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(54) **MULTI-FUNCTION UNIVERSAL FUEL ADDITIVE**

(57) The invention relates to the field of petroleum refining and petrochemistry, and specifically to the composition of a multi-function universal additive and to a fuel composition containing said additive and intended for use in internal combustion engines, and also in boilers and furnaces. The present fuel additive contains aliphatic alcohols, water, carbamide and acetanilide. Use of the

proposed multi-function universal additive in the composition of fuels provides reduced specific fuel consumption, fewer harmful impurities in exhaust and waste gases (CO, CH, soot), and reduced soot formation in the combustion zone. The present additive has dispersant properties in the composition of heavy distillate and residual fuels.

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Description

DESCRIPTION

[0001] This invention relates to the field of oil refining and petrochemistry, in particular to a composition comprising such additive and intended for use in internal combustion engines as well as in boilers and furnaces.

[0002] Today, various additives are known that are used in compositions of modern fuels. There are additives used for bringing fuel quality to standard requirements. The European and US norms strictly limit the sulfur content and aromatic and polycyclic hydrocarbons content of fuels, set a significantly higher level of the cetane number, introduce the index of "fuel lubricating ability". Also, multifunction additive packages for various fuels are in use. Their main purpose is to provide additional performance and ecological properties to fuels which enables to present such fuels as having improved quality.

[0003] An universal additive for fuels used in internal combustion engines is known in the art (RU Patent No. 2034905, published on 10.05.1995; IPC C10L1/18, C10L1/22), which has the following component ratio (in percent by weight):

C ₁ -C ₄ aliphatic alcohol	52-84
Urea	4-12
Acetic acid	4-12
Water	8-24

[0004] According to the inventors, the use of this additive enables to:

- reduce quantity of pollutant emissions of carburetor engines into the atmosphere by a factor of 2.5-7.5 due to improving fuel combustion efficiency;
- reduce black smoke percent of internal combustion engines in operation by a factor of 5-6;
- improve engine power;
- lower fuel consumption during operation of transportation means;
- prolong service life of engines due to preventing deposit from forming on the working surface of the piston-cylinder unit.

[0005] A drawback of this additive is its high corrosivity and extremely low solubility in a hydrocarbon fuel, which narrows its use and reduces field of application.

[0006] Also, a fuel additive is known in the art, which is added in a quantity of 0.0001-0.1 wt.% and comprises aliphatic alcohols, carbamide (urea), water and boric acid (RU Patent No. 2486229, published on 27.06.2013; IPC C10L9/10, C10L1/00, C10L1/10, C10L1/182), while having the following component ratio, in wt.%:

C ₂ -C ₄ aliphatic alcohols	10-97.99
Carbamide (urea)	1-30
Boric acid	0.01-3
Water	1-85

[0007] The additive as claimed may be used for improving combustion of a hydrocarbon fuel (gasoline, diesel fuel, fuel oil or rocket fuel) or products of petrochemical or by-product-coking processes, or products of plant raw stock processing, or water-oil or water-coal fuel, or solid fuel, or gaseous fuel. Another objective of the invention is to develop a fuel that increases combustion temperature as well as raises combustion efficiency and completeness, due to which toxicity of combustion products together with fuel corrosive action on fuel system parts may be reduced. The above-discussed additive is the closest to the claimed solution and has been considered as the prototype. One drawback of the above-discussed solution is that boric acid exhibits weak acidic properties, is practically insoluble in hydrocarbons, and is a toxic substance - its combustion leads to boron oxide emission into the atmosphere.

[0008] The objective of the present invention is to develop a more economical and more ecological fuel having improved consumer and technological characteristics.

[0009] The technical effects of the present invention are:

- reduction of specific fuel consumption and quantities of pollutants in exhaust and waste gases, when the fuel blend comprising the additive of the present invention is used,
- provision of a fuel blend with washing properties,
- raising of stability of heavy distillate and residual fuels.

[0010] The set objective is fulfilled and the technical effects are achieved by improving the additive composition in which acetanilide is substituted for boric acid as well as carbamide content is lowered, the content of the components being, in wt. %:

5	C ₂ -C ₄ aliphatic alcohols	75.0 - 95.0
	Water	4.0 - 20.0
	Carbamide	0.1 - 5.0
	Acetanilide	0.1 - 5.0.

10 **[0011]** Preferably, the additive is intended for direct adding to a fuel in the quantity from 0.005 to 0.006 % on the basis of the fuel weight.

