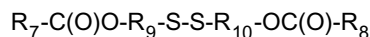
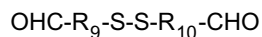
8. The engine oil composition claimed in claim 6, wherein said R_5 and R_6 independently denote a primary alkyl group.

9. The engine oil composition claimed in claim 6, wherein said R_5 and R_6 independently denote propyl group, butyl group, pentyl group, hexyl group, octyl group or lauryl group.

10. The engine oil composition claimed in claim 6, wherein said ZnDTP is added in an amount of 0.04 to 0.2 wt% when calculated as phosphorus (P), relative to the total amount of the engine oil composition.

11. The engine oil composition claimed in any one of claims 1 to 10, wherein said ashless organic polysulfide compound is an organic compound selected from the group consisting of organic compounds expressed by the following formulae.





in which R_7 and R_8 independently denote a straight-chain, branched-chain, alicyclic or aromatic hydrocarbon group in which a straight chain, a branched chain, an alicyclic unit and an aromatic unit may be selectively contained in any combined manner; R_9 and R_{10} independently denote a straight-chain, branched-chain alicyclic or aromatic hydrocarbon group which has two bonding sites and in which a straight chain, a branched chain, an alicyclic unit and an aromatic unit may be selectively contained in any combined manner; R_{11} and R_{12} independently denote a straight-chain or branched-chain hydrocarbon group; and "x" and "y" denote independently an integer of two or more.

12. The engine oil composition claimed in claim 11, wherein said ashless organic polysulfide compound is selected from the group consisting of sulfurized sperm oil, sulfurized pinene oil, sulfurized soybean oil, sulfurized polyolefin, dialkyl disulfide, dialkyl polysulfide, dibenzyl disulfide, di-tertiary butyl disulfide, polyolefin polysulfide, thiadiazol type compound, and sulfurized phenol.

13. The engine oil composition claimed in claim 12, wherein said ashless organic polysulfide compound is the thiadiazol type compound.

14. The engine oil composition claimed in claim 12, wherein said ashless organic polysulfide compound is dialkyl polysulfide and bidenzyl disulfide are preferred.

15. The engine oil composition claimed in any one of claims 11 to 14, wherein said ashless organic polysulfide compound is added in an amount of 0.1-0.3 wt% when calculated as sulfur (S), relative to the total amount of the engine oil composition.

16. The engine oil composition claimed in any one of claims 1 to 15, wherein said molybdenum dithiocarbamate (MoD-TC) in an amount of 300 to 1000 ppm by weight when calculated as molybdenum (Mo), relative to the total weight of the engine oil composition; said zinc dithiophosphate in an amount of 0.04 to 0.2 wt% when calculated as phosphorus (P), relative to the total amount of the engine oil composition; and said ashless organic polysulfide compound in an amount of 0.1 to 0.3 wt% when calculated as sulfur (S), relative to the total amount of the engine oil composition.

Patentansprüche

1. Motoröl-Zusammensetzung, umfassend:

(1) mindestens ein Öl, ausgewählt aus der Gruppe, bestehend aus einem Mineralöl und einem synthetischen Schmieröl, als Basis-Öl,

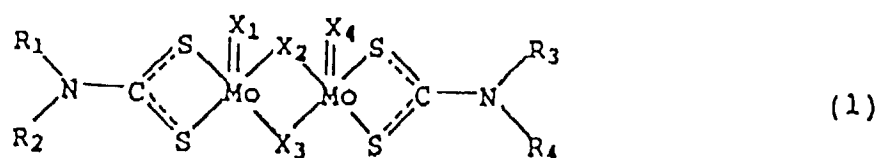
(2) ein Molybdändithiocarbamat (MoDTC) in einer Menge von 50 bis 2000 ppm, gewichtsbezogen, berechnet als Molybdän (Mo), bezogen auf das Gesamtgewicht der Motoröl-Zusammensetzung,

