

26 May 2000

PHOSPHORYLATED THERMAL STABILITY ADDITIVES FOR DISTILLATE FUELS

TECHNICAL FIELD

This invention relates to additives for distillate fuels which reduce deposit formation in fuels that are thermally stressed. More specifically, the invention is directed to a fuel additive that comprises the reaction product of a hydrocarbyl substituted dicarboxylic acid or derivative thereof, a polyhydroxyl compound, and a phosphorus containing compound. This reaction product when added to fuels, such as jet fuels, stabilizes the fuels and reduces or prevents the build up of deposits in the fuel system. The invention also relates to the inclusion of an ester, formed by reacting a) a hydrocarbyl substituted dicarboxylic acid or derivative thereof, with b) a polyhydroxyl compound and a phosphorus-containing compound in a distillate fuel to reduce the thermal degradation of the fuel.

BACKGROUND OF THE INVENTION

When liquid hydrocarbon fuels are subjected to transportation, storage and use, they are exposed to thermal stress. This exposure to elevated temperatures, or thermal stress, causes the fuel to deteriorate. Thermal stress usually results in the formation of sediment, sludge, or gum and can also manifest itself visibly by a color change in the fuel.

Sediment, sludge or gum formation can cause blocking of the fuel system, or at least reduced performance of the fuel system. For example, in modern civil and military jet aircraft the fuel system is used to cool various components, such as engine parts, prior to its combustion

in the engine (turbine). This thermal exposure has been shown to cause the formation of deposits on heat exchangers, fuel lines and on the injection nozzles of the engine. It is apparent that the reduction or elimination of such deposits would be an advancement in the state of the art. It is particularly desirable to reduce deposit formation without the use of reactive nitrogen-containing components in the fuel which can interfere with other commonly used additives.

U.S. Patent 4,292,186 to Chibnik et al. discloses a fuel additive that is a metal salt complex containing a 5- or 6- membered ring. The metal complex is prepared by forming a non-acidic reaction product of a polyalkenyl succinic acid or anhydride and a polyhydric alcohol or aminoalcohol. This reaction product is then reacted with a metal salt, the metal being selected from Groups IB, IIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table. This patent does not suggest nor disclose a fuel additive that is derived from a polyalkenyl succinic acid/alcohol reaction product that is reacted with a phosphorus-containing compound.

EP288246 to Kendall teaches a composition for stabilizing fuel oil which comprises a phosphite compound and a carboxylic acid having from 2-20 carbon atoms. This reference does not disclose the fuel stabilizing additive of this invention

U.S. Patent 5,160,507 to Horodysky discloses an ester-type ashless dispersant that contains additional integral sulfur-ester moieties that are effective in providing thermal stability to fuels. This patent teaches that the sulfur-ester moieties are required for imparting thermal and oxidative stability to hydrocarbon fuels.

U.S. Patent 5,382,266 to Lin et al. relates to an additive that inhibits the degradation of fuel oils. The additive is disclosed as a phosphine or phosphite, such as triphenylphosphite and

triphenylphosphine. This reference does not suggest the reaction product of the present invention as a stabilizer for liquid hydrocarbon fuels.

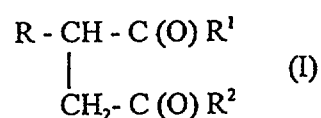
U.S. Patent No. 5,596,130 to Wright et al. discloses a jet fuel additive that is a derivative of (thio)phosphonic acid. This patent specifically discloses the use of a pentaerythritol ester of polyisobutenylthiophosphonic acid in turbine combustion fuel oils to inhibit the formation and emission of soot and smoke from the engine. This reference makes no suggestion or disclosure of the use of a succinic anhydride or dicarboxylic acid to form an ester with a polyol that is subsequently reacted with a phosphorus-containing compound.

WO96/23855 to Dillworth et al. discloses a fuel oil lubricity additive that comprises an ashless dispersant and a carboxylic acid. The carboxylic acid may be in the form of an ester with an alcohol of one or more carbon atoms. This reference does not suggest a stabilizing additive for jet fuel which comprises the reaction product of 1) a hydrocarbyl substituted dicarboxylic acid, or derivative thereof, 2) a polyhydroxyl compound, and 3) a phosphorus containing compound.

