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(54) Title: ADDITIVE MIXTURE FOR THE BACTERICIDAL AND ANTICORROSIVE ADDITIZATION OF FUELS

(57) Abstract: The invention relates to an additive mixture for fuels, which comprises a) at least one N-formal, b) at least one antioxidant and c) at least one corrosion inhibitor. The additive mixture ensures that the additized fuels and lubricants have biocidal and corrosion-inhibiting additization, especially when they comprise proportions of renewable raw materials, such as biodiesel, and when they are in contact with copper-containing surfaces.



WO 2011/006734 A2

Additive mixture for the bactericidal and
anticorrosive additization of fuels

The invention relates to an additive mixture for the bactericidal and anticorrosive additization of fuels. The additive can be formulated as a liquid concentrate or as a semiconcentrate. The invention further relates to the use of the additive mixture for bactericidal and anticorrosive additization of fuels, and to correspondingly additized fuels. The invention also relates to a method for operating a system with a fuel which comprises the components of the inventive additive mixture.

In systems which come into contact with fuels (such as heating oil) (storage tanks, conduits, valves, filters, probes, measuring instruments, burners, etc.), different materials are used, for example plastics, metals and alloys, especially copper-containing materials. Owing to the interaction of long storage times, different compositions of the fuel and external influences such as formation of water of condensation, and oxidative and/or microbial degradation processes, the composition of the fuel can change and lead to undesired consequent phenomena. These consequent phenomena include corrosion, turbidity up to and including precipitation (formation of "sludge"), blockage of filters and material wear. This can lead to failure of the system and to the necessity of expensive repairs. Similar problems arise in fuel-processing systems such as stationary and mobile diesel engines and the corresponding injection systems.

The prior art discloses biocidal compositions for fuels. For example, DE 103 40 830 A1 describes compositions based on formaldehyde depot compounds and antioxidants, and the use thereof for preserving industrial products, for example fuels. An illustrative formaldehyde depot compound is N,N'-methylenebis(5-methyloxazolidine), which is sold by Schülke & Mayr GmbH (Norderstedt, Federal Republic of Germany) as Grotan® OX (Grotamar® 71, Mar® 71). The compositions have very

good storability as concentrates and have a constantly low level of deformation of the plastic vessel containing the concentrate ("neck-in effect").

5 DE 199 61 621 A1 relates to compositions which comprise a bactericidal N-formal, a fungicide and a stabilizer, for use, for example, in fuel additives. The compositions are storage-stable and have good meterability.

10 In the systems mentioned, as well as fossil fuels such as mineral oil, biofuels (such as biodiesel) are increasingly being used, which comprise fatty acid alkyl esters such as fatty acid methyl esters (FAME), for example rapeseed oil methyl ester (RME). This is both because of legal
15 stipulations and financial support and because of the insight that, in the generation of energy from renewable raw materials, the release of CO₂ is climate-neutral. Since the use of biofuels, however, there has been a significant increase in material compatibility problems. It is assumed
20 that biodiesel, for example, leaches copper ions out of copper-containing constituents of the systems. The increased copper ion content in turn accelerates the decomposition of the biodiesel and ultimately leads to the problems mentioned above.

25

WO2009/060057 A2 relates to the use of water-soluble biocides in biodiesel. An example of a biocide is 3,3'-methylenebis(5-methyloxazolidine). To improve the efficacy of the biocides, ethers are proposed. The ethers according to WO2009/060057 A2
30 are needed in a certain amount to dissolve the biocides in the biodiesel. However, ethers readily form peroxides which can convert constituents in biodiesel, inactivate antioxidants and wear away material. The biocidal activity of ethers, moreover, is not comparable to that of formaldehyde
35 depot compounds, and therefore (also as boosters) have to be used at a higher concentration and are therefore uneconomic. Moreover, ethers have a comparatively low flashpoint and can lead to less favorable labelling of products.

For this reason, it is desirable to add to the fuel improved additives which suppress these troublesome influences (decomposition of the biodiesel, formation of sludge) or do not allow them to arise at all, without necessarily needing to use ethers. More particularly, it was an object of the present invention to provide additive mixtures which are suitable for biocidal and anticorrosive additization of those fuels which comprise proportions of renewable raw materials, for example biodiesel. The additive mixtures should also be stable as concentrates and be easy to dose.

It has now been found that, surprisingly, these objects are achieved by an additive mixture which comprises

- a) at least one N-formal,
- b) at least one antioxidant and
- c) at least one corrosion inhibitor.

