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(54) **Friction modifier compound and lubricating oil composition containing the same**

(57) The present invention is directed to chain-hydrocarbon-group-substituted metal phenates having friction reducing ability and various lubricating oil compositions containing the chain-hydrocarbon-group-substituted metal phenates.

A friction modifier comprising a chain-hydrocarbon-group-substituted metal phenate substituted by at least one chain hydrocarbon group, wherein the chain hydrocarbon group has an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement (<sup>13</sup>C-NMR measurement); and a lubricating oil composition containing the metal phenate are disclosed.

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**Description**BACKGROUND OF THE INVENTION5 Field of the Invention

This invention relates to a friction modifier comprising a chain-hydrocarbon-group-substituted metal phenate and a lubricating oil composition containing the same, and more specifically to a friction modifier comprising a specific chain-hydrocarbon-group-substituted metal phenate having excellent friction reducing ability and a lubricating oil composition containing the same.

Description of the Prior Art

15 It is the fundamental theme of lubrication to reduce friction and wear which occur at sliding surfaces of moving parts in machineries, devices, equipments and the like. Technical developments on lubrication technology have conventionally been placed on this theme.

Especially from the need for resource and energy saving, measures for the achievement of low friction and low wear by improvements in the quality of lubricating oils have been investigated from a variety of viewpoints in recent years. As a consequence, it has become an indispensable approach for the production of a lubricating oil excellent in friction characteristics to incorporate additives in base stocks for lubricating oils so that the base stocks can be provided with desired friction characteristics.

Accordingly a number of friction modifiers have been proposed to date, resulting in the use of fatty acids and their metal salts, alcohols, esters, amines and the like - all of which are of the oiliness improver type - and phosphate esters, phosphite esters, zinc dithiophosphate and the like - all of which are of the extreme pressure agent type - in automatic transmission fluids, wet brake oils, sliding surface oils, plastic working oils and the like and also in the use of phosphate esters, phosphite esters, acidic phosphite ester amine salts, molybdenum dithiophosphate, molybdenum dithiocarbamate and the like - all of which are of the extreme pressure agent type - in engine oils, gear oils, cutting oils and the like.

Meanwhile, an automatic transmission fluid was disclosed, which had been obtained by adding magnesium sulfonate used as a metallic detergent, especially over-based magnesium sulfonate having a base number of 300 mg-KOH/g or greater in a base stock in order to improve its friction characteristics (see JP Kokai 62-84190). Further, it has also been proposed to use calcium salicylate as a friction coefficient modifiers for automatic transmission fluids (see JP Kokai 5-163496).

No matter whether these conventionally-proposed friction modifiers are of the organic type or of the metallic type, 35 their friction reducing effects are however not sufficient depending on the use conditions. All of them are still insufficient in assuring stable friction reducing effects as typified by magnesium sulfonate, calcium salicylate and the like the effects of which vary significantly depending on the kind, use conditions and the like of a lubricating base stock, although they provide friction reducing effects to some extents. Therefore they are merely adjuvants for friction modifiers such as phosphate esters and molybdenum dithiocarbamate.

40 In view of the technical developments on friction reducing technology and the circumstances of development of friction modifiers as described above, the present invention has as objects thereof the provision of a novel friction modifier having friction reducing ability and also the provision of a lubricating oil composition containing the friction modifier.

Present Invention

45 It has been discovered that a metal phenate containing at least one chain hydrocarbon group, which has a specific linear portion determinable by a carbon nuclear magnetic resonance measurement (which may hereinafter be referred to as "<sup>13</sup>C-NMR measurement" as needed), has excellent friction reducing ability. It has also been found that its addition to a base stock for lubricating oil makes it possible to furnish a lubricating oil composition having improved friction characteristics and utility in many fields. Based on these findings, the present invention has now been completed.

Namely, the present invention relates in a first aspect thereof to a friction modifier comprising at least one chain-hydrocarbon-group-substituted metal phenate substituted by at least one chain hydrocarbon group, characterized in that said chain hydrocarbon group has an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement (<sup>13</sup>C-NMR measurement).