SUMMARY OF THE INVENTION

As a first aspect of the invention there is disclosed a novel composition of matter. This composition of matter comprises the reaction products of:

- a) a compound of the structural formula

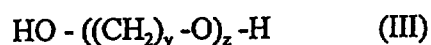


wherein R is hydrocarbyl, preferably an alkyl or alkenyl group having 1 to 300 carbon atoms, preferably 6 to 150 carbon atoms, more preferably 10 to 100 carbon atoms; R¹ and R² are each independently selected from -OH, -Cl, -O-lower alkyl, and when taken together, R¹ and R² are -O-; with

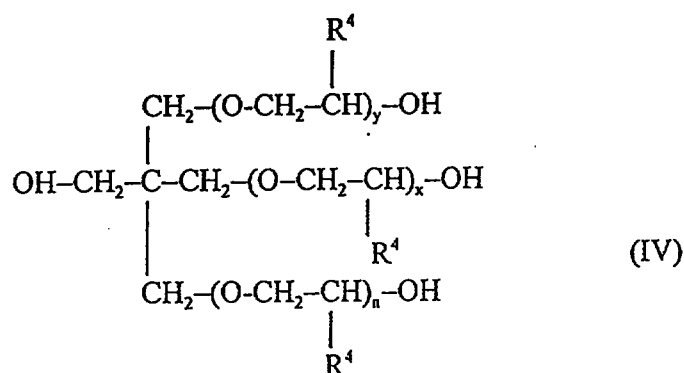
b) a polyhydroxyl alcohol selected from compounds of the structural formulae:



wherein x is an integer of 2 or more, and R³ is a hydrocarbyl group of 1 to 20 carbon atoms;



wherein y is an integer of 1 to 10 and z is an integer of 1 to 100;

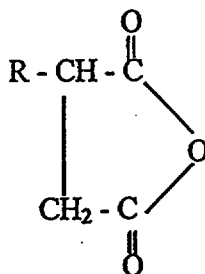


wherein each R⁴ can be independently H or -CH₃; and x, y and n can each independently range from 1 to 20; and mixtures thereof; and

c) a phosphorus containing compound reactive with the reaction product of a) and b).

Hydrocarbyl, as used herein and in the claims, means alkyl, alkenyl, aryl, aralkyl, and alkaryl and may be cyclic or polycyclic and may contain O, N, S or mixtures thereof.

In a preferred embodiment, R¹ and R² are -O-, and thereby the compound (I) is a succinic anhydride of the structural formula



The mole ratio of a) to b) can range from 1:2 to 5:1, more preferably 1:2 to 3:1 and most preferably from about 1:2 to 2:1. The molar ratio of the reaction product of a) and b) (ester) to the phosphorus containing compound can range from 10:1 to 1:10, with 5:1 to 1:5 being more preferred and about 3:1 being most preferred.

The present invention also relates to the use of the physical admixture of the ester and the phosphorus-containing compound in a distillate fuel. For example, the ester can be prepared as described below and then added to a fuel that already contains a phosphorus-containing compound. Alternatively, the ester and the phosphorus-containing compound can be combined in the form of a concentrate or additive package that can be added to the distillate fuel. Thus, there is additionally disclosed, a fuel composition which comprises a distillate fuel and an additive, the additive comprising:

- i) the reaction product of at least one hydrocarbyl substituted dicarboxylic acid or derivative thereof, with a polyhydroxyl compound; and
- ii) phosphorus compound.

The admixture of the ester and the phosphorus containing compound is useful in a method of reducing deposit formation in engines, wherein said deposit formations are a result of distillate fuel subjected to thermal stress. The method comprises fueling said engine with and operating said engine on a fuel composition comprising a distillate fuel and an additive, the additive comprising:

- i) an ester prepared by reacting at least one hydrocarbyl substituted dicarboxylic acid or derivatives thereof, with a polyhydroxyl compound; and
- ii) a phosphorus compound.

The two components, i) and ii), or the three-component reaction product, can be added to the distillate fuel by any conventional method. For example, the two components can be added to the distillate fuel as a single mixture containing both compounds or the individual components can be added separately or in any other desired combination. The additives according to the invention may be added either as a concentrate or as a solution using a suitable carrier solvent, which is compatible with the components and the distillate fuel.

Therefore, the present invention also relates to an additive fluid concentrate for use in distillate fuels containing at least the three-part reaction product set forth above and/or the two part physical admixture described above.

