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(54) ADDITIVE FOR HYDROCARBON FUELS

(57) The invention relates to petrochemistry, in particular to additive compositions for hydrocarbon fuels, mainly to automobile gasoline which are added in order to reduce fuel evaporation losses during storage and can be used for petroleum and fuel storage depots. The inventive additive comprises a butanol-and-polyether mixture which is based on ethylene and propylene oxides and whose molecular mass is equal to 402 conventional units and in which a fluorine-containing chloride of a quaternary ammonium salt of a formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)_2Cl$ is dissolved. Said additive is also comprises an N-perfluorononanyl-β-aminosulfonic acid sodium salt at the following component ratio: 6.0-12.0 mass % fluorine-containing chloride of a quaternary ammonium salt of the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)_2Cl$, 0.2-2.0 mass % N-perfluorononanyl-β-amino-sulfonic acid sodium salt, 30-55 mass % ethylene and propylene oxide-based polyether with the molecular mass of 402 conventional units and 35-60 mass % butanol. Said invention makes it possible to reduce the evaporation of hydrocarbon fuel components during the tank storage thereof and to reuse said additive by preventing additive precipitation on tank walls, in pipelines and filters of engine fuel systems.

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Description

Field of the Invention

[0001] The invention relates to petrochemistry, in particular to additive compositions for hydrocarbon fuels, mainly to automobile gasoline, which are added in order to reduce fuel evaporation losses during storage, and can be used at petroleum and fuel storage depots.

Description of the Prior Art

[0002] An additive is known, which comprises a fluorine-containing surfactant, a polyether with the molecular weight of 2500 which is based on ethylene oxide and propylene oxide, ethylene glycol, and an aliphatic alcohol taken as butanol-1 (see: V.V. Usin, A.V. Ulitko et al. *The environment protection when using fuels and operating means of transportation,* Ulianovsk, UTTsNTIP, 1993, p.25).

[0003] The said additive, however, comprises components in high concentrations and has low efficiency in reducing fuel evaporation losses during storage.

[0004] An additive is also known, which comprises a fluorine-containing surfactant, a polyether with the molecular weight of 3503 which is based on ethylene oxide and propylene oxide, ethylene glycol, and an aliphatic alcohol (see: V.V. Usin, A.V. Ulitko et al. *The environment protection when using fuels and operating means of transportation,* Ulianovsk, UTTsNTIP, 1993, p.34-35). The additive comprises, in % by weight: a fluorine-containing quaternary ammonium salt — 4.5 to 5.5, a polyether with the molecular weight of 3503 which is based on ethylene oxide and propylene oxide — 47.0 to 49.0, ethylene glycol — 4.5 to 5.5, and butanol-1 the rest. The said additive is used for reducing evaporation losses and is added to a hydrocarbon fuel directly in the concentration of 0.2 % by weight. The experience of using the additive proves its insufficient efficiency in reducing evaporation fuel losses during storage.

[0005] The closest, as to its technical essence and achieved result, to the inventive additive is an additive to hydrocarbon fuels, which comprises a butanol-polyether mixture based on ethylene oxide and propylene oxide, in which a fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$ is dissolved (see, RU 2208041 C10L 1/18, 2003). The said additive to hydrocarbon fuels also comprises decanol and a dioctyl ether of phthalic acid in the following component ratio, in % by weight:

Fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$	1.2 to 3.4
Polyether with the molecular weight of 3503 which is based on ethylene oxide and propylene oxide	3.5 to 7.5
Dioctyl ether of phthalic acid	3.5 to 7.5
1:1 mixture of decanol and butanol	the rest.

[0006] The disadvantages of the known solution are its low efficiency in reducing evaporation fuel losses during storage (for A-76 gasoline the evaporation reduction is 30 %) as well as practically complete deposition of these additives on containment walls, pipelines and fuel system filters during fuel pumping and tank drying, which does not enable to use the said additives repeatedly when filling tanks. After fuel has been removed from a tank, it is practically impossible to separate the additive film from the tank surface by way of feeding a new batch of fuel.