55 The present invention also relates in a second aspect thereof to a lubricating oil composition characterized in that said lubricating oil composition comprises:

a lubricating base stock; and

at least one chain-hydrocarbon-group-substituted metal phenate substituted by at least one chain hydrocarbon group, said chain hydrocarbon group having an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement ( $^{13}\text{C}$ -NMR measurement), and said metal phenate having been added in a proportion of from 1 ppm to 10,000 ppm in terms of the metal thereof based on a whole weight of said lubricating oil composition.

The present invention will hereinafter be described in detail.

The chain-hydrocarbon-group-substituted metal phenate, which is used as an effective component of the friction modifier according to the present invention, is formed basically of a phenol component, which carries at least one chain hydrocarbon group bonded thereto, and a metal component. The above metal phenate may be subjected to sulfurization to contain compounds with two or more aromatic groups bonded together by one or more sulfur atoms, respectively, and the above metal phenate may also contain one obtained by subjecting it to an over-basing treatment as needed.

As the chain hydrocarbon group in the chain-hydrocarbon-group-substituted metal phenate according to the present invention, those capable of meeting the following requirements are suitable.

As such, the following requirements can be mentioned:

(i) an alkyl group having an average carbon number of 12 or more per hydroxyl group; and

(ii) said alkyl group having a linearity of 20% or higher, both being as determined by a  $^{13}\text{C}$ -NMR measurement.

Describing about the above requirement (i), it is important for the exhibition of friction reducing effects that the chain hydrocarbon group of the chain-hydrocarbon-group-substituted metal phenate according to the present invention is an alkyl group having an average carbon number of 12 or more per hydroxyl group. In particular, an alkyl group having an average carbon number of from 12 to 40 is preferred. An average carbon number smaller than 12 involves a potential problem that sufficient friction reducing effects may not be obtained.

Describing further, as chain-hydrocarbon-group-substituted metal phenate according to the present invention, one containing at least one or more alkyl groups having 12 to 30 carbon atoms is particularly preferred.

By the way, the term "hydroxyl group" as used herein means an -OH group existing in a chain-hydrocarbon-group-substituted metal phenate in a form as converted under  $^{13}\text{C}$ -NMR measuring conditions.

The term "average carbon number per hydroxyl group" as used herein indicates an average carbon number of an alkyl group as calculated by a  $^{13}\text{C}$ -NMR measurement by supposing that an aromatic carbon bonded to a hydroxyl group is 1.

Specific examples of the above-described alkyl group can include dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, pentatriacontyl, and octatriacontyl.

One of principal features of the present invention resides in that the above alkyl group has a specific linearity as determined by a  $^{13}\text{C}$ -NMR measurement as indicated above under the requirement (ii), and is a requirement indispensable for the unique chain-hydrocarbon-group-substituted metal phenate according to the present invention.

Namely, the chain-hydrocarbon-group-substituted metal phenate according to the present invention is one having an alkyl chain linearity of 20% or higher, preferably 30% or higher as determined by a  $^{13}\text{C}$ -NMR measurement.

Here, the term "alkyl chain linearity" is based on a unique concept established by the present inventors as a result of repetition of numerous experiments, and means the ratio of the number of carbon atoms in a linear portion located 5 or more carbon atoms apart from an end of the alkyl group or 4 or more carbon atoms apart from a branched site of the alkyl group to the total number of carbon atoms in the alkyl group. Accordingly, the alkyl chain linearity varies depending on the substituting site of the aromatic group to the alkyl group or the site of branching of the alkyl group. Specifically, the chain linearity is determined specifically by the following formula from a  $^{13}\text{C}$ -NMR measurement.

$$\text{Alkyl chain linearity (\%)} = \frac{\text{Integral intensity over a chemical shift range of from 29 ppm to 31 ppm}}{\text{Sum of all integral intensity over a chemical shift range of from 5 ppm to 60 ppm}} \times 100$$

Incidentally, the  $^{13}\text{C}$ -NMR measurement was conducted by converting the metal phenate into its corresponding alkyl phenol.

