(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 107 103 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
07.10.2009 Bulletin 2009/41

(21) Application number: **08711738.8**

(22) Date of filing: **21.02.2008**

(51) Int Cl.:
C10L 1/26 *(2006.01)* ***C10L 1/30*** *(2006.01)*

(86) International application number:
PCT/JP2008/052949

(87) International publication number:
WO 2009/090760 (23.07.2009 Gazette 2009/30)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

(30) Priority: **16.01.2008 JP 2008007269**

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(54) **FUEL ADDITIVES**

(57) A fuel additive contains ferrocene and/or ferrocene derivative(s), and lecithin. A fuel additive contains 80 to 99 mass % of ferrocene and/or ferrocene derivative (s), and 1 to 20 mass % of lecithin, and being in the solid state. A fuel additive contains 78 to 99 mass % of ferrocene and/or ferrocene derivative(s), 0.9 to 20 mass % of lecithin and 0.1 to 2 mass % of water, and being in the particle state. A fuel additive containins 2 to 5 mass % of ferrocene and/or ferrocene derivative(s), 5 to 50 mass % of lecithin and mineral oil, and being in the liquid state, wherein the ferrocene and/or ferrocene derivative(s), and the lecithin are dissolved in the mineral oil. The above-mentioned fuel additive is used by being added into a fuel so as to make the concentration of the ferrocene and/or ferrocene derivative(s) and the lecithin in ranges of 1 to 50 ppm, and 0.01 to 500 ppm, respectively.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a fuel additive containing ferrocene and/or ferrocene derivative(s), and, more particularly, relates to a fuel additive containing ferrocene and/or ferrocene derivative(s) to which functions such as combustion promotion, soot reduction, NOx reduction and the like are enhanced by adding lecithin.

DESCRIPTION OF THE RELATED ART

[0002] Conventionally, ferrocene and derivative(s) thereof are used as an additive for various liquid fuels. For instance, ferrocene, derivative(s) thereof and a improvement combustion method of a liquid hydrocarbon in the presence of a fuel additive composition consisting of an aromatic solvent, an aliphatic solvent and/or a petroleum solvent which are liquid organic careers capable of dissolving the ferrocene and derivative(s) thereof are described in JP02-132188A. Moreover, a method of conditioning of diesel engines is described in US Patent 4389220 specification. In accordance with the method, a deposit containing carbon in the combustion chamber is removed, and the fuel consumption per distance traveled is reduced by about 5%, by adding 20-30ppm of ferrocene to the fuel.

[0003] In addition, a method of reducing carbonaceous deposition on the engine and ancillary equipment thereof is proposed in JP Patent 3599337 specification. In accordance with the method, 1-100ppm of ferrocene and derivative(s) thereof, as additives for fuel oil consisting of a heavy residual oil for an internal combustion, are added to a fuel directly, without blending other additives.

[0004] However, ferrocene and ferrocene derivative(s) used for these inventions have a drawback of very low solubility in an aromatic solvent, an aliphatic solvent and a petroleum solvent.

In general, ferrocene is in the solid state. In order to dissolve solid ferrocene, in particular, a large quantity of agitation power and long time, which depend on the size of the solid, are needed. Even if the amount of addition is small, solid ferrocene doesn't dissolve easily either. The trouble occurs in the internal combustion engine when solid ferrocene isn't dissolved beforehand before it adds to the fuel. Therefore, under the present situation, the solid ferrocene is added to a fuel after it is dissolved in a solvent in a solution tank with an agitator.

DISCLOSURE OF INVENTION

[0005] The present invention is made in view of the aforementioned problems of the conventional technology and has an object to provide a fuel additive containing ferrocene and/or ferrocene derivative(s), which can easily and stably be dissolved in a fuel.

[0006] As a result of repeating assiduous studies for achieving the above-mentioned object, the present inventors found the object to be accomplished by using ferrocene and/or ferrocene derivative(s) in combination with lecithin, and have achieved the present invention.

[0007] That is, the fuel additive according to the present invention is characterized by containing ferrocene and/or ferrocene derivative(s), and lecithin.

[0008] The solid fuel additive according to the present invention is characterized by containing 80 to 99 % by mass of ferrocene and/or ferrocene derivative(s), and 1 to 20 % by mass of lecithin. The particulate fuel additive according to the present invention is characterized by containing 78 to 99 % by mass of ferrocene and/or ferrocene derivative(s), 0.9 to 20 % by mass of lecithin and 0.1 to 2 % by mass of water.

