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**(54) Titre :** ADDITIF POUR CARBURANT A FAIBLE TENEUR EN SOUFRE  
**(54) Title:** ADDITIVES FOR LOW-SULFUR FUELS

\[ R-\text{COO}(\text{C}_n\text{H}_{2n+1}\text{-O})_k\text{-H} \]  

**(57) Abrégé/Abstract:**  
The invention relates to fuel compositions containing over 50% percent by weight diesel, gasoline, kerosene, or other hydrocarbons which are liquid at room temperature. The invention is characterized in that the compositions contain 0.001 to 0.1 percent by weight of an additive of formula \((I)\), wherein \(R\) represents a monounsaturated or polyunsaturated alkyene radical with 17 C atoms, \(n\) is 2 or 3 and \(k\) represents a number between 0.5 and 3, with the proviso that the sulfur content in the fuel composition does not exceed a maximum of 0.2 percent by weight.
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(54) Title: ADDITIVES FOR LOW-SULFUR FUELS
(54) Bezeichnung: ADDITIVE FÜR SCHWEFELARME TREIBSTOFFE

R-COO-(C₆H₁₂n+1-O)ₓ-H (1)

(57) Abstract: The invention relates to fuel compositions containing over 50 percent by weight diesel, gasoline, kerosene, or other hydrocarbons which are liquid at room temperature. The invention is characterized in that the compositions contain 0.001 to 0.1 percent by weight of an additive of formula (I), wherein R represents a monounsaturated or polyunsaturated alkylene radical with 17 C atoms, n is 2 or 3 and k represents a number between 0.5 and 3, with the proviso that the sulfur content in the fuel composition does not exceed a maximum of 0.2 percent by weight.

(57) Zusammenfassung: Beansprucht werden Treibstoffzusammensetzungen, enthaltend mehr als 50 Gew.-% Diesel, Benzin, Kerosin, oder andere bei Raumtemperatur flüssige Kohlenwasserstoffe, dadurch gekennzeichnet, dass die Zusammensetzungen ein Additiv der Formel (I) in der R für einen ein- oder mehrfach ungesättigten Alkylendest mit 17 C-Atomen steht und n für 2 oder 3 und k einen Zahl zwischen 0.5 und 3 steht, in Mengen von 0,001 bis 0,1 Gew.-% enthält, mit der massgabe, dass die Treibstoffzusammensetzung einen Schwefelgehalt von maximal 0,2 Gew.-% aufweist.
Additives for Low-sulfur Fuels

This invention relates to low-sulfur fuel compositions which contain certain alkoxylated esters as additives.

Fuels based on petroleum or petroleum derivatives generally contain small amounts of sulfur. Crude oils normally contain between 2 and 0.5% by weight of sulfur. In the combustion of these sulfur-containing fuels, sulfur dioxide is formed as a combustion product and is oxidized in air to sulfuric acid which can cause serious environmental damage in the form of acid rain. Accordingly, there has long been a demand to reduce the sulfur content in petroleum products, more particularly in fuels. However, not only does sulfur have adverse effects, it also serves in the small quantities in which it is normally present as a lubricant improver which is entirely desirable in many technical applications, for example as a fuel for combustion engines. Accordingly, the use of low-sulfur fuels often leads to problems to do with the friction of the correspondingly fuelled machine parts. In order to meet environmental and emission control requirements on the one hand and friction coefficient requirements on the other hand, additives are normally incorporated in the fuels. It is known from WO 94/17160 that esters of carboxylic acids and alcohols containing more than 1 carbon atom are added to low-sulfur fuels, preferably diesel fuels, to adjust the corresponding friction coefficients. Esters of C_{2-50} carboxylic acids and polyols are preferably used. However, the problem arises that, with small additions of expensive additives, the lubricating effect of the fuels thus obtained is not always satisfactory. Accordingly, the problem addressed by the present invention was to provide an additive for low-sulfur fuels which, even in small amounts, would enable the lubricating effect of fuels to be adequately improved.

Accordingly, the present invention relates to fuel compositions
containing more than 50% by weight of diesel, gasoline, kerosene or other hydrocarbons liquid at room temperature, these fuel compositions containing an additive corresponding to formula (I):

\[ R\text{-COO-(C}_n\text{H}_{2n+1}\text{-O)}_k\text{-H} \]  

where \( R \) is a mono- or polyunsaturated alkylene group containing 17 carbon atoms and \( n = 2 \) or 3 and \( k \) is a number of 0.5 to 3, in quantities of 0.001 to 0.1% by weight, with the proviso that the fuel composition has a sulfur content of at most 0.2% by weight.

The fuel compositions according to the invention are further distinguished by the fact that the sulfur content is at most 0.2% by weight, based on the fuel composition.