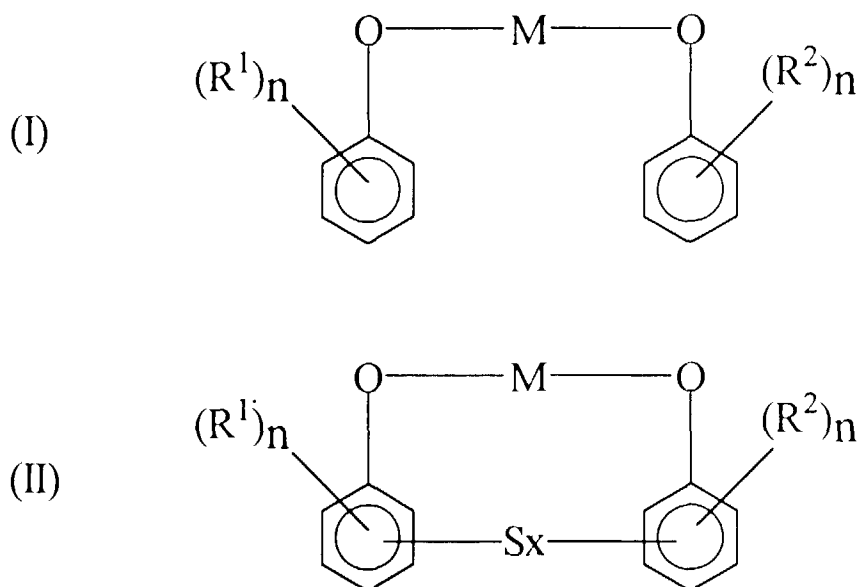
The present inventors were interested in the existence of a correlation between the linearity of the alkyl group or groups in the chain-hydrocarbon-group-substituted metal phenate and its friction reducing effects, and have ascertained that the metal phenate exhibits better friction reducing effects as the alkyl chain linearity becomes higher and also that an alkyl chain linearity lower than 20% cannot exhibit the effects fully although an alkyl chain linearity of 20% or higher, especially of from 30% to 80% shows particularly marked effects.

In the present invention, a chain-hydrocarbon-group-substituted metal phenate excellent in friction reducing effects

can still be obtained provided that its alkyl chain linearity as determined by a  $^{13}\text{C}$ -NMR measurement is 20% or higher, even when the chain-hydrocarbon-group-substituted metal phenate contains two or more hydrocarbon groups per hydroxyl group or is a mixture of two or more different compounds (metal phenates). That is, the overall alkyl chain linearity is 20% or higher. In particular, a metal phenate, hydrocarbon groups of which are each a linear alkyl group having 12 or more carbon atoms, is preferred from the viewpoint that it can substantially improve friction reducing effects.

The metal component represented by M in the formula (I) of the chain-hydrocarbon-group-substituted metal phenate according to the present invention can be an alkali metal or an alkaline earth metal. Further, a metal of an atomic number in a range of from 12 to 56 is also suited. Specific examples of suitable metals can include sodium, potassium, lithium, calcium, magnesium and barium. In addition, aluminum, zinc, tin, chromium, copper, cobalt and the like are also effective. Particularly preferred are alkaline earth metals such as calcium, magnesium and barium.

Typical illustrative compounds of the chain-hydrocarbon-group-substituted metal phenate according to the present invention can be represented by the following formulas (I) to (II):



In each of the above formulas (I) and (II),  $\text{R}^1$  and  $\text{R}^2$  are alkyl groups which may be the same or different, the average carbon number of the total carbon number of  $\text{R}^1$  and the total carbon number of  $\text{R}^2$ , said average total carbon number being equivalent to the number of carbon atoms per hydroxyl group, may preferably be from 12 to 40, and the alkyl chain linearity as determined by a  $^{13}\text{C}$ -NMR measurement is 20% or higher. Specific examples of the alkyl group can include dodecyl, tridecyl, tetradecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, and triacontyl.