[0009] In addition, the liquid fuel additive according to the present invention is characterized by containing mineral oil containing ferrocene and/or ferrocene derivative(s) and lecithin dissolved therein, and having the ferrocene and/or ferrocene derivative(s) content of 2 to 5 % by mass and the lecithin content of 5 to 50 % by mass.

[0010] Furthermore, the fuel additive according to the present invention is characterized by being used by being added into a fuel so as to make the concentration of the ferrocene and/or ferrocene derivative(s) and the lecithin in ranges of 1 to 50 ppm, and 0.01 to 500 ppm, respectively.

BEST MODE OF CARRYING OUT THE INVENTION

[0011] Hereafter, a fuel additive according to this invention will be explained in detail. In this specification, "%" means "mass percentage" unless otherwise specified.

[0012] As mentioned above, a fuel additive according to this invention is the fuel additive that contains ferrocene and/or ferrocene derivative(s) and lecithin. These fuel additives can be in the solid state, especially in the particle state, and in the liquid state.

(1) Ferrocene and ferrocene derivative(s)

[0013] Formally, ferrocene is called bis(cyclopentadienyl)iron, and is also called dicyclopentadienyl iron. Ferrocene derivative(s) used in this invention is(are) compound(s) having a structure in which a dicyclopentadienyl ring having substituents such as an alkyl group. As the ferrocene derivative(s), mention may be made, for example, of ethylferrocene, butylferrocene, acetylferrocene, 2,2-bis-ethyl feroseniru propane and the like.
[0014] For instance, a manufacturing method of ferrocene and derivative(s) thereof (hereinbelow said to be ferrocenes) is disclosed in specification of US Patent No. 2650756, 2769828, 2834796, 2898360, 3035968, 3238158, 3437634, and the like.
[0015] In the present invention, ferrocenes may be a solid such as a fine powder, a coarse particle, a pellet and the like, and may be a liquid. The form of ferrocenes can be suitably chosen depending on the form of a fuel additive of the present invention. It is explained in detail later.
[0016] A fuel additive of the present invention can have a combustion promotion effect, a soot reduction effect, a NOx reduction effect and the like, by containing ferrocenes. In particular, in a diesel engine that is an internal combustion engine, a cleaning effect of the combustion promotion that controls the formation of deposit on a valve, a piston ring, and a combustion chamber is observed. Since the deposit reduces engine output and increases attrition of parts by adhering, controlling formation of the deposit achieves stable driving of a diesel engine. In addition, several percent reduction of fuel consumption can be realized by preventing superfluous air at the time of combustion, by the reforming combustion such as combustion promotion, soot reduction, NOx reduction and the like.

(2) Lecithin

[0017] Lecithin is an animal and plant phospholipid of which the principal ingredients are a glycerophospholipid and a sphingophospholipid. It is obtained by the purification process of various kinds of vegetable oil such as soybean oil, rapeseed oil, rice-bran oil, palm oil, sunflower oil, cocoanut oil, cottonseed oil, corn oil, peanut oil, linseed oil, safflower oil, olive oil and the like. Usually, a vegetable oil is included 1 to 50%. Depending on the contained amount of the vegetable oil and the ratio between saturation acid and unsaturated acid in the vegetable oil, lecithin exists in the liquid form or in the solid form at normal temperature. Moreover, in recent years, a powder lecithin is manufactured from a liquid lecithin by carrying out oil extraction and vacuum drying.
[0018] In the present invention, lecithin may be a liquid, and may be a solid such as a fine powder and the like. The form of lecithin can be suitably chosen depending on the form of a fuel additive of the present invention. It is explained in detail later.

(3) A form of a fuel additive

[0019] A fuel additive of the present invention can be in the solid state, in the particle state, and in the liquid state.

