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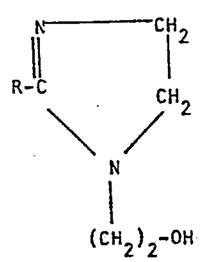
(54) **Corrosion inhibitors for alcohol-based fuels.**

(57) A liquid fuel adapted for use in an internal combustion engine, said fuel comprising 5 to 100 weight percent of one or more alcohols, 0 to 95 weight percent gasoline and, as a corrosion inhibitor, a combination of (A) a member selected from (i) a polymer of one or more C_{16} to C_{18} polyunsaturated aliphatic monocarboxylic acids or (ii) at least one monoalkenylsuccinic acid in which the alkenyl group contains 8 to 30 carbon atoms and (B) at least one substituted imidazoline having the structural formula:



wherein R represents a hydrocarbon alkenyl group having from 7 to 24 carbon atoms.

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CORROSION INHIBITORS FOR ALCOHOL-BASED FUELS

In the past, metal corrosion caused by conventional motor fuels such as gasoline was not much of a problem because such hydrocarbon fuels are inherently non-corrosive. However, with the advent of fuels containing alcohols such as gasohol or straight alcohol fuels, corrosion has become a major problem because such fuels are corrosive. It has been reported that this corrosion is due to the presence of acidic contaminants in such fuels such as formic acid. It is almost impossible to avoid such contaminants because they occur in fuel grade alcohols and are also formed in storage as normal alcohol oxidation products.

It is known from U.S. 4,305,730 that polymerized linoleic acid, especially trimer, is an effective corrosion inhibitor for alcohol-type motor fuels. It has now been discovered that the corrosion inhibiting properties of such polymerized polyunsaturated aliphatic monocarboxylic acids are improved by use of the co-additives described herein. The substituted imidazoline co-additives of the invention, more fully described hereafter, also are known compounds which heretofore have found use, for example, in motor fuel compositions to prevent carburetor icing as disclosed in U.S. 3,036,902.

It is also known from U.S. 2,993,772 that alkenyl succinic acids as well as their anhydrides inhibit and/or prevent the deposit-forming tendency of hydrocarbon fuels during combustion and/or modify the deleterious effect of the formed deposits in both leaded and unleaded fuels particularly in gasoline and jet fuels. It has now also been discovered that a combination of certain substituted imidazolines with a mono-alkenylsuccinic acid wherein the alkenyl group contains 8 to 30 carbon atoms provides corrosion inhibiting properties to fuels containing alcohols such as gasohol or straight alcohol fuels.

According to the present invention, metal corrosion caused by alcohol-type motor fuels is inhibited by adding to the fuel a combination of (A) a member selected from (i) polymerized polyunsaturated aliphatic monocarboxylic acid or (ii) at least one monoalkenylsuccinic acid wherein the alkenyl group contains 8 to 30 carbon atoms and (B) substituted imidazoline.

The invention provides a liquid fuel adapted for use in an internal combustion engine, said fuel comprising from 5 to 100 weight percent of one or more alcohols, from 0 to 95 weight percent gasoline and as a corrosion inhibitor the combination of (A) a member selected from (i) a polymer of one or more C_{16} to C_{18} polyunsaturated aliphatic monocarboxylic acids, (ii) at least one monoalkenylsuccinic acid wherein the alkenyl group contains 8 to 30 carbon atoms and (B) a substituted imidazole.

The additive combination of this invention can be beneficial in any engine fuel containing or consisting of an oxygenate. Such fuels include gasoline-alcohol mixtures referred to as "gasohol" as well as straight alcohol fuels. Useful alcohols are methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, t-butanol, 2-methyl-2-propanol, isobutanol or mixtures thereof such as methanol and t-butanol. Gasohols usually contain 2 to 30 volume percent alcohol. At concentrations above 10 volume percent phase separation problems may be encountered especially in the presence of water.

Phase separation can be minimized by including co-solvents in the gasohol such as ethers, ketones or esters, for example. An especially useful co-solvent is methyl tert-butyl ether which also serves to increase octane value.

The additive combination is used in a corrosion inhibiting amount. A useful range of additive concentration is 1 to 5000 pounds per thousand barrels (ptb). A more preferred range is 5 to 2000 ptb and the most preferred concentration is 5 to 500 ptb.