[0012] The term "C₂-C₄ aliphatic alcohols" is understood as a totality of saturated alcohols comprising one or more hydroxyl groups in carbon atoms, a number of carbon atoms being from two to four, and each atom is coupled with not more than one hydroxyl group.

15 **[0013]** Known solutions do not disclose acetanilide effect on reducing specific fuel consumption and pollutant quantities in exhaust and waste gases, improving fuel washing properties, or raising fuel stability. The inventor unexpectedly found that addition of acetanilide in a quantity from 0.1 to 5% in combination with the other components of the additive has a significant positive effect on these properties.

20 **[0014]** These features of the invention, namely, a combination of C₂-C₄ aliphatic alcohols, water, carbamide and acetanilide in the said ranges of component ratio, are essential features that are conditioned by the cause-and-effect relation therebetween, forming a totality of essential features being sufficient in order, when a fuel blend with the additive according to this invention is in use, to reduce specific fuel consumption and a quantity of impurities present in exhaust and waste gases, provide said fuel blend with washing properties, and raise stability of heavy distillate and residual fuels simultaneously.

25 **[0015]** The proposed additive may be prepared at any enterprise specializing in this industry, because for this well-known materials and standard equipment manufactured by the industry are required.

[0016] The additive may be prepared as follows.

30 *Embodiment 1. Additive for use in a gasoline composition.*

[0017] 800 g of ethylene glycol were put into a 2L Erlenmeyer flask, 17 g of acetanilide were added, and the contents were stirred for 30 minutes until full dissolution. 165 g of distilled water heated to 50°C were put into another 500 mL Erlenmeyer flask, 18 g of carbamide were added, and the contents were stirred for 10 minutes until full dissolution. The carbamide aqueous solution was added into the acetanilide solution while stirring, and the resulting mixture was stirred for 15 minutes. The additive thus obtained, as was intended for use in gasoline, had the following composition, in wt. %:

- carbamide - 1.8
- acetanilide - 1.7
- 40 - ethylene glycol - 80.0
- water - 16.5.

Embodiment 2. Additive for use in a diesel fuel composition.

45 **[0018]** 900 g of isopropyl alcohol were put into a 2L Erlenmeyer flask, 33 g of acetanilide were added, and the contents were stirred for 15 minutes until full dissolution. 44 g of distilled water heated to 50°C were put into another 200 mL Erlenmeyer flask, 23 g of carbamide were added, and the contents were stirred for 10 minutes until full dissolution. The carbamide aqueous solution was added into the acetanilide solution in ethylene glycol while stirring, and the resulting mixture was stirred for 15 minutes. The additive thus obtained, as was intended for use in diesel fuel, had the following composition, in wt. %:

- carbamide - 2.3
- acetanilide - 3.3
- isopropyl alcohol - 90.0
- 55 - water - 4.4.

Embodiment 3. Additive for use in a fuel oil composition.

[0019] 757 g of ethylene glycol were put into a 2L Erlenmeyer flask, 49 g of acetanilide were added, and the contents were stirred for 30 minutes until full dissolution. 152 g of distilled water heated to 50°C were put into another 500 mL Erlenmeyer flask, 42 g of carbamide were added, and the contents were stirred for 10 minutes until full dissolution. The carbamide aqueous solution was added into the acetanilide solution in ethylene glycol while stirring, and the resulting mixture was stirred for 15 minutes. The additive thus obtained, as was intended for use in fuel oil, had the following composition, in wt.%:

- carbamide - 4.2
- acetanilide - 4.9
- ethylene glycol - 75.7
- water - 15.2.

[0020] The additive according to these three particular embodiments was added into the respective fuel in the quantity of 0.005 wt.%.

[0021] The examples provided below, which are not intended to limit the invention in any way, clearly demonstrate the possibility of achieving the claimed technical effect.

Example 1. Reduction of specific fuel consumption and quantity of pollutants in exhaust and waste gases.