(i) Solid fuel additive

[0020] A solid fuel additive of the present invention preferably contains 80 to 99% of ferrocenes and 1 to 20% of lecithin. If the content of the lecithin is less than 1%, the ferrocenes may not dissolve in the fuel easily. If the content of the lecithin is 20%, the ferrocenes solubility enhancement effect may be obtained completely.
The form of ferrocenes is not especially limited as long as it is solid at normal temperature, mention may be made, for example, of a solid form such as a fine powder, a coarse particle, a pellet and the like. In addition, lecithin is preferably in the powder form at normal temperature, more preferably a fine powder of 1 mm or less in particle diameter. It is because the mixture with Ferrocenes may be made more uniform.

(ii) Particulate fuel additive

[0021] A particulate fuel additive of the present invention is one aspect of the above-mentioned solid fuel additive, and is granulated from fine powder ferrocene compound into the shape of a coarse particle. As for the particle diameter, it is preferable to be 0.5 mm to 15 mm, more preferably 1 mm to 10 mm. When the particle diameter is less than 0.5 mm, the handling workability may be inferior due to powder dust. When the particle diameter is more than 15 mm, the solubility may decrease due to decreased deflocculability.
A particulate fuel additive preferably contains 78 to 99% of ferrocenes, 0.9 to 20% of lecithin and 0.1 to 2 % of water. If the content of the lecithin is less than 0.9%, the ferrocenes may not dissolve in the fuel easily. If the content of the lecithin is 20%, the ferrocenes solubility enhancement effect may be obtained completely.
Ferrocenes are preferably in the powder form at normal temperature, more preferably a fine powder of 2 mm or less in

particle diameter. In addition, lecithin is also preferably in the powder form at normal temperature, more preferably a fine powder of 1 mm or less in particle diameter. It is for the convenience of granulation process.
A powder lecithin used in this invention has high hygroscopicity, and obtains suitable tackiness for a granulation by mixed with small amount of water. However, when the content of the water is less than 0.1%, the sufficient tackiness may not be obtained, and when the content of the water is more than 2%, the above-mentioned powder ferrocenes and the above-mentioned powder lecithin may be agglomerated due to high water content.

(iii) Liquid fuel additive

[0022] A liquid fuel additive of the present invention contains mineral oil containing ferrocene and/or ferrocene derivative (s) and lecithin dissolved therein, and preferably the content of the ferrocene and/or ferrocene derivative(s) is 2 to 5 % and the content of the lecithin is 5 to 50 %. If the content of the lecithin is less than 5%, the ferrocenes may not dissolve in the mineral oil easily. If the content of the lecithin is 50%, the effect of enhancing solubility of ferrocenes in mineral oil may be obtained completely.
The ferrocenes may be a solid such as a fine powder, a coarse particle, a pellet and the like, or may be a liquid, preferably a liquid or a fine powder from the viewpoint of shape that dissolves easily in mineral oil. And similarly, the lecithin may also be a liquid, or a solid such as a fine powder and the like, preferably a liquid or a fine powder, because of the shape thereof that dissolves easily in mineral oil.
As used herein, the term "mineral oil" includes hydrocarbon fuel oil , gas oil, kerosene and the like. For example, for use in grade C heavy oil used as a fuel of large-scale diesel engines for marine vessels, grade A heavy oil, grade B heavy oil, gas oil, kerosene and the like can be preferably used, and grade A heavy oil can be more preferably used.

(4) Action and effect of lecithin

[0023] Lecithin in the present invention mainly provides the effect as follows.

i) Enhancement of solubility in fuel of ferrocenes
ii) Dispersing action of sludge in fuel oil
iii) Binder action at the time of granulation to prepare a particulate fuel additive
iv) Deflocculation action in a particulate fuel additive
v) Enhancement of solubility in mineral oil of ferrocenes, in a liquid fuel additive
Each above-mentioned effect is described below.

i) Enhancement of solubility in fuel of ferrocenes

[0024] Ferrocenes have a drawback of low solubility in various fuels, as mentioned above. As used herein, the term "fuel" includes fuels used as a fuel for diesel engines, oil incinerators, boiler devices and the like, such as grade A heavy oil, light oil such as kerosene, gas oil and the like, heavy oil, heavy residue oil, lubricating oil, waste oil and mixed oil thereof, and also fuel emulsion thereof, and solid fuel such as coal and the like, but are not limited thereto, as long as the fuel is not in gaseous form.
[0025] For instance, in case of single ferrocene, a solubility in petroleum solvents such as aromatic solvent other than benzene, toluene and xylene, aliphatic solvent and the like is very low. Thus, in such a solvent as above mentioned, single ferrocene is soluble only up to 3% in concentration at 20 degree C. In addition, ferrocenes concentration in solvent for prolonged stability is preferably 2.5% or less. The same goes for when ferrocenes is dissolved in fuel such as heavy oil and the like. However, by adding the prescribed amount of lecithin, it is possible for ferrocenes to be dissolved up to 5% in concentration, and the stability of the solution is good in a broad temperature region.
The relation between the additive amount of lecithin and the maximum solubility of ferrocenes in grade A heavy oil is shown in Table 1.
[0026]

