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(54) **AGENT FOR INCREASING THE OCTANE NUMBER OF A GASOLINE AUTOMOBILE FUEL**

(57) The invention relates to an agent for increasing the octane number of a gasoline automobile fuel, which agent is a combination of alcohol and a product of reaction between a carbonyl compound and a compound containing at least two hydroxyl groups allowing the formation of cycles with carbonyl compounds, or is the mixtures of the above mentioned products. In a preferred embodiment, mono- or oligosaccharides or diatomic, triatomic or polyatomic alcohols are used as the compounds containing at least two hydroxyl groups allowing the formation of cycles with carbonyl compounds. Pentoses, preferably xylose or arabinose or hexose, substantially glucose, and the mixtures thereof are used as the monosaccharides. Glycols, for example, ethylene glycol are used as diatomic alcohols, glycerin is used as triatomic alcohols and erythritols, for example, pentaerythritol are used as polyatomic alcohols. A compound relating to lower aldehydes or lower ketones, for example, formaldehyde, acetaldehyde, acetone, methylethylketone, diethylketone or cyclohexane, is used as a carbonyl compound. The alcohols correspond to aliphatic alcohols containing up to five carbon atoms, preferably ethanol. The inventive gasoline automobile fuel means a gasoline or an alcohol-gasoline composition.

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Description

FIELD OF THE INVENTION

[0001] The invention relates to agents increasing the octane number of a gasoline automobile fuel, including alcohol-containing gasoline automobile fuel, and can be used to improve the consumer parameters of said types of automobile fuel.

BACKGROUND OF THE INVENTION

[0002] The progress in construction of motor engines and the increased requirements for ecological parameters of automobile fuel influence the ever-growing demand for a high octane gasoline with the proper toxicity level of the exhaust gases according to the present-day standards. The growth in the industrial share of high octane gasoline is impossible without a wide use of antiknock additives promoting increase in the detonation resistance of automobile fuel.

[0003] Nowadays oxygenates including a wide range of oxygen-containing compounds are used as antiknock agents. These are usually the mixtures with difficult to control compositions and containing alcohols, alkyl ethers and esters, carbonyl compounds and their interaction products. Most of them, under the action of air oxygen, can convert into peroxides, leading to a decrease in chemical stability of gasoline and to accumulation of carboxylic acids, causing corrosion of engine and containers and tanks for gasoline storage. A serious drawback of currently widely used methyl-tert-butyl ether is its appreciable toxicity and a low capacity for decomposition that leads to accumulation of toxic products in soil and natural water.

[0004] It is known that cyclic ketals (1.3-dioxolanes), derived via interaction between glycols and carbonyl compounds used as components in fuel compositions, improve ecological characteristics of motor engines. For instance, they reduce the content of solid particles and toxic products of incomplete combustion in the exhaust gases of diesel-fuel engines [US 2004025417, publ. 12.02.2004, FR 2833607, publ. 20.06.2003, AT 311428T, publ. 15.12.2005, JP 7331262, publ. 19.12.1995], improve the ecological characteristics of biodiesel [US 2006199970, publ. 07.09.2006, WO 2006084048, publ. 10.08.2006] and motor gasoline [US 4390345, publ. 28.06.1983, WO 8903242, publ. 20.04.1989].

[0005] CA Pat. 2530219, publ. 03.02.2005 describes the invention concerning an oxygenate production and its application as an additive increasing the capacity of gasoline for inflammation and reducing the content of detrimental emissions into the air. The oxygenate is a product of interaction between glycerol and carbonyl compound, for example acetone, alkylated by tertiary olefin. Alkylation is necessary to reach sufficient solubility of such 1.3-dioxolanes in hydrocarbon fuel and to avoid the influence of unsubstituted hydroxyl on solubility. This fact significantly limits the use of glycerol-based 1.3-dioxolanes as an additive to gasoline.

[0006] The said documents do not contain any information about a capacity of 1.3-dioxolanes to exhibit the antiknock properties toward gasoline.