[0022] The measurement methods, as prescribed and standardized, enable to determine fuel consumption and quantity of each particular component of waste gases. The new European driving cycle (NEDC) is obligatory for Europe. This cycle is used for modeling typical driving manner for European roads. Pollutant emissions by, and fuel consumption in, cars are determined on chassis dynamometers. While a car "runs" on chassis dynamometers in accordance with certain driving cycles (NEDC cycle), calibrated measurement systems determine concentrations of separate exhaust components. Waste gases were analyzed according to the CVS method that comprises the following measurements: determination of CH, CO and CO₂ concentrations with the use of NDIR (Non-Dispersive-Infra-Red) infrared absorption analyzers; determination of NO_x concentration with the use of apparatus operating under the chemiluminescence principle (CLD, chemiluminescence detector); fuel consumption was calculated according to the "carbon balance" method.

[0023] The tests were carried out on the gasoline car "Citroën DS3 Essence" and the diesel car "Renault Megane diesel". The test data (averaged for three runs) are shown in Table 1.

Table 1. Test data for reference fuel before (1) and after (2) use of the additive.

Car	Parameter									
	Consumption, L/100 km		CO ₂ , g/km		CO, g/km		CH, g/km		NO _x , g/km	
	1	2	1	2	1	2	1	2	1	2
Citroën DS3 Essence	5.92	5.41	0.135	0.119	0.601	0.135	0.202	0.045	0.083	0.028
Renault Megane diesel	4.79	4.21	0.125	0.106	0.325	0.195	0.026	0.014	0.292	0.205
1 - reference fuel										
2 - reference fuel + additive										

Example 2.

[0024] Tests for combustion of a heavy fuel (fuel oil) with the additive were carried out on the DKVr 4-13 GM boiler equipped with a GMG-2 burner, a VDN-10-1000 blow fan and a DN-9-1000 smoke exhaustor. Steam flow-rate was measured on the steam conduit according to the standard chart. Air flow-rate was determined according to the design method. The excess air factor and the composition of waste gas components were measured with the use of a Testo 350M/XL gas analyzer. The test data were processed in accordance with the heat engineering methodology proposed by M.B. Ravich [Ravich M.B., Simplified Methodology of Heat Engineering Calculations, M., Publ. House of the USSR Academy of Sciences, 1966, 407 pp.]. This methodology is based on generalized characteristics. Such characteristics may be used for making comparative heat engineering calculations and for calculating heat losses due to waste gases and due to chemical incomplete combustion, without taking an average fuel sample during tests, determining its com-

position and combustion heat.

[0025] The tests were carried out at the following loads on the steam boiler: 40, 60, 80 и 100%. Due to reduction in excess air and improvement in fuel combustion at all operation modes, improvement in the boiler efficiency was observed. The efficiency improvement was 5% at the rated load and 9.5% at the minimal load in comparison with combustion of the standard fuel. The specific fuel consumption exhibited corresponding reduction. The catalytic activity of the composition added to the fuel oil manifested itself in gradual cleaning of heat-exchange surfaces from deposits. The latter disappeared practically completely by the end of the tests. The nitrogen oxides (NO_x) exhaust reduction due to reduction in excess air fed for fuel combustion was 8.5%. Sulfur oxide exhaust reduction, when the boiler was operated on a fuel with the additive, was more significant, amounting to 25%, and after correction of the fuel-air ratio and lowering of the fuel oil heating temperature it was 67% (see Table 2).

Table 2. Performance characteristics of the steam boiler.

Characteristics	Fuel oil	Fuel oil + additive	Fuel oil + additive after adjusting fuel-air ratio
Steam capacity (adjusted value), tons/hour	2.5-3.7	2.3-3.9	3.1-3.9
Air excess beyond the boiler	1.28-2.08	1.11-1.75	1.04-1.25
Waste gases temperature, °C	295-349	298-340	318-336
Efficiency, %	76.18-82.18	80.08-85.35	84.01-86.51
Specific consumption of reference fuel, kg/Gcal	170.0-181.4	166.8-177.6	164.4-168.2
NO _x content of waste gases, mg/m ³	1310-1331	1240-1310	1225-1370
SO ₂ content of waste gases, mg/m ³	117.8-138.6	89.2-96.4	24.1-59.6

Example 3. Washing effect of the additive.

[0026] Washing effect is understood as ability of the additive to prevent deposits in fuel injectors (Port Fuel Injection - PFI) and on intake valves (Intake Valve Deposits - IVD) from forming, thus ensuring that the initial adjustment of an engine remains unchanged. Deposits in the intake system may cause malfunctions during the engine operation, and any deviations from an optimal composition of a fuel mixture reduce power, increase fuel consumption and exhaust gases toxicity.

