

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 835 924 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

15.04.1998 Bulletin 1998/16

(51) Int. Cl.⁶: **C10M 169/04**, C10M 133/04,
C10M 133/16

// (C10N30/04, 40:25)

(21) Application number: **96917714.6**

(22) Date of filing: **17.06.1996**

(86) International application number:
PCT/JP96/01670

(87) International publication number:
WO 97/01619 (16.01.1997 Gazette 1997/04)

(84) Designated Contracting States:
DE FR GB

(30) Priority: **26.06.1995 JP 183564/95**

(71) Applicant: **Kao Corporation**
Chuo-Ku Tokyo 103 (JP)

(72) Inventors:

- **KITA, Kazuo**
deceased (JP)

- **OHTANI, Takashi,**
Kao Corporation
Wakayama-shi, Wakayama 640 (JP)

(74) Representative:

Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann Eitle,
Patent- und Rechtsanwälte,
Arabellastrasse 4
81925 München (DE)

(54) LUBRICATING OIL ADDITIVE AND LUBRICATING OIL COMPOSITION FOR DIESEL ENGINES

(57) A lubricating oil additive for diesel engines comprising one or more members of carboxylic acids, metal salts of carboxylic acids, amine salts of carboxylic acids, and carboxylic acid amides, each having a substituted amino group or substituted amino groups in a molecule, wherein the substituted aminocarboxylic acid compounds have a function of dispersing water-containing calcium sulfate in an oil; and a lubricating oil composition for diesel engines including these lubricating oil additives for diesel engines. When the lubricating oil additives and the lubricating oil compositions for diesel engines of the present invention are added to the lubricating oil, the dispersion function of the water-containing calcium sulfate admixed in the lubricating oil is dramatically improved, and the dispersion functions in oil of the staining components, such as soots, sludges, and the like, mentioned above owned by the lubricating oil are enhanced, so that its detergency is dramatically improved. Therefore, it is made possible to lower the concentration in the amount of the metal-based detergent as well as to lengthen the service life of the lubricating oil.

EP 0 835 924 A1

DescriptionTECHNICAL FIELD

5 The present invention relates to a lubricating oil additive and a lubricating oil composition for diesel engines for land use and marine use. More specifically, the present invention relates to a lubricating oil additive for diesel engines for improving detergency of a lubricating oil and lengthening the service life of the lubricating oil, and to a lubricating oil composition containing the same.

10 BACKGROUND ART

In recent years, there have been increasing demands for high power, low fuel consumption with additional demands for being maintenance-free in diesel engines for land use as well as piston-cylinder type engines for marine use and for electric generators, which in turn require engine oils with high performance and long service life. In particular, the func-
15 tions of deterging the peripheral portions of the piston and frictional portions thereof serve to keep various functions of the oil properly, thereby leading to a long service life of the oil.

In the diesel engines, however, each of the requirements mentioned above has not been yet met under the current circumstances as the deterging function of the oil is lowered by the influence of a combustion gas.

In other words, in the engines for marine use and for electric generators, low-graded fuels containing large amounts of distillation residues of petroleum have been used to reduce costs. Since the low-graded fuels contain large amounts of sulfur compounds, a large amount of sulfur oxides are contained in the combustion gas, and such fuels may further contain nitrogen oxides therein.

These sulfur oxides and nitrogen oxides form dew inside the engines of sulfuric acid and nitric acid, whereby formation of staining components (sludges) in an oil is accelerated, and the staining components are agglomerated and
25 adhered in the engines. In other words, when sulfuric acid or nitric acid is contaminated in the engine oil, the degradation of the oils is accelerated and at the same time agglomeration of unburned combustibles (soots) takes places, and further corrosion increases, thereby accumulating the staining components on such parts as piston grooves, bearing, and the like. As a result, damages may be caused at such energy-transmission parts as piston ring, bearing frictional parts, and the like, thereby causing serious troubles.

In addition, in the diesel engines for land use, owing to the exhaust gas regulation of the recent years, the EGR (Exhaust Gas Recirculation) has begun to be adopted. Therefore, the inside of the engines is more likely to be affected by the combustion gas, so that oxidative degradation of the oil under the combustion gas atmosphere described above is likely to proceed, thereby accelerating the accumulation of the sludges formed on the piston grooves or bearing parts.

In other words, it has been confirmed to the present date that since these acidic substances are included in the
35 lubricating oil, the degradation of the lubricating oil is accelerated, thereby drastically lowering each of functions of the lubricating oil. Therefore, more frequent exchanges and replenishment of the lubricating oils are actually necessary in the present circumstances. In particular, the functions of the lubricating oil lowered by the contamination of the acidic substances are the functions of deterging an internal part of the engine, whereby stains comprising a mixture of degraded products of lubricating oils, combustible products, abrasion powder, and the like accumulate in the peripheral
40 portions of the pistons and cylinder liners, which leads to more serious abrasion in sliding portions of the pistons. As a result, a normal compression ratio cannot be actually obtained, thereby affecting shipping operation and land traveling.

Conventionally, additives so-called "metal-based detergents" have been used against the formation of such acidic substances, whereby the metal-based detergents neutralize the acidic substances formed in the engines, thereby acting as a means for decreasing oxidative degradation of the lubricating oil (Sekiyu Gakkai Shi, Vol. 35, No. 1, 1992,
45 "Development of Overbased Phenate Sulfide and Sulfide-type Salicylate").

Specifically, as detailed below, the metal-based detergents refer to carboxylates, sulfonates, phenolates, or carbonates of alkaline earth metals, such as calcium, magnesium, and the like, each of which is dissolved or dispersed in the form of salts to neutralize the acidic substances mixed therein.

However, since the metal-based detergent contains metal components, such as calcium, and the like, its ash component is high, so that the problem of accumulating residual products takes place in a high-temperature region of the combustion chamber as well as on the wall portion on the side of the piston. In addition, sulfates (including calcium sulfate, and the like) and nitrates (including calcium nitrate, and the like) formed from the metal-based detergents and acidic substances absorb water and adhere onto the piston ring, piston grooves, and other peripheral parts of the piston. These water-absorbed sulfates, nitrates, and the like are likely to act to agglomerate soots, which are unburned
55 combustibles under high-temperature conditions (150° to 300°C), thereby posing such problems of easily forming soot stains.

In lubricating oil compositions for diesel engines, there may be some cases where a reaction product formed between a long-chain alkyl-substituted succinic acid and a polyalkylene-polyamine, or derivatives thereof, as disclosed

in Japanese Patent Laid-Open Nos. 52-102892 and 61-257968, is used (or added) as an ashless dispersant.

The ashless dispersants mentioned above excel in their effects of dispersing non-water containing inorganic substances. However, in the present circumstances, the effects of dispersing water-absorbed inorganic substances (particularly those containing water formed during combustion) are extremely poor.

For the above reasons, in the current circumstances, lubricating oil additives for diesel engines and lubricating oil compositions for diesel engines which can sufficiently show satisfactory performances even in the hostile environments of the internal engines owing to "use of low-graded fuels" and "exhaust gas regulation" have not yet been obtained.

DISCLOSURE OF INVENTION

Accordingly, objects of the present invention are to provide a lubricating oil additive for diesel engines for improving detergency of a lubricating oil for diesel engines for land use and marine use and for lengthening the service life of the lubricating oil, and to provide a lubricating oil composition containing the same.

Under the above circumstances, as a result of conducting intense studies on the stain-formation in the peripheral portions of the pistons and cylinder liner portions owing to the degradation of the lubricating oils for diesel engines and inclusion of the acidic substances, the present inventors have found that soot-like stains in the peripheral portions of the pistons are formed by water absorption of inorganic salts, such as calcium sulfate, and the like. Further, they have found that when a substituted-aminocarboxylic acid compound is added to a lubricating oil, the substituted-aminocarboxylic acid compound being obtainable by treating an aminocarboxylic acid with an active derivative of a hydrocarbon group, the dispersion function of the water-containing calcium sulfate included in the lubricating oil is dramatically improved, so that the dispersion function in oil of the stain components, such as soots and sludges, mentioned above inherently owned by the lubricating oil is enhanced. Therefore, its detergency can be dramatically improved, thereby making it possible not only to make the concentration low in the amount of the metal-based detergent but also to lengthen the service life of the lubricating oil. The present inventors have conducted further studies and thus completed the present invention.

Specifically, the gist of the present invention pertains to the following:

(1) A lubricating oil additive for diesel engines comprising one or more members of carboxylic acids, metal salts of carboxylic acids, amine salts of carboxylic acids, and carboxylic acid amides, each having a substituted amino group or substituted amino groups in a molecule (hereinafter simply referred to as "substituted aminocarboxylic acid compounds"), wherein the substituted aminocarboxylic acid compounds have a function of dispersing water-containing calcium sulfate in an oil;

(2) The lubricating oil additive for diesel engines described in item (1) above, wherein the substituted aminocarboxylic acid compounds have an amino group substituted by a hydrocarbon group or hydrocarbon groups each having 1 to 30 carbon atoms;

(3) The lubricating oil additive for diesel engines described in item (1) or item (2) above, wherein the substituted aminocarboxylic acid compounds have primary or secondary amino groups, each of which is substituted by carboxylic acids, metal salts of carboxylic acids, amine salts of carboxylic acids, or carboxylic acid amides;

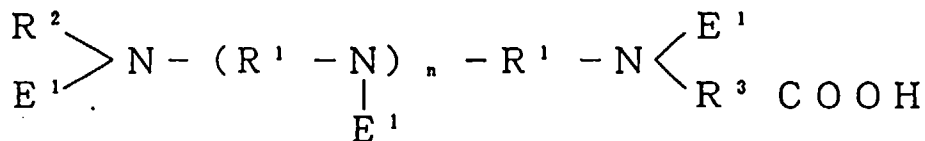
(4) The lubricating oil additive for diesel engines described in any one of items (1) to (3) above, wherein the metal salts of the substituted aminocarboxylic acid compounds are alkali metal salts or alkaline earth metal salts;

(5) The lubricating oil additive for diesel engines described in any one of items (1) to (3) above, wherein the amine salts of the substituted aminocarboxylic acid compounds are carboxylates of primary, secondary or tertiary amines each having 1 to 6 carbon atoms;

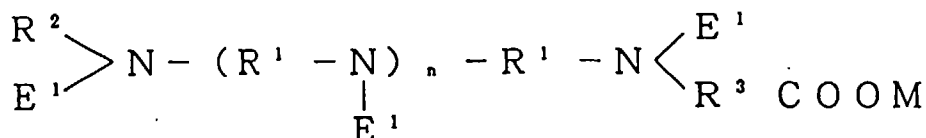
(6) The lubricating oil additive for diesel engines described in any one of items (1) to (3) above, wherein the amides of the substituted aminocarboxylic acid compounds are unsubstituted amides or substituted amides of which one or two hydrogen atoms are substituted by an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group;

(7) The lubricating oil additive for diesel engines described in any one of items (1) to (3) above, wherein the substituted aminocarboxylic acid compounds are represented by the general formula (I):

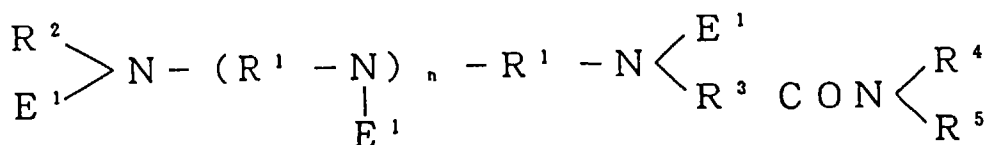
(Acid form)



