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(54) Fuel additive and fuel composition containing the additive

(57) The present invention is directed to a fuel additive excellent in the cleanliness performance for the intake system and combustion chamber(s) of a gasoline engine and also to a fuel composition containing the additive.

A fuel additive is described having as a principal component a polyoxyalkylene glycol having an average molecular weight of from 500 to 5,000 and represented by the following formula (1):

$$HO\text{-}(AO)_n\text{-}H \qquad (1)$$

wherein $(AO)_n$ represents a mixture of oxyethylene groups and oxypropylene groups or solely oxypropylene groups, the A representing an ethylene group or propylene group, and the n representing a positive integer, provided that the content of oxypropylene group(s) is 50 wt% or higher based on the total weight of the oxyalkylene groups and a fuel composition comprising a petroleum fraction as a principal component and 0.001 to 5 wt%, based on the whole weight of the fuel composition, of the fuel additive.

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Description

[0001] This invention relates to a fuel additive and a fuel composition containing the additive, and more specifically to a fuel additive having the property of improving the cleanliness of an intake system and a combustion chamber of a gasoline engine.

[0002] Fuel for internal combustion engines, such as gasoline, is well known to have the tendency of forming sludge, deposit and the like in intake systems and combustion chambers. Deposit in the intake system of an engine becomes a cause of a reduction in its output, a deterioration in its operability and an impairment in its exhaust emission. Especially, as a result of the move toward gasoline engines of significantly high performance in recent years, the engines are now extremely sensitive in performance to such deposit in their intake systems. Although an electronic control type fuel injection device, for example, permits accurate control of an air-fuel ratio and is effective in improving not only the performance of an engine but also its gasoline mileage and exhaust emission, formation of deposit on the associated intake valve results in striking of the deposit by gasoline injected from the fuel injection device, thereby failing to properly control the air/fuel ratio. As a consequence, the operability is adversely affected. Further, deposit in a combustion chamber of an engine becomes a cause of an increase in the octane number requirement of the engine. There has accordingly been a strong demand for the development of an additive which can suppress the formation of deposit in both an intake system and a combustion chamber.

[0003] With the object of improving the cleanliness of the intake valves and intake ports of a gasoline engine, fuels with polyetheramine compounds contained therein are disclosed in JP kokai 55-25489, JP kokoku 55-39278, JP kokoku 56-48556 and JP kokoku 61-33016, and a fuel with a polyisobutene-amine compound contained therein is disclosed in JP kokai 2-261806. These fuels can improve the cleanliness of the intake system of a gasoline engine but, concerning the cleanliness of its combustion chamber, they are not effective but give rather deleterious effect in many instances. Further, JP kokai 4-88091 teaches that a fuel added with a gasoline additive composition, which comprises a polyoxyalkylene glycol having a molecular weight of from 500 to 5,000 or a derivative thereof, an alkylamine and a lubricating oil fraction, can reduce the amount of deposit to be formed on intake valves. However, a fuel with a lubricating oil fraction added therein has been found to deteriorate the cleanliness of combustion chambers of an engine. In addition, JP kokai 3-229797 discloses a fuel which contains a polyetheramine compound. This publication describes that the fuel can improve the cleanliness of the intake system and combustion chambers of a gasoline engine. Its effect has however been found to be insufficient for the improvement of the cleanliness of the intake system and combustion chambers.

[0004] An object of the present invention is to provide a fuel additive comprising a particular polyoxyalkylene glycol with the property of improving the cleanliness of the intake system and combustion chamber of a gasoline engine, and also a fuel composition containing the additive.

[0005] It has been found that a fuel additised with a polyoxyalkylene glycol, which has an average molecular weight of from 500 to 5,000 and contains oxypropylene groups in a proportion of 50 wt% or higher, preferably in the substantial absence of lubricating oil as a diluent can markedly improve the cleanliness of the intake system and combustion chambers of a gasoline engine.

[0006] The present invention provides a fuel additive comprising as a principal component, preferably in the substantial absence of lubricating oil as a diluent, a polyoxyalkylene glycol having an average molecular weight of from 500 to 5,000 and represented by the following formula (1):

$$HO\text{-}(AO)_n\text{-}H \qquad (1)$$

wherein $(AO)_n$ represents a mixture of oxyethylene groups and oxypropylene groups or solely oxypropylene groups, the A representing an ethylene group or propylene group, and the n representing a positive integer, provided that the content of oxypropylene group(s) is 50 wt% or higher based on the total weight of the oxyethylene and oxypropylene groups. In addition, the present invention also provides a fuel composition comprising a petroleum fraction as a principal component and 0.001 to 5 wt%, based on the whole weight of the fuel composition, of the above fuel additive.