[Table 1]

Lecithin (mass %)	Grade A Heavy Oil (mass %)	Maxmum Solubility of Ferrocenes (mass %)
-	97.7	2.3
5.0	90.1	4.1

(continued)

Lecithin (mass %)	Grade A Heavy Oil (mass %)	Maxmum Solubility of Ferrocenes (mass %)
10.0	85.4	4.6
20.0	74.9	5.1
30.0	65.3	4.7
40.0	55.6	4.4
50.0	49.6	4.1
※ The results of stability test for 1 week at room temperature ※ Lecithin = liquid lecithin ※ Grade A Heavy Oil (sulfer content=0. 09%, viscosity=2. 8cst (at 50°C))		

[0027] Thus, since ferrocenes is easily dissolved in a fuel of various combustion facilities or in a fuel additive itself by adding lecithin that has a solubility enhancement effect, and a stable solution can be obtained, it becomes possible to spray ferrocenes in the uniform particle form on a combustion engine. As a result, the action and effect of ferrocenes can be exerted more than enough.

[0028] Lecithin has an oleophilic portion and a hydrophilic portion, and is known to act as a surfactant agent. However, in the present invention, it is considered that lecithin enhances the solubility due to the action of an oleophilic portion. That is, it is considered as follows. When ferrocenes and lecithin are dissolved in a fuel, one part of oleophilic portions of the lecithin promptly adsorb to the surface of the ferrocenes, and another oleophilic portions of the lecithin enhance lipophilic property on the surface of the ferrocenes, therefore, lecithin contribute to the solubility enhancement of ferrocenes in a fuel.
These actions are not seen in any other surfactant agents such as nonionic surfactant and the like, and are peculiar to lecithin.

ii) Dispersing action of sludge in fuel oil.

[0029] This action differs from the above mentioned solubility enhancement action of ferrocene. Lecithin itself acts as a fuel additive, and contributes to long-term stable operation of the combustion facility including a diesel engine.

[0030] Sludge is an insoluble matter, which exists in a fuel oil, especially in a heavy oil, and causes clogging of a strainer and incomplete combustion since it is easy to precipitate. A generation of the sludge arises from change into a hydrocarbon polymer having few hydrogen atoms by oxidation, polymerization and condensation of hydrocarbon that remains in a oil residue in a tank, because of heat-treatment, catalytic cracking, pyrolysis and the like during a purification process of crude oil.

[0031] The above-mentioned change takes place in order of hydrocarbon, malthene, asphaltene, carbine, carboid and carbon. These polymers initially exist in a heavy oil as a macromolecular colloid. It is considered that the colloid has a hydrocarbon such as carbine, carboid and the like as a core with an extremely high C/H ratio, surrounded by some asphaltenes, and covered sequentially with hydrocarbon polymer with a low C/H ratio.

[0032] An asphaltic substance that exists in a heavy oil as such a colloidal particle will not be precipitated and cause the problem of clogging of a strainer, incomplete combustion and the like, as long as it is floating dispersedly as stable colloid. However, this colloidal particle has polarity and adsorptivity property. Therefore, if equilibrium condition is disrupted by heating, adding an oil of a different kind, prolonged storage and the like, the colloidal particles agglutinate together one after another, and get into an aggregate of big particles (micelle colloid), and form sludge by precipitating.

[0033] Specifically, when a light component is added to a heavy oil containing the above-mentioned colloidal particle, hydrocarbon polymers and malthene of the colloid surface layer is dissolved. However, since asphaltene, carboid and the like are unsaturation and have polarity, the colloidal particles agglutinate each other, the huge asphaltene particles are separated, and sludge is formed. In addition, when heat is applied, a colloid surface layer is dissolved and also particle motion is increased because viscosity is reduced by a rise in heat. And sludge is formed by binding and association, since opportunities for collision of the asphaltenes are augmented.