Inventive additives protect fuels to which they are added from infestation by bacteria, yeasts and moulds, and at the same time provide them with the necessary corrosion protection. The advantages of the additive mixtures are found more particularly in the case of addition to fuels which comprise components composed of renewable raw materials, for example biodiesel.

a) N-Formal

Inventive additive mixtures comprise at least one N-formal. The advantages of these active microbicidal ingredients are disclosed in DE 103 40 830 A1. Particularly suitable N-formals are reaction products of formaldehyde and amines (preferably alkanolamines) with a molar formaldehyde excess.

Examples of N-formals are condensation products of paraformaldehyde and isopropanolamine in a molar ratio of 3 : 2, condensation products of paraformaldehyde and

isopropanolamine in a molar ratio of 3 : 2 and urea, and condensation products of paraformaldehyde and isopropanolamine in a molar ratio of 3 : 2 and urea and ethylene glycol.

5

N-Formals which are used with preference in accordance with the invention are N,N'-methylenebis(5-methyloxazolidine), α,α',α'' -trimethyl-1,3,5-triazine-1,3,5-(2H,4H,6H)triethanol, 4,4-dimethyloxazolidine, dimethylolurea, 5-ethyl-3,7-dioxa-1-azabicyclo[3.3.0]octane, 2-(hydroxymethylamino)ethanol, methylenebistetrahydro-1,3-bisoxazine, 5-methylolchloroacetamide, bis(hydroxymethyl)-5,5-dimethylhydantoin, diazolidinylurea, sodium hydroxymethylglycinate and 3,4,4-trimethyloxazolidine, 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol (Grotan® BK), tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazole-2,5-(1H,3H)dione (TMAD) and tetramethylolglycoluril.

Preference is given to low-water formaldehyde depot compounds.

Particular preferred formaldehyde depot compounds are 3,3'-methylenebis(5-methyloxazolidine), 2,2',2''-(hexahydro-1,3,5-triazine-1,3,5-triyl)-triethanol, α,α',α'' -trimethyl-1,3,5-triazine-(2H,4H,6H)triethanol, tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazole-2,5-(1H,3H)-dione, dimethylurea and the products Grotan OF (methylenebis(5-methyloxazolidine) + urea) and Grotan OK (methylenebis(5-methyloxazolidine) + urea + ethylene glycol).

30

A very particularly preferred formaldehyde depot compound is 3,3'-methylenebis(5-methyloxazolidine).

b) Antioxidant

The inventive additive mixture comprises at least one antioxidant. Preferred antioxidants are liquid or are sufficiently soluble in the formaldehyde depot compound at room temperature. Examples of antioxidants are selected from

sterically hindered phenols, amines, vitamin E and derivatives thereof, and alkyl gallates, preferably 3-tert-butyl-4-hydroxyanisole (BHA), 2,6-di-tert-butyl-p-cresol (BHT), 2,6-di-tert-butylphenol, lauryl gallate and vitamin E.

5

Especially preferred as antioxidants are 2,6-di-tert-butylphenol and BHT.

c) Corrosion inhibitor

10 The inventive additive mixture comprises, as a further obligatory component c), at least one corrosion inhibitor. Preferred corrosion inhibitors are liquid or are sufficiently soluble in the formaldehyde depot compound at room temperature. Particularly preferred corrosion inhibitors are
15 triazole derivatives, for example benzotriazole, tolyltriazole or N,N-bis(2-ethylhexyl)((1,2,4-triazol-1-yl)methyl)amine.

Particular preference is given to using N,N-bis(2-ethylhexyl)((1,2,4-triazol-1-yl)methyl)amine, which is
20 supplied by BASF SE (Ludwigshafen, Federal Republic of Germany) as Irgamet® 30.

Amounts of components a), b) and c)

25 In additive mixtures preferred in accordance with the invention, the weight ratio of component b) to component c) is typically 20 : 1 to 1 : 20, preferably 1 : 10 to 10 : 1, especially 1 : 4 to 4 : 1, for example 1 : 1.

30 As explained hereinafter, inventive additives are typically formulated as liquid concentrates or semiconcentrates.

Liquid concentrate

In inventive additive mixtures formulated as liquid
35 concentrates, the proportion of component a) is preferably at least 60% by weight, preferably at least 80% by weight, especially at least 90% by weight, for instance 92% by weight. The proportions of components b) and c) are typically

each at least 0.5% by weight, preferably at least 1% by weight, especially at least 2 by weight, for instance 4% by weight. Particular preference is given to liquid concentrates which consist of components a), b) and c), i.e. comprise no further constituents.

A particularly preferred liquid concentrate consists of:

- a) 92% by weight of 3,3'-methylenebis(5-methyloxazolidine),
- b) 4% by weight of 2,6-di-tert-butylphenol and
- c) 4% by weight of Irgamet 30.