Brief Description of the Invention

[0007] The objective of the invention is to develop and create an additive to hydrocarbon fuels, which would have improved performance and efficiency.

[0008] By achieving the said objective it is possible to obtain technical results comprising a reduction in evaporation of hydrocarbon fuel components when storing them in tanks, as well as in provision of repeated use of an additive by excluding its deposition on tank walls, pipelines and engine fuel system filters.

[0009] The said technical results may be achieved by using a polyether having the molecular weight of 402 as a polyether used in a hydrocarbon fuel additive comprising a butanol-polyether mixture based on ethylene oxide and propylene oxide, in which a fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$ is dissolved, the said additive comprising, in addition, a sodium salt of the N-perfluorinenononail-β-aminosulfonic acid, with the following component ratio, in % by weight:

Fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$	6 to 12

(continued)

Sodium salt of the N-perfluorinenononail-β-aminosulfonic acid	0.2 to 2.0
Polyether with the molecular weight of 402, which is based on ethylene oxide and propylene oxide	30 to 55
Butanol	35 to 60

[0010] The distinctive feature of the invention is that the said additive comprises, in addition, a sodium salt of the N-perfluorinenononail-β-aminosulfonic acid, and a polyether with the molecular weight of 402 is used as the polyether based on ethylene oxide and propylene oxide. In the result of a reaction of the said sodium salt of the N-perfluorinenononail-β-aminosulfonic acid with the said fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$ and butanol fuel evaporation losses are reduced, and the polymeric film sticking to metallic surfaces of fuel tanks is precluded, which enables to use the said additive in tanks repeatedly.

[0011] The additive components content, which ensures obtaining of the above-said results, has been determined experimentally.

[0012] Further, it is advisable that the ratio of a polyether, which has the molecular weight of 402 and is based on ethylene oxide and propylene oxide, and butanol would be 49:40.

Description of the Preferred Embodiment

[0013] In order to prepare the additive, a fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$ is dissolved in a mixture of butanol and a polyether with the molecular weight of 402, which is based on ethylene oxide and propylene oxide. A sodium salt of the N-perfluorinenononail-β-aminosulfonic acid is added to the obtained solution in the quantity from 0.2 to 2.0 % by weight.

[0014] The said fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$ is a wax-like substance having a light-brown color, which is hygroscopically dissolved in alcohols. It has the density from 1560 to 1600 kg/m^3, the melting point of 80°C, the chlorine content from 5.0 to 5.6 % by weight. Its technical designation is "CHAS 9". It is made according to the specification "TU 6-02-2-817-84".

[0015] The polyether having the molecular weight of 402, which is based on ethylene oxide and propylene oxide is a syrupy colorless liquid. The hydroxyl group content is 1.5 to 1.7 %, the acid number is < 0.1 mg KOH/g, the Heppler viscosity at 25°C is 450 to 600 MPa·s, the density is 1010 kg/m^3, the molecular weight is 402. The technical designation is "Laprol-402". It is made according to the specification "TU 6-05-221-484-79".

[0016] Butanol is a colorless clear liquid. It has the density from 800 to 830 kg/m^3, the boiling point is 108°C. It is produced in the industry according to GOST 6006. It is used as a solvent in the paint industry (see, Chemical Encyclopedia in 5 Volumes, V. 1, I.L. Knunyants et al., M., Soviet Encyclopedia Publishers, 1988, p.336-337).

[0017] The sodium salt of the N-perfluorinenononail-β-aminosulfonic acid is a colorless liquid produced by known methods.

[0018] The inventive additive is added to a hydrocarbon fuel after filling a tank with a fuel, e.g., automobile gasoline, in the quantity from 0.015 to 0.025 % by weight. The additive is added to a fuel by pulverizing it.

[0019] In order to establish the quantitative composition of the additive, some samples (see Table 1) have been prepared, which have been tested in a composition with A-76 automobile gasoline according to GOST 2084. Samples 1 - 5 differ in the percentage ratio of the components in the inventive additive.