[0007] The documents describe glycerol alkylation with isobutylene to obtain glycerol polyalkyl ethers as additives to gasoline [DE 4445635, publ. 27.06.1996, EP 0718270, publ. 26.06.1996]. If acetone is used as a solvent, the reaction mixture is a mixture of glycerol tert-butyl ethers with various degree of substitution and having an additive of free glycerol and also it additionally contains the cyclic ketal - 2.2-dimethyl-4-tert-butoxymetyl-1.3-dioxolane and the additive 2.2-dimethyl-4-hydroxymethyl-1.3-dioxolane, containing a free hydroxyl. These reaction mixtures when added to gasoline were shown to exhibit the properties of efficient additives increasing the octane number. To provide the phase compatibility, it is necessary to perform the alkylation of glycerol free hydroxyls, which is more labor- and energy-intensive. However, the presence in the mixture of monoalkylated glycerol as well as the admixtures of free glycerol and unalkylated 4-hydroxymethyl-1.3-dioxolane increases a probability of stratification of the gasoline composition containing this additive. A complex changeable composition of the additive depending on the reaction conditions in a multicomponent system results in instability and unpredictability of its antiknock properties.

[0008] It is known a multifunctional ethanol-based additive to gasoline, providing increased octane number, a lower turbidity temperature, decreased toxicity of exhaust emissions and containing, in addition to ethanol, N-methyl aniline, acetic aldehyde, crotonic aldehyde, ethyl ether and multifunctional additive AUTOMAG [RU Pat. 2148077, publ. 27.04.2000].

[0009] RU Pat. 2068871 C1, publ. 10.11.1996 is directed to an ethanol-based additive to gasoline, containing a co-solvent as a stabilizer which is a waste of hydrolytic production of ethanol from of raw wood, so called "aldehyde-ether-ethanol fraction"(8 - 80 mass %). Introduction of this additive (2 -20 mass %) into gasoline allows to increase its octane number and prevents its stratification at lower temperatures. The hydrolytic production waste in the additive is a mixture of aliphatic alcohols C_3-C_5, esters of methanol and ethanol and formic and acetic acids, furfural and other organic compounds.

[0010] RU Pat. 2129141, publ. 20.04.1999 is directed to a stabilized ethanol-based additive to gasoline, containing N-methyl aniline, ferrocene, and/or its derivatives; wherein ethanol is stabilized with lower aliphatic alcohols, ethers or aldehyde-ether-alcohol fraction derived from the waste of ethanol production from raw wood.

[0011] An object of this invention is to create a universal agent for gasoline automobile fuel, with a higher octane-increasing capability, which can be easily obtained from available chemical industry products or from waste or intermediates of carbohydrate-containing raw material processing.

DISCLOSURE OF THE INVENTION

[0012] As a result of the performed studies it has been found that the combination of alcohol with the product of interaction between a carbonyl compound and a compound containing at least two hydroxyls, allowing the formation of cycles with carbonyl compounds, or mixtures of said products, allows to increase the octane number of gasoline more effectively than any one of said components alone, due to a synergic effect.

[0013] In addition, a problem of phase incompatibility with gasoline fuel arising from the presence of free hydroxyl in the products of interaction between a carbonyl compound and a compound containing at least two hydroxyls allowing the formation of cycles with carbonyl compounds, is avoided.

[0014] Thus, the above mentioned object is solved by the fact that a combination of alcohol and a product of interaction between carbonyl compound and a compound containing at least two hydroxyls allowing the formation of cycles with carbonyl compounds or mixtures of the products, is used as an agent for increasing the octane number of a gasoline automobile fuel.

[0015] Preferably, saccharides or diatomic, triatomic and polyatomic alcohols are used as the compounds containing at least two hydroxyls allowing the formation of cycles with carbonyl compounds.

[0016] Preferably, the said saccharides are monosaccharides. However, oligosaccharides which convert to monosaccharides through interaction with carbonyl compounds, also can be used.

[0017] Pentoses or hexoses as well as their mixtures obtainable via mixing the individual monosaccharides or through technological processes of carbohydrate-containing raw material processing, can be used as monosaccharides.

[0018] Xylose or arabinose are preferably used as pentoses, and glucose is used as hexose.

[0019] Glycols, such as ethylene glycol, are used as diatomic alcohols. Glycerol is used as triatomic alcohol. Erythrites, such as pentaerythritol, are used as polyatomic alcohols.

[0020] A compound belonging to lower aldehydes or lower ketones, for instance formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, diethyl ketone and cyclohexanone, is used as a carbonyl compound.