[0034] Lecithin infiltrates and absorbs to binding portion and/or association of sludge such as carbon, asphaltene and the like, and has a mincing action of sludge by dispersion force by acting as a surfactant agent. Lecithin also has the effect of preventing separation and precipitation of sludge, by preventing mixing of different-type fuels, association of the colloidal particles by heating and the like, by this action.

iii) Binder action at the time of granulation to prepare a particulate fuel additive.

[0035] As mentioned above, when a particulate fuel additive is granulated, lecithin obtains suitable tackiness for a granulation by mixed with small amount of water, and bears a role of a binder.

iv) Deflocculation action in a particulate fuel additive.

[0036] Lecithin contained in particulate fuel additives has deflocculation action to make particles easy to crush when the additive is fed into a fuel. In addition, the crushed additive comes to dissolve very easily by solubility enhancement effect of lecithin.

v) Enhancement of solubility in mineral oil of ferrocenes, in a liquid fuel additive

[0037] Ferrocenes have a very low solubility in mineral oil, and are soluble only up to about 2.5% in concentration. However, by adding the prescribed amount of lecithin, it is possible for ferrocenes to be dissolved up to 5% in concentration, and the stability of the solution is good in a broad temperature region.

(5) Concentration in a fuel of ferrocenes and lecithin.

[0038] It is preferred that the fuel additive according to the present invention for various fuels used for diesel engines, oil incinerators, boiler devices and the like, which are used in a marine vessels, power generating facilities and the like, is added into the fuels so as to make the concentration of ferrocene and/or ferrocene derivative(s) and lecithin in ranges of 1 to 50 ppm, and 0.01 to 500 ppm, respectively.
More specifically, as for usual concentration of ferrocenes, it is preferred that the fuel additive is added sequentially into the fuels in order that the fuels in oil incinerators and boiler devices have ferrocene and/or ferrocene derivative(s) concentration of 1-10 ppm and the fuels in diesel engine have ferrocene and/or ferrocene derivative(s) concentration of 10-50 ppm.
However, in order to greatly improve objective combustion promotion, soot reduction, NOx reduction and the like, several fold to dozens of the continuous additive amount can be temporarily added while a short time, based on the condition of a combustion engine.
[0039] The above-mentioned lecithin has advantageous concentration to dissolve easily and stably ferrocenes in a fuel oil and in fuel additive itself, and to disperse sludge further, in a heavy fuel oil especially.
[0040] In this manner, by dissolving ferrocenes easily and stably with desirable concentration of lecithin, the action and effect of ferrocenes can be exerted more than enough and it can contribute to long-term stabile operation of combustion facilities.

EXAMPLES

[0041] Hereinafter, this invention is further explained in detail on basis of examples and comparative example, but this invention is not limited to these examples.
Evaluation of various characteristics was carried out in the following way.

[Evaluation of a solubility test of ferrocenes]

<u>Solid fuel additive (Example 1 - 4 and Comparative example 1)</u>

[0042] Ferrocene was added to 200 g of grade A heavy oil (sulfur content = 0.09%, viscosity =2.8cst (50 degree C)) as a fuel oil, stirring at 20 degree C and 60 rpm, and the rate of solution until ferrocene concentration reaches 3% was evaluated by measuring the number of seconds. Then, ferrocene was added further in order to produce the stable solution of maximum concentration, and stability after still standing for one week at room temperature was evaluated. The results are shown in Table 2.

<u>Liquid fuel additive (Example 5 - 7 and Comparative example 2)</u>

[0043] While stirring at 20 degree C and 60 rpm, the fuel additives were prepared by compositions shown in Table 3, and the rate of solution until ferrocene is completely dissolved in grade A heavy oil was evaluated by measuring the number of seconds. Stability of the obtained solution after still standing for one week at room temperature was evaluated. The test was done on a 200 g scale. The results are shown in Table 3.