The present invention further relates to a jet fuel composition comprising as a major portion a jet fuel and as a minor portion an additive comprising the three-part reaction product set forth above and/or the two part physical admixture described above.

The methods and additives of the instant invention effectively stabilize the distillate fuels during storage. The term "stabilized" as used herein, means that particulate formation in the distillate fuel and color deterioration of the fuel are inhibited. The term "particulate formation" is meant to include the formation of insoluble solids, sediment and gum.

An additional aspect of the invention is directed to a process for inhibiting the degradation of distillate fuels and for stabilizing fuels which comprises adding to the distillate fuel an effective inhibiting amount of the three part reaction product described herein or the admixture described herein. The invention is also directed to a method of reducing deposit formation in engines, the method comprises fueling the engine with, and operating the engine on, a fuel composition comprising a distillate fuel and an additive that is the three-part reaction product described herein or the admixture described herein.

The present invention is also directed to a process for inhibiting the thermal degradation of jet fuel which comprises adding to said jet fuel an effective amount of a reaction product derived from reacting a hydrocarbyl substituted dicarboxylic acid, or derivative thereof with a polyhydroxyl compound to create a first reaction product (the ester), and thereafter reacting said first reaction product with a phosphorus containing compound. This process is also possible using the three-component reaction product where all three components are reacted simultaneously or by using an admixture of the ester and the phosphorus containing compound.

This invention also discloses a stabilized distillate fuel composition comprising a distillate fuel and an effective stabilizing amount of the novel composition of matter described herein. There is further disclosed a composition comprising a major amount of a liquid

hydrocarbon fuel and 0.0005 to 2% by weight of the product obtained by reacting a hydrocarbyl substituted dicarboxylic acid, or derivative thereof with a polyhydroxyl compound and a phosphorus containing compound.

DETAILED DESCRIPTION OF THE INVENTION

Subjecting distillate fuels to thermal stress tends to result in significant deposit formation. The function of the present invention is to reduce deposit formation anywhere in the fuel and exhaust systems. In jet fuel compositions, for instance, this includes reducing deposit formation in the fuel nozzles and spray rings, and on surfaces such as heat exchangers, manifolds, actuators and turbine vanes and blades. In other distillate fuel compositions, such as diesel fuel, the addition of the additives of the present invention serves to prevent injector deposits and to increase fuel stability.

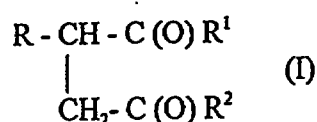
Suitable phosphorus compounds for forming the additives of the present invention include phosphorus compounds or mixtures of phosphorus compounds capable of introducing a phosphorus atom into the reaction product of the polyhydroxyl compound and the hydrocarbyl substituted dicarboxylic acid, or derivative thereof. Any phosphorus compound, organic or inorganic, capable of undergoing such a reaction can be used. Accordingly, use can be made of inorganic phosphorus compounds such as the inorganic phosphorus acids and the inorganic phosphorus oxides, including their hydrates. Typical organic phosphorus compounds include full and partial esters of phosphorus acids, such as the mono-, di- and triesters of phosphorus acid, thiophosphoric acid, dithiophosphoric acid, trithiophosphoric acid and the

tetrathiophosphoric acid; the mono-, di- and triesters of phosphorus acid, thiophosphorus acid, dithiophosphorus acid and trithiophosphorus acid; the trihydrocarbyl phosphine oxides; the trihydrocarbyl phosphine sulfides; the mono- and dihydrocarbyl phosphonates and their mono-, di- and trithio analogs; the mono- and dihydrocarbyl phosphonites, and their mono- and dithio analogs; and the like. Thus, use can be made of such compounds as, for example, phosphorous acid (H_3PO_3 , sometimes depicted as $\text{H}_2(\text{HPO}_3)$, and sometimes called ortho-phosphorus acid or phosphonic acid), phosphoric acid (H_3PO_4 , sometimes called orthophosphoric acid), hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$), metaphosphoric acid (HPO_3), pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), hypophosphorus acid (H_3PO_2 , sometimes called phosphinic acid), pyrophosphorus acid ($\text{H}_4\text{P}_2\text{O}_5$, sometimes called pyrophosphonic acid), phosphinous acid (H_3PO), tripolyphosphoric acid ($\text{H}_5\text{P}_3\text{O}_{10}$), tetrapolyphosphoric acid ($\text{H}_6\text{P}_4\text{O}_{13}$), trimetaphosphoric acid ($\text{H}_3\text{P}_3\text{O}_9$), phosphorus trioxide, phosphorus tetroxide, phosphorus pentoxide and the like. Partial or total sulfur analogs such as phosphorotetrathioic acid (H_3PS_4), phosphoromonothioic acid ($\text{H}_3\text{PO}_3\text{S}$) and phosphorodithioic acid ($\text{H}_3\text{PO}_2\text{S}_2$) can also be used in forming the additives according to this invention.