Fuels in the context of the present invention are understood to be any energy-yielding working materials of which the free combustion energy is converted into mechanical work. Such materials include all types of motor and aircraft fuels which are liquid at room temperature and normal pressure. Motor fuels, for example for automobile and truck engines, generally contain hydrocarbons, for example gasoline or higher-boiling petroleum fractions.

Diesel fuels are low-inflammability mixtures of liquid hydrocarbons which are used as fuels for constant-pressure or compression-ignition engines (diesel engines) and which consist predominantly of paraffins with impurities in the form of olefins, naphthenes and aromatic hydrocarbons. Their composition is variable and depends in particular upon the production method. Diesel is obtained, for example, from gas oil by cracking or from tars obtained in the low-temperature carbonization of brown coal or hard coal. Typical products have densities of 0.83 to 0.88 g/cm³, boiling points in the range from 170 to 360°C and flash points of 70 to 100°C. Diesel oils for stationary plant and for marine engines are similar in composition to
heavy fuel oil while those for automobiles, buses and trucks correspond to fuel oil.

During combustion in a diesel engine, air is taken into the cylinder, heated to 550-900°C by high compression (compression ratio 14:1 to 25:1), so that a jet of diesel injected in ignites spontaneously and reaches a combustion pressure of 50-80 bar at a combustion temperature of 1500-2200°C so that the piston is moved and work is done. 13 m³ air are used in the combustion of 1 liter of diesel in the diesel engine. The combustion energy released amounts to ca. 42,000 kJ/kg.

A key factor for the usability of diesel fuels is their ignition response which is quantitatively expressed by the cetane number. Ignition response is the capacity of a motor fuel to ignite relatively easily or with relative difficulty in an engine operating on the diesel principle. With every fuel, this requires not only atomization, pressure and temperature, but also a conditioning interval (ignition delay) before discernible combustion. Good ignition response of a fuel means favorable starting behavior and quiet running of the diesel engine by virtue of a short conditioning interval or small ignition delay. With a large ignition delay, the known phenomenon of “knocking” comes audibly into play. The requirements for diesel fuels are a cetane number of 20 to 40 for slow-running engines and a cetane number of > 45 for small and fast-running engines. Other desirable properties include a low pour point, a low content of incom bustible or soot-forming substances and a low sulfur content.

The fuel compositions according to the invention contain diesel, gasoline, kerosene or other hydrocarbons liquid at room temperature, for example hexane or pentane. Fuel compositions containing diesel as fuel are particularly preferred. In principle, the fuel compositions according to the invention may also contain mixtures of, for example, gasoline and kerosene in any ratio.

The additives of formula (I) are alkoxylated carboxylic acid esters
known per se. It is one of the key aspects of the present invention that the carboxylic acids must be unsaturated carboxylic acids containing 11 to 17 carbon atoms in the alkyl chain. Compounds of formula (I), in which R is an unsaturated group containing 17 carbon atoms, are particularly preferred. Oleic acid is particularly preferred for the purposes of the invention. The alkoxylation, i.e. the reaction of the acid with ethylene oxide and/or propylene oxide, is carried out in known manner, cf. for example US 5,326,891 or US 5,292,910 which describe the synthesis of such compounds where the acids are reacted with the alkoxydes in the presence of selected hydrotalcite catalysts to form the required alkoxylated compounds. Also of relevance in this regard is the disclosure of WO 98/25878 which describes a process for the synthesis of these "short-ethoxylated" fatty acids by reaction of the fatty acids in the presence of alkanolamines.

One feature of the present additives of formula (I) is that the number of alkoxide units per molecule is strictly limited and is preferably 1, i.e. 1 part acid and 1 part alkoxide have reacted. Since, in addition, the use of modern catalysts does not provide for uniform products, mixtures of different alkoxylated compounds are usually present which is expressed in the partly broken number k in formula (I). Compounds of formula (I) where n = 2, i.e. ethoxylated fatty acids, are particularly preferred. The index k should preferably have a value of 0.5 to 1.5, compounds of formula (I) where k = 1 being most particularly preferred. Compounds of formula (I) where k = 1 and n = 2 are also preferred. The fuel compositions according to the invention contain the additives of formula (I) in quantities of preferably 0.001 to 0.01% by weight and more preferably 0.001 to 0.005% by weight. Oleic acid esters containing 1 part ethylene oxide are particularly preferred.

In a particularly preferred embodiment, the additives of formula (I) according to the invention are used in fuel compositions with an extremely
low sulfur content, i.e. a sulfur content of 0.005 to at most 0.05% by weight. In a most particularly preferred embodiment, they are used in fuel compositions with a sulfur content below 0.005% by weight. The aromatics content of the claimed fuel compositions should be below 25% by volume and is preferably below 20% by volume. Fuel compositions containing less than 5% by volume of aromatics are particularly preferred, fuel compositions free from aromatics being most particularly preferred.