[0007] The present invention is concerned with the fuel additive and also with the fuel composition containing the fuel additive, as described above. As preferred embodiments, the present invention embraces the following additives and fuel composition:

(1) The fuel additive as described above, in which the polyoxyalkylene glycol has an average molecular weight of from 1,000 to 3,000.

(2) The fuel additive as described above under (1), in which, in the formula (1) representing the polyoxyalkylene

glycol, A represents a propylene group.

(3) The fuel composition as described above, in which the content of the fuel additive is from 0.05 to 0.5 wt% based on the whole weight of the fuel composition.

[0008] The present invention will hereinafter be described in detail.

(A) Fuel Additive

[0009] The fuel additive according to the present invention contains as a principal component the polyoxyalkylene glycol represented by the formula (1). In the formula, A may be mixed alkylene group formed of an ethylene group and a propylene group. Preferably, it is a propylene group. In the fuel additive according to the present invention, it is important that the content of oxypropylene group(s) in the polyoxyalkylene glycol is 50 wt% or higher, preferably 60 to 100 wt%, for example 70 to 90 wt%. A content of oxypropylene group(s) lower than 50 wt% leads to insufficient solubility in fuel and also to formation of sludge and deposit in a greater amount.

[0010] Further, the average molecular weight of the polyoxyalkylene glycol in the present invention is from 500 to 5,000. An average molecular weight lower than 500 leads to a substantial reduction in the preventive effect against the formation of sludge and deposit. An average molecular weight higher than 5,000, on the other hand, results in such a polyoxyalkylene glycol as acting by itself is a cause for sludge and deposit formation. The preferred average molecular weight is from 1,000 to 3,000.

[0011] The polyoxyalkylene glycol in the present invention can be prepared by method(s) known per se in the art. For example, it can be prepared by subjecting ethylene oxide and propylene oxide as raw materials to ring-opening polymerization in the presence of a catalyst. Usable examples of the polymerization catalyst can include metal alkoxides [$Al(OR)_3$, $Zn(OR)_2$ and the like] and organometal compounds [$Al(C_2H_5)_3$, $Zn(C_2H_5)_2$ and the like]. In the polyoxyalkylene glycol for use in the present invention, oxyethylene groups and oxypropylene groups may be arranged regularly, randomly or as blocks. Since the reactivity of ethylene oxide is higher than that of propylene oxide, the polyoxyalkylene glycol is in the form of a block polymer in many instances. The proportion of oxypropylene groups in the polyoxyalkylene glycol for use in the present invention can be controlled at 50 wt% or higher based on the average molecular weight of the polyoxyalkylene glycol by adjusting the ratio between ethylene oxide and propylene oxide. Further, it is possible to produce a polymer, the average molecular weight of which is from 1,000 to 5,000, by controlling its polymerization conditions to adjust its polymerization degree and then isolating it by a distillation method and the like. Such polymers have been produced to date for use as surfactants and also as raw materials for urethane rubber. "Pluronic" series commercially available from Asahi Denka Kogyo K.K. can be mentioned as examples.

[0012] Besides the polyoxyalkylene glycol represented by the formula (1), the fuel additive according to the present invention may contain, at low concentrations, impurities, polymers of low molecular weights, polymers of high molecular weights and the like, which are formed as byproducts in the course of the production. If desired, the fuel additive can be used in a form dissolved in a diluent. As the diluent, a known organic solvent can be used. Illustrative can be saturated aliphatic hydrocarbons such as n-hexane, n-heptane and isooctane, aromatic hydrocarbons such as toluene and xylene, and fuels such as gasoline. No particular limitation is imposed on the amount of such a diluent insofar as it is in a range not impairing the performance of the fuel additive according to the present invention. In general, however, the diluent can be used in a proportion of from 0.05 to 20 parts by weight per every part by weight of the polyoxyalkylene glycol of the present invention.