[0021] Aliphatic alcohols containing up to 5 carbon atoms, preferably ethanol, are used as an alcohol.

[0022] Gasoline automobile fuel in this invention means gasoline or gasoline - alcohol fuel composition.

[0023] An essential condition necessary to provide a high octane rating is the presence in the claimed agent of both alcohol and the products of carbonyl compound interaction with a compound containing at least two hydroxyls, capable of forming the cycles with carbonyl compounds or mixtures of said products. Alcohols are insufficiently effective antiknock agents. According to our data and [US 4541836, publ. 17.09.1985], the introduction of anhydrous ethanol (up to 10 %) into gasoline increases the octane number of the fuel by 2-4 units.

[0024] Study of octane-increasing activity of cyclic ketals of monosaccharides, which are one of the examples of the product of interaction between carbonyl compound and a compound, containing at least two hydroxyls allowing the formation of cycles with carbonyl compounds, using a standard hydrocarbon mixture, has shown that pure ketals, formed by monosaccharides and acetone, do not actually increase the octane number of hydrocarbons. For instance, introduction of acetone - arabinose ketal into the mixture of iso-octane - n-heptane (4:1) in an amount of 8 mass %, does not actually influence its octane number. A similar effect has been shown for triatomic alcohol-based ketals: the 10% content of glycerol - acetone cyclic ketal in gasoline increases the octane number by 1.4 units; for glycerol - methyl ethyl ketone ketal by 0.9 units; for other ketals the increase in the octane number is not more than the measurement error.

[0025] Addition of ethanol into the system increases the octane number of the model mixture: for arabinose - acetone ketal (weight ratio of ketal : ethanol is 0.75:1.0) by 10.4 units; for xylose - acetone ketal (weight ratio of ketal : ethanol is 0.75 : 1.0) by 13.1 units; for glycerol - acetone ketal (weight ratio of ketal : ethanol is 1.0:1.0) by 12.6 units. This suggests a synergic effect of the pair "alcohol - cyclic ketal", providing a high octane-increasing activity of the claimed agents.

[0026] It should be noted that the order of introduction of alcohol and said product of interaction of carbonyl compound and a compound containing at least two hydroxyls allowing the formation of cyclic ketals with carbonyl compounds doesn't influence the achievement of octane-increasing effect of the claimed agent. The essential fact is only the presence of the combination of said components no matter whether they are mixed before introduction into gasoline automobile fuel or they are mixed in the gasoline automobile fuel. Due to this, the claimed agent exhibits the octane-increasing effect for both gasoline and alcohol-containing gasoline compositions.

[0027] The presence of alcohol additive helps to avoid the problem of phase compatibility with gasoline of the cyclic ketals and acetals having free hydroxyls. In presence of alcohol, these compounds, regardless of the nature of alkyl substituents, form a monophase stable system with gasoline.

[0028] Glycerol-based cyclic ketals are known to promote the increase in phase stability of alcohol-containing gasoline

[GB Pat. 811406, publ.. 02.04.1959, US 4390344, publ. 28.06.1983]. This fully relates to monosaccharide-based cyclic ketals. For instance, addition of cyclic ketals or mixtures of monosaccharide-based cyclic ketals (3 - 8 weight %) to the two-phase system containing gasoline and 10 volume % water-containing ethanol results in a homogeneous system. Thus, the presence of the said ketals stabilizes the gasoline phase homogeneity allowing the increase in the threshold water concentration followed by its isolation as a separate phase. Therefore, in order to compound the hydrocarbon and alcohol, it becomes possible to use not only dry ethanol but also rectificate containing 3.6 % water, and hydrous alcohol containing up to 5% water.

EMBODIMENTS OF THE INVENTION

[0029] The product of a carbonyl compound interaction with a compound containing at least two hydroxyls allowing the formation of cycles with carbonyl compounds, which is needed for realization of the invention, can be obtained as follows.

[0030] One group of compounds, containing at least two hydroxyls allowing the formation of cycles with carbonyl compounds, is saccharides.

[0031] Both individual monosaccharides and their mixtures, for instance a pentose fraction derived, as described below from a vegetable raw material, are used as saccharides.