The liquid concentrate is prepared by initially charging component a) (for example 3,3'-methylenebis(5-methyloxazolidine)) and then dissolving component b) (such as 2,6-di-tert-butylphenol or BHT) and component c) (such as Irgamet 30) while stirring. The product is clear and colourless to pale yellow.

Inventive liquid concentrates are used prophylactically in fuels which are yet to be microbially infested in concentrations of 20 to 100 mg/l (ppm), and in fuels which have already been contaminated in amounts of 200 to 1000 ppm.

Semiconcentrate

In inventive additive mixtures which have been formulated as a semiconcentrate, the proportion of component a) is typically at least 5% by weight, preferably at least, preferably at least 10% by weight, especially at least 15% by weight, for instance 20% by weight. Components b) and c) are typically present in an amount of in each case at least 0.1% by weight, preferably at least 0.25% by weight, especially at least 0.5% by weight, for instance 0.9% by weight.

Semiconcentrates comprise, as well as the inventive components a), b) and c), a carrier. Examples of carriers are selected from diesel oil, biodiesel oil, fatty acid methyl

esters, mineral oil (e.g. ShellSol A 150), aliphatic or aromatic hydrocarbons (such as toluene), alkylbenzenes, for example Marlican (RG), and mixtures thereof. The amount of the carrier in the concentrate is preferably at least 50% by weight, more preferably at least 60% by weight, especially at least 70% by weight, for instance 78% by weight.

A particularly preferred semiconcentrate comprises:

- a) 20% by weight of 3,3'-methylenebis(5-methyloxazolidine),
- b) 0.9% by weight of 2,6-di-tert-butylphenol
- c) 0.9% by weight of Irgamet 30

and, as the remainder, a hydrocarbon as a carrier which is soluble in FAME-containing hydrocarbons, for example diesel fuel. For example, the carriers used are, for example, ShellSol A 150 or alkylbenzene (Marlican).

To prepare the semiconcentrate, the carrier is initially charged and component a) (such as 3,3'-methylenebis(5-methyloxazolidine)), component b) (such as 2,6-di-tert-butylphenol or BHT) and component c) (such as Irgamet 30) are dissolved while stirring. The product is clear and colourless to pale yellow.

Inventive semiconcentrates are used prophylactically in fuels which are yet to be microbially infested in concentrations of 100 to 500 ppm, and in fuels which have already been contaminated in amounts of 1000 to 5000 ppm.

The invention further relates to the use of the inventive additive mixture for biocidal and anticorrosive additization of fuels, and to the protection thereof from oxidative degradation.

According to the invention, the corrosion of copper in particular as a constituent of the materials of systems

through which the fuel flows or in which it is stored. As mentioned above, the corrosion of copper presented a problem especially when the fuel comprises proportions of renewable raw materials, for example FAME. The proportion of renewable raw materials (such as FAME) which is typically present in the fuel is up to 100% by volume, preferably up to 20% by volume, especially up to 10% by volume, such as 5 to 7% by volume.

According to the invention, components a), b) and c) are used in the fuel in an amount which ensures effective protection from microbial attack and from oxidative and corrosive influences. In the fuel, the proportion of component a) should be at least 5 ppm, more preferably at least 100 ppm and especially preferably at least 200 ppm, for example 500 ppm. The proportions of components b) and c) should each be at least 0.25 ppm, preferably at least 5 ppm and more preferably at least 10 ppm, for example 25 ppm.

The invention further relates to the use of the inventive liquid concentrate for producing a semiconcentrate.

Components a), b) and c) are used - in combination - in fuels, preferably in the form of the inventive liquid concentrates or semiconcentrates. They are used in accordance with the invention in lubricants, cooling lubricant concentrates and emulsions, transformer oils, fuels, biofuels, biodiesels, diesel fuels, kerosenes, heavy oils, heating oils, mineral oils, all of which are referred to here as fuels. They are preferably used in fuels with proportion of material composed of renewable raw materials, especially biodiesel.

The inventive formulations can be combined with further active biocidal ingredients, functional additives and auxiliaries, as disclosed, for example, in WO2009/060057 A2, DE 10 2006 035013 A1 or DE 103 40 830 A1.

The combination of components a), b) and c) is used in fuels preferably by adding a liquid concentrate or a semiconcentrate. Alternatively, it is possible to add components a), b) and c) individually, but this alternative is not preferred.

The invention further relates to a method for operating a system with a fuel, in which the additive mixture described is added to the fuel, or in which the components are added individually.

The invention also relates to a fuel which comprises components a), b) and c) in such an amount that the concentration (based in each case on the fuel)

- of component a) is at least 5 ppm, preferably at least 100 ppm and especially at least 200 ppm, for instance 500 ppm;
- of component b) is at least 0.25 ppm, preferably at least 5 ppm and especially at least 10 ppm, for instance 25 ppm; and
- of component c) is at least 0.25 ppm, preferably at least 5 ppm and especially at least 10 ppm, for instance 25 ppm.