(3) Zinkdithiophosphat (ZnDTP) in einer Menge von 0,01 bis 0,2 Gew.%, berechnet als Phosphor (P), bezogen auf die Gesamtmenge der Motoröl-Zusammensetzung, und

(4) eine aschelose organische Polysulfidverbindung in einer Menge von 0,01 bis 0,4 Gew.%, berechnet als Schwefel (S), bezogen auf die Gesamtmenge der Motoröl-Zusammensetzung,

mit der Maßgabe, daß die Motoröl-Zusammensetzung kein borhaltiges Additiv enthält, wenn die aschelose organische Polysulfidverbindung keine Verbindung von Thiadiazol-Typ ist.

2. Motoröl-Zusammensetzung gemäß Anspruch 1, worin das genannte Molybdändithiocarbamat (MoDTC) eine Verbindung der folgenden Formel (1) ist:



worin R_1 bis R_4 , unabhängig voneinander, eine geradkettige oder verzweigte Alkyl- oder Alkenylgruppe mit 4 bis 18 Kohlenstoffatomen und X_1 bis X_4 , unabhängig voneinander, ein Sauerstoff- oder Schwefelatom bedeuten, wobei das Verhältnis zwischen der Zahl des oder der Sauerstoffatome und derjenigen des oder der Schwefelatome bezüglich X_1 bis X_4 1/3 bis 3/1 beträgt.

3. Motoröl-Zusammensetzung gemäß Anspruch 2, worin die genannten Reste R_1 bis R_4 , unabhängig voneinander, die Alkylgruppe bedeuten.

4. Motoröl-Zusammensetzung gemäß Anspruch 2, worin die genannten Reste R_1 bis R_4 , unabhängig voneinander, eine Butyl-, 2-Ethylhexyl-, Isotridecyl- oder eine Stearylgruppe bedeuten.

5. Motoröl-Zusammensetzung gemäß einem der Ansprüche 1 bis 4, worin das genannte MoDTC in einer Zugabemenge von 300 bis 1000 ppm, gewichtsbezogen, berechnet als Molybdän (Mo), bezogen auf das Gesamtgewicht der Motoröl-Zusammensetzung, verwendet wird.

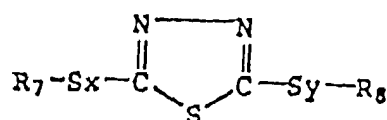
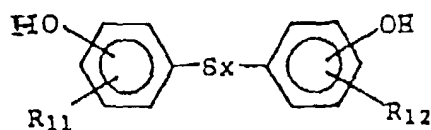
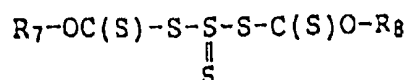
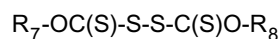
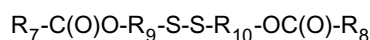
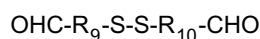
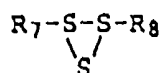
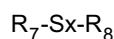
6. Motoröl-Zusammensetzung gemäß einem der Ansprüche 1 bis 5, worin das genannte Zinkdithiophosphat (ZnDTP) eine Verbindung der Formel (2) ist:



worin R_5 und R_6 , unabhängig voneinander, eine geradkettige oder verzweigte Alkylgruppe oder eine gerade oder

verzweigte Arylgruppe mit 3 bis 18 Kohlenstoffatomen bedeuten.

7. Motoröl-Zusammensetzung gemäß Anspruch 6, worin die genannten Reste R_5 und R_6 , unabhängig voneinander, eine Alkylgruppe bedeuten.
8. Motoröl-Zusammensetzung gemäß Anspruch 6, worin die genannten Reste R_5 und R_6 , unabhängig voneinander, eine primäre Alkylgruppe bedeuten.
9. Motoröl-Zusammensetzung gemäß Anspruch 6, worin die genannten Reste R_5 und R_6 , unabhängig voneinander, eine Propyl-, Butyl-, Pentyl-, Hexyl-, Octyl- oder eine Laurylgruppe bedeuten.
10. Motoröl-Zusammensetzung gemäß Anspruch 6, worin das genannte ZnDTP in einer Menge von 0,04 bis 0,2 Gew. % zugefügt wird, berechnet als Phosphor (P), bezogen auf die Gesamtmenge der Motoröl-Zusammensetzung.
11. Motoröl-Zusammensetzung gemäß einem der Ansprüche 1 bis 10, worin die genannte aschelose organische Polysulfidverbindung eine organische Verbindung ist, ausgewählt aus der Gruppe, bestehend aus organischen Verbindungen der folgenden Formel:



worin R_7 und R_8 , unabhängig voneinander, eine geradkettige, verzweigte, alicyclische oder aromatische Kohlenwasserstoffgruppe, worin eine geradkettige, eine verzweigte, eine alicyclische Einheit und eine aromatische Einheit selektiv in jeder kombinierten Weise enthalten sein können, R_9 und R_{10} , unabhängig voneinander, eine ge-

radkettige, verzweigte alicyclische oder aromatische Kohlenwasserstoffgruppe mit 2 Bindungsstellen, worin eine geradkettige, eine verzweigte, eine alicyclische Einheit und eine aromatische Einheit selektiv in jeder kombinierten Weise enthalten sein können, R_{11} und R_{12} , unabhängig voneinander, eine geradkettige oder verzweigte Kohlenwasserstoffgruppe und "x" und "y", unabhängig voneinander, eine ganze Zahl von 2 oder mehr bedeuten.

12. Motoröl-Zusammensetzung gemäß Anspruch 11, worin die genannte aschelose Polysulfidverbindung aus der Gruppe ausgewählt ist, bestehend aus mit Schwefel behandeltem Potwalöl, mit Schwefel behandeltem Pinenöl, mit Schwefel behandeltem Sojabohnenöl, mit Schwefel behandeltem Polyolefin, Dialkyldisulfid, Dialkylpolysulfid, Dibenzylidisulfid, Di-t-butylidisulfid, Polyolefinpolysulfid, einer Verbindung vom Thiadiazol-Typ und aus mit Schwefel behandeltem Phenol.
13. Motoröl-Zusammensetzung gemäß Anspruch 12, worin die genannte aschelose Polysulfidverbindung die Verbindung vom Thiadiazol-Typ ist.
14. Motoröl-Zusammensetzung gemäß Anspruch 12, worin die genannte aschelose organische Polysulfidverbindung Dialkylpolysulfid und insbesondere Dibenzylidisulfid ist.
15. Motoröl-Zusammensetzung gemäß einem der Ansprüche 11 bis 14, worin die genannte aschelose organische Polysulfidverbindung in einer Menge von 0,1 bis 0,3 Gew.% zugefügt wird, berechnet als Schwefel (S), bezogen auf die Gesamtmenge der Motoröl-Zusammensetzung.
16. Motoröl-Zusammensetzung gemäß einem der Ansprüche 1 bis 15, worin das genannte Molybdändithiocarbamat (MoDTC) in einer Menge von 300 bis 1000 ppm, gewichtsbezogen, berechnet als Molybdän (Mo), bezogen auf das Gesamtgewicht der Motoröl-Zusammensetzung, das genannte Zinkdithiophosphat in einer Menge von 0,04 bis 0,2 Gew.%, berechnet als Phosphor (P), bezogen auf die Gesamtmenge der Motoröl-Zusammensetzung, und die genannte aschelose organische Polysulfidverbindung in einer Menge von 0,1 bis 0,3 Gew.%, berechnet als Schwefel (S), bezogen auf die Gesamtmenge der Motoröl-Zusammensetzung, enthalten sind.

