LUBRICITY IMPROVER FOR DIESEL OIL

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Abstract
A fuel oil composition is comprised of diesel oil and a lubricity additive of the formula (I):

\[ R-COO-\{(\text{AO})_n\}-H \]  

wherein \( R \) is an alkyl or alkenyl group having from 5 to 19 carbon atoms, \( AO \) is a \( \text{CH}_2\text{CH}_2 \) or \( \text{C}_2\text{H}_4 \) group and \( n \) is a number of 0.5 to 6, wherein the additive is a liquid at 21°C. and having a narrow homolog distribution. The compounds of formula (I) are particularly useful in diesel oils having low sulfur content.
LUBRICITY IMPROVER FOR DIESEL OIL

FIELD OF THE INVENTION

[0001] This invention relates to the use of additives for improving the lubricity of diesel oil, to a low-sulfur diesel oil containing these additives and to a process for improving the lubricity of diesel oils.

[0002] The course of efforts to improve the emission behavior of diesel fuels, both the contents of polyaromatic compounds and the contents of long-chain alkanes in diesel oil have been reduced in recent years. In addition, attempts have been made to reduce the sulfur content to very low levels, i.e. to values of at most 0.05% by weight and preferably 0.03% or lower. As a result of these changes in the composition of diesel fuels, problems have arisen in the use of conventional ester-based lubricity enhancers. Partial precipitations can often occur to the considerable detriment of fuel quality.

[0003] Accordingly, there is a need for lubricity enhancers which could also be used in low-sulfur diesel oils. These additives would be effective in small quantities and, at the same time, would not lose their effect, even at low temperatures.

[0004] It has now been found that certain alkylated compounds solve this problem.

[0005] In a first embodiment, the present invention relates to the use of fatty acid alkylene glycol esters which are liquid at 21° C. and which correspond to general formula (I):

\[ R-\text{COO}-\text{(AO)}_n=\text{H} \]  

(1)

[0006] where R is an alkyl or alkenyl group containing 5 to 19 carbon atoms, AO stands the groups CH₂CH₃ or CH₃, and n is a number of 0.5 to 6, as an additive for improving the lubricity of diesel oil.

[0007] Ester and alkoxylation thereof are already known from WO 96/23855 as additives for improving the lubricity of diesel oils. However, WO 96/23855 does not disclose the compounds according to the present invention with their low degrees of alkoxylation. The only compounds actually mentioned are a sorbitan mono-oleate and a glycerol mono-oleate.

[0008] Diesel oils or diesel oils or simply diesel are low-flammability 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 contents of olefins, napthenes and aromatic hydrocarbons. Their composition is variable and is dependent in particular on the production method. Typical products have densities of 0.83 to 0.88, boiling points in the range from 170 to 360° C. and solidus points of 70 to 100° C. Diesel oil is obtained in the distillation of petroleum from gas oil, during cracking, from the tar obtained in the low-temperature carbonization (or hydrogenation) of lignite or hard coals and by hydrogenation of the coal extract. Diesel oils for stationary installations and for marine engines are similar in composition to heavy heating oil; diesel oils for automobiles, buses and trucks correspond in composition to heating oil. During combustion in a diesel engine, air is drawn into the cylinder, heated to 550-900° C. by high compression (compression ratio 14:1 to 25:1), so that a jet of injected diesel ignites spontaneously and reaches a combustion pressure of 50 to 80 bar at a combustion temperature of 1,500 to 2,200° C., so that the piston is moved and work is done. The combustion of 1 liter of diesel in a diesel engine requires 13 m³ of air; the combustion energy released amounts to around 42,000 kJ/kg. A key factor for the usability of diesel fuels is their ignition response which is now 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. The quality features of diesel fuels also include low-temperature behavior which can be described by the cloud point or—nowadays preferably—by the cold filter plugging point (CFPP) which is the temperature at which diesel fuel "sucked" through blocks a filter. Other desirable properties include a low pour point, a low content of incombustible or soak-forming substances and a low sulfur content. The additives according to the invention are particularly suitable for use in low-sulfur diesel oils, i.e. diesel oil with a sulfur content of at most 0.05% by weight and preferably 0.03% by weight or lower. For Europe, the standards and tests for diesel fuel are specified in DIN-EN 590 (05/1993).