[0032] As a source of a mixture of saccharides to obtain the products used in the claimed agent, it is appropriate to utilize cheap agricultural wastes having no nutritional and feeding values, such as cereals straw, and other waste of grain processing used to produce bioethanol.

[0033] The raw material is pretreated. It includes refinement to form 2.0 - 0.5 mm particles, chemical separation of accompanying components (waxes, fats, terpenes, soluble pectins, proteins, lignines, inorganic substances) by extraction with ethanol - benzene mixture, subsequent acid hydrolysis and separation of a carbohydrate fraction by the known procedures [Yu.I. Kholkin "Technology of hydrolysis industries", Moscow, Timber Industry, 1989]. The resulting mixtures of monosaccharides making 25 - 30 weight % of raw material are so - called "pentose fraction", primarily containing xylose and arabinose with glucose admixture.

[0034] Table 1 lists the product composition of pretreatment and hydrolysis of various raw materials.

Table 1. The product composition of pretreatment and hydrolysis of various raw materials.

Raw material	Yield of various fractions, weight %					Overall yield of pentose fraction, weight %
	Pretreatment			Hydrolysis		
	Waxes, fats, terpenes	Ashes	Pentose fraction	Cellulose, lignine	Pentose fraction	
Wheat straw	6	6	4	59	25	29
Rice straw	4	5	5	61	25	30
Dried silver grass	5	5	5	55	30	35

[0035] The products are obtained by the interaction of these substances with carbonyl compounds under acid catalysis with elimination of the formed water by one of the known methods [Ed. N.K. Kochetkov, "Methods of carbohydrate chemistry", Mir, Moscow, 1967, p.165]. To separate by-products poorly soluble in hydrocarbons, the reaction mixture is extracted with benzene or other suitable solvent. The extract is evaporated and used as a component of the agent to increase the octane number. Likewise, one can use di- and oligosaccharides, hydrolyzable through interaction with carbonyl compounds, and also giving the mixtures of the corresponding products.

[0036] As carbonyl compounds, lower aldehydes or ketones can be used; in the first case, the interaction is the acetalization reaction, and the reaction products are cyclic acetals; in the second case, the interaction reaction is the ketalization reaction, and the reaction products are cyclic ketals.

[0037] Since such monosaccharides contain at least two pairs of hydroxyls capable, upon interaction with carbonyl compounds, to form cycles, the derivatives, containing both one and two cyclic groups per monosaccharide molecule can be obtained. To maximize the octane-increasing effect, the reaction is conducted in presence of an excess of carbonyl compound, which provides the maximal depth of conversion to form products containing two oxygen-containing cycles. Table 2 exemplifies the physical and chemical characteristics of products of interaction between saccharides (individual monosaccharides, disaccharides, monosaccharide mixtures) and acetone.

Table 2. Physical and chemical characteristics of cyclic products, derived via interaction of monosaccharides and acetone.

Products of interaction between saccharides and acetone	Phase state, m.p. °C
Cyclic diketal obtained by ketalization of D-glucose with acetone (glucose - acetone diketal)	Solid, 110
Cyclic diketal obtained by ketalization of D-arabinose with acetone (arabinose - acetone diketal)	Solid, 48-49
Cyclic diketal obtained by ketalization of D-xylose with acetone (xylose - acetone diketal)	Thick oil
A mixture of cyclic diketals of glucose and fructose, obtained by ketalization of saccharose with acetone	Solid, 95-99
A mixture of cyclic diketals, obtained by ketalization of the mixture of monosaccharides isolated from dried silver grass with acetone	Thick oil

[0038] The cyclic diketals of monosaccharides and acetone showed in table 2 are solid at room temperature or viscous liquid products, soluble in alcohol; their mixtures with alcohol are soluble in gasoline.

[0039] When using pentose fraction isolated from the hydrolyzate of carbohydrate-containing raw material, the total yield of the mixture of cyclic diketals is 57 - 70% depending on the type of material from which the pentose fraction was derived. The dried silver grass is a promising material for obtaining claimed additives since it is the richest source of pentoses and provides the highest yield of resulting mixture of cyclic diketals.

[0040] Table 3 shows the weight content of the mixture obtained upon acetone ketalization of pentose fraction isolated from silver grass.

