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(54) **Friction modifier comprising metal sulfonate and lubricating oil composition containing the same**

(57) Novel metal sulfonates having friction reducing ability and also various lubricating oil compositions containing the metal sulfonates are disclosed. The metal sulfonates which provide a friction modifier comprise a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal. The hydrocarbon group of the organic sulfonic group is a

chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto. The chain hydrocarbon group has an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement (¹³C-NMR measurement). Lubricating oil compositions added with the metal sulfonate are also provided.

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DescriptionBACKGROUND OF THE INVENTIONField of the Invention

This invention relates to a friction modifier comprising a metal sulfonate and to a lubricating oil composition with the metal sulfonate added therein, and more specifically to a friction modifier comprising a metal sulfonate containing a specific chain hydrocarbon group and to a lubricating oil composition with the metal sulfonate added therein.

Description of the Prior Art

From the need for resource and energy saving measures in all the industrial fields in view of environmental conservation, reductions in friction and wear through improvements in lubricating oils have also been investigated in the field of lubricating oils from a variety of viewpoints in recent years with a view to lowering fuel consumption rates. As a result, it has already become indispensable 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, 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 wet brake oils, automatic transmission fluids, 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 oil was disclosed, which had been obtained by adding magnesium sulfonate, which is used as a metallic detergent, for example, for the dispersion of sludge occurring in lubricating oils, the solubilization of a precursor and the neutralization of an acid, especially over-based magnesium sulfonate having a base number of 300 mg-KOH/g or greater in a base stock, in order to improve friction characteristics (see JP Kokai 62-84190). Further, a lubricating oil making combined use of a metallic detergent, such as calcium sulfonate, barium sulfonate or magnesium sulfonate, with a molybdenum dialkyldithiocarbamate was also proposed (see JP Kokai 62-215697).

These metal sulfonates, when employed singly, are however still insufficient in friction reducing effects, so that they are merely friction modifier adjuvants for use in combination with friction modifiers such as phosphate esters and molybdenum dithiocarbamate. If a metal sulfonate having still higher friction reducing ability is identified, it is therefore believed it will find utility in a much wider range of fields and hence to have a significantly-increased industrial value. There is accordingly an outstanding intense desire for the development of such a metal sulfonate.

In view of the circumstances of development of friction modifiers as described above, the present invention has as objects thereof the provision of a novel metal sulfonate having friction reducing ability and also the provision of a lubricating oil composition with the metal sulfonate added.

Present Invention

It has been discovered that a metal sulfonate having an alkyl group, which has a specific linear portion determinable by carbon nuclear magnetic resonance measurement (^{13}C -NMR measurement) (hereinafter referred to as ^{13}C -NMR measurement, as needed), has excellent friction reducing ability. Having been interested in its effectiveness as a friction modifier, 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 a variety of technical fields. Based on these findings, the present invention has now been completed.

The present invention relates in a first aspect thereof to a friction modifier comprising a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, characterized in that said hydrocarbon group is a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, and said chain hydrocarbon group has an alkyl chain linearity of 20% or higher as determined by ^{13}C -NMR measurement.

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

a base stock; and

a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, said hydrocarbon group being a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon

group bonded thereto, said chain hydrocarbon group having an alkyl chain linearity of 20% or higher as determined by ^{13}C -NMR measurement, and said metal sulfonate 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 metal sulfonate which is used as the friction modifier according to the present invention is composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, and is a compound which can be represented, for example, by the following formula (I):



It may consist of one type of the compound or may be a mixture of two or more compounds having different hydrocarbon groups. In the formula (I), R in the organic sulfonic group RSO_3 is a hydrocarbon group, which is a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto. Illustrative of the chain hydrocarbon group can be alkyl groups, each of which has 12-40 carbon atoms on average per organic sulfonic group as measured by ^{13}C -NMR and calculated supposing that there is one carbon atom bonded to a sulfonic group. It is particularly preferred to contain at least one or more alkyl groups having 12-30 carbon atoms. Specific examples of the alkyl group can include dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, pentatriacontyl, and octatriacontyl.