(B) Fuel Composition

[0013] The fuel composition according to the present invention is obtained by mixing, in a fuel composed of a petroleum fraction as a principal component, the fuel additive of the present invention at a content of from 0.001 to 5 wt% based on the whole weight of the fuel composition. No particular limitation is imposed on the manner of mixing such as the order of mixing. A content lower than 0.001 wt% cannot reduce the formation of sludge and deposit to a sufficient extent in the intake system and combustion chambers of a gasoline engine, whereas a content higher than 5 wt% leads to an increase in the amount of sludge and deposit formed. The preferred content ranges from 0.05 to 0.5 wt%. Specific examples of the fuel can be fuels for spark ignition engines, such as No. 1 and No. 2 "motor gasolines" specified under JIS K2202 and the "aviation gasoline" stipulated under JIS K2206. These "motor gasolines" should include reformed motor gasolines, cracked motor gasolines, low-lead motor gasolines, unleaded motor gasolines, and the like.

[0014] The petroleum fraction employed in the fuel composition according to the present invention can be a petroleum fraction having a 10%-distillation temperature of 70°C or lower and a 97%-distillation temperature of 205°C or lower, as distillation properties, and an existent gum content of 5 mg/100 ml or lower. Illustrative can be petroleum fractions produced by atmospheric distillation of crudes such as paraffin base crude, naphthene base crude, mixed base crude,

special crudes, and mixtures thereof, as well as petroleum fractions obtained as a result of treatment of heavy petroleum fractions, which have been produced by atmospheric distillation of such crude, by combining hydrocracking, catalytic cracking, catalytic reforming and the like. These petroleum fractions can be used either singly or in combination. Components other than the petroleum fraction can include gas oil fractions derived from oil shale, oil sand, coal and the like; and gas oil fractions synthetically available from methanol.

[0015] The fuel composition according to the present invention can also contain one or more known fuel additives as desired to extents not impairing its performance. Examples of the known fuel additives can include surface ignition preventing agents such as tricresyl phosphate (TCP) and trimethyl phosphate; metal deactivators led by salicylidene derivatives such as N,N'-salicylidene diaminopropane; anti-icing additives such as alcohols and succinimide; corrosion inhibitors such as aliphatic amine salts, sulfonate salts and alkylamine phosphates; antistatic agents such as anionic, cationic and amphoteric surfactants; coloring agents such as azo dyes; phenols such as 2,6-di-tert-butyl-p-cresole; and antioxidants typified by aromatic amines such as phenyl-à-naphthylamine. These additives can be used either singly or in combination. The amount of each additive can be, but is not limited to, 0.5 wt% or smaller.

[0016] In addition, the fuel composition according to the present invention may also contain an oxygen-containing compound to an extent not impairing its performance. Illustrative can be methanol, ethanol, methyl tert-butyl ether, and ethyl tert-butyl ether. The amount of the oxygen-containing compound can be, but is not limited to, in a range of from 0.1 to 10% based on the whole weight of the fuel composition.

EXAMPLES

[0017] The present invention will hereinafter be described in further detail by the following examples. It should however be borne in mind that the present invention is by no means limited by the following examples. In the following examples, the following petroleum fraction and Compound 1 were used. A quantitation method of oxypropylene groups and a cleanliness performance test method will also be described.

(1) Petroleum fraction (base fuel)

[0018] Properties of a petroleum fraction used as a base fuel are shown in Table 1.

TABLE 1

Specific gravity (g/cm^3, at 15°C)	0.7486
Distillation properties (°C)	
Initial boiling point	31.5
10%	43.0
50%	99.0
90%	144.0
End point	178.0
Road octane number	100
Existent gum (mg/100 mℓ)	
Unwashed	2.1
Washed	0.3
Hydrocarbon type (vol%)	
Aromatics	36.9
Olefins	16.1
Sulfur (wppm)	9

(2) Compound 1

[0019] A polyoxyalkylene glycol represented by the formula

$$HO\text{-}(EO)_a\text{-}(PO)_b\text{-}(EO)_c\text{-}H \quad (2)$$

wherein E is an ethylene group, P is a propylene group, a+c is 2.4, b is 16.4, and the content of oxypropylene groups is 88.5 wt%; ("Pluronic L31, trade name; product of Asahi Denka Kogyo K.K.). Its average molecular weight is 1,075.

(3) Quantitation of oxypropylene groups

[0020] The content of the oxypropylene groups contained in Compound 1 was determined by 13C-NMR spectroscopy.

(4) Cleanliness performance test method

[0021] After a test engine shown in Table 2 was operated under operation conditions presented in Table 3, the test engine was disassembled. Deposit (hereinafter called "IVD") formed on its intake valves and deposit (hereinafter called "CCD") formed in its combustion chambers were scraped off and their weights were measured.