[0020] The additive efficiency has been evaluated according to the quantity of evaporated fuel under storage in the static conditions for two days, as compared to the fuel without the additive and the fuel with the additive according to the closest analogous solution. The additive test results are given in Table 2.

[0021] The evaporation tests have been conducted in the static conditions in glasses with the evaporation area of 13.8 cm^2 at the air temperature from 18°C to 20°C and the relative humidity from 85% to 95%. The error in determining evaporation is $\pm$0.05 g/day/m^2.

[0022] An analysis of the results given in Table 2 enables to draw a conclusion that the most preferred are Samples 1 and 2 of the additive, though all the tested compositions in the above-stated conditions reduce the quantity of gasoline evaporated from the surface.

[0023] The efficiency of the additives has been also evaluated according to a reduction in fuel evaporation when the repeatedly used compositions have been pulverized over the fuel surface — when drying and subsequent filling of a tank with a fuel. As can be seen in Table 2, the efficiency of the inventive additive is practically not reduced because it is not deposited on the surfaces.

Table 1.

Additive composition, in % by weight	SAMPLES				
	1	2	3	4	5
Fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$	10	9	8	6	12
Laprol-402	49	40	55	33.5	30
Butanol	40	49.5	35	60	57.8
Sodium salt of the N-perfluorinenononail-β-aminosulfonic acid	1	1.5	2	0.5	0.2

Table 2.

Parameter	A-76 gasoline w/o additive	With the prototype additive in the quantity of 0.001 % by weight	With the inventive additive in the quantity of 0.02 % by weight				
			Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Loss of gasoline weight (in grams for 2 days)	6.0	4.2	3.4	3.8	4.1	4.0	3.7
Reduction of evaporation, rel. %	-	30.0	43.3	36.6	31.7	33.3	38.3
Octane number, units	76.0	75.8	76.1	76.0	75.9	76.0	76.2
Loss of gasoline weight (in grams for 2 days) after the second fill of the tank	6.0	5.9	3.5	3.9	4.3	4.4	4.5
Reduction of evaporation, rel. %	-	1.70	41.7	35.0	27.3	26.7	25.0

Claims

1. An additive for hydrocarbon fuels comprising a butanol-polyether mixture based on ethylene oxide and propylene oxide, in which a fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$ is dissolved, wherein a polyether having the molecular weight of 402 is used as the polyether in the said mixture, the said additive further comprising a sodium salt of the N-perfluorinenononail-β-aminosulfonic acid and having the following component ratio, in % by weight:

Fluorine-containing chloride of a quaternary ammonium salt having the formula $C_8F_{17}CONCHC_3H_6N(C_2H_4OH)CH_3)_2Cl$	6 to 12
Sodium salt of the N-perfluorinenononail-β-aminosulfonic acid	0.2 to 2.0
Polyether with the molecular weight of 402, which is based on ethylene oxide and propylene oxide	30 to 55
Butanol	35 to 60

2. The additive according to Claim 1, wherein the ratio of the polyether, which has the molecular weight of 402 and is

based on ethylene oxide and propylene oxide, and butanol is 49:40.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2004/000216

A. CLASSIFICATION OF SUBJECT MATTER
C10L 1/18, 1/22, 1/24

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)
C10L 1/18, 1/20, 1/22, 1/24,

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2208040 C1 (GOSUDARSTVENNY NAUCHNO-ISSLEDOVATELSKY INSTITUT MINISTERSTVA OBORONY ROSSYSKOI FEDERATSII (PO PRIMENENIJU TOPLIV, MASEL, SMAZOK I SPETSIALNYKH ZHIDKOSTEI-25 GOSNII MO RF PO KHIMOTOLOGII) 10.07.2003	1-2
A	SU 1816794 A1 (USIN V.V. et al) 23.05.1993	1-2
A	JP 62-100592 A (TAKEHARA: KK) 11. 05. 1987	1-2
A	US 2912416 A (SHELL DEVELOPMENT COMPANY) 10. 11. 1959	1-2

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"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)
"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
"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
"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
"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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 September 2004 (29.09.2004)	**14 October 2004 (14.10.2004)**
Name and mailing address of the ISA/	Authorized officer
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