If diesel is selected as the actual fuel, it should have a cetane number below 50 and preferably below 45. The cetane number of the diesel should be below 50.

The addition of the compounds of formula (I) leads to a good broad effect of the corresponding fuels, the HFRR value at 60°C being 600 μm, preferably at most 500 μm and more particularly 400 μm or less. The HFFR (high-frequency reciprocating rig) value is used to measure the friction of fuels in use. A detailed description of this method can be found in ISO/TC22/SC7/WG6/N188.

The fuels according to the invention may contain other typical additives, for example cetane number improvers (saltpeter or nitrous ester), corrosion inhibitors, flow enhancers, surfactants (which keep the fuel injectors clean), defoamers and smoke reducers.

In choosing the additives for the fuel compositions according to the invention, it is important to bear in mind that the use of, for example, fatty alcohols and/or alkoxylated fatty alcohols and/or alkanolamides and/or derivatives thereof is preferably ruled out. Fuel compositions which contain only the additives of formula (I) for reducing friction are most particularly preferred.

The use of the above-defined compounds of formula (I) in fuels, more particularly in diesel fuels, leads on the one hand to satisfactory lubrication behavior of the fuels without any of the adverse ecological consequences typical of low-sulfur fuels. In addition, the fuels containing
the additives according to the invention show excellent low-temperature behavior with no flocculation, even at low temperatures.

Examples

An oleic acid ester containing 1 mol ethylene oxide per mol fatty acid was tested for its effectiveness in reducing the friction coefficient of diesel (HFRR) by comparison with a commercially available glycerol mono-oleic acid ester (GMO). The additive was used in a quantity of 50 ppm. Additive-free diesel was used as the reference fuel.

The HFRR value of the additive-free diesel was 591 μm. A value of 529 μm was measured for the GMO-containing diesel whereas the additive according to the invention achieved an HFRR value of 500 μm.
CLAIMS
1. A fuel composition containing more than 50% by weight of diesel, gasoline, kerosene or other hydrocarbons liquid at room temperature, characterized in that the compositions contain an additive corresponding to formula (I):

\[ R\text{-COO-}(C_nH_{2n+1})_k\text{-H} \]  

where R is a mono- or polyunsaturated alkylene group containing 10 to 17 carbon atoms, n has a value of 2 or 3 and k has a value of 0.5 to 3, in quantities of 0.001 to 0.1% by weight, with the proviso that the fuel composition has a sulfur content of at most 0.2% by weight.

2. A fuel composition as claimed in claim 1, characterized in that it contains compounds of formula (I) where n has a value of 2 as additives.

3. A fuel composition as claimed in claims 1 and 2, characterized in that it contains compounds of formula (I) where k has a value of 0.5 to 1.5 as additives.

4. A fuel composition as claimed in claims 1 to 3, characterized in that it contains compounds of formula (I) where k has a value of 1 as additives.

5. A fuel composition as claimed in claims 1 to 4, characterized in that it contains compounds of formula (I) where k has a value of 1 and n has a value of 2.

6. A fuel composition as claimed in claims 1 to 5, characterized in that it contains compounds of formula (I) where R is an unsaturated group containing 17 carbon atoms.

7. A fuel composition as claimed in claims 1 to 6, characterized in that it contains the additives of formula (I) in quantities of 0.001 to 0.01% by weight and preferably in quantities of 0.001 to 0.005% by weight.

8. A fuel composition as claimed in claims 1 to 7, characterized in that the sulfur content of the fuel is in the range from 0.005 to 0.05.
9. A fuel composition as claimed in claims 1 to 8, characterized in that the sulfur content of the fuel is below 0.005% by weight.

10. A fuel composition as claimed in claims 1 to 9, characterized in that the content of aromatics is below 25% by volume, preferably below 20% by volume and more particularly below 5% by volume.

11. A fuel composition as claimed in claims 1 to 10, characterized in that the fuel does not contain any aromatics.

12. A fuel composition as claimed in claims 1 to 11, characterized in that diesel is selected as the fuel.

13. A fuel composition as claimed in claim 12, characterized in that the cetane index of the diesel is below 50 and preferably below 45.

14. A fuel composition as claimed in claims 12 and 13, characterized in that the cetane number of the diesel is below 50.

15. A fuel composition as claimed in claims 1 to 14, characterized in that the HFRR friction coefficient at 60°C is at most 500 µm.

16. A fuel composition as claimed in claims 1 to 15, characterized in that the composition is free from fatty alcohols and/or alkoxylated fatty alcohols and/or alkanolamides and/or derivatives thereof.
R-COO-(C_{n}H_{2n+1}-O)_{k}-H