The inventive liquid concentrates or semiconcentrates have the following advantages:

- they are clear, homogeneous, fluid, low-viscosity, free-flowing, low-odour, readily distributable, readily incorporable, possess good stability (cold stability, storage stability, sufficient thermal stability) and are easy to handle;
- they have a broad profile of action: they are bactericidally, fungicidally and algicidally active,

protect from oxidative degradation, give a good coating on the surfaces to be treated, protect from corrosion, especially in the case of nonferrous metals;

- 5 - they protect systems and materials which come into contact with fuels, especially biofuels;
- they effectively prevent sludge formation in fuel systems and vessels;
- 10 - they improve the shelf life of the treated products;
- they improve the lubricant properties of the treated products;
- 15 - they possess good compatibility with a multitude of materials;
- they have good solubility in different bases, such as
- 20 oils;
- they possess good dissolution capacity for further/additional additives;
- 25 - no additional solvents are required and
- they enhance the calorific value of heating oil.

The advantages of the invention are evident more particularly from the examples which follow.

Examples

Unless stated otherwise, all percentages are based on weight.

Example 1

Materials used:

- 3,3'-methylenebis(5-methyloxazolidine)
- brass 63 (100×20×1 mm), Cat.No.: 16-24 from Riegger Industriehandel, Reinbek, Federal Republic of Germany
- E-copper ((100×20×1 mm), Cat.No.: 15-54 from Riegger
- diesel fuel to EN 590, with 5% (V/V) fatty acid methyl ester

Procedure: The solutions and the metal sheet were each introduced into a 500 ml wide-neck bottle. Solutions 1A-1C were not stirred; solutions 1D-1G were stirred with a magnetic stirrer. The appearance of the solutions was assessed visually.

Sample	Experiment	Start	After 4 weeks	After 6 weeks
1A	Cu sheet in diesel; without stirring	clear yellow solution	clear yellow solution	clear yellow solution
1B	Cu sheet in diesel + 500 ppm of 3,3'-methylenebis(5-methyloxazolidine); without stirring	clear yellow solution	clear yellow solution	slightly turbid yellow solution
1C	Cu sheet in diesel + 50 ppm of 3,3'-methylenebis(5-methyloxazolidine); without stirring	clear yellow solution	clear yellow solution	turbid yellow solution
1D	Cu sheet in diesel; with stirring	clear yellow solution	clear yellow solution	clear yellow solution

Sample	Experiment	Start	After 4 weeks	After 6 weeks
1E	Cu sheet in diesel + 500 ppm of 3,3'-methylenebis(5-methyloxazolidine); with stirring	clear solution yellow	clear solution yellow	highly turbid solution, some dark coating on the sheet and at the base of the bottle
1F	Cu sheet in diesel + 50 ppm of 3,3'-methylenebis(5-methyloxazolidine); with stirring	clear yellow solution	clear yellow solution	clear yellow solution, fluff in the solution
1G	Brass sheet in diesel + 500 ppm of 3,3'-methylenebis(5-methyl-oxazolidine); with stirring	clear yellow solution	clear yellow solution	turbid yellow solution, some dark coating on the sheet and at the base of the bottle

Example 2

Materials used:

- 3,3'-methylenebis(5-methyloxazolidine)
- semiconcentrate 2: 20% 3,3'-methylenebis(5-methyloxazolidine), 0.9% di-tert-butylphenol, 0.9% Irgamet 30; dissolved in ShellSol A 150
- E-copper (100x20x1 mm), Cat.No.: 15-54 from Riegger
- diesel fuel to EN 590, with 5% (V/V) fatty acid methyl ester content

Procedure: The solutions and the metal sheet were each introduced into a 500 ml wide-neck bottle and stirred at room temperature with a magnetic stirrer.

Sample	
2A	Diesel, stirred
2B	Diesel + copper sheet, stirred
2C	Diesel + 500 ppm of 3,3'-methylenebis(5-methyloxazolidine); stirred
2D	Diesel + copper sheet + 500 ppm 3,3'-methylenebis(5-methyloxazolidine)
2E	Diesel + 2500 ppm of semiconcentrate 2, stirred
2F	Diesel + copper sheet + 2500 ppm of semiconcentrate 2, stirred