As the metal sulfonate according to the present invention, one having an alkyl chain linearity of 20% or higher, especially of from 30% to 80% as determined by a ^{13}C -NMR measurement is preferred.

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 atoms apart from an end of the alkyl group or 4 or more atoms apart from a branched site of the alkyl group to the total number of carbon atoms in the alkyl group. Its value is dependent on the bonding site of an aromatic group and the site of branching of the alkyl group.

In the present invention, the alkyl chain linearity has been determined specifically by the following formula from a ^{13}C -NMR measurement.

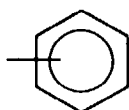
Alkyl chain linearity (%) =

$$\frac{\text{Integral intensity over a chemical shift range of from 29 ppm to 31 ppm}}{\text{Sum of all integral intensity over a chemical shift range of from 5 ppm to 60 ppm}} \times 100$$

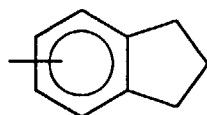
Incidentally, the ^{13}C -NMR measurement was conducted by converting the metal sulfonate into its corresponding sulfonic acid.

The present inventors recognized the existence of a correlation between the alkyl chain linearity and the friction reducing effects of its metal sulfonate, and have ascertained that the metal sulfonate exhibits better friction reducing effects as the linearity becomes higher and also that a linearity lower than 20% cannot exhibit the effects fully although a linearity of 20% or higher, especially of from 30% to 80% shows particularly marked effects.

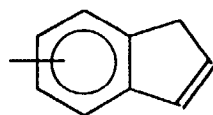
Even when the metal sulfonate contains two or more chain hydrocarbon groups per organic sulfonic group or is a mixture of two or more different compounds (metal sulfonates), the metal sulfonate exhibits friction reducing effects and is effective as a metal sulfonate according to the present invention provided that the alkyl chain linearity as determined by a ^{13}C -NMR measurement is 20% or higher. In particular, a metal sulfonate, the chain hydrocarbon groups of which are each an alkyl group having 12 or more carbon atoms and a linearity of 20% or higher, is preferred from the viewpoint of making it possible to substantially increase friction reducing ability. The aromatic group bonded to the chain hydrocarbon groups can be either monocyclic or fused polycyclic. Those represented by the following structural formulas (a) to (g), respectively, are effective, with a phenyl group being particularly preferred.



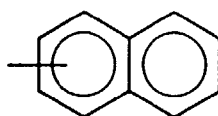
(a)



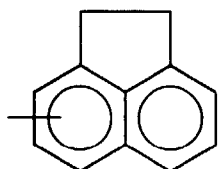
(b)



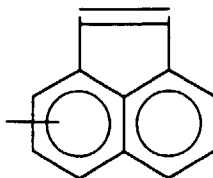
(c)



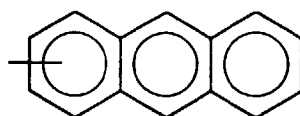
(d)



(e)



(f)

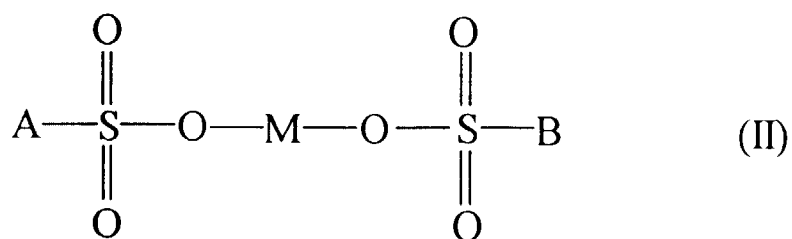


(g)

The metal component represented by M in the above-described metal sulfonate (formula (I)) $(\text{RSO}_3)_x\text{M}$ 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 can include sodium, potassium, lithium, calcium, magnesium and barium. In addition, aluminum, zinc, tin, chromium, copper, cobalt and the like are also effective. Of these, calcium, magnesium, barium and the like are particularly preferred.