(Salt form)



(Amide form)



(I)

wherein R^1 represents an alkylene group having 2 to 4 carbon atoms; R^2 represents an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, or an aralkyl group having 7 to 30 carbon atoms; R^3 represents a linear or branched alkylene group having 1 to 5 carbon atoms, a linear or branched alkenylene group having 2 to 5 carbon atoms, or phenylene group; R^4 and R^5 , which may be identical or different, each represents hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group; E^1 represents hydrogen atom, R^2 , $-R^3COOH$, $-R^3COOM$, or $-R^3CONR^4R^5$; n is an integer of 0 to 4; and M represents an alkali metal, an alkaline earth metal, or a primary, secondary, or tertiary ammonium having an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group, with the proviso that a total number of carbon atoms in R^2 in a molecule is 10 to 210;

(8) A lubricating oil composition for diesel engines, wherein 0.05 to 10% by weight of the lubricating oil additives for diesel engines as defined in any one of items (1) to (7) above is added;

(9) The lubricating oil composition for diesel engines described in item (8) above, further containing a metallic detergent;

(10) A lubricating oil composition for diesel engines characterized in that 0.05 to 10% by weight of one or more members of the lubricating oil additives for diesel engines as defined in any one of items (1) to (7) above, 0.5 to 50% by weight of a metallic detergent, 0.1 to 10% by weight of an ashless dispersant, and 0.01 to 5% by weight of an extreme-pressure lubricant are added to a base oil;

(11) A method for dispersing water-containing calcium sulfate in an oil, comprising adding the additives as defined in any one of items (1) to (7) above to a lubricating oil for diesel engines; and

(12) Use of the additives as defined in any one of items (1) to (7) above for dispersing water-containing calcium sulfate in a lubricating oil for diesel engines.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view showing a hot tube tester used in Example 2.

Figure 2 is a view showing piston landing portions, which are sites for evaluation of detergency used in Example 3.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in detail below.

The lubricating oil additive for diesel engines of the present invention comprises one or more members of carboxylic acids, metal salts of carboxylic acids, amine salts of carboxylic acids, and carboxylic acid amides, each having a substituted amino group or substituted amino groups in a molecule, wherein the substituted aminocarboxylic acid compounds have a function of dispersing water-containing calcium sulfate in an oil. These substituted aminocarboxylic acid compounds are obtainable by reacting amino group of an aminocarboxylic acid with an active derivative of a hydrocarbon group.

Here, the substituted amino group means an amino group whose one or two hydrogen atoms are substituted by a hydrocarbon group having 1 to 30 carbon atoms. In particular, the hydrocarbon groups are a linear or branched alkyl group having 1 to 30 carbon atoms, a linear or branched alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, or a linear or branched aralkyl group having 7 to 30 carbon atoms. When two hydrogen atoms are substituted, these substituents may be identical or different. Also, an unsubstituted amino group may be also be included in a molecule.

The carboxylic acid residual groups are an alkyl group having 1 to 22 carbon atoms, an alkenyl group having 2 to 22 carbon atoms, an aryl group having 6 to 22 carbon atoms, or an aralkyl group having 7 to 22 carbon atoms, each of which may contain each of the elements of O, S, N, amide group, carboxyl group, an N-substituted polyalkylene-polyamine, or the like.

The metal salts of the substituted aminocarboxylic acid compounds include salts of alkali metal ions, such as Na ions, K ions, Li ions, and the like, or salts of alkaline earth metal ions, such as Ca ions, Mg ions, Ba ions, and the like.

The amine salts of the substituted aminocarboxylic acid compounds may be salts of any of primary, secondary, or tertiary amines. The substituents for these amines include an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group.

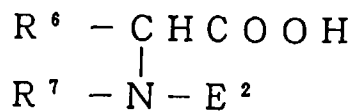
The amides of the substituted aminocarboxylic acid compounds include unsubstituted amides ($-RCONH_2$), or amides substituted by an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group.

The aminocarboxylic acid compounds usable in the lubricating oil additive for diesel engines of the present invention, and the like will be explained concretely hereinbelow.

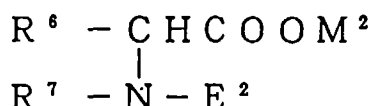
(1) Substituted aminocarboxylic acid compounds each having a substituted amino group at α -position of carboxylic acids

Examples of the substituted aminocarboxylic acids include those represented by the general formula (II):

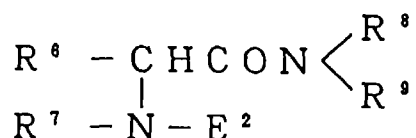
(Acid form)



(Salt form)



(Amide form)



(II)

In the formula, R^6 represents hydrogen atom, or represents a linear or branched alkyl group having 1 to 21 carbon atoms, a linear or branched alkenyl group having 2 to 21 carbon atoms, an aryl group having 6 to 21 carbon atoms, or a linear or branched aralkyl group having 7 to 21 carbon atoms, each of which may have O atom, S atom, or N atom, amide group, or carboxyl group. Concrete examples of the linear or branched alkyl groups include methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, nonadecyl group, eicosyl group, heneicosyl group, 2-methylpropyl group, 1-methylbutyl group, 1-ethylbutyl group, 2-ethylhexyl group, 1-methyloctyl group, 10-methylundecyl group, 8-methylheptadecyl group, 1-methylhexyl group, 3,5,5-trimethylhexyl group, 2-heptylundecyl group, isodecyl group, isotridecyl group, and the like.

Concrete examples of the linear or branched alkenyl groups include vinyl group, 1-propenyl group, 2-propenyl group, 1-butenyl group, 1-hexenyl group, 1-octenyl group, 1-decenyl group, 1-dodecenyl group, 1-tetradecenyl group, 1-hexadecenyl group, 9-octadecenyl group, 1-eicosenyl group, 1-methylvinyl group, 2-methyl-1-propenyl group, 1-methyl-1-propenyl group, 1-methyl-1-butenyl group, 1-ethyl-1-butenyl group, and the like.

Concrete examples of the aryl groups include phenyl group, methylphenyl group, ethylphenyl group, propylphenyl group, butylphenyl group, pentylphenyl group, hexylphenyl group, heptylphenyl group, octylphenyl group, nonylphenyl group, decylphenyl group, isodecylphenyl group, dodecylphenyl group, tridecylphenyl group, tetradecylphenyl group, isotridecylphenyl group, di(methyl)phenyl group, di(ethyl)phenyl group, di(butyl)phenyl group, di(pentyl)phenyl group, di(hexyl)phenyl group, tri(methyl)phenyl group, tri(ethyl)phenyl group, tri(propyl)phenyl group, tri(butyl)phenyl group, naphthyl group, and the like.

Concrete examples of the aralkyl groups include 1-phenylethyl group, 2-phenylethyl group, 3-phenylpropyl group, 4-phenylbutyl group, 6-phenylhexyl group, 10-phenyldecyl group, 14-phenyltetradecyl group, 2-phenylpropyl group, 3-phenylhexyl group, 2-phenyloctyl group, and the like.

Concrete examples of the groups having carboxyl group include carboxymethyl group, 1-carboxyethyl group, 2-carboxyethyl group, 3-carboxypropyl group, 10-carboxydecyl group, and the like.

Concrete examples of the groups having amide group include N-ethylaminocarbonylmethyl group, 2-(N-butylaminocarbonyl)ethyl group, 3-(N,N-dimethylaminocarbonyl)propyl group, and the like.

Concrete examples of the groups having O atom, S atom, and N atom include ethoxymethyl group, 2-(ethoxy)ethyl group, 2-(butyloxy)propyl group, 2-(dodecyloxy)ethyl group, 2-(octadecyloxy)propyl group, 3-(ethyloxy)propyl group, 2-ethoxyethoxymethyl group, 2-ethoxypropoxymethyl group, 2-(2'-ethoxyethoxy)ethoxymethyl group, mercaptomethyl group, 2-mercaptoethyl group, 3-mercaptopropyl group, propylthiomethyl group, 2-(butylthio)ethyl group, 3-(pentylthio)propyl group, 2-aminoethyl group, 2-N,N-dimethylaminoethyl group, 3-N-methylaminopropyl group, and the like.

R^7 represents a linear or branched alkyl group having 1 to 30 carbon atoms, a linear or branched alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, or a linear or branched aralkyl group having 7 to 30 carbon atoms. Concrete examples of the linear or branched alkyl groups include those alkyl groups listed under R^6 , docosyl group, tricosyl group, tetracosyl group, triacontyl group, 1-methylheneicosyl group, 1-methyltetracosyl group, 1-methyloctacosyl group, and the like.

Concrete examples of the linear or branched alkenyl groups include those alkenyl groups listed under R^6 , 13-docosenyl group, 1-methyldocosyl group, 1-methyloctadecenyl group, and the like.

Concrete examples of the aryl groups include those aryl groups listed under R^6 , and octadecylphenyl group, eicosylphenyl group, tetracosylphenyl group, di(octyl)phenyl group, di(nonyl)phenyl group, di(dodecyl)phenyl group, tri(hexyl)phenyl group, tri(octyl)phenyl group, and the like.

Concrete examples of the aralkyl groups include those aralkyl groups listed under R^6 , 2-phenyldodecenyl group, 2-phenyloctadecenyl group, and the like.

Concrete examples of the mercaptoalkylene groups include 1-mercaptoethylene group, 2-mercaptopropylene group, 2-methylthiotrimethylene group, and the like.

Concrete examples of the aminoalkylene groups include 2-aminopropylene group, 2-N-ethylaminotrimethylene group, 2-N,N-dimethyltrimethylene group, and the like.

R^8 and R^9 may be identical or different, and each represents hydrogen atom, an alkyl group having 1 to 6 carbon atoms, more preferably 2 to 4 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group. The amides represented by $-NR^8R^9$ may be $-NH_2$, but a greater preference is given to those having such substituents as an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group at N-position. Concrete examples of the alkyl groups and the alkenyl groups include those alkyl groups or alkenyl groups listed under R^6 having up to 6 carbon atoms.

E^2 represents hydrogen atom or as defined in R^7 . M^2 represents an alkali metal ion or an alkaline earth metal ion, or primary, secondary, or tertiary ammonium. The suitable metal ions include Na ions, K ions, Ca ions, and Mg ions. Also, the ammoniums include those ammoniums having an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group. Concrete examples of the alkyl groups and the alkenyl groups include those alkyl groups or alkenyl groups each being listed under R^6 having up to 6 carbon atoms.

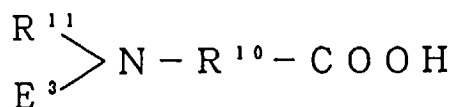
In order to secure the solubility to oils, it is desired that the total number of carbon atoms of $R^6 + R^7 + E^2$ is preferably from 10 to 60, more preferably from 10 to 40, still more preferably from 12 to 30.

Concrete examples of the compounds represented by the general formula (II) include acid forms, such as N,N-didecylaminoacetic acid, N-octadecenylaminoacetic acid, N-nonylphenylaminoacetic acid, 2-N-octadecenylaminohexanoic acid, 2-N-octylaminodecanoic acid, 2-N-(1'-methylheptadecyl)aminododecanoic acid, 2-N-octadecylaminosuccinic acid, 2-N,N-diethylaminosuccinic acid, and the like, alkali metal salt forms thereof, alkaline earth metal salt forms thereof, amine salt forms thereof, and amide forms thereof.