[0044]

[Table 2]

		Example				Comparative Example
		1	2	3	4	1
additive composition [%]	Ferrocene	80	98	94.5	79	100
	Lecithin (Solid)	20	2	5	20	-
	Water	-	-	0.5	1	-
	Total	100	100	100	100	100
solubility rate		180	370	290	175	660
dissolved concentration		4.8	3.5	4.1	4.9	3.0
stability test		very good	good	very good	good	no good

Lecithin (Solid) means a powdered lecithin in the solid state, lecithin(liquid) means a lecithin in the liquid state.
Stability test:
"very good"mesns complete dissolution,
"good" mesns almost dissolution,
"passed" mesns a little insoluble matter was observed,
"no good" mesns too much insoluble matter was observed.

[0045]

[Table 3]

		Example			Comparative Example
		5	6	7	2
additive composition [%]	Ferrocene	3.5	5.0	4.0	2.5
	Lecithin (Liquid)	5	20	50	-
	Water	-	-	-	-
	Grade A Heavy Oil	92	75	46	97.5
	Total	100	100	100	100
solubility rate		110	190	120	580
dissolved concentration		3.5	5.0	4.0	2.5
stability test		very good	good	good	passed

Lecithin(Solid) means a powdered lecithin in the solid state, lecithin (liquid) means a lecithin in the liquid state.
Stability test:
"every good"mesns complete dissolution.
"good" mesns almost dissolution,
"passed" mesns a little insoluble matter was observed,
"no good" mesns too much insoluble matter was observed.

Results

[0046] The rate of solution of solid fuel additives of the present invention (Example 1 - 4) until ferrocene concentration

reaches 3% is very fast as compared with comparative example 1. The concentration of a stable solution of comparative example 1 is 3% but with many insoluble matters, while the concentration of a stable solution of example 1-4 is allowed to be 3.5 to 5.0%. In addition, the evaluations of stability after storing for one week of Example 1 - 4 are "very good" or "good". Thus, it was confirmed that a solid fuel additive of this invention was very excellent in all aspects of solution rate of ferrocene, dissolved concentration and stability evaluation.
At the time of preparation of fuel additive, the rate of solution of liquid fuel additives of the present invention (Example 5 - 7) until ferrocene is completely dissolved in grade A heavy oil is very fast as compared with comparative example 2. In addition, the evaluations of stability after storing for one week are "very good" or "good". Thus, it was confirmed that a liquid fuel additive of this invention was very excellent in all aspects of solution rate of ferrocene, dissolved concentration and stability evaluation.

[Dispersing effect of sludge]

[0047] Sludge dispersion tests of examples and comparative examples described in Table 2 and Table 3 were done. The tests were applied to The Japanese Shipowners' Association method.

Operating procedure

[0048]

(1) Into a test tube, 0.1g of grade C heavy oil was taken, and 20 ml of normal heptane was added to this test tube. In addition, 0.02m1 (1/1000) of fuel additive of Examples 1-7 or comparative examples 1-2 was added.
(2) The test tube was sealed and strongly shaken 20 times or more until thoroughly mixed.
(3) The test tube was settled at room temperature and the dispersion state of every elapsed time was evaluated by the following standard.

Evaluation standard

[0049]

A ... Complete dispersion and no precipitation
B ... Dispersion and precipitation
It is referred to as B1, B2 and B3 in order of increasing amount of precipitation.
C ...No dispersion and precipitated almost

The results are shown in Table 4.
[0050]

[Table 4]

		soon after mixed	8 hours after	24 hours after	48 hours after
Example	1	A	A	A	A~B1
	2	A	A~B1	B1~B2	B2
	3	A	A	A~B1	B1
	4	A	A	A	A~B1
	5	A	A	A-B1	B1
	6	A	A	A	A~B1
	7	A	A	A	A~B1
Comparative Example	1	A	C	C	C
	2	A	C	C	C

(continued)

	soon after mixed	8 hours after	24 hours after	48 hours after
Additive-free	A	C	C	C
※ Properties of Grade C heavy oil applied to the evaluation Density(15°C) : 0. 955 Viscosity(50°C): 358cst Sulfer content(%) : 3. 07 Carbon Residue contend(%) : 11. 6 Asphaltene(%) : 6. 94				

Results

[0051] A solid fuel additive of this invention (Examples 1-4) and a liquid fuel additive of this invention (Examples 5-7) have a very excellent effect of sludge dispersion as compared with comparative example 1, 2 and additive-free. Comparative examples 1 and 2, which do not contain lecithin, had no effect at all and were the same as additive-free grade C heavy oil. An effect of lecithin was the result of being proportional to an additive amount in general.