In each formula, M is appropriately an alkaline earth metal, although it can be other divalent metals described above. n indicates the number of alkyl groups substituted on the aromatic group and is an integer of from 1 to 5, preferably an integer of 1 to 2. In the respective formulas, they can be the same or different. Further, x is an integer of from 1 to 5 in the formula (II).

In the present invention, the chain-hydrocarbon-group-substituted metal phenate can specifically be a metal salt of an alkylphenol or alkylphenol sulfide, which can be a basic salt or over-based salt in addition to a neutral salt. Its salt type can be chosen as desired depending on its application. The metal salt of the alkylphenol or alkylphenol sulfide can be prepared by a reaction between the alkyl phenol or alkylphenol sulfide and a metal compound, for example, an oxide, hydroxide, alkoxide or the like. The over-based salt can be obtained by a method known *per se*, in the art. On the other hand, the alkylphenol sulfide can be produced by reacting the alkylphenol with sulfur or a sulfur-containing compound such as hydrogen sulfide and is obtained in the form of a mixture that two or more phenol groups are bonded by one or more sulfur atoms, respectively.

A metal phenate mixture with an alkyl chain linearity controlled within the above-described specific range can also be obtained by mixing various metal phenates of different alkyl chain linearities.

According to the present invention, a friction modifier comprising such a specific chain-hydrocarbon-group-substituted metal phenate as described above can be provided. This friction modifier is oil-soluble. It can be used by dissolv-

ing it in a hydrocarbon or another solvent and diluting the resultant concentrate as needed or as a component of an additive package in combination with other additives.

A description will next be made about the lubricating oil composition according to the present invention.

The lubricating oil composition according to the present invention contains the lubricating base stock and the chain-hydrocarbon-group-substituted metal phenate.

No particular limitation is imposed on the base stock for use in the lubricating oil composition according to the present invention. The base stock can be any one of mineral base stocks, synthetic base stocks and vegetable base stocks, or can be a blended base stock of two or more of these base stocks.

As a mineral base stock, it is possible to use, for example, a mineral oil obtained by the treatment of a lubricating oil fraction, which is in turn available by vacuum distillation of an atmosphere distillation residue of paraffin-base, neutral or naphthene-base crude oil, through a refining step such as solvent refining, hydrocracking, hydro-refining, catalytic dewaxing, solvent dewaxing or clay treatment; a mineral oil obtained by subjecting a vacuum distillation residue to solvent deasphalting and then treating the resulting deasphalted oil through the above-described refining step; a mineral oil obtained by isomerizing wax components; or a blended oil thereof. In the above solvent refining, an aromatic extraction solvent such as phenol, furfural or N-methylpyrrolidone can be used, whereas as a solvent for the solvent dewaxing, liquefied propane, MEK/toluene, MEK/MIBK, or the like can be used. Among the above-described mineral base stocks, hydro-refined oil is preferred from the standpoint of quality such as oxidation stability, and one containing, for example, 2 wt% or less of aromatic hydrocarbons and 90 wt% or more of saturated hydrocarbons can be used although the preferred mineral base stock varies depending on the application purpose of the lubricating oil.

Examples of synthetic base stocks, on the other hand, can include poly( $\alpha$ -olefin) oligomers; polybutene; alkylbenzenes; polyol esters such as trimethylolpropane esters and pentaerythritol esters; polyoxyalkylene glycols; polyoxyalkylene glycol esters; polyoxyalkylene glycol ethers; dibasic acid esters; phosphate esters; and silicone oils. These base stocks can be used either singly or in combination.

Further, usable examples of vegetable base stocks can include rape seed oil, palm oil, coconut oil, olive oil and sunflower oil.