Likewise, use can be made of organic phosphorus compounds such as mono-, di- and triesters of phosphoric acid (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates, monohydrocarbyl diacid phosphates and mixtures thereof), mono-, di- and triesters of phosphorus acid (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites and mixtures thereof), esters of phosphonic acids (both "primary" and "secondary"), esters of phosphinic acids, phosphoryl halides, halophosphites,

halophosphates, tertiary pyrophosphate esters and the partial sulfur analogs of any of the foregoing organic phosphorus compounds and the like, wherein each hydrocarbyl group contains up to about 100 carbon atoms, preferably up to about 50 carbon atoms, more preferably up to about 24 carbon atoms and most preferably up to about 12 carbon atoms.

The hydrocarbyl substituted dicarboxylic acids, and derivatives thereof (e.g., acid halides, acid esters and acid anhydrides), suitable for use in the present invention may be compounds of the structural formula



wherein R is hydrocarbyl, preferably an alkyl or alkenyl group having 1 to 300 carbon atoms, preferably 6 to 150 carbon atoms, more preferably 10 to 100 carbon atoms; R¹ and R² are each independently selected from -OH, -Cl, -O-lower alkyl, and when taken together, R¹ and R² are -O-.

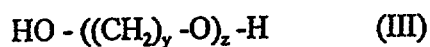
Preferred hydrocarbyl substituted dicarboxylic acids include hydrocarbyl substituted succinic anhydrides. The hydrocarbyl substituent is usually a polyolefin, and preferably a polyisobutylene group, having a number average molecular weight of from about 500 to 5000, more preferably 600 to 3000 and most preferably from about 950 to about 2000.

Suitable polyhydroxyl alcohols for use in the present invention include any compound that contains 2 or more hydroxyl groups (-OH) and which will react with the selected hydrocarbyl substituted dicarboxylic acid will be useful in preparing the fuel additives according to the invention.

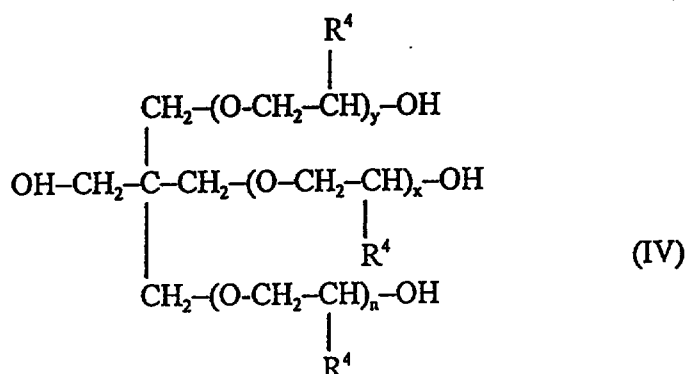
Preferred polyhydroxyl alcohol are selected from compounds of the structural formulae:



wherein x is an integer of 2 or more, and R^3 is a hydrocarbyl group of 1 to 20 carbon atoms;



wherein y is an integer of 1 to 10 and z is an integer of 1 to 100;



wherein each R^4 can be independently H or $-CH_3$; and x , y and n can each independently range from 1 to 20; and mixtures thereof.

Representative compounds of the above formulae, suitable for use in the present invention, include alkyl diols, alkyl triols, glycols, glycerol, pentaerythritol, tripentaerythritol, trimethylolethane, triethylolpropane, 1,2,6-hexanetriol, sorbitol, inositol and polyvinyl alcohol. Pentaerythritol propoxylates and pentaerythritol ethoxylates are also useful polyols in preparing the additives according to the invention. The preferred polyol for use in the present invention is pentaerythritol.