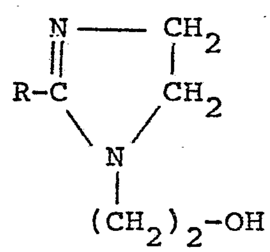
Component A (i) is a polymer of one or more 16 to 18 carbon polyunsaturated aliphatic monocarboxylic acids. Examples of these are tall oil fatty acid, oleic acid, linoleic acid and linolenic acid including mixtures thereof. The polymers comprise mainly dimers and trimers of the polyunsaturated acids. Suitable polymers of linoleic acid are available commercially. Mixtures high in trimer content are most preferred.

The monoalkenylsuccinic acids(Component Aii) are well known in the art. These acids may be readily prepared by the condensation of an olefin with maleic anhydride followed by hydrolysis (see U.S. Pat. No. 2,133,734 and U.S. Pat. No. 2,741,597). Suitable monoalkenylsuccinic acids include octenylsuccinic acid, decenylsuccinic acid, undecenylsuccinic acid, dodecenylsuccinic acid, pentadecenylsuccinic acid, octadecenylsuccinic acid and isomers thereof having alkenyl groups of various hydrocarbon structures. The preferred monoalkenylsuccinic acid is dodecenylsuccinic acid, more preferably, dodecenylsuccinic acid prepared from propylene tetramer.

While an alkenyl group ranging from 8 to 30 carbon atoms is preferred as indicated above, it is contemplated that substantially any alkenylsuccinic acid or its equivalent anhydride may be employed in the fuels of the present invention provided it is sufficiently soluble in the fuel to be effective in combination with the substituted imidazoline compounds of the invention as a corrosion inhibitor. Further, since relatively pure olefins are difficult to obtain and are often too expensive for commercial use, alkenylsuccinic acids prepared as mixtures by reacting mixed olefins with maleic anhydride may be employed in this invention as well as relatively pure alkenyl succinic acids. Mixed alkenylsuccinic acids wherein the alkenyl group averages 6-8, 8-10 and 10-12 carbon atoms are commercially available.

Component B of the combination is a substituted imidazoline.

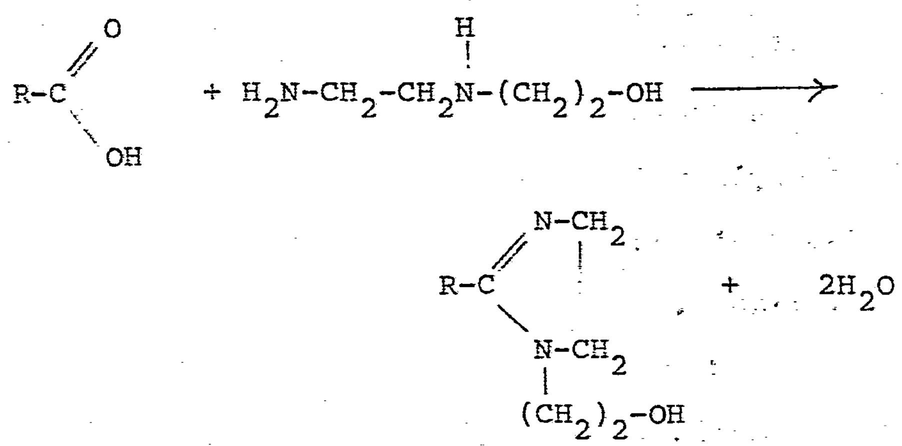
The substituted imidazoline used in this invention can be represented by the following general formula (I):



(I)

in which R is a hydrocarbon alkenyl group having from 7 to 24 carbon atoms.

The imidazolines having Formula I which are useful in this invention may be readily obtained by reacting suitable organic acids with N-(2-hydroxyethyl)ethylene diamine. This reaction involves the elimination of 2 molecules of water between the acid and the amine. This reaction is represented by the following equation:



In addition to the imidazoline, small amounts of a corresponding linear amino amide are also obtained. This amino amide is the result of eliminating only one molecule of water between the acid and the amine. Methods of preparing the imidazolines are well known. Useful procedures are described in Wilson, U.S. 2,267,965, and Wilkes, U.S. 2,214,152. As can be seen from the reaction equation given above, the R group in the imidazoline is the alkenyl residue of the particular acid which is used in its preparation. In other words, the R group will have one carbon atom less than the acid which is used to prepare the imidazoline.