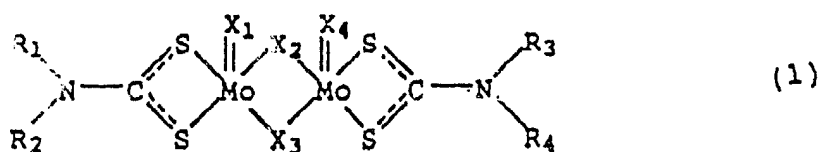
Revendications

1. Composition d'huile pour moteur comprenant :

- (1) au moins une huile choisie dans le groupe constitué par une huile minérale et un lubrifiant synthétique comme huile de base ;
- (2) du dithiocarbamate de molybdène (DTCMo) à raison de 50 à 2000 ppm, cette quantité étant exprimée en poids de molybdène (Mo), par rapport au poids total de la composition d'huile pour moteur ;
- (3) du dithiophosphate de zinc (DTPZn) à raison de 0,01 à 0,2 % en poids, ce pourcentage étant exprimé en poids de phosphore (P) par rapport au poids total de la composition d'huile pour moteur ; et
- (4) un composé polysulfure organique sans cendres à raison de 0,01 à 0,4 % en poids, ce pourcentage étant exprimé en poids de soufre (S) par rapport au poids total de la composition d'huile pour moteur ;

une condition à satisfaire étant que la composition d'huile pour moteur ne doit pas contenir un additif contenant du bore dans le cas où le composé polysulfure organique sans cendres n'est pas un composé du type thiadiazole.

2. Composition d'huile pour moteur selon la revendication 1, dans laquelle ledit dithiocarbamate de molybdène (DTC-Mo) est un composé exprimé par la formule suivante (I) :



dans laquelle R_1 à R_4 indiquent, de manière indépendante, un groupe alkyle à chaîne droite ou ramifiée ou un

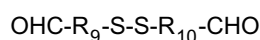
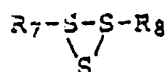
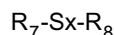
groupe alcényle à chaîne droite ou ramifiée ayant de quatre à dix-huit atomes de carbone ; et X_1 à X_4 indiquent, de manière indépendante, un atome d'oxygène ou un atome de soufre, le rapport entre le nombre d'atome ou atomes d'oxygène et le nombre d'atome ou atomes de soufre dans X_1 à X_4 étant de 1/3 à 3/1.

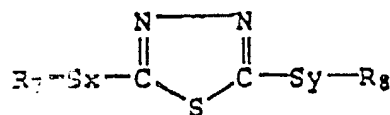
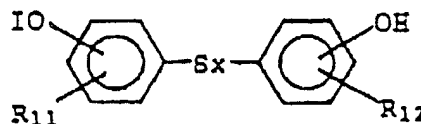
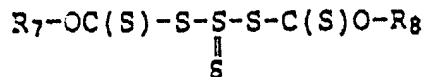
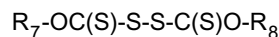
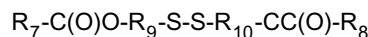
3. Composition d'huile pour moteur selon la revendication 2, dans laquelle lesdits groupes R_1 à R_4 indiquent, de manière indépendante, un groupe alkyle.
4. Composition d'huile pour moteur selon la revendication 2, dans laquelle lesdits groupes R_1 à R_4 indiquent, de manière indépendante, un groupe butyle, un groupe 2-éthylhexyle, un groupe isotridécyle ou un groupe stéaryle.
5. Composition d'huile pour moteur selon l'une quelconque des revendications 1 à 4, dans laquelle ledit DTCMo est ajouté à raison de 300 à 1000 ppm, cette quantité étant exprimée en poids de molybdène (Mo) par rapport au poids total de la composition d'huile pour moteur.
6. Composition d'huile pour moteur selon l'une quelconque des revendications 1 à 5, dans laquelle ledit dithiophosphate de zinc (DTPZn) est un composé exprimé par la formule (2) :



dans laquelle R_5 et R_6 indiquent, de manière indépendante, un groupe alkyle à chaîne droite ou ramifiée ou un groupe aryle à chaîne droite ou ramifiée ayant trois à dix-huit atomes de carbone.