In conducting the reaction of the hydrocarbyl substituted dicarboxylic acid with the polyhydroxyl compound, any temperature at which the desired reaction occurs at a satisfactory

reaction rate can be used. Typically the reaction is conducted in a solvent, such as mixed xylenes and thus an appropriate reaction temperature is the reflux temperature of the mixture. Ordinarily, the phosphorylation reaction (whether conducted concurrently or separately) is conducted at temperatures in the range of 80 to 200°C, more preferably 100 to 180°C. However, departures from those ranges can be made whenever deemed necessary or desirable. These reactions may be conducted in the presence or absence of an ancillary diluent or liquid reaction medium.

Numerous catalysts may be used to prepare the compounds of the invention, for example, any material that supplies a free proton may be used. Representative of such catalysts includes sulfuric acid, acidic ion exchange resin and hydrocarbon soluble sulfonic acids. Base catalysts are also useful and include the hydrocarbon soluble tertiary amines.

The additives of the present invention are used in a fuel in any amount sufficient to reduce the formation of deposits in the fuel and exhaust systems of an engine, such as an internal combustion engine or a jet engine. Preferably, the additive is used in an amount of from about 1 to about 1000 mg per liter of fuel, more preferably in the range of from about 5 to about 200, and most preferably from about 10 to about 100 mg per liter of fuel on an active ingredient basis, i.e., excluding diluent or solvent. The preferred distillate fuels for use in the present invention are diesel fuels and jet fuels, more preferably, JP-8, Jet-A fuels and Jet-A1 fuels.

The inventive additives are typically added to the fuel at ambient temperatures and pressures. The inventive additives are preferably added to the distillate fuel prior to any appreciable deterioration of the fuel. However, the additives are also effective even after some deterioration has occurred.

Other components which may be used with the additives of the present invention include ashless dispersants, antioxidants, metal deactivators, corrosion inhibitors, conductivity improves (e.g., static dissipators), fuel system icing inhibitors, distillate fuel stabilizers, cetane improvers and demulsifiers. The various additional components that can be included in the distillate fuel compositions of this invention are used in conventional amounts. Thus, the amounts of such optional components are not critical to the practice of this invention. The amounts used in any particular case are sufficient to provide the desired functional property to the fuel composition.

EXAMPLE I

Preparation of Thermal Stability Additive

To a one (1) liter reaction flask fitted with a condensor, the following materials were added:

1)	polyisobutenyl succinic anhydride (PBSA) (molecular weight = 1050 gms/mole)	135.43 gms (0.129 moles)
2)	pentaerythritol	13.77 gms (0.101 moles)
3)	mixed xylenes (solvent)	75.50 gms
4)	Amberlyst™ 15 resin (catalyst)	1.30 gms

The mixture was heated to reflux (about 175°C) and stirred for four (4) hours. The mixture was filtered to remove the catalyst and the filtrate was returned to the reaction vessel. Diethyl phosphite (4.75 gms) (0.034 moles) was then added to the mixture. The molar ratio of PBSA to pentaerythritol to phosphite was thus 1.0:0.78:0.26. The mixture was heated at reflux for about one (1) hour with stirring. About 2.0 ml of water was removed by azeotropic distillation. The xylenes were then removed by vacuum distillation. The final product contained

0.656% by weight phosphorus. The resulting product was tested in the Hot Liquid Process Simulator (HLPS) described below.

HLPS Test

To evaluate the inventive additives and their effects on fuel compositions subjected to thermal stress, this sample and others described below were tested using the Hot Liquid Process Simulator (HLPS) test. In this test all additives were evaluated in a typical Jet A fuel which is pumped for 250 minutes at 2.0 ml per minute over a tube heated to 320°C. The weight of the deposits which accumulate on the tube are recorded. Low deposit weight numbers indicate an effective additive in this test. The results for a Control (untreated fuel) and a fuel treated with the additive prepared in this Example are set forth in Table I below. All treat rates are based on active ingredients, i.e., excluding diluents or carrier fluids.

TABLE I

Sample	Treat Rate	HLPS Deposit
Control	0	460 µg
Example I	25 mg/l	110 µg

PTS Test

Another test used in the petroleum industry to evaluate the thermal stabilizing properties of a fuel additive is the Pad Thermal Stability (PTS) test. Treated and untreated samples of No. 2 diesel fuel are heated to 150°C for four (4) hours, cooled to room temperature and then filtered through Whatman No. 1 filter paper. White light reflectance from the filter paper is then

measured. A higher reflectance indicates an effective additive in this test. The results for the additive prepared in Example I and a Control are set out in Table

II.