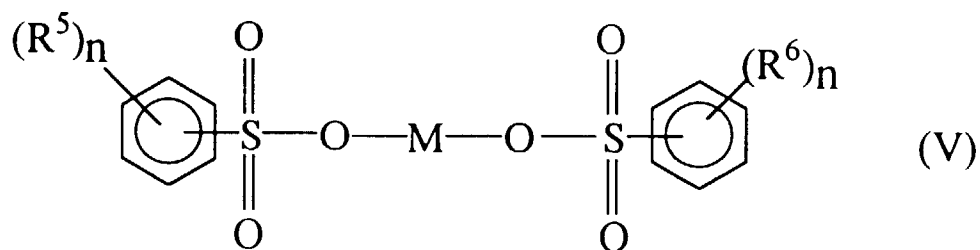
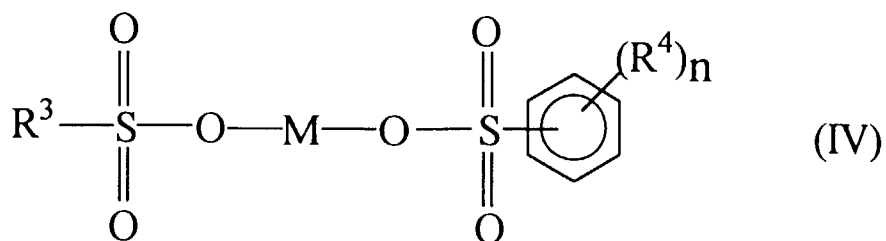
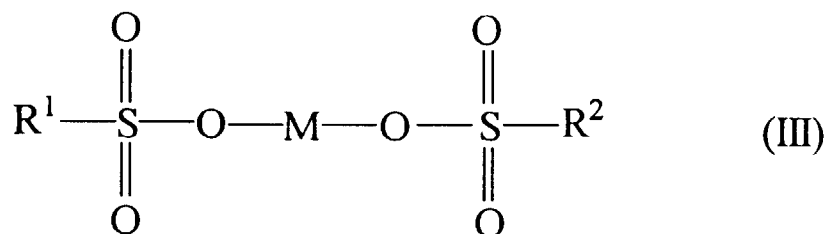
In the above formula (I), x is a value corresponding to the valence of the metal component M.

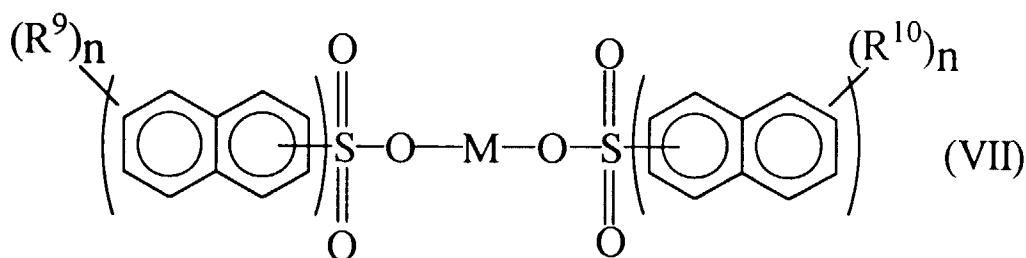
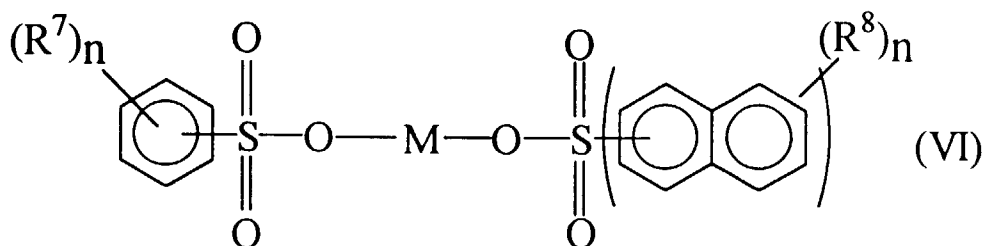
Typical illustrative compounds of the metal sulfonate according to the present invention can be represented by the following formula (II):