As a lubricating base stock such as that described above, it is possible to use a blended base stock obtained by suitably blending plural base stocks so that the blended base stock has a viscosity and other properties desired for the intended application of the lubricating oil composition. For example, it is preferred to control the kinematic viscosity at 100°C in a range of from 2 mm<sup>2</sup>/s to 30 mm<sup>2</sup>/s, especially from 3 mm<sup>2</sup>/s to 10 mm<sup>2</sup>/s for a lubricating oil for internal combustion engines, the kinematic viscosity at 100°C in a range of from 2 mm<sup>2</sup>/s to 30 mm<sup>2</sup>/s, especially from 3 mm<sup>2</sup>/s to 15 mm<sup>2</sup>/s for an automatic transmission fluid, and the kinematic viscosity at 4°C in a range of from 10 mm<sup>2</sup>/s to 1,000 mm<sup>2</sup>/s, especially from 20 mm<sup>2</sup>/s to 500 mm<sup>2</sup>/s.

The chain-hydrocarbon-group-substituted metal phenate for use in the lubricating oil composition according to the present invention can be added to the lubricating base stock in a proportion of from 0.01 to 10 wt%, preferably from 0.05 to 5 wt% based on the whole weight of the lubricating oil composition or in a proportion of from 1 ppm to 10,000 ppm, preferably from 50 ppm to 5,000 ppm in terms of the metal, although the proportion varies depending on the application field of the lubricating oil.

To the lubricating oil composition according to the present invention, it is possible to add selected ones of viscosity index improvers, ashless dispersants, anti-oxidants, extreme pressure agents, wear inhibitors, metal deactivators, pour-point depressants, rust inhibitors, other friction modifiers and other additives as needed.

Illustrative usable examples of the viscosity index improvers can include polymethacrylates, polyisobutylenes, ethylene-propylene copolymers, and hydrogenated styrene-butadiene copolymers. These viscosity index improvers are used generally in a proportion of from 3 wt% to 35 wt%.

Illustrative of the ashless dispersants can be polybutenylsuccinimides, polybutenylsuccinamides, benzylamines, and succinate esters. They can be used generally in a proportion of from 0.05 wt% to 7 wt%.

Illustrative examples of the anti-oxidants can include amine-type anti-oxidants such as alkylated diphenylamines, phenyl- $\alpha$ -naphthylamine and alkylated phenyl- $\alpha$ -naphthylamines; phenolic anti-oxidants such as 2,6-di-*t*-butylphenol and 4,4'-methylene-bis(2,6-di-*t*-butylphenol); and zinc dithiophosphate. They can be used generally in a proportion of from 0.05 wt% to 5 wt%.

Illustrative of the extreme pressure agents can be dibenzyl sulfide and dibutyl disulfide. They can be used generally in a proportion of from 0.05 wt% to 3 wt%.

Illustrative examples of the metal deactivators can include benzotriazole, benzotriazole derivatives, and thiadiazole. They can be used generally in a proportion of from 0.01 wt% to 3 wt%.

Illustrative of the pour-point depressants can be ethylene-vinyl acetate copolymers, chlorinated paraffin-naphthalene condensation products, polymethacrylates, and polyalkylstyrenes. They can be used generally in a proportion of from 0.1 wt% to 10 wt%.

Illustrative of the wear inhibitors can be phosphate esters, zinc thiophosphate, and sulfur compounds. They can be used generally in a proportion of from 0.01 wt% to 5 wt%.

As preferred embodiments of the present invention, it is possible to provide:

(i) a friction modifier for lubricating oils, which comprises chain-hydrocarbon-group-substituted metal phenate substituted by at least one chain hydrocarbon group, wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 per hydroxyl group and an alkyl chain linearity of 20% or higher as determined by a  $^{13}\text{C}$ -NMR measurement.

(ii) a friction modifier for lubricating oils, which comprises chain-hydrocarbon-group-substituted metal phenate substituted by at least one chain hydrocarbon group, wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 per hydroxyl group and an alkyl chain linearity of 25% or higher as determined by a  $^{13}\text{C}$ -NMR measurement.