Copper content mg/l (ppm)	2 days	1 week	2 weeks	3 weeks	6 weeks
2A	0.1	0.1	0.2	not determined	0.1
2B	1.3	1.5	1.8	1.6	2.3
2C	0.1	0.1	0.1	0.1	0.2
2D	0.6	0.6	0.8	1.0	1.0
2E	0.1	<0.1	<0.1	<0.1	0.2
2F	not determined	0.5	not determined	0.7	0.7
Appearance	2A	2B	2C	2D	2E
Start	clear yellow	clear yellow	clear yellow	clear yellow	clear yellow
					2F
					clear yellow

	solution	solution	solution	solution	solution	solution
after 1 week	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 2 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 3 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 5 weeks	clear yellow solution	clear yellow solution	clear yellow liquid	turbid yellow solution	clear yellow solution	clear yellow solution
after 10 weeks	clear yellow solution	turbid yellow liquid	clear yellow solution	red sludge at the base of a turbid yellow liquid	clear yellow solution	clear yellow solution
after 11 weeks	clear yellow solution	red sludge at the base of a turbid yellow liquid	clear yellow solution	red sludge at the base of a turbid yellow liquid	clear yellow solution	clear yellow solution
after 12 weeks	clear yellow solution	red sludge at the base of a turbid yellow liquid	clear yellow solution	red sludge at the bottom of a turbid yellow liquid	clear yellow solution	clear yellow solution

Appearance	2A	2B	2C	2D	2E	2F
after 13 weeks	clear yellow solution	red sludge at the base of a turbid yellow liquid	turbid	red sludge at the base of a turbid yellow liquid	somewhat more intense yellow	somewhat more intense yellow
after 14 weeks	clear yellow solution	red sludge at the base of a turbid yellow liquid	turbid, a little brown sludge at the base	red sludge at the base of a turbid yellow liquid	somewhat more intense yellow	somewhat more intense yellow, brown crumbs in the solution
after 15 weeks	clear yellow solution	red sludge at the base of a turbid yellow liquid	turbid, a little brown sludge at the base	red sludge at the base of a turbid yellow liquid	somewhat more intense yellow	somewhat more intense yellow, brown crumbs in the solution
after 20 weeks	clear yellow solution	red sludge at the base of a turbid yellow liquid	turbid, a little brown sludge at the base	red sludge at the base of a turbid yellow liquid	slightly turbid, somewhat more intense yellow	slightly turbid, somewhat more intense yellow, brown crumbs/fluff in the solution

Example 3

Materials used:

- Concentrate X: 92% 3,3'-methylenebis(5-methyloxazolidine) + 4% BHT + 4% benzotriazole
- Concentrate Y: 92% 3,3'-methylenebis(5-methyloxazolidine) + 4% 2,6-di-tert-butylphenol + 4% Irgamet 30
- E-copper (100x20x1 mm), Cat.No.: 15-54 from Riegger
- diesel fuel to EN 590, with 5% (V/V) fatty acid methyl ester content

Procedure: The solutions and the metal sheet were each introduced into a 500 ml bottle and stirred with a magnetic stirrer.

Sample	
3A	Diesel + 500 ppm of concentrate X, stirred
3B	Diesel + 500 ppm of concentrate X + copper sheet, stirred
3C	Diesel + 500 ppm of concentrate Y, stirred
3D	Diesel + copper sheet + 500 ppm of concentrate Y; stirred

Copper content mg/l (ppm)	Blank value	3 weeks	6 weeks
3A	0.2	0.2	0.16
3B	0.2	1.4	2.1
3C	0.2	0.2	0.25
3D	0.2	0.7	0.67

Appearance	3A	3B	3C	3D
Start	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 3 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 6 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 7 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 8 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 9 weeks	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 10 weeks	clear yellow solution	slightly turbid, brown fluff	clear yellow solution	clear yellow solution
after 11 weeks	clear yellow solution	turbid, brown sludge at the base	clear yellow solution	clear, intensely yellow solution
after 12 weeks	clear yellow solution	turbid, brown sludge at the base	clear yellow solution	clear, intensely yellow solution
after 17 weeks	slightly turbid, yellow	turbid, brown sludge at the base	very slightly turbid, yellow	turbid, fluff/crumbs in the solution

Example 4

Materials used:

- 3,3'-Methylenebis(5-methyloxazolidine)
- Semiconcentrate 4: 20% 3,3'-methylenebis(5-methyloxazolidine), 0.9% di-tert-butylphenol, 0.9% Irgamet 30; dissolved in ShellSol A 150
- Diesel fuel to EN 590, with 5% (V/V) fatty acid methyl ester content
- Copper naphthenate (copper content: 7.97%; stock solution: 12.55 g of copper naphthenate are dissolved/100 g of toluene, corresponding to 1% copper)