Table 3. Composition of the mixture obtained by acetone ketalization of pentose fraction isolated from dried silver grass.

Products of ketalization	Content, weight %
Xylose - acetone diketal	77
Arabinose - acetone diketal	14
Glucose - acetone diketal	6
Diacetone alcohol	3

[0041] Monosaccharides ketalization products are nontoxic. Experiments with mice of SHK line (nursery "Stolbovaja") have shown that the preparations of cyclic diketals based on arabinose and glucose in olive oil, administered per os to the animals in doses ranging from 100 to 6000 mg/kg, are well tolerated by animals during 30 days and cause no changes in their state of health.

[0042] Cyclic monosaccharides diketals are stable in the agent for increasing the octane number; they can be hydrolyzed to form non-toxic products. It is their major advantage over toxic, undegradable alkyl ethers, such as methyl tert-butyl ether widely used as a component of oxygenates.

[0043] Another group of compounds containing at least two hydroxyls, allowing the formation of cycles with carbonyl compounds, is composed of di-, tri- and polyatomic alcohols.

[0044] The reaction products of di-, tri- and polyatomic alcohols with carbonyl compounds - cyclic acetals and ketals - are obtained by one-step synthesis using available large-tonnage products of industrial production (glycerol, ethylene glycol, pentaerythritol, paraformaldehyde, acetaldehyde, acetone, etc.) by the known procedures in the conditions of acid catalysis with azeotropic elimination of water [A. Terney "Modern Methods of Organic Chemistry," Volume 2, Moscow: Mir, 1981, pp. 20]. In the case when the azeotropic elimination of water is carried out in the presence of methyl ethyl ketone, the reaction product is a mixture of cyclic compounds, which can also be used as a part of the claimed octane-increasing agent.

[0045] Cyclic acetals and ketals of di-and triatomic alcohols are fluids, readily soluble in alcohol; their mixtures with alcohol are readily soluble in gasoline.

[0046] Another example of cyclic acetal, which can be used as a component of the claimed agent for increasing the octane number, is pentaerythritol diformal, which is the product of the interaction between pentaerythritol and formaldehyde. Pentaerythritol is available large-tonnage product of chemical industry and is a polyatomic alcohol with branched structure, containing four hydroxyls. Their paired interaction with formaldehyde forms two dioxane cycles. Pentaerythritol diformal is a solid product soluble in alcohol.

[0047] Octane-increasing activity of the clamed agents has been investigated using n-heptane and model hydrocarbon mixtures of isooctane - n-heptane 1:1 and 4:1. The measurements are carried out by the standard method according to GOST (GOST is the state standard specification in Russian Federation) 8226-82 "Fuel for the engines. Research method to determine the octane number" (method 1) and by the express method (method 2) which gives the results similar to those obtained by standard methods. Express method uses the instrument for measuring gasoline detonation resistance (Octanometer OK-2m (manufacturing company "Plus Radio"), applicable for express determination of the octane number of gasolines during their production and also for research works and for the inspection of gasoline quality by consumers. The Octanometer OK-2m operation principle is based on measuring the parameters of the reaction of cold-flame oxidation of gasolines followed by determination of a detonation resistance, equivalent to the motor and research methods. In this case, the comparison standards are taken to be the parameters of the reactions of cold-oxidation control fuels, manufactured according to GOST 511-82.

[0048] Tables 4 and 5 list the octane-increasing effect of agents, containing various individual cyclic ketals and acetals and various aliphatic alcohols, on n-heptane, and model hydrocarbon isooctane - n-heptane mixtures.

Table 4. Octane-increasing effect of agents, based on glycerol - acetone cyclic ketal in the presence of alcohols of various structures on n-heptane.

Agent composition	Content of cyclic ketal in the agent, wt %	Content of the agent in n-heptane, vol %	The increase of octane number, ΔON	Method for octane number (ON) determination
Cyclic ketal of glycerol and acetone + ethanol	50	20	47.3	2
Cyclic ketal of glycerol and acetone + iso-butanol	62.5	16	30.0	2

Table 5. Octane-increasing effect of the agents, including various individual cyclic acetals and ketals as well as various alcohols, on model mixtures of iso-octane - n-heptane of various content.