(iii) A lubricating oil composition comprising:

a lubricating base stock; and

chain-hydrocarbon-group-substituted metal phenate, wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 per hydroxyl group and a chain linearity of 20% or higher as determined by a  $^{13}\text{C}$ -NMR measurement, and said metal phenate having been added in a proportion of from 1 ppm to 10,000 ppm in terms of the metal thereof based on the whole weight of the lubricating oil composition.

(iv) A lubricating oil composition comprising:

a base stock composed of a hydro-refined oil containing 2 wt% or less of aromatic hydrocarbons and 90% or more of saturated hydrocarbons; and

chain-hydrocarbon-group-substituted metal phenate, wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 per hydroxyl group and an alkyl chain linearity of 20% or higher as determined by the  $^{13}\text{C}$ -NMR measurement, and said metal phenate having been added in a proportion of from 1 ppm to 10,000 ppm in terms of the metal thereof based on the whole weight of the lubricating oil composition.

(v) A lubricating oil composition comprising:

a lubricating base stock; and

metal phenate substituted by at least one chain hydrocarbon group, wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 a hydroxyl group and an alkyl chain linearity of 20% or higher as determined by the  $^{13}\text{C}$ -NMR measurement, said metal phenate having been added in a proportion of from 1 ppm to 10,000 ppm in terms of the metal thereof based on the whole weight of the lubricating oil composition, and at least one of 4 wt% to 30 wt% of a viscosity index improver, 0.1 wt% to 5 wt% of an ashless dispersant, 0.1 wt% to 2.5 wt% of an extreme pressure agent, 0.1 wt% to 3 wt% of an anti-oxidant, 0.1 wt% to 3 wt% of a wear inhibitor, 0.15 wt% to 8 wt% of a pour-point depressant and 0.01 wt% to 2 wt% of a metal deactivator can be added.

As has been described above, the friction modifier according to the present invention, which comprises the chain-hydrocarbon-group-substituted metal phenate, is useful for various fuels and lubricating oils, and the lubricating oil composition according to the present invention, which contains the friction modifier, can be used as hydraulic working oils, wet brake oils, sliding surface oils, plastic working oils, cutting oils and the like in addition to automatic transmission fluid compositions, lubricating oil compositions for internal combustion engines, and gear oils. It can also be used without limitations in lubricating oils and fuel oils in any fields insofar as the friction reducing effects of the metal phenate can be exhibited.

### Examples

The present invention will next be described specifically by Examples and Comparative Examples. It is however to be noted that the Examples and the like are to primarily demonstrate the friction reducing effects of certain chain-hydrocarbon-group-substituted metal phenates (hereinafter may be referred to as "metal phenates" as needed) according to

the present invention and that the present invention shall not be limited by these Examples and the like.

The alkyl chain linearities of metal phenates employed in the following Examples and the like and, as performance evaluation of lubricating oil compositions, friction coefficients were measured by the following methods.

5 (i) Measuring method of alkyl chain linearity:

Each metal phenate was converted into its corresponding alkylphenol, and under the following measuring conditions, its  $^{13}\text{C}$ -NMR spectrum was measured. Further, its alkyl chain linearity was calculated in accordance with the below-described formula.

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Measuring conditions

Used instrument	EX400 (manufactured by JEOL Ltd.)
Observed nucleus	$^{13}\text{C}$
15 Observing frequency	100.50 MHz
Measuring mode	Inverse gated $^1\text{H}$ decoupling
Internal standard	TMS (= 0 ppm)
Relaxation reagent	$\text{Cr}(\text{acac})_3$
Solvent	$\text{CDCl}_3$
20 Quantity of sample	300 mg
Temperature	30°C

25 Alkyl chain linearity (%) =  $\frac{\text{Integral intensity over the chemical shift range of from 29 ppm to 31 ppm}}{\text{Sum of all integral intensity over the chemical shift range of from 5 ppm to 60 ppm}} \times 100$

(ii) Performance evaluation

Friction coefficient measuring method:

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Concerning each lubricating oil composition added with its corresponding metal phenate in a predetermined proportion, its friction coefficient was measured under the following conditions by using "LFW-1" as a testing machine.