In the above formula (II), A and B may be the same or different and are each (i) an alkyl group or (ii) an aromatic group with at least one alkyl group bonded thereto, and the alkyl groups are those capable of providing 20% or higher as an average linearity of the whole alkyl groups as determined by a ^{13}C -NMR measurement. Further, the aromatic group can be at least one aromatic group selected from the group consisting of the above-described structural formulas (a) to (g). In addition, M in the formula represents the above-described divalent metal, with an alkaline earth metal being preferred.

Accordingly, more specific illustrative examples of the metal sulfonate according to the present invention can be represented by the following formulas (III) to (VII):





In the above formulas (III) to (VII), R^1 to R^{10} are alkyl groups and as already described, the average total carbon numbers of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 and R^{10} , said average total carbon numbers being equivalent to the numbers of carbon atoms per the corresponding organic sulfonic acids, may preferably be from 12 to 40, and R^1 to R^{10} have alkyl chain linearities of 20% or higher as determined by ^{13}C -NMR measurement.

In each of the above formulas (III) to (VII), each n represents the number of alkyl groups bonded to the associated aromatic group and may stand for an integer of 1 to 5, preferably of 1 to 3. In each formula, two n values can be the same or different.

Further, M_s in the formulas (III) to (VII) are preferably alkaline earth metals, although they can be other divalent metals described above.

No particular limitation is imposed on a process for the preparation of a metal sulfonate according to the present invention, which contains one or more alkyl groups which are large in chain length and high in linearity. It is possible to adopt, for example, a process in which a sulfonic acid available by sulfonation of an alkyl-substituted aromatic hydrocarbon obtained from a petroleum fraction or of an alkyl-substituted aromatic hydrocarbon, which is an alkylation product of an aromatic hydrocarbon by an olefinic hydrocarbon, is neutralized with an alkali metal oxide, hydroxide, alkoxide or the like, followed by the adjustment of a quantity of a metal.

Further, a metal sulfonate according to the present invention, which has a specific alkyl chain linearity, can be prepared by mixing various metal sulfonates of different alkyl chain linearities so that the overall alkyl chain linearity is controlled to fall within the above-described particular range.

In the present invention, the metal sulfonate 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. A basic salt can be one prepared by a conventional process, and can be prepared, for example, by dispersing $M(\text{OH})_2$ or $M\text{CO}_3$ (wherein M represents an alkaline earth metal or the like) in a colloidal form in a sulfonate. A conventionally-adopted preparation process can be relied upon.

As has been described above, the present invention provides a friction modifier, especially a friction modifier for lubricating oils, which is composed of a particular metal sulfonate. This friction modifier is oil-soluble. It can be used by dissolving 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.

No particular limitation is imposed on the base stock employed 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-methyl-pyrrolidone 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 oxidation stability and the like, and one containing, for example, 2 wt% or less of aromatic hydrocarbons and 90 wt% or more of saturated hydrocarbons can be used.

Examples of synthetic base stocks, on the other hand, can include poly(α -olefin) oligomers of lubricating viscosity; 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, soybean oil, coconut oil, olive oil and sunflower oil.

The lubricating base stock employed in the lubricating oil composition according to the present invention can be produced by suitably preparing a blended base stock so that the blended base stock has properties desired for the intended application of the lubricating oil composition. Concerning viscosity, for example, it is preferred to control the kinematic viscosity at 100°C in a range of from 2 mm²/s to 30 mm²/s, especially from 3 mm²/s to 10 mm²/s for a lubricating oil for internal combustion engines, the kinematic viscosity at 100°C in a range of from 2 mm²/s to 30 mm²/s, especially from 3 mm²/s to 15 mm²/s for an automatic transmission fluid, and the kinematic viscosity at 40°C in a range of from 10 mm²/s to 1,000 mm²/s, especially from 20 mm²/s to 500 mm²/s.