[0009] The fatty acid alkylene glycols are products of the addition of ethylene oxide (EO) or propylene oxide (PO) or both EO and PO onto fatty acids with the formula RCOOH, in which R is as defined above. Compounds which contain only EO (CH₂—CH₂ groups) or only propylene oxide groups (C₃H₆ groups) are preferred, the ethoxylated compounds being particularly preferred.

[0010] Typical examples are capric acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isodecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and the technical mixtures thereof which are obtained, for example, in the pressure hydrolysis of natural fats and oils, in the reduction of aldehydes from Roelen’s oxo synthesis or as monomer fraction in the dimerization of unsaturated fatty acids, Technical C₁₂₃₄ fatty acids, such as coconut oil, palm oil, palm oil kernel oil or tallow fatty acid for example, are preferred. Ethoxylated or ethoxyalted and propoxylated fatty acids with a degree of alkoxylation n between 1 and 2 are particularly preferred. The fatty acids may be just propoxylated fatty acids or ethoxylated and propoxylated fatty acids; the ethoxylated and propoxylated fatty acids may be both random and block compounds.

[0011] The alkoxylates used in accordance with the invention are ethoxylated and/or propoxylated fatty acids which are also known as fatty acid alkylene glycols. They are known compounds and may be obtained by reaction of carboxylic acids with alkylene oxide in the presence of amines as catalysts, for example in accordance with DE-A-
In this process, however, the low-alkoxylated compounds are obtained in yields of well below 90% of the theoretical. In this process, the ethoxylation is carried out in the presence of alkanolamines as catalysts and gives distinctly higher yields.

However, for the propoxylated fatty acids and for the ethoxylated and propoxylated fatty acids, WO 99/06518 discloses a process which gives good yields of more than 90% of the theoretical for the low-propoxylated and ethoxylated/propoxylated fatty acids. This is achieved by carrying out the propoxylation or propoxylation/ethoxylation of the fatty acids in the presence of alkanolamines. Typical examples of alkanolamines suitable as basic catalysts are monoethanolamine, diethanolamine and, preferably, triethanolamine. The alkanolamines are used in quantities of typically 0.1 to 5% by weight and preferably 0.5 to 3.0% by weight, based on the fatty acids. The propoxylation and/or ethoxylation/propoxylation reaction can be carried out in a known manner. Normally, the fatty acid and the catalyst are introduced into a stirred autoclave which is freed from traces of water before the reaction by alternate evacuation and purging with nitrogen. The fatty acid is then reacted with the propylene oxide or with the ethylene oxide/propylene oxide mixture in a molar ratio of 1:0.5 to 1:1.5 which can be introduced into the pressure reactor in portions through a siphon after heating. The fatty acids are preferably reacted with 1 to 2 mol propylene oxide or with 1 to 2 mol of the ethylene oxide/propylene oxide mixture. The reaction may be carried out at temperatures of 80 to 180°C and preferably at temperatures in the range from 100 to 120°C and under autogenous pressures of 1 to 5 and preferably 2 to 3 bar. After the end of the reaction, it is advisable to stir the reaction mixture for a certain time (15 to 90 mins.) at the reaction temperature. The autoclave is then cooled and vented and, if desired, acids, such as lactic acid or phosphoric acid for example, are added to the product in order to neutralize the basic catalyst.

According to the invention, liquid compounds corresponding to general formula (I) above may generally be used. Compounds (I) where n is a number of 0.5 to 2.5 and, more particularly, 0.5 to 1.5 are preferred, the odd numbers being obtained by averaging via the different degrees of alkoxylation of the individual compounds. A value of n indicates a proportion of unesterified acids. However, additives (I) where n is 1 or greater are preferred.

It has also been found that, where alkoxyates of formula (I) are used, particularly good results are obtained when they are so-called narrow-range alkoxyates. Preferably, more than 90% of a homolog should be present in the compounds of formula (I). Homologs of formula (I) where n=1 are particularly preferred.