Friction materials:	Steel/steel
35 Load:	200 lb
Oil temperature:	80°C
Revolution speed:	600 rpm
Measuring period:	30 min

40 Example 1

Provided was Calcium Phenate 1 (total base number: 85 mg-KOH/g), which had an average alkyl carbon number of 19 per hydroxyl group and an alkyl chain linearity of 45.3%. A lubricating oil composition was formulated by adding the phenate to a refined mineral oil "100SN" (4.2 mm<sup>2</sup>/s at 100°C) as a lubricating base stock in a proportion of 140 ppm in terms of calcium based on the whole weight of the lubricating oil composition. The friction coefficient of the resultant lubricating oil composition was measured by the above-described method. It was found to be 0.10.

Example 2

50 A lubricating oil composition was formulated in exactly the same manner as in Example 1 except that the proportion of Calcium Phenate 1 was increased from 140 ppm to 560 ppm in terms of calcium. When subjected to a performance evaluation, its friction coefficient was found to be 0.09.

Example 3

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Provided was Calcium Phenate 2 (total base number: 260 mg-KOH/g), which had an average alkyl carbon number of 20 per hydroxyl group and an alkyl chain linearity of 28.2%. A lubricating oil composition was formulated by adding the phenate to a lubricating base stock, which was the same as that employed in Example 1, in a proportion of 950 ppm

in terms of calcium based on the whole weight of the lubricating oil composition. The resultant lubricating oil composition was subjected to the above-described performance evaluation. Its friction coefficient was found to be 0.09.

#### Example 4

A lubricating oil composition was formulated in exactly the same manner as in Example 3 except that the proportion of Calcium Phenate 2 was increased from 950 ppm to 1,900 ppm in terms of calcium. The resultant lubricating oil composition was subjected to a performance evaluation. Its friction coefficient was found to be 0.09.

#### Example 5

A lubricating oil composition was formulated in exactly the same manner as in Example 3 except that the proportion of Calcium Phenate 2 was increased to 5,700 ppm in terms of calcium. The resultant lubricating oil composition was subjected to a performance evaluation. Its friction coefficient was found to be 0.09.

#### Comparative Example 1

The lubricating base stock, i.e., the purified mineral oil alone was subjected to a performance evaluation. Its friction coefficient was found to be 0.14.

#### Comparative Example 2

Provided was Calcium Phenate 3 (total base number: 250 mg-KOH/g), which had an average alkyl carbon number of 20 per hydroxyl group and an alkyl chain linearity of 15.5%. A lubricating oil composition was formulated by adding the phenate to a refined mineral oil, which was the same as that employed in Example 1, in a proportion of 950 ppm in terms of calcium based on the whole weight of the lubricating oil composition. As a result of a performance evaluation, its friction coefficient was found to be 0.14. No advantageous effect was available from the addition of Calcium Phenate 3 the alkyl chain linearity of which is lower than 20%.

#### Comparative Example 3

A lubricating oil composition was formulated in exactly the same manner as in Comparative Example 2 except that the proportion of Calcium Phenate 3 was increased to 5,700 ppm in terms of calcium. The resultant lubricating oil composition was subjected to a performance evaluation. Its friction coefficient was found to be 0.13.

The kinds and properties of the calcium phenate used in the Examples and the like are shown in Table 1, and the results of the performance evaluations of the lubricating oil compositions are summarized in Table 2.

TABLE 1

Kind	Average Alkyl Carbon Number Per Hydroxyl Group	Alkyl Chain Linearity	Total Base Number
Calcium Phenate 1	19	45.3%	85 mg-KOH/g
Calcium Phenate 2	20	28.2%	260 mg-KOH/g
Calcium Phenate 3	20	15.5%	250 mg-KOH/g



TABLE 2

	Example					Comparative Example		
	1	2	3	4	5	1	2	3
Base stock	Refined mineral oil, 100SN							
Proportion of additive (Ca conc., ppm)								
Calcium Phenate 1	140	560	-	-		-	-	-
Calcium Phenate 2	-	-	950	1900	5700	-	-	-
Calcium Phenate 3	-	-	-	-		-	950	5700
Performance evaluation								
Friction coefficient	0.10	0.09	0.09	0.09	0.09	0.14	0.14	0.13