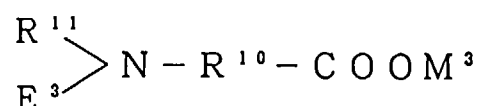
(2) Substituted aminocarboxylic acid compounds each having substituted amino group at ω -position of carboxylic acids

Examples of the substituted aminocarboxylic acids include those represented by the general formula (III):

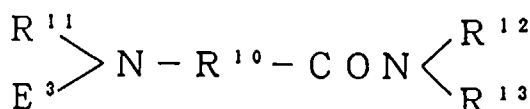
(Acid form)



(Salt form)



(Amide form)



(III)

In the formula, R^{10} represents a linear or branched, alkylene group, alkenylene group, or aralkylene group having 1 to 21 carbon atoms, and each of the groups may have O atom, S atom, N atom, amide group, or carboxyl group.

Concrete examples of the linear or branched alkylene groups include methylene group, ethylene group, propylene group, trimethylene group, butylene group, 1,2-dimethylethylene group, 1,1-dimethylethylene group, 2,2-dimethylethylene group, tetraethylene group, pentylene group, pentamethylene group, hexylene group, hexamethylene group, octylene group, octamethylene group, decylene group, decamethylene group, dodecylene group, dodecamethylene group, tetradecylene group, tetradecamethylene group, hexadecylene group, hexadecamethylene group, octadecylene group, octadecamethylene group, and the like.

Concrete examples of the linear or branched alkenylene groups include vinylene group, 1-propenylene group, 2-propenylene group, 1-ethylvinylene group, 2-ethylvinylene group, 1,1-dimethylvinylene group, 1,2-dimethylvinylene group, 2,2-dimethylvinylene group, 1-hexenylene group, 1-decenylene group, 1-dodecenylene group, 1-hexadecenylene group, 1-octadecenylene group, 1-eicosenylene group, and the like.

Concrete examples of the arylene groups include phenylene group, methylphenylene group, ethylphenylene group, propylphenylene group, butylphenylene group, pentylphenylene group, hexylphenylene group, heptylphenylene group, octylphenylene group, nonylphenylene group, decylphenylene group, isodecylphenylene group, dodecylphenylene group, tridecylphenylene group, tetradecylphenylene group, isotridecylphenylene group, di(methyl)phenylene group, di(ethyl)phenylene group, di(butyl)phenylene group, di(pentyl)phenylene group, di(hexyl)phenylene group, tri(methyl)phenylene group, tri(ethyl)phenylene group, tri(propyl)phenylene group, tri(butyl)phenylene group, naphthylene group, and the like.

Concrete examples of the aralkylene groups include 1-phenylethylene group, 1-phenylmethylethylene group, 1-naphthylethylene group, 2-naphthylethylene group, 2-phenylethylene group, and the like.

Concrete examples of the groups each having carboxyl groups include 2-carboxytrimethylene group, 2-carboxyte-

tramethylene group, and the like.

Concrete examples of the groups each having amide group include aminocarbonylmethylene group, N,N-dimethylaminocarbonylmethylene group, 2-N-ethylaminocarbonylmethylene group, and the like.

Concrete examples of the groups each having O atom, S atom, or N atom include 2-oxatetramethylene group, 2-oxa-4-methyltetramethylene group, and the like.

R¹¹ represents a linear or branched alkyl group having 1 to 30 carbon atoms, a linear or branched alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, or a linear or branched aralkyl group having 7 to 30 carbon atoms. Concrete examples of R¹¹ include those listed under R⁷.

R¹² and R¹³ may be identical or different, and each represents hydrogen atom, or an alkyl group having 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group. The amides represented by -NR¹²R¹³ may be -NH₂, but it is more preferred that the amides have an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group at N-position. Concrete examples of R¹² and R¹³ include those listed under R⁶ and R⁹.

E³ represents hydrogen atom or as defined in R¹¹ above.

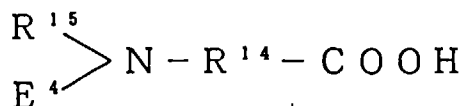
M³ represents an alkali metal ion, an alkaline earth metal ion, or a primary, secondary, or tertiary ammonium ion. The suitable metal ions include Na ions, K ions, Ca ions, or Mg ions. In addition, the ammonium ions may have an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group, each of which may have hydroxyl group or hydroxyl groups. Concrete examples of the substituents include those listed under M².

In order to secure the solubility to oils, it is desired that the total number of carbon atoms of R¹⁰ + R¹¹ + E³ is preferably from 10 to 60, more preferably from 10 to 40, still more preferably from 12 to 30.

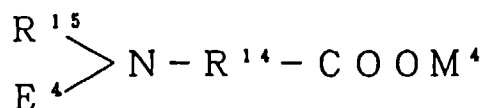
Concrete examples of the compound represented by the general formula (III) include acid forms, such as 5-(N,N-dioctylamino)pentanoic acid, 5-(N-octadecenylamino)pentanoic acid, p-N-dodecylaminobenzoic acid, 3-(p-N-decylaminophenyl)propionic acid, 3-(3'-N,N-dipropylaminopropoxy)propionic acid, 3-(3'-N-octadecylaminopropylthio)propionic acid, and the like, alkali metal salt forms thereof, alkaline earth metal salt forms thereof, amine salt forms thereof, and amide forms thereof.

(3) The substituted aminocarboxylic acids represented by the general formula (IV):

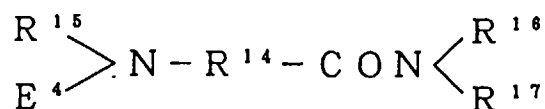
(Acid form)



(Salt form)



(Amide form)



(IV)

are suitably used for the lubricating oil additives for diesel engines of the present invention.

In the formula, R^{14} represents a linear or branched alkylene group having 1 to 5 carbon atoms. Concrete examples thereof include those alkylene groups listed under R^{10} having 1 to 5 carbon atoms.

R^{15} represents an alkyl group having 10 to 22 carbon atoms, an alkenyl group having 10 to 22 carbon atoms, an aryl group having 6 to 22 carbon atoms, or an aralkyl group having 10 to 22 carbon atoms. Concrete examples of R^{15} include those listed under R^7 having 10 to 22 carbon atoms.

R^{16} and R^{17} each represents hydrogen atom, or an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group. The amides represented by $-\text{NR}^{14}\text{R}^{15}$ may be $-\text{NH}_2$, but it is more preferred that the amides have an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group at N-position. Concrete examples of R^{16} and R^{17} include those listed under R^8 and R^9 .

E^4 represents hydrogen atom or $-\text{R}^{14}\text{-COOH}$ in a case where the compound represented by the general formula (IV) takes an acid form, or $-\text{R}^{14}\text{-COOM}^4$ in a case where the compound takes a salt form, or $-\text{CON}(\text{R}^{16})\text{R}^{17}$ in a case where the compound takes an amide form.

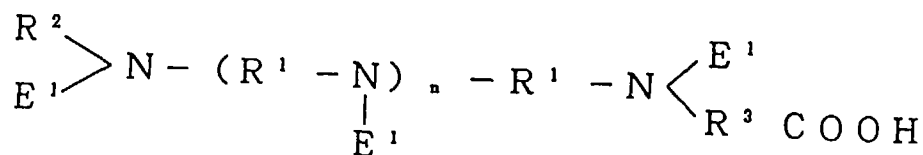
M^4 represents an alkali metal ion, an alkaline earth metal ion, or a primary, secondary, or tertiary ammonium ion. The suitable metal ions include Na ions, K ions, Ca ions, and Mg ions. In addition, the ammoniums may have an alkyl group or an alkenyl group each having 1 to 6 carbon atoms, or phenyl group. Concrete examples of the M^4 include those listed under M^2 .

In order to secure the solubility to oils, the total number of carbon atoms of $\text{R}^{14} + \text{R}^{15} + \text{E}^4$ is preferably from 12 to 32, more preferably from 12 to 24.

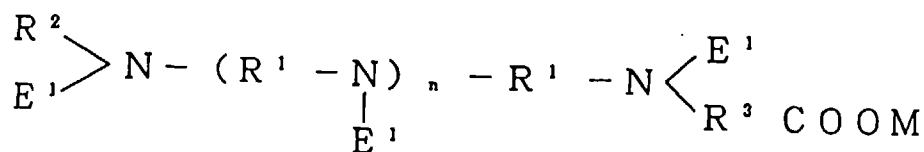
Concrete examples of the compound represented by the general formula (IV) include acid forms, such as N-dodecyl-2,2'-aminoacetic acid, N-nonylphenyl-2,2'-aminodiacetic acid, N-decyl-3,3'-aminodipropionic acid, N-octadecenyl-3,3'-aminodipropionic acid, N-butylphenyl-3,3'-amino-di(2-methylpropionic acid), and the like, alkali metal salt forms thereof, alkaline earth metal salt forms thereof, amine salt forms thereof, and amide forms thereof.

(4) The substituted aminocarboxylic acids represented by the general formula (I):

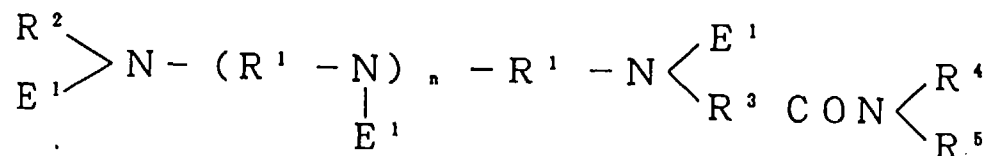
(Acid form)



(Salt form)



(Amide form)



(I)

are suitably used for the lubricating oil additives for diesel engines of the present invention.

In the formula, R^1 represents an alkylene group having 2 to 4 carbon atoms. Concrete examples thereof include ethylene group, trimethylene group, tetramethylene group, and the like.

n is from 0 to 4. When n exceeds 4, the resulting compound becomes viscous, so that its handleability becomes poor.

R^2 represents an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, or an aralkyl group having 7 to 30 carbon atoms. Concrete examples of R^2 include those listed under R^7 .

R^3 represents a linear or branched alkylene group having 1 to 5 carbon atoms, a linear or branched alkenylene group having 2 to 5 carbon atoms, or phenylene group. Concrete examples of R^3 include those listed under R^{10} having up to 5 carbon atoms.

R^4 and R^5 may be identical or different, and each represents hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group. Concrete examples of R^4 and R^5 include those listed under R^8 and R^9 .

E^1 represents hydrogen atom, R^2 , or $-R^3COOH$ in a case where the compound takes an acid form; or E^1 represents hydrogen atom, R^2 , or $-R^3COOM^1$ group in a case where the compound takes a salt form; or E^1 represents hydrogen atom, R^2 , or $-R^3CONR^4R^5$ in a case where the compound takes an amide form.

M^1 represents an alkali metal ion, an alkaline earth metal ion, or a primary, secondary, or tertiary ammonium. These ammoniums may have an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group. Concrete examples of M^1 include those listed under M^2 . The total number of carbon atoms of all R^2 's

in a molecule is from 10 to 150, preferably from 10 to 100, more preferably from 10 to 80. When the total number of carbon atoms is less than 10, the solubility to oils becomes poor.