The metal sulfonate according to the present invention can exhibit sufficient friction reducing effects when 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, oxidation inhibitors, 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 oxidation inhibitors can include amine-type oxidation inhibitors such as alkylated diphenylamines, phenyl- α -naphthylamine and alkylated phenyl- α -naphthylamines; phenolic oxidation inhibitors such as 2,6-di-*t*-butylphenol and 4,4'-methylene-bis(2,6-di-*t*-butyl-phenol); 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 a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, in which the hydrocarbon group is a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, and wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 per organic sulfonic group and an alkyl chain linearity of 20% or higher as determined by a ¹³C-NMR measurement.

(ii) A friction modifier for lubricating oils, which comprises metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, in which the hydrocarbon group is a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, and wherein the chain hydrocarbon group is an alkyl group having an average carbon number of from 12 to 40 per organic sulfonic group and has an alkyl chain linearity of 30% or higher as determined by a ¹³C-NMR measurement.

(iii) A lubricating oil composition comprising:

a lubricating base stock;

a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, said hydrocarbon group being a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, said chain hydrocarbon group being an alkyl group, which has an average carbon number of from 12 to 40 per organic sulfonic group, and having an alkyl chain linearity of 20% or higher as determined by a ^{13}C -NMR measurement, and said metal sulfonate 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 the lubricating oil composition.

(iv) A lubricating oil composition comprising:

a lubricating base stock;

a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, said hydrocarbon group being a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, said chain hydrocarbon group being an alkyl group, which has an average carbon number of from 12 to 40 per organic sulfonic group, and having an alkyl chain linearity of 20% or higher as determined by a ^{13}C -NMR measurement, and said metal sulfonate 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 the lubricating oil composition; and

at least one additive selected from the group consisting of viscosity index improvers, ashless dispersants, oxidation inhibitors, extreme pressure agents, metal deactivators, pour-point depressants and wear inhibitors.

As a more preferable embodiment of the lubricating oil composition according to the present invention, there is provided a lubricating oil composition comprising as a base stock a hydro-refined oil, which contains 2 wt% or less of aromatic hydrocarbons and 90 wt% or more of saturated hydrocarbons, and a calcium sulfonate containing 1 to 2 $\text{C}_{14}\text{-}_{24}$ alkyl groups per organic sulfonic group and having an alkyl chain linearity of 40% or higher as determined by a ^{13}C -NMR measurement, said calcium sulfonate having been added in a proportion of from 50 ppm to 5,000 ppm in terms of calcium based on the whole weight of the lubricating oil composition.

As has been described above, the metal sulfonate according to the present invention can be used as a friction modifier in hydraulic working oils, wet brake oils, sliding surface oils, plastic working oils, cutting oils and the like in addition to lubricating oils for internal combustion engines, automatic transmission fluids and gear oils. Without being limited to them, the metal sulfonate can be used without limitations in any other oils insofar as it can exhibit its friction reducing effects.

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 unique effects of the alkyl group or groups in the metal sulfonate 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 the metal sulfonates employed in the following Examples and the performance evaluation of the lubricating oil compositions were measured or conducted by the following methods.

(i) Measuring method of alkyl chain linearity

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

Measuring conditions	
Used instrument	EX400 (manufactured by JEOL Ltd.)
Observed nucleus	^{13}C

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(continued)

Measuring conditions	
Observing frequency	100.50 MHz
Measuring mode	Inverse gated ¹ H decoupling
Internal standard	TMS (= 0 ppm)
Relaxation reagent	Cr(acac) ₃
Solvent	CDCl ₃
Quantity of sample	300 mg
Temperature	30°C

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

Measuring method of friction coefficients

Concerning lubricating oil compositions with corresponding metal sulfonates added in predetermined proportions, their friction coefficients were measured under the following conditions by using "LFW-1" as a testing machine.