Acids which are useful in preparing the imidazolines are hydrocarbon mono-carboxylic acids having up to about 20 carbon atoms. The preferred acids are unsaturated organic acids such as 9,10 decylenic acid, octenoic acid, oleic acid, linoleic acid and the like. Preferred acids are commonly obtained as hydrolysis products of natural materials. These acids thus obtained are mixtures. For example, acids obtained from olive oil, typically, are a mixture of about 83 percent oleic acid, 6 percent palmitic acid, 4 percent stearic acid and 7 percent linoleic acid. This mixture is quite useful for preparing imidazolines to be used in this invention. Organic acid mixtures obtained on saponifying and acidulating babassu oil, castor oil, peanut oil or palm oil are examples of useful acids. Several imidazoline compounds which can be used in the present invention are available commercially. A preferred imidazoline is 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline.

The weight ratio of component A to component B in the combination can vary over a wide range, typically 1 to 10 parts A to 1 to 10 parts B. In a preferred embodiment, the weight ratio is about 0.5-5 parts component A for each part component B. In a more preferred embodiment there are 0.6-4.0 parts component A per each part component B. The most preferred ratio is 1:1.

Components A and B can be separately added to the fuel. More preferably components A and B are pre-mixed to form a package and this package is added to the fuel in an amount sufficient to provide the required degree of corrosion protection.

Most preferably components A and B are also pre-mixed with a solvent to make handling and blending easier. Suitable solvents include alcohols (e.g., methanol, ethanol, isopropanol), ketones (acetone, methyl ethyl ketone), esters (tert-butyl acetate) and ethers (e.g., methyl tert-butyl ether).

Aromatic hydrocarbons are very useful solvents. These include benzene, toluene, xylene and the like. Excellent results can be obtained using xylene.

The concentration of the active components A and B in the package can vary widely. For example, the active content can range from 5 weight percent up to the solubility limit of A or B in the solvent. With xylene, a total active content of 5-60 weight percent is generally used, especially about 50 weight percent.

Tests were conducted to measure the anticorrosion properties of the additive combination. In the tests, the corrosion of steel cylinder rods (1/8 in. x 3 in.) (0.3175 cm x 7.62 cm) semisubmersed in test fluid was measured under different test conditions. The rods were first cleaned with carborundum 180, polished with crocus cloth, washed with acetone and then dried at room temperature.

Each rod was weighed and then semisubmersed in 10 milliliters of the test fluid in a sealed bottle for the specified time at the specified temperature.

At the end of the test period, the rods were removed from the fuel, and after loose deposits were removed with a light brush, the rods were washed and dried as at the start of the test and then reweighed. Any change in rod weight was recorded. Loss of weight indicated corrosion.

A series of three tests were carried out lasting 7 days, 14 days and 30 days, respectively. The series of tests were conducted in fuels comprising 5 volume percent methanol and 5 volume percent t-butanol in gasoline (indolene) containing 0.5 weight percent of 5.0 percent acetic acid in water. The tests were conducted at 25°C.

The test additives added to the test fuels were equal weight mixtures (100 ptb) of either (i) predominantly oleic acid dimer or predominantly oleic acid trimer or (ii) dodecenylsuccinic acid prepared from dodecene or propylene tetramer in combination with 2-heptadecenyl-1-(2-hydroxyethyl)imidazoline and 50 ptb of each individual component.

The results of these tests which are set out in the table below demonstrate the excellent anticorrosion properties of a fuel containing an additive combination of the invention.