With regard to the choice of compounds of formula (I) suitable for the purposes of the invention, it is essential for the ester to be liquid at 21°C (room temperature). Accordingly, compounds of formula (I) based on fatty acid mixtures of sunflower oil, tall oil, soybean oil or rapeseed oil are particularly suitable. In addition, fatty acids containing at least one olefinic double bond are also preferably selected as the fatty acid component. Besides unbranched fatty acids, fatty acids with one or more branches may also be used for the production of the additives of formula (I). Additives based on oleic acid (a C_{18} unsaturated fatty acid) are particularly preferred. Particular mention is made in this regard of the 1-E0-oleic acid ester (in formula (I), n=1, R=C_{17} unsaturated).

According to the invention, the additives of formula (I) are added to the diesel oil in quantities of 10 to 1,000 ppm, preferably in quantities of 10 to 250 ppm and more particularly in quantities of 10 to 100 ppm. Preferably, less than 100 ppm of the additive is used. As mentioned above, the quantity of additive should be kept to a minimum. This is achieved in accordance with the invention.

Other additives, more particularly cetane number improvers (saltpeter or nitrous ester), corrosion inhibitors, flow enhancers, surfactants (which keep the fuel injectors clean), defoamers and occasionally smoke reducers are introduced into the diesel as additives. Exhaust gases from diesel fuels contain more nitrogen oxides and 30 to 100 times more particles ("soot") than those from spark ignition fuels after catalytic cleaning. Such additives may also be used in combination with the additives according to the invention. Preferably, however, no other additives should be used to improve lubricity.

The present invention also relates to a diesel oil with a sulfur content of at most 0.05% by weight which contains additives of formula (I) for improving lubricity, preferably in quantities of 10 to 1,000 ppm and more particularly in quantities of less than 100 ppm. In a preferred embodiment, the diesel oil is free from acetylated nitrogen-containing compounds and from free alcohols, more particularly C_{20-22} fatty alcohols and derivatives thereof, more particularly alkoxyated derivatives.

The diesel oil according to the invention should contain less than 0.05% by weight of sulfur and should have a distillation point (95%- to ASTM-D86) of at most 350°C. The so-called flash point should be at least 38°C.

A fuel oil composition comprising diesel oil and a lubricity additive of the formula (I):

\[ R\text{--COO--}(AO)_{n}\text{--H} \]  

wherein \( R \) is an alkyl or alkenyl group having from 5 to 19 carbon atoms, \( AO \) is a \( CH_{2}CH_{2} \), or \( CH_{2} \) group and \( n \) is a number of 0.5 to 6, wherein the additive is a liquid at 21°C and having a narrow homolog distribution.

The composition of claim 15 wherein \( n \) is equal to from 0.5 to 2.5.

The composition of claim 16 wherein \( n \) is equal to from 0.5 to 1.5.

The composition of claim 15 wherein the compound of formula (I) is the product of the process comprising reacting ethylene and/or propylene oxide and a fatty acid selected from the group consisting of sunflower oil fatty acid, rapeseed oil fatty acid, tall oil fatty acid and/or soybean oil fatty acid.
19. The composition of claim 15 wherein the amount of
the compound of formula (I) in the fuel oil composition is
from 10 to 1,000 ppm.

20. The composition of claim 19 wherein the amount of
the compound of formula (I) in the fuel oil composition is
from 10 to 250 ppm.

21. The composition of claim 20 wherein the amount of
the compound of formula (I) in the fuel oil composition is
from 10 to 100 ppm.

22. The composition of claim 15 wherein the diesel oil has
a sulfur content of up to 0.05% by weight.

23. The composition of claim 15 wherein the composition
is free from other lubricity additives.

24. The composition of claim 15 wherein the composition
is free from acylated nitrogen-containing compounds.

25. The composition of claim 15 wherein the composition
is free from a C_{n-22} fatty alcohol and/or a derivative thereof.

26. The composition of claim 15 wherein the derivative is
an alkoxylate.

27. A process for improving the lubricity of diesel adding
to diesel fuel up to 1,000 ppm of an additive of claim 15.

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