TABLE II

Sample	Treat Rate (mg/liter)	Reflectance (%)
Control	0	55.4
Example I	25	91.4

These two tests amply demonstrate that an additive according to the invention is highly effective in reducing the thermal degradation of fuels. Further, the reaction product according to this invention does not require nitrogen (unlike the succinimide and amine dispersants) and will therefore be less likely to interfere with other commonly used fuel additives such as water separators and coalescers.

EXAMPLE II

The procedure described in Example I was used, except that there was no addition of diethyl phosphite. Therefore, this Example is a control and was only the ester between the succinic anhydride and the pentaerythritol. Phosphorus content was zero (0). The molar ratio of PBSA to the pentaerythritol was 1.00:0.78.

EXAMPLE III

To a one (1) liter reaction flask, fitted with a condensor, the following materials were added:

- | | | |
|----|--|--------------------------|
| 1) | polyisobutenyl succinic anhydride (PBSA)
(molecular weight = 1400 gms/mole) | 238.74 gms (0.171 moles) |
| 2) | pentaerythritol | 17.86 gms (0.130 moles) |
| 3) | xylene | 123.28 gms |
| 4) | Amberlyst™ 15 | 106 gms |

The mixture was heated to reflux (about 180°C) and stirred for four (4) hours. About 2.6 ml of water generated by the reaction was removed by azeotropic distillation. The product was then filtered and the solvent removed by vacuum distillation. As no phosphorus was added, this sample would also serve as a control.

EXAMPLE IV

The following materials were added to a 2-liter reaction flask fitted with a condenser:

- | | | |
|----|--|--------------------------|
| 1) | PBSA (molecular weight of about 2200 gms/mole) | 312.21 gms (0.142 moles) |
| 2) | pentaerythritol | 14.97 gms (0.110 moles) |
| 3) | sulfuric acid (catalyst) | 4.0 drops |
| 4) | xylene | 136.0 gms |

The molar ratio of the PBSA to the pentaerythritol was 1:0.77. This mixture was heated to reflux and stirred for four (4) hours. About 3.0 ml of water was azeotropically removed. The product was then filtered and solvents were removed by vacuum distillation. This sample also served as a control.

EXAMPLE V

Base Catalyzed

The following materials were added to a two-(2) liter reaction flask:

- 1) polyisobutenyl succinic anhydride (PBSA)
(molecular weight = 1050 gms/mole) 576.84 gms (0.549 moles)
- 2) pentaerythritol 86.34 gms (0.635 moles)
- 3) diethyl phosphite 33.46 gms (0.242 moles)
- 4) N,N-dimethyl-cyclohexylamine (catalyst) 4.0 drops
- 5) xylenes 188.8 gms

The molar ratio of the PBSA to pentaerythritol to phosphite was 1:1.16:0.44. The mixture was heated to reflux (about 173°C) and stirred for four (4) hours. About 10.5 ml of water was azeotropically removed from the reaction product which was then filtered. The phosphorus content of the final reaction product (without solvent) was 0.663% by weight.

Table III sets forth various additives that were added to fuels and tested using the HLPS test and/or the PTS Test. In some of the testing, the ester products without reacted phosphorus, such as, the reaction product of Example II, were combined with free (unreacted) sources of phosphorus, for example, Sample Nos. 8 and 9.

TABLE III

Sample No.	Additive(s)	Treat Rate (mg/liter)	Phosphorus Concentration µg/l	PTS* % Reflectance	HLPS Jet Fuel µg of deposit
1	Controls/Blanks	-	-	55.4	460
2	Example I	9.1	60	90.7	-
3	Example II	10.0	0	84.9	-
4	Example III	25.0	0	88.3	-
5	Example IV	25.0	0	77.8	-
6	Example V	10	66	92.6	-
7	Example V	25	165	-	60
8	Example II plus diethylphosphite (DEP)	10.0/0.27 (DEP)	61	86.4	-

9	Example II plus dibutylphosphite (DBP)	10.0/0.38 (DBP)	61	84.8	-
10	1050 PBSA/sorbitol (molar ratio 1:0.88)	25.0	0	74.2	-
11	1050 PBSA/sorbitol/DEP (molar ratio 1:0.88:0.29)	25.0	164	85.8	-
12	Example II	25.0	0	88.7	370
13	Example I	25	165	91.4	110,140**
14	Example II plus DEP	25.0/0.73 (DEP)	165	90.0	210
15	Primene 81R***	10.0	0	84.9	-
16	Succinimide dispersant	10.0	0	68.8	-

* PTS test performed in diesel fuel, 4 hours at 150°C

** Two runs

*** Commercial diesel fuel stabilizer supplied by Rohm & Haas

From the data contained in Table III, it is evident that the reaction products according to the invention are effective fuel stabilizers. Especially preferred are the base catalyzed products (Example V). The lower molecular weight PBSAs for example 1050 molecular weight (Example V) are also preferred in the preparation of the fuel stabilizers according to the invention.