[0027] Washing components for gasoline are surfactants comprising polar groups connected to one or more polymeric hydrocarbon tailings. Polar groups are functional groups of a washing component and usually are amines that are absorbed onto metal surfaces and/or onto forming deposit. A polymeric hydrocarbon tailing represents long-chain molecules of polyisobutylene and ensures good solubility in a fuel by ensuring dispersion of particles-precursors of deposit formation.

[0028] The BASF Keropur® additives are based on polyisobutylene amine (for gasolines) and polyisobutylene succinimide (for diesel fuels) that are produced from high-reactivity polyisobutylene (PIB) synthesized in accordance with the patented BASF technology. The Keropur® (Puradd® in the US) washing additives synthesized on the basis of high-reactivity PIB are highly efficient. BASF produces high-reactivity PIB from pure polyisobutylene according to the patented technology, and its composition comprises more than 90% of alpha-olefins.

[0029] The most common washing components for gasolines are based on a PIB-amine active group; however, already for a long time Afton Chemical Corporation has used the patented technology on the basis of the Mannich base, which technology was developed in the early 1970s when Afton Chemical for the first time started commercial production of Mannich washing components based on the PIB-phenol.

[0030] Most US manufacturers add washing additives to gasoline for cars in a concentration from 100 to 200 mg/kg (ppm). However, European manufacturers tend to prevent deposits from forming on valves practically to the fullest degree, and, therefore, add washing additives in a concentration from 300 to 600 mg/kg (ppm).

[0031] A required level of washing properties may be established, for example, in accordance with the recommendations issued by the Worldwide Fuel Charter (WWFC).

[0032] According to the EPA (US Environmental Protection Agency) rules, all additives for gasolines should be certified. The additive ability to prevent deposits from forming on intake valves is assessed on a BMW engine according to ASTM D 5500 method. Tests are carried out in the reference fuel having the prescribed composition. The test fuel is produced

by mixing commercial components in certain proportions. It is considered that the quality of 65% of US gasoline complies with these requirements.

[0033] Tests are carried on a car for two weeks. When a base fuel without washing additives is used, the minimum quantity of deposits formed at intake valves after the trip of 10,000 miles should be not less than 290 mg per valve. After testing the base fuel, a fuel with a washing additive is tested. A washing additive should ensure that deposits are reduced to a level not more than 100 mg per valve.

[0034] Also, the tests are aimed at assessing the additive influence on the fuel tendency to form deposits in the combustion chamber (Combustion Chamber Deposits, CCD). The CCD parameter enables to monitor side effects of washing additives. Some additives, though having good washing properties, may contribute to increased deposit formation in the engine combustion chamber, and an extremely high concentration of such an additive may caused increased deposit formation. Deposit quantity in a combustion chamber, when gasoline with an additive is used, should not be higher than 1,300 mg per cylinder or 140% in comparison to the use of the base fuel.

[0035] Comparative tests of the composition claimed for protection and its prototype, which were carried out according to the ASTM D 5500 method, showed the results displayed in Table 3.

Table 3. Comparative tests of fuels according to the ASTM D 5500 method.

Parameter	Fuel		
	Reference	Reference + #4 according to the prototype 0.003%	Reference + the additive 0.005%
Quantity of deposits on intake valves, mg per valve	360	350	196
Deposits in the combustion chamber, mg per cylinder	1618	1680	856

[0036] Thus, the proposed composition exhibits prominent washing effect as well as reduces deposit formation in the combustion chamber.

Example 4. Dispersion properties of the additive in compositions of heavy distillate and residual fuels.

[0037] It is known in the practice that residual fuels are unstable substances, since their constituent resins (solid pyrobitumens, carbenes and carboides) have density values from 1,070 to 1,300 kg/m³, which is above the density of residual fuel liquid part. Under the action of the natural gravitation, these solid substances, when stored in reservoirs and used in equipment, precipitate in the form of deposits on reservoir bottoms, in fuel filters, pipelines, heaters, engine injection nozzles, thus interfering with the fuel combustion process and requiring that equipment should be periodically cleaned from their sediments. Instability of residual fuels becomes even more actual nowadays, since, when oil processing becomes deeper, they comprise more products of secondary oil processing, namely, leavings of the viscosity breaking and thermal cracking of straight-run products - fuel oil and tar oil. These products are characterized (contrary to straight-run fuel oil and tar oil) by higher aggregative instability of pyrobitumens, which results in their accelerated deposition. Residual fuels, which composition comprise residual cracking products, may not be stored for a long time due to their increased physical instability.