Sample	Test setup
4A	Diesel
4B	Diesel + 500 ppm of 3,3'-methylenebis(5-methyloxazolidine)
4C	Diesel + 2500 ppm of semiconcentrate 4
4D	Diesel + 1 ppm of copper + 500 ppm of 3,3'-methylenebis(5-methyloxazolidine)
4E	Diesel + 5 ppm of copper + 500 ppm of 3,3'-methylenebis(5-methyloxazolidine)
4F	Diesel + 1 ppm of copper + 2500 ppm of semiconcentrate 4
4G	Diesel + 5 ppm of copper + 2500 ppm of semiconcentrate 4
4H	Diesel + 1 ppm of copper (after 2 weeks)
4I	Diesel + 5 ppm of copper (after 2 weeks)

All samples are stirred in a 250 ml screwtop bottle with a magnetic stirrer at room temperature. The appearance changed as follows:

Appearance	4A	4B	4C	4D	4E	4F	4G	4H	4I
Start	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution		
after 2 weeks	clear yellow solution	clear yellow solution	clear yellow solution	turbid yellow liquid	turbid yellow liquid	clear yellow solution	clear yellow solution	clear yellow solution	clear yellow solution
after 3 weeks	clear yellow solution	clear yellow solution	clear yellow solution	turbid yellow liquid	dark sludge in turbid yellow liquid	clear yellow solution	clear yellow solution	clear yellow solution	turbid yellow liquid
after 4 weeks	clear yellow solution	clear yellow solution	clear yellow solution	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid	clear yellow solution	clear yellow solution	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid
after 5 weeks	clear yellow solution	clear yellow solution	clear yellow solution	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid	clear yellow solution	turbid, flocs	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid
after 6 weeks	clear yellow solution	clear yellow solution	clear yellow solution	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid	clear yellow solution	turbid, flocs	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid
after 7 weeks	clear yellow solution	clear yellow solution	clear yellow solution	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid	turbid, flocs	turbid, flocs	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid

weeks	solution	yellow solution	yellow solution	in turbid yellow liquid	sludge in turbid yellow liquid	yellow, flocs	flocs	sludge in turbid yellow liquid	sludge in turbid yellow liquid
after 12 weeks	clear yellow solution	clear yellow solution	clear yellow solution	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid	turbid, yellow, flocs	turbid, flocs	dark sludge in turbid yellow liquid	dark sludge in turbid yellow liquid

Example 5

Materials used:

- EL heating oil, low-sulfur (purely mineral, no fatty acid methyl esters)
- Fatty acid methyl esters
- 3,3'-Methylenebis(5-methyloxazolidine)
- Semiconcentrate X: 20% 3,3-methylenebis(5-methyloxazolidine), 0.9% di-tert-butylphenol, 0.9% Irgamet 30; dissolved in ShellSol A 150
- E-copper (100×20×1 mm) Cat.No.: 15-4 from Riegger

Diesel sample	Composition (% by vol.)
5A	100% heating oil + 0% biodiesel
5B	90% heating oil + 10% biodiesel
5C	80% heating oil + 20% biodiesel
5D	70% heating oil + 30% biodiesel

Sample	Experiment
5A1	5A + Cu
5A2	5A + 500 ppm of 3,3-methylenebis(5-methyloxazolidine)
5A3	5A + 500 ppm of 3,3-methylenebis(5-methyloxazolidine) + Cu
5A4	5A + 2500 ppm of semiconcentrate X
5A5	5A + 2500 ppm of semiconcentrate X + Cu
5B1	5B + Cu
5B2	5B + 500 ppm of 3,3-methylenebis(5-methyloxazolidine)
5B3	5B + 500 ppm of 3,3-methylenebis(5-methyloxazolidine) + Cu
5B4	5B + 2500 ppm of semiconcentrate X
5B5	5B + 2500 ppm of semiconcentrate X + Cu

Sample	Experiment
5C1	5C + Cu
5C2	5C + 500 ppm of 3,3-methylenebis(5-methyloxazolidine)
5C3	5C + 500 ppm of 3,3-methylenebis(5-methyloxazolidine) + Cu
5C4	5C + 2500 ppm of semiconcentrate X
5C5	5C + 2500 ppm of semiconcentrate X + Cu
5D1	5D + Cu
5D2	5D + 500 ppm of 3,3-methylenebis(5-methyloxazolidine)
5D3	5D + 500 ppm of 3,3-methylenebis(5-methyloxazolidine) + Cu
5D4	5D + 2500 ppm of semiconcentrate X
5D5	5D + 2500 ppm of semiconcentrate X + Cu

The appearance of the individual sample changed as follows:

	Start	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks	After 11 weeks
5A1	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution
5A2	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear, red, sediment on the metal and at the base
5A3	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	Slightly turbid, sediment at the base