The data also confirm that the reaction product of the ester (succinic anhydride and/or dicarboxylic acid with the alcohol) with the phosphorus containing compound is more effective than the physical mixture of the ester and the phosphorus compound. See Sample Nos. 2 versus Sample Nos. 8 or 9.

The HLPS results, shown in Table I, demonstrate that the additives of the present invention provide fuel compositions which exhibit significantly reduced deposit formation upon being subjected to thermal stress as compared to untreated fuel compositions. As with the PTS

test, the phosphorus containing reaction product is more effective than the physical mixture of the ester the phosphorus compound. Compare Sample No. 13 with Sample No. 14.

The exposure of distillate fuels to heat, either during transportation or when used as a heat sink, causes fuel to form deposits in the fuel system. This is highly undesirable and the petroleum industry is continually searching for additives that will reduce or prevent the formation of such deposits. The additives according to this invention satisfy that need in an effective and economical manner.

This invention is susceptible to considerable variation in its practice. Accordingly, this invention is not limited to the specific exemplifications set forth herein. Rather, this invention is within the spirit and scope of the appended claims, including any equivalents thereof, available as a matter of law.

I claim:

1. A fuel composition which comprises a distillate fuel and an additive, wherein the additive comprises the reaction product of:
 - i) at least one hydrocarbyl substituted dicarboxylic acid, or derivative thereof;
 - ii) a polyhydroxyl compound; and
 - iii) a phosphorus compound.
2. The composition of claim 1 wherein component i) is a hydrocarbyl substituted succinic anhydride.
3. The composition of claim 1 wherein said phosphorus compound is an organic phosphorus compound.
4. The composition of claim 1 wherein said phosphorus compound is an inorganic phosphorus-containing acid or anhydride, including partial sulfur analogs thereof.
5. The composition of claim 2 wherein said hydrocarbyl group is a polyisobutenyl group having a number average molecular weight of from about 500 to 5,000.
6. The fuel composition of claim 1 wherein said additive is present in an amount sufficient to reduce the formation of deposits in the fuel system and the exhaust system of an engine operating on said fuel composition.
7. The fuel composition of claim 1 wherein said additive is present in an amount of from about 1 to about 1000 mg per liter of fuel.
8. The fuel composition of claim 1 wherein said additive is present in an amount of from about 30 to about 200 mg per liter of fuel.



9. The fuel composition of claim 1 wherein said distillate fuel is selected from diesel fuel or jet fuel.
10. The fuel composition of claim 9 wherein said jet fuel is selected from JP-8 jet fuel, Jet-A fuel and Jet A-1 fuel.
11. The fuel composition according to claim 1 further comprising additives selected from the group consisting of ashless dispersants, antioxidants, metal deactivators, corrosion inhibitors, conductivity improvers, fuel system icing inhibitors, distillate fuel stabilizers, cetane improvers and demulsifiers.
12. A method of reducing deposit formation in engines, wherein said deposit formations are a result of distillate fuel subjected to thermal stress, which comprises fueling said engine with and operating said engine on the fuel composition of claim 1.
13. A composition of matter comprising the reaction products of:
 - a) at least one compound of the structural formula:

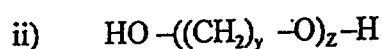


wherein R is a hydrocarbyl radical of 1 to 300 carbon atoms; R^1 and R^2 are each independently selected from the group of $-\text{OH}$, $-\text{Cl}$, $-\text{O}$ -lower alkyl; and when R^1 and R^2 are taken together $-\text{O}-$;

- b) at least one polyhydroxyl alcohol selected from:
 - i) $\text{R}^3 - (\text{OH})_x$