Agent composition	Content of cyclic ketal or acetal in the agent, wt %	Content of the agent in model hydrocarbon mixture, vol. %	The increase of octane number, ΔON		Method for octane number (ON) determination
			Model mixture iso-octane -n-heptane 1:1	Model mixture iso-octane -n-heptane 4:1	
Cyclic diketal of arabinose and acetone + ethanol	25	5	2.7	2.5	2
		10	5.8	5.7	
	33	5	2.5	2.5	
		10	5.9	5.7	
	50	5	2.5	2.5	
		10	5.7	5.2	
	43	18.2	-	10.4	1
Cyclic diketal of glucose and acetone + ethanol	25	5	2.9	2.1	2
		10	6.0	5.2	
	33	5	3.6	3.0	
		10	7.2	5.8	
	20	26	-	16.0	1

(continued)

Agent composition	Content of cyclic ketal or acetal in the agent, wt %	Content of the agent in model hydrocarbon mixture, vol. %	The increase of octane number, ΔON		Method for octane number (ON) determination
			Model mixture iso-octane -n-heptane 1:1	Model mixture iso-octane -n-heptane 4:1	
Cyclic diketal of xylose and acetone + ethanol	33	30	-	9.8	2
	43	18.2	-	13.1	1
Cyclic diketal of xylose and acetone + iso-propanol	33	30	-	9.5	2
Cyclic diketal of xylose and acetone + n-butanol	33	30	-	5.6	2
Cyclic ketal of ethylene glycol and acetone +methanol	50	20	-	6.6	2
Cyclic ketal of ethylene glycol and acetone + ethanol	50	20	-	10.3	2
Cyclic ketal of ethylene glycol and acetone + iso-propanol	50	20	-	9.8	2
Cyclic ketal of ethylene glycol and acetone + n-butanol	50	20	-	4.8	2
Cyclic ketal of ethylene glycol and acetone + n-alcohol	50	20	--	4.5	2
amyl Cyclic ketal of glycerol and acetone + ethanol	50	20	-	12.6	2
Cyclic ketal of glycerol and acetone + n-butanol	50	20	-	7.2	2
Cyclic acetal of glycerol and acetaldehyde + ethanol	50	20	-	16.5	2

(continued)

Agent composition	Content of cyclic ketal or acetal in the agent, wt %	Content of the agent in model hydrocarbon mixture, vol. %	The increase of octane number, ΔON		Method for octane number (ON) determination
			Model mixture iso-octane -n-heptane 1:1	Model mixture iso-octane -n-heptane 4:1	
Cyclic acetal of pentaerythritol and formaldehyde + ethanol	50	20	-	19.6	2

[0049] The data in Tables 4 and 5 confirm the known fact that the lower the octane number of the initial hydrocarbon mixture, the greater the effect produced by introduction of octane-increasing agent. The magnitude of the octane-increasing effect in the tested concentration range is approximately proportional to the weight content of the agent in the mixture. In addition, these data indicate that the synergetic octane-increasing effect of cyclic ketals and acetals is manifested in the presence of alcohols of various structures.

[0050] Table 6 shows the octane-increasing activity of agents containing ethanol in combination with mixtures of cyclic ketals of various structures.

Table 6. Octane-increasing effects of ethanol-containing agents comprising the mixtures of cyclic ketals on the model hydrocarbon mixture iso-octane - n-heptane 4:1 (data are obtained by Method 1).

Mixture of ketals containing in the agent	Content of the mixture of cyclic ketals in the agent, wt %	Content of the agent in model hydrocarbon mixture, vol. %	The increase of octane number, ΔON
Mixture of cyclic diketals obtained by ketalization with acetone of pentose fraction of wheat straw hydrolyzate	9.1	29.5	22.6
Mixture of cyclic diketals obtained by ketalization with acetone of pentose fraction of dried silver grass	50	20	19.6
Mixture of cyclic ketals arabinose-acetone + glycerol-acetone (1:1)	32.9	24.3	14.8

[0051] A number of octane-increasing agents were tested using automobile gasoline and straight-run gasoline fraction.

[0052] Table 7 shows the examples of the octane-increasing effects of the claimed agents based on monosaccharides, added to automobile gasoline.

Table 7. Octane-increasing effect of agents, containing cyclic ketals and ethanol, on automobile gasoline with ON = 77.6 (data are obtained by Method 1).