[Measurement of combustion rate]

[0052] When 10 mg of fuel oil (grade C heavy oil, the same oil as used for effect evaluation of the above-mentioned sludge dispersion), to which was added liquid fuel additive (examples 5-7) of this invention or liquid fuel additive of the comparative example 2, was heated to 500 degree C with a rate of temperature rise of 100 degree C/min.) and combusted (m1 represents mass of an end point of carbon residue generation), and kept at 500 degree C by using Differential thermal analysis system TG/DTA6300 (made by Seiko Instruments Inc.), TG (thermogravimetric analysis) carbon residue combustion rate constant was computed from the mass reduction curve of generated carbon residue (m2 represents mass of 95% burned point). The quantity of airflow was 100ml/min. Following formula (I) was used for the calculating method. * 1, *2

$$\text{TG carbon residue combustion rate constant} = \text{AxTxIn}(m1/m2)/\text{tau} \ldots \text{(I)}$$

A: constant
T: temperature
m1: mass of an end point of carbon residue generation
m2: mass of 95% burned point
tau: (m2-m1) time
*1 Shibayama et al., the Japan Society of Mechanical Engineers collected papers, 34 (260), 769 (1968)
*2 Hou et al., the Japan Society of Mechanical Engineers collected papers, 54 (507) 3301 (1988)
The test results are shown in Table 5.
[0053]

[Table 5]

		additive amount	TG carbon residue combustion rate constant	relative rate constant
Example	5	500 ppm	16.21	1.030
	6	500 ppm	16.26	1.033
	7	500 ppm	16.51	1.048
	5	1000 ppm	19.20	1.220
	6	1000 ppm	19.76	1.255
	7	1000 ppm	19.55	1.242
Comparative Example	2	1000 ppm	15.74	1
	2	2000 ppm	18.27	1.161
※ relative rate constant = relative constant that assumed "1,000ppm of comparison example 2" to be 1				

Results

[0054] As compared with 1000ppm addition of comparative example 2, as for 1000ppm addition of liquid fuel additive of this invention (examples 5-7), high TG carbon residue combustion rate constant (relative velocity constant) was obtained. Since the content of ferrocene was high level, it was a foregone conclusion. However, also as for 500ppm addition of Examples 5-7, TG carbon residue combustion rate constant (relative velocity constant) was higher than that of 1000ppm addition of the comparative example 2. In addition, as for 1000ppm addition of Examples 5-7, TG carbon residue combustion rate constant (relative velocity constant) was higher than that of 2000ppm addition of the comparative example 2.
This can be imagined to be a synergistic effect between solubility enhancement and sludge dispersion of lecithin on ferrocene. As for the comparative example 2 that does not contain lecithin, it is considered that solubility is insufficient also in fuel oil because ferrocene is unstable in liquid additive. Additionally, it is considered that the effect was inferior to example 5-7 since there is not a sludge decentralization effect either when a relative content of ferrocenes was the same.

[A system examination by a diesel engine]

[0055] The system examination of a cargo boat with a diesel engine of the following specification was done, by using solid fuel additive of this invention (example 3) and solid fuel additive of comparative example 1.
The system examination was done, namely, in a solution tank with an agitator, 9.0Kg of solid fuel additive was dissolved in 360 liters of grade A heavy oil, and was added of 1/1000 into the fuel (grade C heavy oil) line from this solution tank with injection pump. (The additive amount of fuel additive was 25ppm.)
A solid fuel additive of Example 3 or comparative example 1 was added by the above-mentioned method over four months alternately per one month (30 days) (one month x 2 times for each solid fuel additive). Then, a fuel consumption and condition of dirt of a heat exchanger by visual observation was compared. Next, water-wash was performed and dirt removal performance was compared.

Specification of a cargo boat

[0056]

Gross tonnage: 160,000 t
Deadweight tonnage: 300,500 t
Continuous maximum power: 21,300 kW x 74 rpm
Number of cylinders: ten pieces
Revolutions of a turbosupercharger: 10,000 rpm

Fuel consumption: 90,000 L/day (additive-free)

Test results are shown in Table 6.