Friction materials	steel/steel
Load	200 lb.
Oil temperature	80°C
Revolution speed	600 rpm
Measuring period	30 minutes

Example 1

Provided was Calcium Sulfonate I of the following characteristics:

- Average number of alkyl carbons per organic sulfonic group 31
- Alkyl chain linearity 47.2%
- Calcium content 2.8 wt%
- Total base number 25 mg-KOH/g

A lubricating oil composition was formulated by adding the sulfonate to a solvent-refined mineral oil "100N" (kinematic viscosity at 100°C: 4.2 mm²/s) 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 0.09.

Example 2

A lubricating oil composition was formulated in exactly the same manner as in Example 1 except that the proportion of Calcium Sulfonate 1 was increased from 140 ppm to 560 ppm in terms of calcium. The resultant lubricating oil composition was subjected to a performance evaluation. Its friction coefficient was found to be 0.08, thereby indicating an improvement in friction characteristics.

Example 3

Provided was Calcium Sulfonate 2 of the following characteristics:

- Average number of alkyl carbons per organic sulfonic group 35

- Alkyl chain linearity 39.9%
- Calcium content 12 wt%
- Total base number 300 mg-KOH/g

5 A lubricating oil composition was formulated by adding the sulfonate to the same lubricating base stock as that employed in Example 1 in a proportion of 1,200 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 0.10.

10 Example 4

A lubricating oil composition was formulated in exactly the same manner as in Example 3 except that the proportion of Calcium Sulfonate 2 was increased from 1,200 ppm to 2,400 ppm in terms of calcium. The resultant lubricating oil composition was subjected to a performance evaluation. Its friction coefficient was found to be 0.08.

15 Example 5

Provided was Calcium Sulfonate 3 of the following characteristics:

- 20 - Average number of alkyl 1 carbons per organic sulfonic group 26
- Alkyl chain linearity 31.0%
- Calcium content 11.8 wt%
- Total base number 295 mg-KOH/g

25 A lubricating oil composition was formulated by adding the sulfonate to the same lubricating base stock as that employed in Example 1 in a proportion of 2,400 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.

30 Example 6

A lubricating oil composition was formulated in exactly the same manner as in Example 5 except that the proportion of Calcium Sulfonate 3 was increased from 2,400 ppm to 4,800 ppm in terms of calcium. The resultant lubricating oil composition was subjected to a performance evaluation. Its friction coefficient was found to be 0.08.

35 Comparative Example 1

Provided was Calcium Sulfonate 4 of the following characteristics:

- 40 - Average number of alkyl carbons per organic sulfonic group 33
- Alkyl chain linearity 17.2%
- Calcium content 12 wt%
- Total base number 300 mg-KOH/g

45 A lubricating oil composition was formulated by adding the sulfonate to the same lubricating base stock as that employed in Example 1 in a proportion of 2,400 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 0.13.

50 Comparative Example 2

Provided was Calcium Sulfonate 5 of the following characteristics:

- Average number of alkyl carbons per organic sulfonic group 31
- Alkyl chain linearity 12.6%
- 55 - Calcium content 11.7 wt%
- Total base number 295 mg-KOH/g

A lubricating oil composition was formulated by adding the sulfonate to the same lubricating base stock as that

employed in Example 1 in a proportion of 2,400 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 found to be 0.14.

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 Sulfonate 5 was increased from 2,400 ppm to 4,800 ppm in terms of calcium. Its friction coefficient was found to be 0.13. The calcium sulfonate, the alkyl chain linearity of which is low, was also found to be unable to bring about any substantial advantageous effects on friction characteristics despite the increase in its proportion.

Comparative Example 4

The solvent-refined mineral oil "100N" (kinematic viscosity at 100°C: 4.2 mm²/s), which was employed as a lubricating base stock in Example 1, was subjected by itself to a performance evaluation. Its friction coefficient was found to be 0.14.