Concrete examples of the compound represented by the general formula (I) include acid forms, such as 3-[2'-(N-decylamino)ethylamino]propionic acid, 3-(3'-N-oleylamino)propylamino]-2-methylpropionic acid, 2-(N,N-dioc-
 tylamino)ethylaminoacetic acid, N,N'-dihexylethylenediamine diacetic acid, N-octadecylpropylenediamine triacetic acid, N,N'-diolelpropylenediamine tripropionic acid, N,N'-di-2-ethylhexylethylenediamine di(2-methylpropionic acid), and the like, alkali metal salt forms thereof, alkaline earth metal salt forms thereof, amine salt forms thereof, and amide forms thereof.

The substituted aminocarboxylic acid compounds usable in the present invention can be prepared by the following methods.

(1) The substituted aminocarboxylic acids represented by the general formula (II) or (III) can be synthesized by a reaction comprising treating a known aminocarboxylic acid with a hydrocarbon group.

The means for treating an amino group of the known aminocarboxylic acids are not particularly limited, and it is convenient to use chlorinated hydrocarbons as active derivatives of the hydrocarbon groups.

In the case where an aminocarboxylic acid is in a solid form, it may be previously dissolved in a small amount of a chlorinated hydrocarbon prior to reaction, or it may be dissolved in such solvents as paraffinic hydrocarbons, aromatic hydrocarbons, alcohols, and the like prior to reaction. In a case where an aminocarboxylic acid is in a liquid form or has a low melting point, it may be used in reaction without dilution. However, in a case where the reactivity is vigorous, it may be preferably diluted with a solvent.

A chlorinated hydrocarbon is added dropwise to the aminocarboxylic acid prepared by the method described above at a temperature of 50° to 200°C. The temperature of the dropwise addition differs depending upon the kinds of the chlorinated hydrocarbons used. Smaller the number of carbon atoms of the chlorinated hydrocarbons, higher the reactivity, so that the dropwise addition may be carried out at a low temperature. Therefore, in the case of treating with those chlorinated hydrocarbons having a relatively large number of carbon atoms, the reaction has to be carried out at a high temperature. For instance, in a case of treating with a chlorinated hydrocarbon having a number of carbon atoms of about 10, the dropwise addition may be carried at a temperature of around 100°C, and thereafter, the temperature is raised to a temperature of about 130°C to carry out reaction and allow maturation. In a case of treating with a chlorinated hydrocarbon having a number of carbon atoms of less than 10, the dropwise addition is carried at a temperature of 100°C or less, and in a case of treating with a chlorinated hydrocarbon having a number of carbon atoms of exceeding 10, the dropwise addition is carried at a temperature higher than 100°C. The reaction time is usually from 10 to 18 hours from initiation of the dropwise addition.

In the reaction mixture, aside from the desired product, unreacted chlorinated hydrocarbons and hydrogen chloride are co-present therein. Therefore, in order to isolate the desired product, the reaction mixture is neutralized with sodium hydroxide, and then washed with water, and thereafter, the unreacted product is distilled off under reduced pressure. In a case where washing with water is difficult, a concentrated aqueous sodium hydroxide is added dropwise to the neutralized mixture to form a sodium salt again with the reaction product. Subsequently, a cationic exchange resin, water and an organic solvent are added to the formed salt, and the resulting mixture was stirred and mixed, to convert the sodium salt into an acid form. Thereafter, the organic solvent is collected. The collected organic solvent is removed under reduced pressure of 5 to 10 Torr at a temperature of 80° to 200°C, to give a hydrocarbon-substituted aminocarboxylic acid usable in the present invention.

In this reaction, smaller the number of carbon atoms of the chlorinated hydrocarbon used, higher the reactivity. For instance, when the chlorinated hydrocarbon having a small number of carbon atoms is used in excess amounts, a mixture of a mono-substituted product and a di-substituted product is produced, wherein hydrogen atom or hydrogen atoms of an amino group is substituted with a chlorinated hydrocarbon or chlorinated hydrocarbons.

The metal salts or the amine salts can be prepared by, for instance, adding NaOH, Ca(OH)₂ or an amine to the resulting product in an acid form, and stirring the mixture at a temperature of from room temperature to 80°C for about one hour (salt-formation reaction). In the case of the metal salts, the salts are formed while dissolving NaOH or Ca(OH)₂.

The amide form is prepared by dissolving primary amine or secondary amine in a product in an acid form, and stirring the resulting mixture for one hour at a temperature of 80° to 150°C under, as occasion demands, reduced pressure (5 to 10 mm Hg). By the above reaction, a carboxylic acid and an amine undergo dehydration condensation, to give a carboxamide.

In the cases where handleability is difficult as in the case where the compound is a solid, the compound may be dissolved in an organic solvent, such as hydrocarbons, and the like, and then the mixture undergoes salt-formation reaction or amide-formation reaction.

(2) The substituted aminocarboxylic acids represented by the general formula (IV) can be synthesized by a reaction comprising treating a carboxylic acid with a primary amine or secondary amine.

The above reaction may be carried out by the reaction between a primary amine or secondary amine and a polymerizable compound having a double bond or double bonds. Concrete examples of the polymerizable compounds having a double bond or double bonds include methacrylic acid ester, acrylic acid ester, methacrylic acid amide, and the like.

Specifically, while stirring under a nitrogen gas stream, methacrylic acid ester or acrylic acid ester is added dropwise at a temperature of from 60° to 100°C to a primary amine or secondary amine. The dropping speed is not limited, and the dropwise addition is carried out over a period of about two to three hours so as not to cause heat generation. After the dropwise addition is terminated, the reaction mixture is kept at the same temperature for 5 to 15 hours to carry out reaction and allow maturation of the reaction mixture.

After the reaction is terminated, the mixture is cooled to a temperature of not more than 40°C, and about 48%-sodium hydroxide is added dropwise thereto. After the dropwise addition is terminated, the mixture is saponified at 80°C for about two hours. The saponified mixture is dehydrated under reduced pressure (about 5 mm Hg) at 150°C, to give a desired sodium salt product.

In order to convert the salt product into an acid form, concentrated hydrochloric acid is added to the resulting aqueous sodium salt solution. The mixture is extracted with an organic solvent and washed with water, and then the solvent is removed by topping treatment. Alternatively, the sodium salt is dissolved in water and an organic solvent, and then the resulting mixture is mixed and stirred together with a cationic exchange resin, to thereby give an acid form. Subsequently, the solvent layer is collected and dried, and then the solvent is distilled off.

The amide form may be prepared in the same manner as the method described in (1) above.

(3) The substituted aminocarboxylic acid compounds represented by the general formula (I) can be synthesized by a reaction comprising treating an alkylenediamine derivative with a polymerizable carboxylic acid having a double bond or double bonds and a chlorinated hydrocarbon or chlorinated hydrocarbons, or by treating an alkylenediamine derivative with a monochlorocarboxylic acid and a chlorinated hydrocarbon and chlorinated hydrocarbons.

For instance, carboxylic acid compounds of alkylenediamines, alkyl-substituted alkylenediamines, polyalkylene-polyamines, or alkyl-substituted polyalkylene-polyamines may be prepared by adding dropwise a chlorinated hydrocarbon and a polymerizable carboxylic acid having a double bond or double bonds to an alkylenediamine, an alkyl-substituted alkylenediamine, a polyalkylene-polyamine, or an alkyl-substituted polyalkylene-polyamine, or by adding dropwise a chlorinated hydrocarbon and a monochlorocarboxylic acid to the above alkylenediamine derivatives, to carry out reaction with the above amines by substituting hydrogen atom or hydrogen atoms of an amino group with carboxyl group or carboxyl groups or an alkyl group or alkyl groups.

The preparation conditions are as follows. In the case where an alkylenediamine derivative is treated with a chlorinated hydrocarbon, the preparation conditions are substantially the same as those described in (1). In the case where an alkylenediamine derivative is treated with a polymerizable carboxylic acid having a double bond or double bonds, the preparation conditions are substantially the same as those described in (2). In the case where an alkylenediamine derivative is treated with a monochlorocarboxylic acid, a monochlorocarboxylic acid ester (or an alkali metal salt thereof, an alkaline earth metal salt thereof, or an amide thereof) is added dropwise to an alkyl-substituted alkylenediamine heated to a temperature of 50° to 150°C, and then the reaction mixture is stirred for 5 to 18 hours to carry out reaction and allow maturation of the resulting mixture. The dropping speed is such that the dropwise addition is carried out over a period of about three to four hours so as not to cause heat generation. The reaction temperature may be as follows. In the case where the reaction mixture contains a primary amine moiety, the reaction temperature may be from 50° to 120°C, and in the case where the reaction mixture contains a secondary amine moiety alone, the reaction temperature may be from 100° to 150°C. In this reaction, since hydrochloric acid is formed, the reaction is neutralized with NaOH and then subjected to desalting (by the same manner as (1)) and purification. In addition, the reactions (1) to (3) are carried out under an N₂ gas stream (atmosphere).

The starting materials usable in the above preparation methods are as follows.

The aminocarboxylic acids in (1) include aminoacetic acid, aminopentanoic acid, aminocaproic acid, aminocaprylic acid, aminodecanoic acid, aminododecanoic acid, aminoundecanoic acid, aminotetradecanoic acid, aminohexadecanoic acid, aminooctadecanoic acid, aminoeicosanoic acid, aminobenzoic acid, aminophenylacetic acid, aminonicotinic acid, aminonaphthoic acid, aminophenylpropionic acid, aminohippuric acid, aminobutyric acid, alanine, valine, norvaline, leucine, norleucine, isoleucine, methionine, cystine, aspartic acid, glutamic acid, histidine, lysine, arginine, and the like. Here, a preference is given to aminopentanoic acid, aminocaproic acid, aminocaprylic acid, aminodecanoic acid, aminododecanoic acid, aminotetradecanoic acid, aminohexadecanoic acid, aminooctadecanoic acid, aminobenzoic acid, aminophenylacetic acid, and aminophenylpropionic acid, and a greater preference is given to aminocaproic acid, aminocaprylic acid, aminododecanoic acid, aminobenzoic acid, and aminophenylacetic acid.

Concrete examples of the chlorinated hydrocarbons usable in the reactions of (1) and (3) are 1-chlorohexane, 1-chlorooctane, 1-chlorododecane, 1-chlorooctadecane, 1-chloro-2-ethylhexane, 1-chlorooctadecene, 1-chloro-3-phenylpropane, 1-chloro-4-methylbenzene, 1-chloro-2-heptylundecane, 1-chloro-3,5,5-trimethylhexane, and the like. Here, a preference is given to 1-chlorohexane, 1-chlorooctane, 1-chlorododecane, 1-chloro-2-ethylhexane, and 1-chlorooctadecane.

Concrete examples of the primary amines usable in the reaction of (2) are capric amine, laurylamine, myristylamine, palmitylamine, stearylamine, oleylamine, behenylamine, and the like. Among them, laurylamine, myristylamine, palmitylamine, stearylamine, and oleylamine are suitably used.

Concrete examples of the secondary amines usable in the reaction of (2) are dihexylamine, dicaprylamine, dicapric amine, dilaurylamine, dimyristylamine, dipalmitylamine, distearylamine, dioleylamine, dibehenylamine, di-2-ethylhexylamine, dibenzylamine, and the like. A preference is given to dicaprylamine, dicapric amine, dilaurylamine, dimyristylamine, and dioleylamine.