[0038] The most efficient method of controlling formation of deposits in fuels comprising residual products of oil processing is the introduction of additives possessing dispersion properties. As practices show, an efficient additive that may be used for this purpose is the VNII NP-102 additive developed in Russia, which not only prevents deposits from forming in residual fuels, but also ensures washing-out of already formed deposits from fuel systems. The VNII NP-102 additive is prescribed by GOST 10585-75 for addition (in a concentration of at least 0.2 wt.%) to F5 and F12 admiralty fuel oils. Its latest (and improved) analog is the VNII NP-200 additive (working concentration is from 0.05 to 0.2 wt.%).

[0039] The proposed composition, after being added to fuel oil in a concentration from 0.005 to 0.006 wt.%, exhibits pronounced dispersion properties manifesting themselves in prevention of deposit formation, water emulsification, washing-out of deposits already formed.

[0040] In order to evaluate efficiency of the proposed composition and compare it with the existing analog, the method according to RU Patent No. 2462708 "Method for determining efficiency of dispersant additives to residual fuels" was used. According to the measurement results, the efficiency of the VNII NP-200 additive (0.2 wt.%) is 145%, and that of the composition proposed in this invention (0.005 wt.%) is 512%.

[0041] The pronounced dispersion properties of the composition were demonstrated during tests at an iron and steel plant using fuel oil as the fuel for open-hearth furnaces and continuous heating furnaces. According to the certificate

and the incoming inspection results, the fuel oil used comprises 1.2% of sulfur. In order to carry out tests, 10 liters of the proposed additive were added to the 200 m³ supplying tank. The tank was left heated for 12 hours. Before start of the tests a sample of fuel oil was taken, which, according to the laboratory analysis, showed the sulfur content of 1.5%. This may be explained only by the fact that additional 600 kg of sulfur were contained in the bottom deposit (in heavy fractions, the sulfur content was greater) that was dispersed by the introduced additive.

Claims

1. A fuel additive, comprising aliphatic alcohols, water, and carbamide, **characterized in that** it additionally comprises acetanilide, and the component ratio being, in wt. %:

C ₂ -C ₄ aliphatic alcohols	75.0 - 95.0	4.0 - 20.0
water	0.1 - 5.0	
carbamide	0.1 - 5.0	
acetanilide		

2. The fuel additive according to Claim 1, intended for introduction directly into a fuel in a quantity from 0.005 to 0.006% on the basis of the fuel weight.

INTERNATIONAL SEARCH REPORT

International application No
PCT/RU2016/000117

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L1/10
ADD.

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

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 017 368 A (STEINMANN HENRY W [US]) 25 January 2000 (2000-01-25) column 4, line 15 - line 30; example 1; tables 1-6	1,2
Y	----- RU 2 034 905 C1 (KOLLEKTIVNOE MALOE N PROIZV VN [RU]) 10 May 1995 (1995-05-10) cited in the application abstract	1,2
Y	& DATABASE WPI Week 199602 Thomson Scientific, London, GB; AN 1996-018923 & RU 2 034 905 C1 (ADIOZ RES PRODN ENTERP) 10 May 1995 (1995-05-10) abstract ----- -/-	1,2

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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INTERNATIONAL SEARCH REPORT

International application No PCT/RU2016/000117

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 1 789 302 A (CALCOTT WILLIAM S ET AL) 20 January 1931 (1931-01-20) column 1, line 1 - line 8; claim 9 column 2, line 75 - line 83 -----	1,2

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/RU2016/000117

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6017368	A	25-01-2000	NONE
RU 2034905	C1	10-05-1995	NONE
US 1789302	A	20-01-1931	NONE

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- RU 2034905 [0003]
- RU 10051995 [0003]
- RU 2486229 [0006]
- RU 2462708 [0040]

Non-patent literature cited in the description

- **RAVICH M.B.** Simplified Methodology of Heat Engineering Calculations, M. Publ. House of the USSR Academy of Sciences, 1966, 407 [0024]