	Start	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks	After 11 weeks
5A4	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution
5A5	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution, a little fluff	clear red solution, a little fluff	clear red solution, a little fluff
5B1	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution, a little fluff	slightly turbid, crumbs	slightly turbid, crumbs
5B2	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment at the base
5B3	clear red solution	turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid

	Start	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks	After 11 weeks
5B4	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment at the base
5B5	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment at the base
5C1	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	turbid	turbid	turbid, has become lighter
5C2	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment a the base
5C3	clear red solution	turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid

	Start	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks	After 11 weeks
5C4	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment at the base
5C5	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment at the base
5D1	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	turbid	turbid	decolorized to orange, turbid and sediment
5D2	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid, a little sediment at the base	slightly turbid, a little sediment a the base
5D3	clear red solution	turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid	dark sludge in turbid red liquid

	Start	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks	After 5 weeks	After 6 weeks	After 11 weeks
5D4	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid	slightly turbid
5D5	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	clear red solution	slightly turbid	slightly turbid

Evaluation of the examples

Example 1 shows that 3,3'-methylenebis(5-methyloxazolidine) is incompatible as an additive to diesel oil (with 5% FAME) with a time delay and in a concentration-dependent manner and more particularly in turbulent flow, when it comes into contact with copper or nonferrous metal. 3,3-Methylenebis(5-methyloxazolidine) is thus, as an additive to diesel/biodiesel, associated with disadvantages when there is contact with nonferrous metal. The biocide, which in principle has good suitability, is thus not very suitable owing to its incompatibility.

Example 2 shows that diesel fuel with 5% FAME can leach considerable amounts of copper salt out of copper sheet (2B). In the case of addition of 3,3'-methylenebis(5-methyloxazolidine), the copper wear is lower (2D), and in the case of addition of inventive semiconcentrate with ShellSol A 150 significantly lower (2F). The formation of sludge in the solution correlates with the amount of copper salt released. Even in the absence of copper sheet, the performance of the inventive semiconcentrate is somewhat better than that of 3,3'-methylenebis(5-methyloxazolidine) (see 2E compared to 2C).

Example 3 shows that diesel fuel with 5% FAME in contact with copper sheet is protected better by addition of a concentrate composed of 92% 3,3'-methylenebis(5-methyloxazolidine), 4% 2,6-di-tert-butylphenol and 4% Irgamet 30 than by addition of a likewise inventive concentrate composed of 92% 3,3'-methylenebis(5-methyloxazolidine), 4% BHT and 4% benzotriazole.

In **Example 4**, a defined amount of copper salt (copper naphthenate, dissolved in toluene) is added to diesel

fuel with 5% FAME (**4D** to **4I**). WHEN 3,3'-methylenebis(5-methyloxazolidine) is added, there is incompatibility depending on the copper concentration (**4D**, **4E**). An addition of inventive semiconcentrate significantly improves the stability of the diesel fuel (**4F**, **4G**). Diesel fuel with 5% FAME leads, after addition of copper salt, to the formation of sludge (see **4H**, **4I**). Diesel fuel with 5% FAME without addition of copper salt is stable (**4A**), and likewise in the case of addition of 3,3'-methylenebis(5-methyloxazolidine) (**4B**) or inventive semiconcentrate (**4C**). This demonstrates that inventive semiconcentrates are also suitable for products which do not have a proportion of material composed of renewable raw materials.

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Example 5 shows the unfavourable influence of FAME (10 to 30% by volume) on diesel fuel when the latter is in contact with Cu. An addition of 3,3'-methylenebis(5-methyloxazolidine) worsens the compatibility further (e.g. **5C3** compared to **5C1**); only an addition of inventive semiconcentrate gives a stable liquid in the presence of copper sheet (e.g. **5C5**).

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This shows that an N-formal such as 3,3'-methylenebis(5-methyloxazolidine) is incapable of protecting FAME-containing liquids which are in contact with nonferrous metals against microbial degradation. Only the combination with sufficient amounts of antioxidant and corrosion inhibitor leads to a product which protects FAME-containing liquids which are in contact with nonferrous metals from microbial degradation. FAME-containing liquids are then storage-stable and do not form undesired precipitates.