TABLE

7-DAY TESTS

Additives	Weight Reduction (mg.)
none	7.5
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline	5.6
oleic acid dimer	1.7
oleic acid trimer	1.8
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + oleic acid dimer	1.1
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + oleic acid trimer	0.5
dodecenylsuccinic acid from dodecene	5.7
dodecenylsuccinic acid from propylene tetramer	3.8
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + dodecenylsuccinic acid from dodecene	0.1
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + dodecenylsuccinic acid from propylene tetramer	0.1

14-DAY TESTS

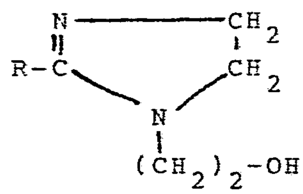
Additives	Weight Reduction (mg.)
none	10.3
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline	5.7
oleic acid dimer	3.7
oleic acid trimer	4.7
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + oleic acid dimer	0.4
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + oleic acid trimer	0.1
dodecenylsuccinic acid from dodecene	10.5
dodecenylsuccinic acid from propylene tetramer	8.9
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + dodecenylsuccinic acid from dodecene	0.4
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + dodecenylsuccinic acid from propylene tetramer	0.2

30-DAY TESTS

Additives	Weight Reduction (mg.)
none	12.1
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline	4.4
oleic acid dimer	6.5
oleic acid trimer	9.3
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + oleic acid dimer	1.1
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + oleic acid trimer	0.2
dodecenylsuccinic acid from dodecene	15.1
dodecenylsuccinic acid from propylene tetramer	15.1
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + dodecenylsuccinic acid from dodecene	0.9
2-heptadecenyl-1-(2-hydroxyethyl)imidazoline + dodecenylsuccinic acid from propylene tetramer	0.9

CLAIMS:

1. A liquid fuel adapted for use in an internal combustion engine, said fuel comprising 5 to 100 weight percent of one or more alcohols, 0 to 95 weight percent gasoline and, as a corrosion inhibitor, a combination of (A) a member selected from (i) a polymer of one or more C_{16} to C_{18} polyunsaturated aliphatic monocarboxylic acids or (ii) at least one monoalkenylsuccinic acid in which the alkenyl group contains 8 to 30 carbon atoms and (B) at least one substituted imidazoline having the structural formula:



wherein R represents a hydrocarbon alkenyl group having from 7 to 24 carbon atoms.

2. A liquid fuel as claimed in Claim 1 wherein said polymer of one or more C_{16} to C_{18} polyunsaturated aliphatic monocarboxylic acids comprises linoleic acid dimer, trimer or a mixture thereof.

3. A liquid fuel as claimed in either Claim 1 or Claim 2 wherein said monoalkenylsuccinic acid is dodecenylsuccinic acid.

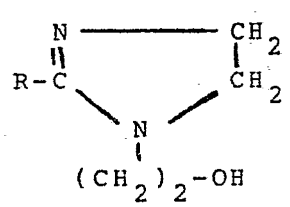
4. A liquid fuel as claimed in any one of Claims 1 to 3 wherein said substituted imidazoline is 2-heptadecenyl-1-(2-hydroxy-ethyl)imidazoline.

5. A liquid fuel as claimed in any one of Claims 1 to 4 wherein the weight ratio of component A to component B in the combination is from 1:10 to 10:1, preferably 1:1.

6. A liquid fuel as claimed in any one of Claims 1 to 5 wherein the corrosion inhibitor is present at an amount ranging from 1 to 5000 pounds (0.45 to 2250 kg) per thousand barrels, preferably 5 to 500 pounds (2.25 to 225 kg) per thousand barrels.

7. A liquid fuel as claimed in any one of claims 1 to 6 wherein said fuel comprises a major amount of a hydrocarbon distillate in the gasoline distillation range and from 2 to 30 volume percent of one or more alkanols containing from 1 to 4 carbon atoms.

8. A corrosion inhibitor concentrate comprising a solvent containing 5 to 60 weight percent of a combination of (A) a polymer of one or more C_{16} to C_{18} polyunsaturated aliphatic monocarboxylic acids and (B) at least one substituted imidazoline having the structural formula:



in which R is a hydrocarbon alkenyl group having from 7 to 24 carbon atoms.

9. A method of preparing a liquid fuel comprising blending a fuel comprising 5 to 100 weight

percent of one or more alcohols and 0 to 95 weight percent gasoline with, as a corrosion inhibitor, a combination as defined in any one of Claims 1 to 5, the components of said combination being either premixed or added separately.

10. A method as claimed in Claim 9 wherein the corrosion inhibitor is present at an amount ranging from 1 to 5000 pounds (0.45 to 2250 kg) per thousand barrels, preferably 5 to 500 pounds (2.25 to 225 kg) per thousand barrels or the fuel is as defined in Claim 7.