[0057]

[Table 6]

		Example 3	Comparative Example 1
fuel consumption	first	2,597 KL	2,660 KL
	second	2,566 KL	2,647 KL
dirt of a heat exchange mechanism	first	Very little deposit adhered to the surface.	A deposit almost adhered to the entire surface thinly.
	second	same as above	same as above
removability of dirt of a heat exchange mechanism by flushing with water	first	removed by easy rinsing with water	A lot of time of washing with water was needed until removed.
	second	same as above	same as above
※ General Properties of a fuel oil (Grade C heavy oil) Density(15°C) : 0. 984 Viscosity(50°C) : 401 cst Sulfer content(%) :3. 61 Carbon Residue content(%) : 13. 4 Asphaltene(%) : 8. 98			

[0058] Since it was an examination with real ship, fuel consumption was influenced by a wind, flow of tide, difference of output and the like, however, since the results of two examinations became comparable, the evaluation can be judged to be credible.

As for a solid fuel additive of this invention (Example 3), although the additive amount of ferrocene itself was more slightly fewer than comparative example 1, the results showed that the fuel consumption was also less. This means that the combustion efficiency was improved synthetically and synergistically, because lecithin enhances solubility of ferrocene and a stabilized fuel atomization was realized by dispersion effect of sludge of lecithin itself. In addition, since the combustion promotion effect was enhanced, dirt of a heat exchanger was cleaner than comparative example 1. And an advantage such as the dirt was removed by easy rinsing with water was observed.

In the same way, when fuel additive of Example 3 was dissolved in a solution tank, it was dissolved by prompt breakup and dispersion thoroughly in about 10 minutes just after the addition and it was confirmed that neither a precipitation nor a float at all were seen in the solution tank during the procedure. On the other hand, as for a fuel additive of comparative example 1, a float was partially seen in about 30 minutes after stirring and, as for the inside of a solution tank, a precipitate and a float of ferrocene insoluble were seen also during the procedure.

INDUSTRIAL APPLICABILITY

[0059] According to this invention, by using ferrocene and/or ferrocene derivative(s) together with lecithin, the fuel additive in which the ferrocene and/or the ferrocene derivative(s) contained can be dissolved easily and stably can be provided.

Claims

1. A fuel additive containing ferrocene and/or ferrocene derivative(s), and lecithin.

2. The fuel additive according to claim 1, containing 80 to 99 mass % of said ferrocene and/or ferrocene derivative(s), and 1 to 20 mass % of said lecithin, and being in the solid state.

3. The fuel additive according to claim 1, containing 78 to 99 mass % of said ferrocene and/or ferrocene derivative(s), 0.9 to 20 mass % of said lecithin and 0.1 to 2 mass % of water, and being in the particle state.

4. The fuel additive according to claim 1, containing 2 to 5 mass % of said ferrocene and/or ferrocene derivative(s), 5 to 50 mass % of said lecithin and mineral oil, and being in the liquid state, wherein the ferrocene and/or ferrocene derivative(s), and the lecithin are dissolved in said mineral oil.

5. The fuel additive according to any one of claims 1 to 4, wherein said additive is used by being added into a fuel so as to make the concentration of said ferrocene and/or ferrocene derivative(s) and said lecithin in ranges of 1 to 50 ppm, and 0.01 to 500 ppm, respectively.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/052949

A. CLASSIFICATION OF SUBJECT MATTER
C10L1/26(2006.01)i, *C10L1/30*(2006.01)i

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)
C10L1/26, C10L1/30

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus(STN), JST7580(JDream2), JSTPlus(JDream2)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2-132188 A (Velino Ventures Inc.), 21 May, 1990 (21.05.90), Claims & US 4998876 A & EP 359390 A1	1-5
A	JP 2-279790 A (Exxon Chemical Patents Inc.), 15 November, 1990 (15.11.90), Claims & US 5135669 A & EP 386923 A1	1-5
A	GB 1497531 A (NITROCHEMIE G.M.B.H.), 12 January, 1978 (12.01.78), Example 1 (Family: none)	1-5

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 March, 2008 (21.03.08)	01 April, 2008 (01.04.08)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

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- **Shibayama et al.** *Japan Society of Mechanical Engineers collected papers,* 1968, vol. 34 (260), 769 **[0052]**
- **Hou et al.** *Japan Society of Mechanical Engineers collected papers,* 1988, vol. 54 (507), 3301 **[0052]**