The measurement results of the friction coefficients in the above Examples and Comparative Examples and the calcium sulfonates employed therein are summarized in Table 1 and Table 2, respectively. From these results, it is appreciated that an alkyl chain linearity of 20% or higher in a metal sulfonate provides a low friction coefficient even if the metal sulfonate is added in a small proportion (Examples 1 and 2) whereas a lower alkyl chain linearity cannot provide a low friction coefficient even if the proportion of the metal sulfonate is increased (Comparative Example 3). From a comparison between Comparative Example 2 and Comparative Example 4, it is indicated that use of a metal sulfonate having a linearity lower than 20% results in a lubrication oil composition the friction coefficient of which is the same as that of the base stock alone. It has therefore been elucidated that the alkyl chain linearity is a primary element governing friction characteristics.

TABLE I

	Example						Comparative Example			
	1	2	3	4	5	6	1	2	3	4
Base stock	Refined Mineral Oil									
<u>Additive (Ca concentration, ppm)</u>										
Ca-sulfonate 1	140									
Ca-sulfonate 1		560								
Ca-sulfonate 2			1,200							
Ca-sulfonate 2				2,400						
Ca-sulfonate 3					2,400					
Ca-sulfonate 3						4,800				
Ca-sulfonate 4							2,400			
Ca-sulfonate 5								2,400		
Ca-sulfonate 5									4,800	
<u>Performance evaluation</u>										
Friction coefficient	0.09	0.08	0.10	0.08	0.09	0.08	0.13	0.14	0.13	0.14

TABLE 2

Kind	Average Alkyl Carbon Number Per Organic Sulfonic Group	Alkyl Chain Linearity	Ca Content	Total Base Number (TBN)
Ca-sulfonate 1	31	47.2%	2.8%	25 mg-KOH/g
Ca-sulfonate 2	35	39.9%	12%	300 mg-KOH/g
Ca-sulfonate 3	26	31.0%	11.8%	295 mg-KOH/g
Ca-sulfonate 4	33	17.2%	12%	300 mg-KOH/g
Ca-sulfonate 5	31	12.6%	11.7%	295 mg-KOH/g

From this it is readily seen that a metal sulfonate having an alkyl chain linearity of 20% or higher is useful as a

friction modifier for lubricating oils, and can improve the friction characteristics of lubricating oil compositions.

Claims

1. A friction modifier comprising a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, characterized in that said hydrocarbon group is a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, and said chain hydrocarbon group has an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement (^{13}C -NMR measurement).
2. The friction modifier comprising a metal sulfonate 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 organic sulfonic group as measured by ^{13}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% to 80% as determined by ^{13}C -NMR measurement.
5. A lubricating oil composition characterized in that said lubricating oil composition comprises:
 - a base stock; and
 - a metal sulfonate composed of an organic sulfonic group, which contains a hydrocarbon group, and a metal, said hydrocarbon group being a chain hydrocarbon group or an aromatic group with at least one chain hydrocarbon group bonded thereto, said chain hydrocarbon group being an alkyl group, said chain hydrocarbon group having an alkyl chain linearity of 20% or higher as determined by a carbon nuclear magnetic resonance measurement (^{13}C -NMR measurement), and said metal sulfonate 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 wherein the chain hydrocarbon group is an alkyl group.
7. The lubricating oil composition of claim 6 wherein the chain hydrocarbon group is one or more alkyl group each of which has 12-40 carbon atoms on average per organic sulfonic group as measured by ^{13}C -NMR measurement.
8. The lubricating oil composition of claim 5, 6 or 7 wherein the chain hydrocarbon group has an alkyl chain linearity of 30% to 80% as determined by ^{13}C -NMR measurement.
9. The lubricating oil composition of claim 5, 6 or 7 further containing at least one additive selected from the group consisting of viscosity index improvers, ashless dispersants, oxidation inhibitors, extreme pressure agents, metal deactivators, pour point depressants, and wear inhibitors.