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Claims

1. Additive mixture for fuels, which comprises
- 5 a) at least one N-formal,
b) at least one antioxidant and
c) at least one corrosion inhibitor.
- 10 2. Additive mixture according to Claim 1, characterized in that the N-formal is selected from N,N'-methylenebis(5-methyloxazolidine), α,α',α'' -trimethyl-1,3,5-triazine-1,3,5-(2H,4H,6H)-triethanol, 4,4-dimethyloxazolidine, dimethylol-
15 urea, 5-ethyl-3,7-dioxa-1-azabicyclo[3.3.0]octane, 2-(hydroxymethylamino)ethanol, methylene-bistetrahydro-1,3-bisoxazine, 5-methylolchloroacetamide, bis(hydroxymethyl)-5,5-dimethylhydantoin, diazolidinylurea, sodium hydroxymethylglycinate and 3,4,4-trimethyloxazolidine, 2,2',2''-
20 (hexahydro-1,3,5-triazine-1,3,5-triyl)triethanol, tetrahydro-1,3,4,6-tetrakis(hydroxylmethyl)imidazo[4,5-d]imidazole-2,5-(1H,3H)dione (TMAD) and tetramethylolglycoluril, especially
25 N,N'-methylenebis(5-methyloxazolidine).
3. Additive mixture according to Claim 1 or 2, characterized in that the antioxidant is selected from sterically hindered phenols, amines, vitamin
30 E and derivatives thereof, and alkyl gallates, preferably 3-tert-butyl-4-hydroxyanisole (BHA), 2,6-di-tert-butyl-p-cresol (BHT), 2,6-di-tert-butylphenol, lauryl gallate and vitamin E, especially 2,6-di-tert-butylphenol and BHT.
- 35 4. Additive mixture according to any of the preceding claims, characterized in that the corrosion inhibitor is a triazole derivative, preferably benzotriazole, tolyltriazole or N,N-bis(2-

ethylhexyl)((1,2,4-triazol-1-yl)methyl)amine,
especially N,N-bis(2-ethylhexyl)((1,2,4-triazol-1-yl)methyl)amine.

- 5 5. Additive mixture according to any of the preceding
 claims, characterized in that the weight ratio of
 component b) to component c) is 20 : 1 to 1 : 20,
 preferably 1 : 10 to 10 : 1, especially 1 : 4 to 4
 : 1, for instance 1 : 1.
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6. Additive mixture according to any of the preceding
 claims, characterized in that it is present as a
 liquid concentrate and the proportion of component
 a) is at least 60% by weight, preferably at least
15 80% by weight, especially at least 90% by weight,
 for instance 92% by weight.
7. Additive mixture according to any of the preceding
 claims, characterized in that it is present as a
20 liquid concentrate and the proportions of
 components b) and c) are each at least 0.5% by
 weight, preferably at least 1% by weight,
 especially at least 2% by weight, for instance 4%
 by weight.
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8. Additive mixture according to any of Claims 1 to
 5, characterized in that it is present as a
 semiconcentrate in a carrier and the proportion of
 component a) is at least 5% by weight, preferably
30 at least 10% by weight, especially at least 15% by
 weight, for instance 20% by weight.
9. Additive mixture according to any of claims 1 to 5
 and 8, characterized in that it is present as a
35 semiconcentrate and the proportions of components
 b) and c) are each at least 0.1% by weight,
 preferably at least 0.25% by weight, especially at
 least 0.5% by weight, for instance 0.9% by weight.

10. Additive mixture according to Claim 8 or 9, characterized in that the semiconcentrate comprises, as carriers, diesel oil, biodiesel oil, fatty acid methyl esters, mineral oil, aliphatic
5 or aromatic hydrocarbons or mixtures thereof in an amount of at least 50% by weight, preferably at least 60% by weight, especially at least 70% by weight, for instance 78% by weight.
- 10 11. Use of the liquid concentrate according to Claim 6 or 7 for producing a semiconcentrate.
12. Use of the additive mixture according to any of the preceding claims for biocidal and corrosion-inhibiting additization of fuels, the corrosion of
15 copper preferably being inhibited.
13. Use according to Claim 12, characterized in that the fuel comprises proportions of renewable raw materials, preferably fatty acid methyl esters.
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14. Use according to Claim 13, characterized in that the proportion is up to 100% by volume, preferably up to 20% by volume, especially up to 10% by
25 volume, such as 5 to 7% by volume.
15. Use according to any of Claims 12 to 14, wherein the liquid concentrate is used in an amount of 20 to 1000 ppm, or the semiconcentrate in an amount
30 of 100 to 5000 ppm.
16. Method for operating a system with fuel, in which the additive mixture according to any of Claims 1 to 10 is added to the fuel.
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17. Fuel which comprises components a), b) and c) according to any of Claims 1 to 10 in such an amount that the concentration

- of component a) is at least 5 ppm, preferably at least 100 ppm and especially at least 200 ppm, for instance 500 ppm;
- 5 - of component b) is at least 0.25 ppm, preferably at least 5 ppm and especially at least 10 ppm, for instance 25 ppm; and
- 10 - of component c) is at least 0.25 ppm, preferably at least 5 ppm and especially at least 10 ppm, for instance 25 ppm,

based in each case on the fuel.