Example №	Ketal containing in the agent	Content of ketal in the agent, wt.%	Content of agent in gasoline, vol.%	The increase of octane number, ΔON
1	Cyclic diketal of arabinose and acetone	25	5	5.7
2			10	11.9
3			15	13.8
4		33	5	5.2
5			10	11.1
6			15	13.4
7			20	14.5
8		50	5	2.7
9			10	6.1
10			15	11.7
11	Cyclic diketal of glucose and acetone	25	5	5.4
12			10	11.4
13			15	14.7
14		33	5	4.9
15			10	9.7
16			15	14.3
17			20	15.0
18*	Mixture of cyclic diketals, obtained by ketalization of pentose fraction of hydrolyzate of dried silver grass by acetone	50	20	17.0*
* The results have been obtained using commercial gasoline AI-80				

[0053] Table 8 lists the test results for some types of fuel compositions, including a straight-run gasoline fraction and octane-increasing agents containing cyclic ketals on the basis of glycerol, ethylene glycol and ethanol.

Table 8. Test results of various types of octane-increasing agents, containing cyclic ketals on the basis of glycerol, ethylene glycol and ethanol in the gasoline fraction.

Cyclic ketal (CK)	Ratio CK : ethanol (vol.) in the agent composition	Content of the agent in gasoline, vol.%	The increase of octane number, ΔON	Temperature of exfoliation $T_{exfol.}$, °C
Ketal of acetone and glycerol	1 : 2	15	9.3	below - 30
	1 : 1	20	13.4	below - 30
Ketal of methyl ethyl ketone and glycerol	1 : 1	10	5.9	-22.7
	2: 1	15	10.3	-28.5
	1: 2	15	7.6	-26.9
	1 : 1	20	12.5	below -30

(continued)

Cyclic ketal (CK)	Ratio CK : ethanol (vol.) in the agent composition	Content of the agent in gasoline, vol.%	The increase of octane number, ΔON	Temperature of exfoliation $T_{exfol.}$, °C
Ketal of cyclohexanon and glycerol	1 : 1	10	4.2	below -30
	2: 1	15	8.0	below -30
	1: 2	15	5.7	below -30
	1 : 1	20	10.6	below -30
Ketal of acetone and ethylene glycol	1 : 1	10	2.8	-16.3
	2: 1	15	5.7	-17.6
	1: 2	15	5,0	-17.2
	1 : 1	20	9.3	-28.9

[0054] If a ready gasoline - alcohol composition is used as gasoline fuel, the cyclic ketal or a mixture of cyclic ketals is added in the required amount directly to the gasoline - alcohol composition.

[0055] Data in Tables 9 and 10 show the effect of cyclic ketals on octane characteristics of gasoline-alcohol composition.

Table 9. Effect of monosaccharide-based cyclic diketals on octane characteristics of gasoline-alcohol composition with 10 vol.% ethanol.

Cyclic ketal (CK)	CK amount added to gasoline-alcohol composition, wt %	The increase of octane number, ΔON
Cyclic diketal of arabinose and acetone	8	7.0
Cyclic diketal of xylose and acetone	8	9.2
Cyclic diketal of glucose and acetone	5	6.1
Mixture of cyclic diketals of monosaccharides from wheat straw	3	4.3

Table 10. Effect of cyclic ketals, based on ethylene glycol and glycerol, on the change of octane number in gasoline-alcohol composition.

Cyclic ketal (CK)	The increase of octane number, ΔON			
	Gasoline-alcohol composition with 5% vol ethanol		Gasoline-alcohol composition with 10 vol. % ethanol	
	Content of CK 5 vol. %	Content of CK 10 vol. %	Content of CK 5 vol. %	Content of CK 10 vol. %
Ketal of acetone and glycerol			5.1	8.9
Ketal of methyl ethyl ketone and glycerol	3.8	8.0	3.5	8.1
Ketal of cyclohexanon and glycerol	2.2	5.8	1.7	6.3
Ketal of acetone and ethylene glycol	0.8	3.6	1.0	5.1

[0056] Phase stability of gasoline - alcohol compositions, quantitatively characterized by exfoliation temperature, is measured according to GOST 5066-91 using low-temperature thermostat KRIO-VT (company TERMEX-II). Table 11 data show the effect of glycerol or ethylene glycol- based cyclic ketals on phase stability of alcohol - gasoline compositions at lower temperatures.