Concrete examples of the alkylenediamines, the alkyl-substituted alkylenediamines, the polyalkylene-polyamines, the alkylalkylenediamines, and the alkyl-substituted polyalkylene-polyamines each usable in the reaction of (3) include ethylenediamine, propylenediamine, butylenediamine, diethylenetriamine, dipropylenetriamine, dibutylenetriamine, triethylenetetramine, tripropylenetetramine, tributylenetetramine, tetraethylenepentamine, tetrapropylenepentamine, tetrabutylenepentamine, pentaethylenhexamine, pentapropylenhexamine, pentabutylenhexamine, stearylethylenediamine, stearylpropylenediamine, stearylbutylenediamine, oleylethylenediamine, oleylpropylenediamine, oleylbutylenediamine, stearyldiethylenetriamine, oleyldiethylenetriamine, and the like. A preference is given to ethylenediamine, propylenediamine, stearylethylenediamine, stearylpropylenediamine, oleylethylenediamine, and oleylpropylenediamine.

The polymerizable carboxylic acids having a double bond or double bonds usable in the reactions of (2) and (3) include derivatives of acrylic acid and methacrylic acid. Concrete examples thereof include acrylic acid amides including carboxamides formed between diethanolamine and acrylic acid or acrylic acid esters, such as methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, and the like; carboxamides formed between acrylic acids and dibutylamine; and carboxamides formed between acrylic acids and dihexylamine; and methacrylic acid amides including carboxamides formed between diethylamine and methacrylic acid or methacrylic acid esters, such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate, and the like; carboxamides formed between methacrylic acids and diethanolamine; carboxamides formed between methacrylic acids and dibutylamine; carboxamides formed between methacrylic acids and dihexylamine, and the like.

The chlorocarboxylic acids usable in the reaction of (3) include esters, alkali metal salts, alkaline earth metal salts, and amides of chloroacetic acid, 3-chloropropionic acid, 4-chlorobutyric acid, 5-chlorovaleric acid, 5-chloropentenoic acid, 3-chloropropenoic acid, and 4-chlorobutenoic acid. Concrete examples thereof include esters of chloroacetic acids, such as methyl chloroacetate, ethyl chloroacetate, hexyl chloroacetate, octyl chloroacetate, and the like; and an amide formed between chloroacetic acid and diethylamine; an amide formed between chloroacetic acid and diethanolamine; an amide formed between chloroacetic acid and dibutylamine; an amide formed between chloroacetic acid and dihexylamine, and the like.

The aminocarboxylic acid compounds of the present invention prepared as described above are effective in the adsorption of inorganic substances by the synergism of amino groups and carboxyl groups, effectively acting to disperse a sludge component (inorganic substances) formed in a long-term use of a lubricating oil. As a means for evaluating the dispersing function of the inorganic substances in oils described above, the dispersibility in oils of a water-containing calcium sulfate is remarked as a means for evaluation in the present invention, of which the conventional ashless dispersant is considered to show poor dispersibility.

The aminocarboxylic acid compounds of the present invention may be added in a range of from 0.05 to 10% by weight to the lubricating oil, to thereby exhibit dispersion effects of the inorganic substances in oils. The preferred range of the added amount is from 0.2 to 3.0% by weight. When the added amount is less than 0.05% by weight, sufficient dispersion effects cannot be achieved, and when the added amount exceeds 10% by weight, it is not economically advantageous.

The aminocarboxylic acid compounds of the present invention may be used alone as a lubricating oil additive. Further, a metallic detergent may be added together therewith, to give a lubricating oil composition for diesel engines of the present invention. The metallic detergents are not particularly limited as long as they are those conventionally used as conventional lubricating oil additives. Concrete examples thereof include neutral salts which are alkaline earth metal salts of organic acids such as petroleum sulfonic acids (hereinafter referred to as "petroleum sulfonate-based metallic detergents"); synthetic sulfonic acids; alkylphenol sulfide polymers (hereinafter referred to as "phenate-based metallic detergents"); alkyl salicylic acids (hereinafter referred to as "salicylate-based metallic detergents," or overbased compounds containing alkaline earth metal carbonates. The amount of the above metallic detergents formulated in the lubricating oil composition for diesel engines of the present invention differs depending upon the fuels used, and in the fuels for vessel use, the amount of the metallic detergents is preferably 5.0 to 10% by weight in the lubricating oil.

The aminocarboxylic acid compounds of the present invention may be formulated together with ashless dispersants and extreme-pressure lubricants to the base oil, to give a lubricating oil composition for diesel engines of the present invention. The above base oils are not particularly limited, and natural mineral oils and synthetic oils, which usually have viscosities of from 20 mm²/s to 250 mm²/s at 40°C, may be usable. Here, the mineral oils refer to paraffinic hydrocarbons, aromatic hydrocarbons, or mixtures thereof. The synthetic oils include poly α -olefins, esters, polyglycols, and the like. The ashless dispersants are not particularly limited, and concrete examples thereof include amides and imides formed between hydrocarbon-substituted carboxylic acids (dicarboxylic acids or monocarboxylic acids) or derivatives thereof and polyethylene-polyamines, the hydrocarbon-substituted carboxylic acids including polyolefin-substituted maleic acids, polybutene-substituted succinic acid derivatives, fatty acids, and the like, and the polyethylene-polyamines including ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and the like. Typical examples of the imides include alkenylsuccinic acid imides having large molecular weights, and the like.

It is preferred that the ashless dispersant is formulated in the lubricating oil composition for diesel engines of the present invention in an amount of 0.1 to 10% by weight. In addition, the extreme-pressure lubricants are not particularly limited, and concrete examples of the extreme-pressure lubricants include zinc dialkyldithiophosphates, zinc alkylphosphates, alkaline earth metal salts of alkyl phosphates, alkyl phosphates, and fatty acids. It is preferred that the extreme-pressure lubricant is formulated in the lubricating oil composition for diesel engines of the present invention in an amount of 0.01 to 5% by weight.

In the lubricating oil composition for diesel engines of the present invention, the following additives may be further added in an amount so as not to impair the effects of the present invention, depending upon areas, conditions and required properties in which the lubricating oil compositions are used: Pour point depressants and viscosity index modifiers, such as polymers of lauryl methacrylate having a molecular weight of from 10,000 to 100,000; antioxidants, such as tert-butyl paracresol; metal deactivators, such as triphenyl phosphite; and dimethyl silicone defoaming agents having a viscosity of 10 to 100,000 mm²/s at 25°C.

The present invention will be further described by means of the working examples and comparative examples, without intending to restrict the scope of the present invention to these working examples, and the like.

Example 1. Dispersion Test (1) of Calcium Sulfate

The dispersion effects of water-absorbed calcium sulfate in oil were studied. The lubricating oil compositions listed in Table 1 (lubricating oil compositions prepared by adjusting to 30 TBN (30 mg/g $\cdot$ KOH) with a metal-based detergent were used as testing oils, and each of the dispersion states of calcium sulfate in oil was observed.

The testing method was as follows. Sulfuric acid which was diluted to a concentration of 60% by water was added to each of the testing oils, and the mixture was stirred for a given period of time. Thereafter, each of the dispersion states of the calcium sulfate formed was observed and evaluated.

Supplemental Description) Calcium sulfate formed by including sulfuric acid in the testing oil has the property of absorbing water, so that sulfuric acid previously diluted with water is used to easily form water-absorbed calcium sulfate (theoretical water content: 3.63 mol per mol of CaSO₄).

(Testing Method)

1) A test tube having an inner diameter of 30 mm was charged with 50 g of each lubricating oil, and sulfuric acid which was previously diluted with water to a concentration of 60% was added in an amount for neutralizing a 9 TBN (9 mg/g $\cdot$ KOH) portion of the testing oil (0.65 g of 60% sulfuric acid in 50 g of 30 TBN testing oil).

2) Next, the test tube was heated to a temperature of 50°C, and the mixture was stirred with an agitator (flat type stirring blade: 120 mm $\times$ 18 mm) for 10 minutes (By stirring for 10 minutes, sulfuric acid is entirely neutralized by the calcium content in the testing oil.).

3) After the stirring was terminated, the mixture was allowed to stand for 30 minutes at a temperature of 50°C. Thereafter, the dispersion state of calcium sulfate was evaluated by gross examination.

(Evaluation Method)

- A: The state in which calcium sulfate was dispersed in oil without being adhered to or precipitated on the vessel wall.
- B: The dispersion state in which a part of calcium sulfate was adhered to or precipitated on the vessel wall.
- C: The state in which equal to or greater than one-half of the calcium sulfate content was adhered to or precipitated on the vessel wall.
- D: The state in which substantially all of calcium sulfate were adhered to or precipitated on the vessel wall.

(Starting Materials to be Formulated)

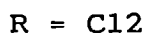
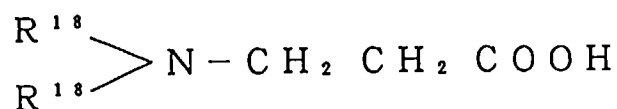
Metallic detergent: A salicylate-based metallic detergent was used (A product, which was a synthesized product having alkaline value of 200 TBN, being used.).
 5 Ashless dispersant: Commercially available alkyl(polybutenyl)succinimide (bis type) was used.
 Extreme-pressure lubricant: Commercially available zinc alkyl(number of carbon atoms of about 8; primary type)dithiophosphate was used.
 Mineral oil: Commercially available natural paraffinic mineral oil (viscosity of 120 cSt at 40°C) was used.

10 The preparation methods of the aminocarboxylic acids of the present invention used in the present test were described in the following section. Incidentally, the structures of the prepared compounds were determined by infrared absorption spectroscopy, molecular weight measurement (GPC), acid value, saponification value, total amine value, partial amine value, and the like.

15 (Preparative Product No. 1)

Reaction Product of Secondary Laurylamine (1 mol) and Acrylic Acid (1 mol)

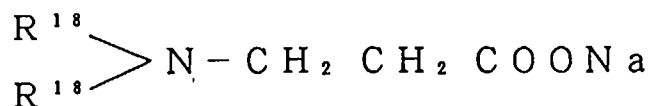
20 The temperature was controlled to 80°C while stirring secondary laurylamine (1 mol) under a nitrogen gas stream. Ethyl acrylate (1 mol) was added dropwise thereto over a period of four hours. After the dropwise addition was terminated, the mixture was reacted and matured for eight hours. Thereafter, the reaction mixture was cooled to a temperature of equal to or lower than 40°C, and a 48%-sodium hydroxide aqueous solution (1 mol) was added dropwise over a period of two hours. After the dropwise addition was terminated, the temperature was raised to 80°C, and the mixture
 25 was saponified for two hours. Five-hundred mL of toluene was added to the resulting mixture, and 1 mol of hydrochloric acid was further added for neutralization. Thereafter, the toluene layer was repeatedly washed with water to a point where the pH of the washing liquid is about neutral. The solvents were distilled off, to give the following compound (N,N-dilauryl-β-aminopropionic acid).