TABLE 2

Engine type	4-stroke O.H.C.
Bore x stroke (mm)	65 x 58
Number of cylinders	2
Total displacement (mℓ)	359
Compression ratio	8.5:1
Maximum output (ps/rpm)	12.2/3600
Maximum torque (kg-cm/rpm)	240/3000

TABLE 3

Engine speed (rpm)	3000
Load (W)	2400
Coolant temperature (°C)	82
Air/fuel ratio	12
Test duration (hours)	20
Lubricating oil	"Esso Super Flow" (10W-30)

EXAMPLE

[0022] A fuel composition was prepared by mixing Compound 1 in the petroleum fraction shown in Table 1. A cleanliness performance test was conducted on the thus-prepared fuel composition. The content of Compound 1 in the fuel composition and the results of the cleanliness performance test are shown in Table 4. The results of the cleanliness performance test were presented in terms of changes (%) relative to the cleanliness performance of the base fuel not added with Compound 1.

TABLE 4

	Example
Content in fuel composition (wt%)	
Compound 1	0.1
Cleanliness performance (change *1%)	
IVD*2	- 60
IVD*3	- 42

*1 Change: Percentage (%) of a change relative to the cleanliness performance of the base fuel

*2 IVD: Change in the amount of deposit formed on the intake valves.

*3 CCD: Change in the amount of deposit formed in the combustion chambers.

[0023] As is evident from Table 4, the fuel composition according to the present invention, which contained Compound 1, achieved substantial reductions in both IVD and CCD compared with the fuel which did not contain Compound 1.

Claims

1. A fuel additive comprising as a principal component a polyoxyalkylene glycol having an average molecular weight of from 500 to 5,000, and represented by the formula

$$HO\text{-}(AO)_n\text{-}H$$

wherein $(AO)_n$ represents a mixture of oxyethylene groups and oxypropylene groups or solely oxypropylene groups, the A representing an ethylene group or propylene group, and the n representing a positive integer, provided that the content of oxypropylene group(s) is 50 wt% or higher based on the total weight of the oxyethylene and oxypropylene groups.

2. A fuel additive according to claim 1, wherein said polyoxyalkylene glycol has an average molecular weight of from 1,000 to 3,000.

3. A fuel additive according to claim 1 or 2, wherein, in the formula (1) representing said polyoxyalkylene glycol, A represents a propylene group.

4. A fuel additive according to claim 1 or 2 wherein, in the formula (1) representing said polyoxyalkylene glycol, $(AO)_n$ represents a mixture of oxyethylene and oxypropylene groups.

5. A fuel composition comprising a petroleum fraction as a principal component and 0.001 to 5 wt%, based on the whole weight of said fuel composition, of a fuel additive according to any preceding claim.

6. A fuel composition according to claim 5, wherein the content of said fuel additive is from 0.05 to 0.5 wt% based on the whole weight of said fuel composition.

7. A method for reducing deposit formation in the intake system and combustion chamber of gasoline fueled engines comprising running the gasoline fueled engine on a gasoline fuel containing a fuel additive according to any one of claims 1 to 4.

8. The method of claim 7 wherein the fuel contains from 0.001 to 5 wt% of the polyoxyalkylene glycol.

9. The method of claim 8 wherein the fuel contains from 0.05 to 0.5 wt% of the polyoxyalkylene glycol.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 6034

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 548 616 A (SUNG ET AL.) 22 October 1985 * the whole document * ---	1,2,4-6	C10L1/18 C10L10/00
X	US 3 030 939 A (BRANDT ET AL.) 24 April 1962 * the whole document * ---	1,2,4-6	
X	FR 2 096 298 A (SHELL) 11 February 1972 * page 2; claim 18 * * page 12 * ---	1-3,5-9	
X	GB 2 261 441 A (ETHYL) 19 May 1993 * abstract; claim 8 * * page 8, line 8 - line 22 * * page 13, line 1 - line 16 * * page 15 * ---	1-9	
X	EP 0 647 700 A (ETHYL) 12 April 1995 * page 5, line 49; example 2 * ---	1-3,5,7,8	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	EP 0 654 524 A (TONEN) 24 May 1995 * page 6, line 1 - line 10; examples C1,D1 * * page 6, line 55 - line 56 * ---	1-9	C10L
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 November 1998	De La Morinerie, B

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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 6034

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 2 425 845 A (TOUSSAINT ET AL.) 19 August 1947 * claim 9 *	1,2,4	
X	EP 0 569 228 A (ETHYL) 10 November 1993 * abstract * * page 11, line 4 - line 5 * * page 10, line 16 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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