From the above Examples and Comparative Examples, it is apparent that a low frictional coefficient can be obtained from a chain-hydrocarbon-group-substituted metal phenate of an alkyl chain linearity of 20% or higher even if it is added in a small proportion (Example 1), but it is also clear from a comparison among Comparative Examples 1, 2 and 3 that a metal phenate of an alkyl chain linearity lower than 20% cannot bring any significant improvement in frictional coefficient even if its proportion is increased. From these results, it has become evident that the alkyl chain linearity is a principal factor governing friction reducing ability.

From this it is seen that a in-hydrocarbon-group-substituted metal phenate having an alkyl chain linearity of 20% or higher has high friction reducing effects, is useful as a friction modifier especially for lubricating oils, and can improve the friction characteristics of lubricating oil compositions.

### Claims

1. A friction modifier comprising chain-hydrocarbon-group-substituted metal phenate substituted by at least one chain hydrocarbon group, characterized in that said chain hydrocarbon group has an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement ( $^{13}\text{C}$ -NMR measurement).
2. The friction modifier comprising chain-hydrocarbon-group-substituted metal phenate as defined in claim 1, wherein said chain hydrocarbon group is an alkyl group.
3. The friction modifier of claim 2 wherein the chain hydrocarbon group is one or more alkyl group each of which has 12-40 carbon atoms on average per hydroxyl group as measured by  $^{13}\text{C}$ -NMR measurement.
4. The friction modifier of claim 1, 2 or 3 wherein the chain hydrocarbon group has an alkyl chain linearity of 30% or higher as determined by  $^{13}\text{C}$ -NMR measurement.
5. A lubricating oil composition characterized in that said lubricating oil composition comprises:
  - a lubricating base stock; and
  - chain-hydrocarbon-group-substituted metal phenate according to any one of claims 1 to 4, the said metal phenate having been added in a proportion of from 1 ppm to 10,000 ppm in terms of the metal thereof based on a whole weight of said lubricating oil composition.
6. The lubricating oil composition of claim 5 further containing at least one additive selected from viscosity index improvers, ashless dispersants, anti-oxidation inhibitors, extreme pressure agents, wear inhibitors, metal deactivators, pour point depressants, rust inhibitors, and other friction modifiers.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 0773

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.6)
X	EP 0 486 893 A (IDEMITSU KOSAN CO) 27 May 1992 * abstract * * page 2, line 54 - page 3, line 7 * * page 3, line 22-30 * * page 4, line 45-47 * * page 4, line 55 - page 5, line 5 * * page 5, line 10-12 * * examples 1-7,10,11 * ---	1-6	C10M159/22 C10M135/30 C10M129/10 C10M129/91 C07G17/00 //C10N10:04, 30:06
X	WO 95 14751 A (BP CHEMICALS ADDITIVES ;COOK STEPHEN JAMES (GB); ROBINSON PAUL KRI) 1 June 1995 * abstract * * page 3, line 6-22 * * claim 10 * ---	1-6	
X	EP 0 095 322 A (OROBIS LTD) 30 November 1983 * page 5, line 11-27 * * claim 13 * ---	1-6	
X	US 5 320 762 A (CAMPBELL CURTIS B) 14 June 1994 * column 2, line 63 - column 3, line 60 * * examples 5-9 * ---	1-6	C10M C07G
X	EP 0 662 509 A (BP CHEMICALS ADDITIVES) 12 July 1995 * page 2, line 30 - page 3, line 16 * ---	1-4	
A	EP 0 620 268 A (ETHYL PETROLEUM ADDITIVES LTD) 19 October 1994 * abstract * * page 2, line 30-38 * * page 5, line 7-8 * * example 2 * -----	1-6	
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>16 September 1998</b>	Examiner <b>Perakis, N</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>			

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