40 (Preparative Product No. 2)

Sodium Salt of Reaction Product of Secondary Laurylamine (1 mol) and Acrylic Acid (1 mol)

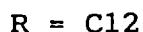
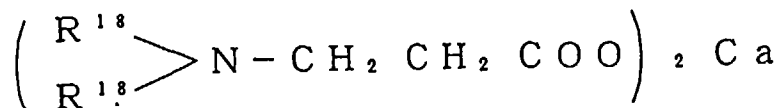
45 Preparative Product No. 1 was used, and sodium hydroxide (amount equivalent to 1 mol) was added thereto, and the mixture was stirred and dissolved at a temperature of 60°C, to give the following compound (sodium N,N-dilauryl-β-aminopropionate).



(Preparative Product No. 3)

Calcium Salt of Reaction Product of Secondary Laurylamine (1 mol) and Acrylic Acid (1 mol)

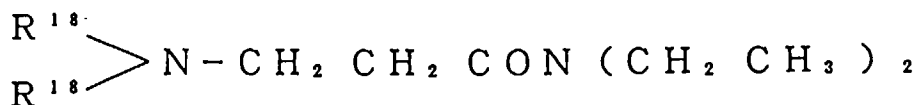
Preparative Product No. 1 was used, and calcium hydroxide (amount equivalent to 0.5 mol) was added thereto, and the mixture was stirred and dissolved at a temperature of 80°C, to give the following compound (calcium N,N-dilauryl-β-aminopropionate).



(Preparative Product No. 4)

Ethylamine Amide of Reaction Product of Secondary Laurylamine (1 mol) and Acrylic Acid (1 mol)

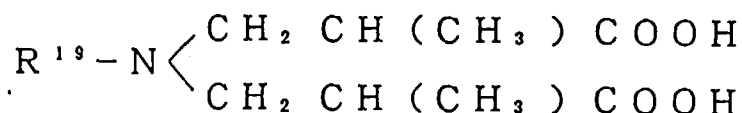
Preparative Product No. 1 was used, and diethanolamine (amount equivalent to 1 mol) was added thereto, and the mixture was stirred at a temperature of 80°C for one hour. Further, the temperature was raised to 120°C to carry out dehydration reaction for three hours, to give the following compound (N',N'-diethylamide of N,N-dilauryl-β-aminopropionic acid).



(Preparative Product No. 5)

Reaction Product of Primary Oleylamine (1 mol) and Methacrylic Acid (2 mol)

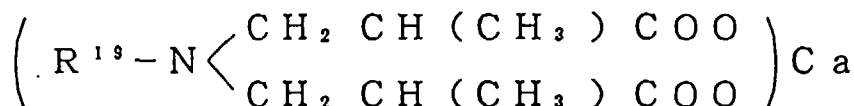
The temperature was controlled to 80°C while stirring primary oleylamine (1 mol) under a nitrogen gas stream. Ethyl methacrylate (1 mol) was added dropwise thereto over a period of four hours. After the dropwise addition was terminated, the mixture was kept at the same temperature for eight hours for reaction and maturation. Thereafter, the reaction mixture was cooled to a temperature of equal to or lower than 40°C, and a 48%-sodium hydroxide aqueous solution (2 mol) was added dropwise over a period of two hours. After the dropwise addition was terminated, the temperature was raised to 80°C, and the mixture was saponified for two hours. Subsequently, the mixture was cooled to a temperature of 40°C, and then 1000 ml of water and 1000 ml of toluene were added thereto. One-hundred grams of a cationic exchange resin was added to the resulting mixture, and the mixture was stirred. Thereafter, the toluene layer was subjected to topping treatment, to give the following compound (N-oleyl-3,3'-amino-N,N-di-2-methylpropionic acid).



(Preparative Product No. 6)

Calcium Salt of Reaction Product of Primary Oleylamine (1 mol) and Methacrylic Acid (2 mol)

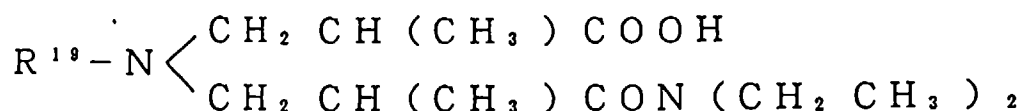
Preparative Product No. 5 was used, and calcium hydroxide (amount equivalent to 1 mol) was added thereto, and the mixture was stirred and dissolved at a temperature of 80°C, to give the following compound (calcium salt of N-oleyl-3,3'-amino-N,N-di-2-methylpropionic acid).



(Preparative Product No. 7)

Diethylamine amide of Reaction Product of Primary Oleylamine (1 mol) and Methacrylic Acid (2 mol)

Preparative Product No. 5 was used, and diethylamine (1 mol) was added thereto, and the mixture was stirred at a temperature of 80°C for one hour. Further, the temperature was raised to 120°C to carry out dehydration reaction for three hours, to give the following compound (mono-N',N'-diethylamide of N-oleyl-3,3'-amino-N,N-di-2-methylpropionic acid).

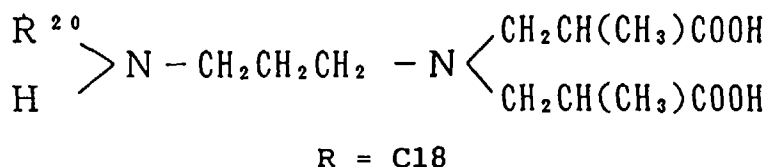


(Preparative Product No. 8)

Reaction Product of Stearyl Propylenediamine (1 mol) and Methacrylic Acid (2 mol)

The temperature was controlled at 80°C while stirring stearyl propylenediamine (1 mol) under a nitrogen gas stream. Ethyl methacrylate (2 mol) was added dropwise thereto over a period of four hours. After the dropwise addition was terminated, the mixture was reacted and matured for eight hours. Thereafter, the reaction mixture was cooled to a temperature of equal to or lower than 50°C, and a 48%-sodium hydroxide aqueous solution (2 mol) was added dropwise over a period of two hours. After the dropwise addition was terminated, the temperature was raised to 80°C, and the mixture was saponified for two hours. Subsequently, 500 ml of toluene was added thereto, and 1 mol of hydrochloric acid was further added to the resulting mixture for neutralization. Thereafter, the toluene layer was repeatedly washed

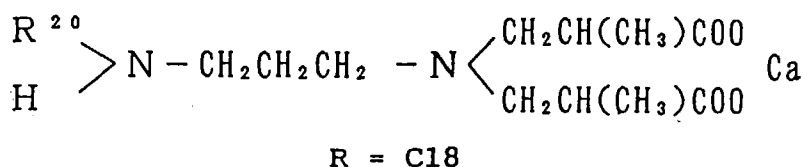
with water to a point where the pH of the washing liquid is about neutral. By the above procedures, the following compound (3-(N-(3'-(N'-stearyl amino)propyl)amino)-N,N-di-2-methylpropionic acid) was obtained.



(Preparative Product No. 9)

Calcium Salt of Reaction Product of Stearyl Propylenediamine (1 mol) and Methacrylic Acid (2 mol)

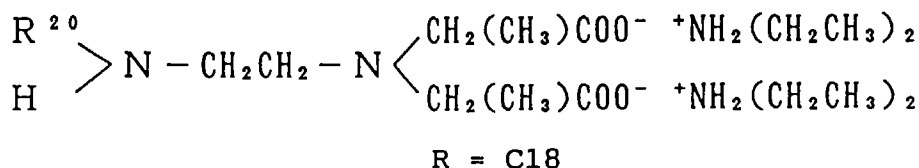
Preparative Product No. 8 was used, and an equivalent amount of calcium hydroxide (1 mol) was added thereto, and the mixture was stirred and dissolved at a temperature of 80°C, to give the following compound (calcium 3-(N-(3'-(N'-stearyl amino)propyl)amino)-N,N-di-2-methylpropionate).



(Preparative Product No. 10)

Diethylamine Salt of Reaction Product of Stearyl Propylenediamine (1 mol) and Methacrylic Acid (2 mol)

Preparative Product No. 8 was used, and an equivalent amount of diethylamine (2 mol) was added thereto, and the mixture was stirred and dissolved at a temperature of 40°C, to give the following compound (diethylamine salt of 3-(N-(3'-(N'-stearyl amino)propyl)amino)-N,N-di-2-methylpropionic acid).



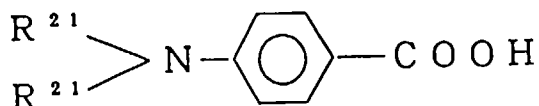
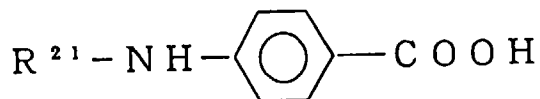
(Preparative Product No. 11)

Reaction Product of Aminobenzoic Acid (1 mol) and Lauryl Chloride (2 mol)

Aminobenzoic acid (1 mol) was mixed with lauryl chloride (0.5 mol), and the temperature of the resulting mixture was gradually raised to 150°C while stirring the mixture under a nitrogen gas stream. After raising the temperature, the remaining lauryl chloride (1.5 mol) was added dropwise to the mixture over a period of three hours. After the dropwise addition was terminated, the mixture was reacted and matured at the same temperature for seven hours. After the reaction, the reaction mixture was cooled to room temperature, and the toluene solvent was added, and the mixture was

washed with water. Further, the solvent and water were distilled off under reduced pressure (4 mm Hg) at a temperature of 110°C, and the temperature was raised to 180°C under reduced pressure conditions and kept at that temperature for one hour to remove unreacted products. Accordingly, the following compounds (N-lauryl-p-aminobenzoic acid and N,N-dilauryl-p-aminobenzoic acid) were obtained.

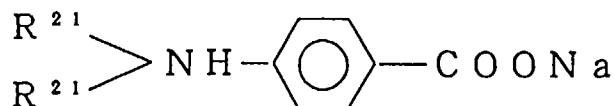
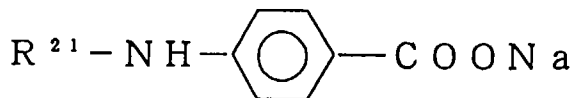
A mixture of:



(Preparative Product No. 12)

Sodium Salt of Reaction Product of Aminobenzoic Acid (1 mol) and Lauryl Chloride (2 mol)

Preparative Product No. 11 was used, and an equivalent amount of sodium (0.5 mol) was added thereto, and the mixture was stirred and dissolved at a temperature of 50°C, to give the following compound (sodium N-lauryl-p-aminobenzoate and sodium N,N-dilauryl-p-aminobenzoate).



Results

Each of the aminocarboxylic acid compounds prepared in this example was added to a testing oil, to evaluate the dispersion effects of calcium sulfate. The results are shown in Tables 1 and Table 2.

Table 1

Composition of Lubricating Oil and Evaluation Results

Test No.	Aminocarboxylic Acids of Present Invention	Composition of Testing Oil (% by weight)					Evaluation Results
		Aminocarboxylic Acids of Present Invention	Metallic Detergent	Ashless Dispersant	Extreme-Pressure Lubricant	Mineral Oil	
1	Comparative Example 1	0	15	1.5	0.5	Bal.	D
2	Comparative Example 2	0	15	0	0.5	Bal.	D
3	Comparative Example 3	0	15	0	0	Bal.	D
4	Preparation No. 1	0.5	15	0	0.5	Bal.	B
5	Preparation No. 2	0.5	15	0	0.5	Bal.	A
6	Preparation No. 3	0.5	15	0	0.5	Bal.	A-B
7	Preparation No. 4	0.5	15	0	0.5	Bal.	A
8	Preparation No. 5	0.5	15	0	0.5	Bal.	A-B

Remarks:

Metallic detergent: A salicylate-based metallic detergent was used (A product, which was a synthesized product having alkaline value of 200 TBN, being used.).