7. Composition d'huile pour moteur selon la revendication 6, dans laquelle lesdits groupes R_5 et R_6 indiquent, de manière indépendante, un groupe alkyle.
8. Composition d'huile pour moteur selon la revendication 6, dans laquelle lesdits groupes R_5 et R_6 indiquent, de manière indépendante, un groupe alkyle primaire.
9. Composition d'huile pour moteur selon la revendication 6, dans laquelle lesdits groupes R_5 et R_6 indiquent, de manière indépendante, un groupe propyle, un groupe butyle, un groupe pentyle, un groupe hexyle, un groupe octyle ou un groupe lauryle.
10. Composition d'huile pour moteur selon la revendication 6, dans laquelle ledit DTPZn est ajouté à raison de 0,04 à 0,2 %, ce pourcentage étant exprimé en poids de phosphore (P), par rapport au poids total de la composition d'huile pour moteur.
11. Composition d'huile pour moteur selon l'une quelconque des revendications 1 à 10, dans laquelle ledit composé polysulfure organique sans cendres est un composé organique choisi dans le groupe constitué par les composés organiques exprimés par les formules suivantes :





dans lesquelles R_7 et R_8 indiquent, de manière indépendante, un groupe hydrocarbure à chaîne droite, à chaîne ramifiée, alicyclique ou aromatique, la chaîne droite, la chaîne ramifiée, l'unité alicyclique et l'unité aromatique pouvant être choisies de manière à être présentes dans une combinaison quelconque ; R_9 et R_{10} indiquent, de manière indépendante, un groupe hydrocarbure à chaîne droite, à chaîne ramifiée, alicyclique ou aromatique qui a deux sites de liaison, la chaîne droite, la chaîne ramifiée, l'unité alicyclique et l'unité aromatique pouvant être choisies de manière à être présentes dans une combinaison quelconque ; R_{11} et R_{12} indiquent, de manière indépendante, un groupe hydrocarbure à chaîne droite ou à chaîne ramifiée, « x » et « y » indiquent, d'une manière indépendante, un nombre entier égal à deux ou plus.

12. Composition d'huile pour moteur selon la revendication 11, dans laquelle ledit composé polysulfure organique sans cendres est choisi dans le groupe constitué par l'huile de spermaceti sulfurée, un pinène sulfuré, une huile de soja sulfurée, une polyoléfine sulfurée, un disulfure de dialkyle, un polysulfure de dialkyle, un disulfure de dibenzyle, un disulfure de di-tert.-butyle, un polysulfure de polyoléfine, un composé du type thiadiazol et un phénol sulfuré.

13. Composition d'huile pour moteur selon la revendication 12, dans laquelle ledit composé polysulfure organique sans cendres est un composé du type thiadiazol.

14. Composition d'huile pour moteur selon la revendication 12, dans laquelle ledit composé polysulfure organique sans cendres est, de préférence un polysulfure de dialkyle ou le disulfure de dibenzyle.

15. Composition d'huile pour moteur selon l'une quelconque des revendications 11 à 14, dans laquelle ledit composé polysulfure organique sans cendres est ajouté à raison de 0,1 - 0,3 % en poids, ce pourcentage étant exprimé en poids de soufre (S), par rapport au poids total de la composition d'huile pour moteur.

16. Composition d'huile pour moteur selon l'une quelconque des revendications 1 à 15, dans laquelle ledit dithiocarbamate de molybdène (DTCMo) est présent à raison 300 à 1000 ppm, cette quantité étant exprimée en poids de molybdène (Mo), par rapport au poids total de la composition d'huile pour moteur ; ledit dithiophosphate de zinc est présent à raison de 0,04 à 0,2 % en poids, ce pourcentage étant exprimé en poids de phosphore (P), par rapport au poids total de la composition d'huile pour moteur ; et ledit composé polysulfure organique sans cendres étant présent à raison de 0,1 à 0,3 % en poids, ce pourcentage étant exprimé en poids de soufre (S), par rapport au poids total de la composition d'huile pour moteur.