Table 11. Stabilizing effect of cyclic ketals on gasoline-alcohol composition.

Cyclic ketal (CK)	Content of CK, vol. %	Temperature of exfoliation, °C	
		Gasoline-alcohol composition with 5 vol. % ethanol	Gasoline-alcohol composition with 10 vol. % ethanol
Without CK	0	- 5.8	- 10.4
Ketal of acetone and glycerol	5		below- 30
	10		below - 30
Ketal of methyl ethyl ketone and glycerol	5	-22.7	-26.9
	10	-28.5	below - 30
Ketal of cyclohexanone and glycerol	5	below - 30	below - 30
	10	below - 30	below - 30
Ketal of acetone and ethylene glycole	5	- 16.3	-17.2
	10	-17.6	-28.9

[0057] Thus, the results listed indicate that the claimed agents show the evident octane-increasing and stabilizing effects on alcohol-containing gasoline fuel.

[0058] Experiments on model systems showed that the claimed octane-increasing agents are poorly liable to gumming formation. So, Russian state standard specifications afford content of gums up to 6.0 mg/100 cm^3 fuel, but the real gum formation in the agent composition, containing 10% acetone - glycerol cyclic ketal, is 0.6 mg/100 cm^3 of fuel, and in the agent composition, containing 30% acetone - glycerol cyclic ketal, is 3.0 mg/100 cm^3. Regarding the known effects of said compositions on decrease in detrimental products in exhaust gases, one can state that the former can render a complex positive effect on the internal combustion engine work.

Claims

1. An agent for increasing the octane number of a gasoline automobile fuel, wherein the agent is a combination of alcohol and product of interaction between carbonyl compound and a compound containing at least two hydroxyls, allowing the formation of cycles with said carbonyl compounds, or mixtures of said products.

2. The agent of claim 1, wherein the compounds, containing at least two hydroxyls, allowing the formation of cycles with carbonyl compounds, are saccharides or diatomic alcohols, or triatomic alcohols, or polyatomic alcohols.

3. The agent of claim 2, wherein the saccharides are monosaccharides and oligosaccharides.

4. The agent of claim 3, wherein the monosaccharides are pentoses, preferably, xylose or arabinose, or hexoses, preferably glucose, as well as mixtures thereof.

5. The agent of claim 2, wherein the diatomic alcohols are glycols, for example, ethylene glycol.

6. The agent of claim 2, wherein the triatomic alcohol is glycerol.

7. The agent of claim 2, wherein the polyatomic alcohols are erythritols, for example, pentaerythritol.

8. The agent of claim 1, wherein the carbonyl compound is that referring to lower aldehydes or lower ketones, preferably formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, diethyl ketone or cyclohexanone.

9. The agent of claim 1, wherein the alcohol is the aliphatic alcohol containing up to five carbon atoms, preferably ethanol.

10. The agent of claim 1, wherein the gasoline automobile fuel is gasoline.

11. The agent of claim 1, wherein the gasoline automobile fuel is a gasoline - alcohol composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2009/000266

A. CLASSIFICATION OF SUBJECT MATTER

C10L 1/02 (2006.01); C10L 1/18 (2006.01); C10L 10/10 (2006.01)

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 1/02, C10L 1/18, C10L 10/10

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)

PAJ, Esp@senet, RUPAT, EPATIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4541836 A (UNION CARBIDE CORPORATION) 17.09.1985, the claims	1-11
A	RU 2246527 C1 (BAKLANOV A.V.) 20.02.2005	1-11
A	RU 2263135 C2 (OBSCHESTVO S OGRANICHENNOI OTVETSTVENNOSTJU "STANDART") 27.10.2005	1-11
A	EP 0718270 A2 (WESSENDORF RICHARD DR.) 26.06.1996	1-11
A	GB 811406 A (BADISCHE ANILIN & SODA-FABRIK AKTIENGESELLSHAFT) 02.04.1959	1-11

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

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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
31 August 2009 (31.08.2009)	08 October 2009 (08.10.2009)
Name and mailing address of the ISA/ RU Facsimile No.	Authorized officer Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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