Ashless dispersant: Commercially available alkyl(polybutenyl)succinimide (bis type) was used.

Extreme-pressure lubricant: Commercially available zinc alkyl (number of carbon atoms of about 8; primary type) dithiophosphate was used.

Mineral oil: Commercially available natural paraffinic mineral oil (viscosity of 120 mm²/s at 40°C) was used.

Table 2
Composition of Lubricating Oil and Evaluation Results

Test No.	Aminocarboxylic Acids of Present Invention	Composition of Testing Oil (% by weight)					Evaluation Results
		Aminocarboxylic Acids of Present Invention	Metallic Detergent	Ashless Dispersant	Extreme-Pressure Lubricant	Mineral Oil	
9	Preparation No.6	0.5	15	0	0.5	Bal.	B
10	Preparation No.7	0.5	15	0	0.5	Bal.	A
11	Preparation No.8	0.5	15	0	0.5	Bal.	A
12	Preparation No.9	0.5	15	0	0.5	Bal.	A-B
13	Preparation No.10	0.5	15	0	0.5	Bal.	A
14	Preparation No.11	0.5	15	0	0.5	Bal.	A
15	Preparation No.12	0.5	15	0	0.5	Bal.	A

Remarks:

Metallic detergent: A salicylate-based metallic detergent was used (A product, which was a synthesized product having alkaline value of 200 TBN, being used.).
Ashless dispersant: Commercially available alkyl(polybutenyl)succinimide (bis type) was used.
Extreme-pressure lubricant: Commercially available zinc alkyl (number of carbon atoms of about 8; primary type) dithiophosphate was used.
Mineral oil: Commercially available natural paraffinic mineral oil (viscosity of 120 mm²/s at 40°C) was used.

As is clear from Table 1, the aminocarboxylic acid compounds prepared in Example all showed improvements in dispersion effects of calcium sulfate at a concentration of 0.5% by weight, thereby showing improvement in precipitation of calcium sulfate and adhesion state of calcium sulfate to the vessel walls. On the other hand, the dispersion effects of

the conventionally used ashless dispersant were extremely poor for the water-containing calcium sulfate.

Example 2. Detergency Test (1)

The detergency of the lubricating oil composition was evaluated using a hot tube testing device shown in Figure 1. Specifically, a lubricating oil (testing oil), which was previously subjected to degradation treatment, and air were supplied into a glass tube heated to a given temperature, and the state of adhesion of the staining components owing to degradation of the lubricating oil was observed and evaluated by the Racker scoring.

〈Set Conditions〉

Amount of testing oil supplied: 6 ml/16 hours.

Amount of air supplied: 10 ml/minutes.

Temperature of the heating portion: 280° to 320°C.

〈Method of Pre-Treatment of Lubricating Oil〉

Estimating the acid substances (sulfuric acid) contaminated, unburned combustibles (soots) and abrasion powder (iron powder) during actual operation, each of the testing oils was pre-treated under the following conditions.

Specifically, carbon black, iron powder, and sulfuric acid were mixed to each of the testing oils in the proportions shown below and stirred at 100°C for 10 minutes to conduct tests using a hot tube testing device.

Carbon black: 0.2% by weight, to the testing oil.

Iron powder with a particle size of 5 μm or less: 0.05% by weight, to the testing oil.

Sulfuric acid: 0.8% by weight, to the testing oil.

〈Evaluation Method〉

The glass tube after the 16-hour test was evaluated in reference to a given standard color, and scores of 1 to 10 are given.

Score 1: Staining state of the glass tube is most severely shown, and discolored to a black carbide color.

Score 5: Staining state of the glass tube is moderate shown, and discolored to a pale yellowish color.

Score 10: Staining state of the glass tube is least shown, substantially having the same state as the glass tube before testing.

The compositions of the testing oils are shown in Tables 3 and 4, and the evaluation results are shown in Tables 5 and 6.

As is clear from Tables 5 and 6, in the detergency of the lubricating oils, a high-temperature detergency was improved for the lubricating oils where any twelve kinds of the aminocarboxylic acids of the present invention were added. In particular, at a temperature of 320°C, carbide stains are formed in the products without the aminocarboxylic acids, whereas no carbide stains were adhered in the lubricating oil compositions of the present invention containing the aminocarboxylic acids. Therefore, when the aminocarboxylic acids of the present invention are added to the lubricating oils, the deterging and dispersion effects of the lubricating oils are improved, so that effects of inhibiting the stains in the glass tubes are observed.

Table 3

Composition of Lubricating Oil						
Test No.	Aminocarboxylic Acids of Present Invention	Composition of Testing Oil (% by weight)				
		Aminocarboxylic Acids of Present Invention	Metallic Detergent	Ashless Dispersant	Extreme-Pressure Lubricant	Mineral Oil
16	Comparative Example 1	0	15	1.5	0.5	Bal.
17	Comparative Example 2	0	7.5	1.5	0.5	Bal.
18	Comparative Example 3	0	15	0	0.5	Bal.
19	Preparation No. 1	0.5	15	0	0.5	Bal.
20	Preparation No. 2	0.5	15	0	0.5	Bal.
21	Preparation No. 3	0.5	15	0	0.5	Bal.
22	Preparation No. 4	0.5	15	0	0.5	Bal.
23	Preparation No. 5	0.5	15	0	0.5	Bal.
Remarks: Metallic detergent: A salicylate-based metallic detergent was used (A product, which was a synthesized product having alkaline value of 200 TBN, being used.). Ashless dispersant: Commercially available alkyl(polybutenyl)succinimide (bis type) was used. Extreme-pressure lubricant: Commercially available zinc alkyl (number of carbon atoms of about 8; primary type)dithiophosphate was used. Mineral oil: Commercially available natural paraffinic mineral oil (viscosity of 120 mm ² /s at 40 °C) was used.						

Table 4

Composition of Lubricating Oil						
Test No.	Aminocarbox- ylic Acids of Present Inven- tion	Composition of Testing Oil (% by weight)				
		Aminocarbox- ylic Acids of Present Inven- tion	Metallic Deter- gent	Ashless Dis- persant	Extreme- Pressure Lubricant	Mineral Oil
34	Preparation No. 6	0.5	15	0	0.5	Bal.
25	Preparation No. 7	0.5	15	0	0.5	Bal.
26	Preparation No. 8	0.5	15	0	0.5	Bal.
27	Preparation No. 9	0.5	15	0	0.5	Bal.
28	Preparation No. 10	0.5	15	0	0.5	Bal.
29	Preparation No. 11	0.5	15	0	0.5	Bal.
30	Preparation No. 12	0.5	15	0	0.5	Bal.
Remarks: Metallic detergent: A salicylate-based metallic detergent was used (A product, which was a synthesized product having alkaline value of 200 TBN, being used.). Ashless dispersant: Commercially available alkyl(polybutenyl)succinimide (bis type) was used. Extreme-pressure lubricant: Commercially available zinc alkyl (number of carbon atoms of about 8; primary type)dithiophosphate was used. Mineral oil: Commercially available natural paraffinic mineral oil (viscosity of 120 mm ² /s at 40 °C) was used.						

Table 5

Results for Hot Tube Test				
Test No.	Aminocarboxylic Acids of Present Invention	Scores at Each Testing Temp. (10 being the full score)		
		280°C	300°C	320°C
16	Comparative Example 1	8.5	6.0	1.0
17	Comparative Example 2	7.0	4.0	1.0
18	Comparative Example 3	8.0	5.5	1.0
19	Preparation No. 1	9.0	7.5	2.0-3.0
20	Preparation No. 2	9.0	8.0	4.0
21	Preparation No. 3	9.5	8.5	4.5
22	Preparation No. 4	10	9.0	5.0
23	Preparation No. 5	10	9.0	6.0

Table 6

Results for Hot Tube Test				
Test No.	Aminocarboxylic Acids of Present Invention	Scores at Each Testing Temp. (10 being the full score)		
		280°C	300°C	320°C
24	Preparation No. 6	10	8.5	5.5
25	Preparation No. 7	9.5	8.0	4.0
26	Preparation No. 8	9.5	7.0	3.0
27	Preparation No. 9	10	8.5	5.5
28	Preparation No.10	9.0	7.0	3.0
29	Preparation No.11	10	9.5	5.0
30	Preparation No.12	10	9.5	5.5

Metallic detergent: A salicylate-based metallic detergent was used (A product, which was a synthesized product having alkaline value of 200 TBN, being used.).
 Ashless dispersant: Commercially available alkyl(polybutenyl)succinimide (bis type) was used.
 Extreme-pressure lubricant: Commercially available zinc alkyl(number of carbon atoms of about 8; primary type)dithiophosphate was used.
 Mineral oil: Commercially available natural paraffinic mineral oil (viscosity of 120 mm²/s at 40°C) was used.

Example 3. Engine Test (1)

The detergency for the piston was evaluated using a four-cylinder diesel engine SD-22 (manufactured by Nissan Motor, Co., Ltd.). Incidentally, the fuel was a mixture of Fuel Oil A and light oil (1:1), whose sulfur content was adjusted to 3% in fuel by using TNPS (di-tertiary-nonyl polysulfide).

Details of test conditions and type of the engine used are set forth below:

(Engine Used)

Type: four-cycles, four-cylinders, water-cooling diesel engine.
 Exhaust gas capacity: 2.2 liters.
 5 Combustion system: Ante-chamber type.
 Bore × Stroke: 80 mm × 83.6 mm.
 Compression ratio: 22.2.

(Conditions of Engine Test)

10 Engine testing time: 100 hours
 Engine rotational speed: 3000 rpm (torque: 8 kg-m)
 Fuel: Fuel Oil A/light oil (1:1) + TNPS (S = 3%)

15 (Evaluation Sites and Evaluation Criteria of Detergency)

Evaluation site of detergency: Piston landing portions (Top Landing, Second Landing, Third Landing, see Figure)

Evaluation criteria of detergency: The staining state around the piston landing portions was classified according to the following criteria and evaluated. The lubricating oil compositions used in the engine test is shown in Table 7, and the
 20 results for the engine test is shown in Table 8.

- F: Adhesion of carbon found, substantially on entire surfaces.
- E: Adhesion of carbon found, adhering on equal to or greater than one-third the area in the peripheral direction of the piston.
- 25 D: Adhesion of carbon found, adhering on equal to or less than one-third the area in the peripheral direction of the piston.
- C: Discoloration to pale yellowish color, discoloring on equal to or more than one-third the area in the peripheral direction of the piston.
- 30 B: Discoloration to pale yellowish color, discoloring on equal to or less than one-third the area in the peripheral direction of the piston.
- A: No discoloration.

Table 7

Lubricating Oil Composition for Engine Test						
Test No.	Aminocarboxylic Acids of Present Invention	Composition of Testing Oil (% by weight)				
		Aminocarboxylic Acids of Present Invention	Metallic Detergent	Ashless Dispersant	Extreme-Pressure Lubricant	Mineral Oil
25	Comparative Example 1	0	15	1.5	0.5	Bal.
26	Comparative Example 2	0	15	0	0.5	Bal.
27	Preparation No. 2	0.5	15	1.5	0.5	Bal.
28	Preparation No. 7	0.5	15	1.5	0.5	Bal.
29	Preparation No. 10	0.5	15	1.5	0.5	Bal.
30	Preparation No. 12	0.5	15	1.5	0.5	Bal.

Table 8

Lubricating Oil Composition for Engine Test					
Test No.	Aminocarboxylic Acids of Present Invention	Results for Engine Test			
		Top Landing	Second Landing	Third Landing	
25	Comparative Example 1	E	D	B	
26	Comparative Example 2	E	D	B-C	
27	Preparation No. 2	C	B-C	A	
28	Preparation No. 7	D	B-C	A	
29	Preparation No. 10	D	B	A	
30	Preparation No. 12	D	B	A	

Four compounds used in Examples 1 and 2 were added to each of the lubricating oils to conduct an engine test by using SD-22 manufactured by Nissan Motors, Co., Ltd. The engine test was carried out for a 100-hour operation using a light oil in which the sulfur concentration was adjusted to 3% to evaluate the piston detergency after testing.

A piston detergency of higher by 1 rank was confirmed for the lubricating oils in which the aminocarboxylic acids of the present invention were added. In particular, stains at second and third landing portions were reduced.

As described above, the aminocarboxylic acid compounds of the present invention have excellent dispersion effects of calcium sulfate, and show improvements in the piston detergency in the actual engine.

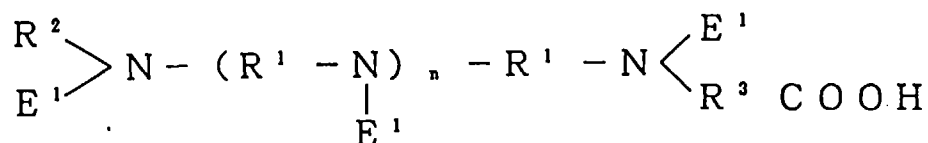
INDUSTRIAL APPLICABILITY

When the lubricating oil additives and the lubricating oil compositions for diesel engines of the present invention are added to the lubricating oil, the dispersion function of the water-containing calcium sulfate admixed in the lubricating oil is dramatically improved, and the dispersion functions in oil of the staining components, such as soots, sludges, and the like, mentioned above owned by the lubricating oil are enhanced, so that its detergency is dramatically improved. Therefore, it is made possible to lower the concentration in the amount of the metal-based detergent as well as to lengthen the service life of the lubricating oil.

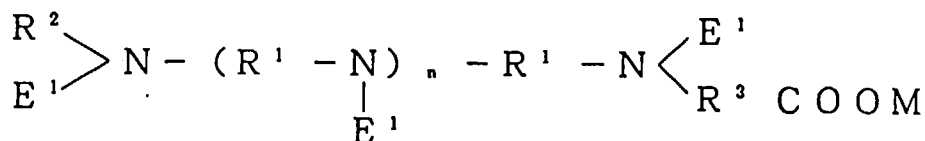
Claims

1. A lubricating oil additive for diesel engines comprising one or more members of carboxylic acids, metal salts of carboxylic acids, amine salts of carboxylic acids, and carboxylic acid amides, each having a substituted amino group or substituted amino groups in a molecule (hereinafter simply referred to as "substituted aminocarboxylic acid compounds"), wherein the substituted aminocarboxylic acid compounds have a function of dispersing water-containing calcium sulfate in an oil.
2. The lubricating oil additive for diesel engines according to claim 1, wherein said substituted aminocarboxylic acid compounds have an amino group substituted by a hydrocarbon group or hydrocarbon groups each having 1 to 30 carbon atoms.
3. The lubricating oil additive for diesel engines according to claim 1 or claim 2, wherein said substituted aminocarboxylic acid compounds have primary or secondary amino groups, each of which is substituted by carboxylic acids, metal salts of carboxylic acids, amine salts of carboxylic acids, or carboxylic acid amides.
4. The lubricating oil additive for diesel engines according to any one of claims 1 to 3, wherein said metal salts of the substituted aminocarboxylic acid compounds are alkali metal salts or alkaline earth metal salts.
5. The lubricating oil additive for diesel engines according to any one of claims 1 to 3, wherein said amine salts of the substituted aminocarboxylic acid compounds are carboxylates of primary, secondary or tertiary amines each having 1 to 6 carbon atoms.
6. The lubricating oil additive for diesel engines according to any one of claims 1 to 3, wherein said amides of the substituted aminocarboxylic acid compounds are unsubstituted amides or substituted amides of which one or two hydrogen atoms are substituted by an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group.
7. The lubricating oil additive for diesel engines according to any one of claims 1 to 3, wherein said substituted aminocarboxylic acid compounds are represented by the general formula (I):

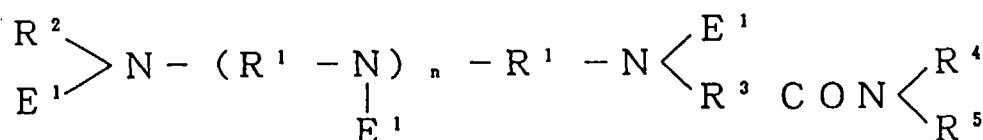
(Acid form)



(Salt form)



(Amide form)



(I)

wherein R¹ represents an alkylene group having 2 to 4 carbon atoms; R² represents an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, or an aralkyl group having 7 to 30 carbon atoms; R³ represents a linear or branched alkylene group having 1 to 5 carbon atoms, a linear or branched alkenylene group having 2 to 5 carbon atoms, or phenylene group; R⁴ and R⁵, which may be identical or different, each represents hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group; E¹ represents hydrogen atom, R², -R³COOH, -R³COOM, or -R³CONR⁴R⁵; n is an integer of 0 to 4; and M represents an alkali metal, an alkaline earth metal, or a primary, secondary, or tertiary ammonium having an alkyl group having 1 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, or phenyl group, with the proviso that a total number of carbon atoms in R² in a molecule is 10 to 210.

8. A lubricating oil composition for diesel engines, wherein 0.05 to 10% by weight of the lubricating oil additives for diesel engines as defined in any one of claims 1 to 7 is added.
9. The lubricating oil composition for diesel engines according to claim 8, further containing a metallic detergent.
10. A lubricating oil composition for diesel engines characterized in that 0.05 to 10% by weight of one or more members of the lubricating oil additives for diesel engines as defined in any one of claims 1 to 7, 0.5 to 50% by weight of a metallic detergent, 0.1 to 10% by weight of an ashless dispersant, and 0.01 to 5% by weight of an extreme-pressure lubricant are added to a base oil.
11. A method for dispersing water-containing calcium sulfate in an oil, comprising adding the additives as defined in any one of claims 1 to 7 to a lubricating oil for diesel engines.

- 12.** Use of the additives as defined in any one of claims 1 to 7 for dispersing water-containing calcium sulfate in a lubricating oil for diesel engines.

5

10

15

20

25

30

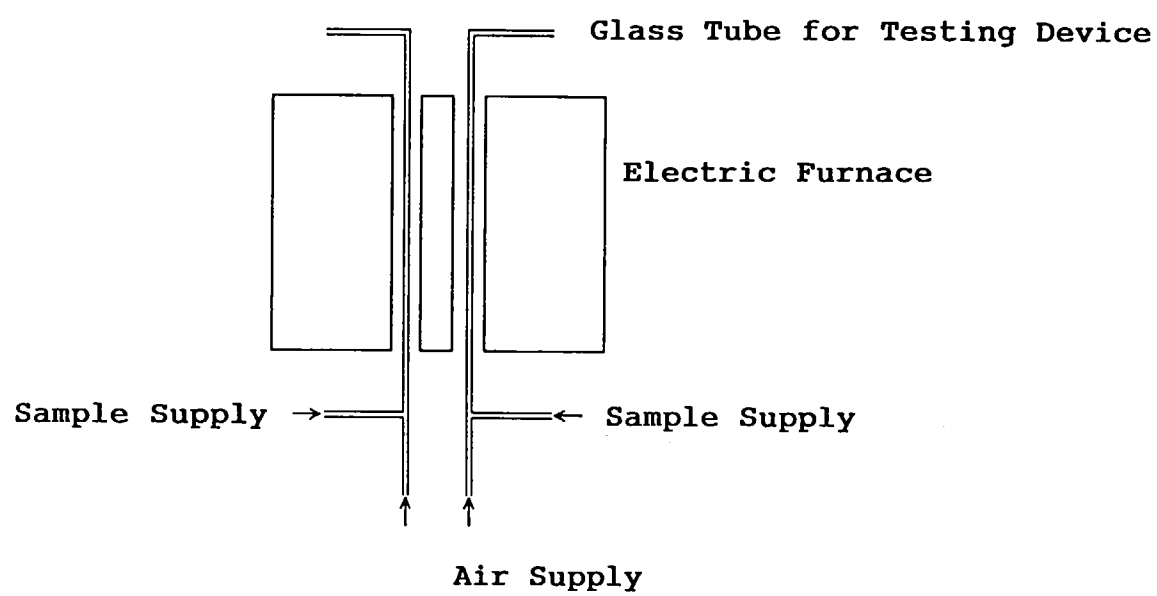
35

40

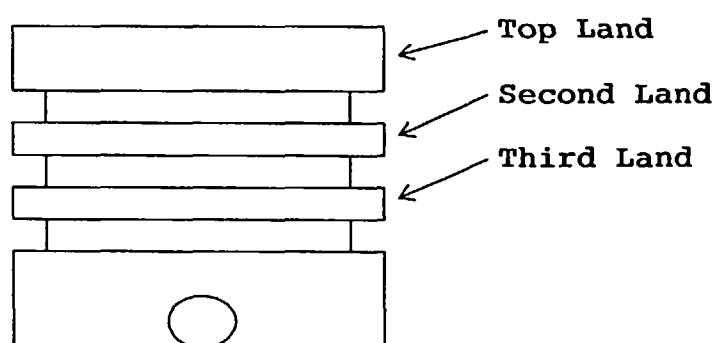
45

50

55



F I G. 1



F I G. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01670

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ C10M169/04, C10M133/04, C10M133/16, C10N30:04, C10N40:25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ C10M169/04, C10M133/04-133/20, C10N30:04, C10N40:25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 52-102892, A (Shell Internationale Research Maatschappij N.V.), August 29, 1977 (29. 08. 77), Claim & BE, 851615, A & FR, 2341358, A & GB, 1506786, A	1 - 12
A	JP, 61-257968, A (Sheburon Research Co.), November 15, 1986 (15. 11. 86), Claim & BR, 8601619, A & US, 4647390, A & US, 4648886, A & CA, 1270255, A	1 - 12
A	JP, 02-194096, A (Akzo N.V.), July 31, 1990 (31. 07. 90), Claim & AU, 8945896, A & CA, 2004544, A & BR, 8906197, A & US, 5062978, A & EP, 372628, B1 & DE, 68906514, E & ES, 2040986, T3 & SG, 9401601, A	1 - 12
A	JP, 5-508188, A (The Lubrizol Corp.), November 18, 1993 (18. 11. 93), Example 11 & WO, 92/18589, A1 & US, 5490945, A	1 - 12

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search September 3, 1996 (03. 09. 96)	Date of mailing of the international search report September 17, 1996 (17. 09. 96)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01670

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P	JP,7-316576, A (Kao Corp.), December 5, 1995 (05. 12. 95), Claim (Family: none)	1 - 12

Form PCT/ISA/210 (continuation of second sheet) (July 1992)