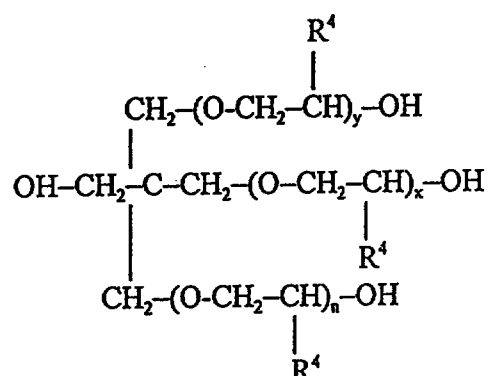


wherein x is an integer of 2 or more and R³ is a hydrocarbyl group of 1 to 20 carbon atoms;



wherein y is an integer of 1 to 10 carbon atoms and z is an integer of 1 to 100; and

iii)



wherein each R⁴ can be independently H or -CH₃; and x, y and n can each independently range from 1 to 20; and

iv) mixtures thereof; and

c) at least one phosphorus-containing compound.

14. The composition according to claim 13 wherein R¹ and R² are -O-; R is polyalkenyl; the polyhydroxyl alcohol is selected from the group consisting of alkyl diols, alkyl triols, pentaerythritol, dipentaerythritol, tripentaerythritol, pentaerythritol propoxylate, pentaerythritol ethoxylate, sorbitol, glycols and mixtures thereof; and the phosphorus-containing compound is selected from the group consisting of dialkyl phosphites, trialkyl



phosphites, phosphorus pentaoxide, phosphoric acid, phosphorous acid, hypophosphorus acid and mixtures thereof.

15. The composition according to claim 13 wherein R is a polyolefin having a number average molecular weight from about 500 to about 5,000; the polyhydroxyl alcohol is pentaerythritol and the phosphorus containing compound is selected from diethyl phosphite, dibutylphosphite and mixtures thereof.
16. The composition according to claim 13 wherein the mole ratio of component (a) to component (b) is in the range of from 1:2 to 5:1.
17. A method of reducing deposit formation in engines, wherein said deposit formations are a result of distillate fuel subjected to thermal stress, which comprises fueling said engine with and operating said engine on the fuel composition comprising a major amount of fuel and a minor amount of the composition of matter of claim 13.
18. A method of stabilizing a fuel, wherein said method comprises adding to a fuel to be stabilized the composition of claim 13.
19. A fuel composition which comprises a distillate fuel and an additive, the additive comprising an admixture of:
 - a) the reaction product of at least one hydrocarbyl substituted dicarboxylic acid, or derivative thereof, with a polyhydroxyl compound; and
 - b) phosphorus compound.
20. The fuel composition of claim 19 wherein the hydrocarbyl substituted dicarboxylic acid, or derivative thereof, is a hydrocarbyl substituted succinic anhydride.



21. The fuel composition according to claim 19 wherein the phosphorus compound is an organic phosphorus compound.
22. The fuel composition according to claim 19 wherein the phosphorus compound is an inorganic phosphorus-containing acid or anhydride, including partial sulfur analogs thereof.
23. The fuel composition according to claim 19 wherein said hydrocarbyl group is a polyisobutenyl group having a number average molecular weight of from about 500 to 5,000.
24. The fuel composition according to claim 19 wherein said additive is present in an amount of from about 1 to about 1000 mg per liter of fuel.
25. The fuel composition according to claim 19 wherein said distillate fuel is selected from diesel fuel or jet fuel.
26. A method of reducing deposit formation in engines, wherein said deposit formations are a result of distillate fuel subjected to thermal stress, which comprises fueling said engine with and operating said engine on the fuel composition of claim 19.
27. An additive fluid concentrate for use in distillate fuels comprising an admixture of:
 - a) the reaction product of at least one hydrocarbyl substituted dicarboxylic acid, or derivative thereof, with a polyhydroxyl compound; and
 - b) phosphorus compound.
28. A method of stabilizing a fuel, wherein said method comprises adding to a fuel to be stabilized the additive fluid concentrate of claim 27.



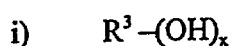
29. An additive fluid concentrate for use in distillate fuels comprising the reaction product of:

- a) at least one compound of the structural formula:

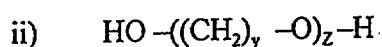


wherein R is a hydrocarbyl radical of 1 to 300 carbon atoms; R^1 and R^2 are each independently selected from the group of $-\text{OH}$, $-\text{Cl}$, $-\text{O}$ -lower alkyl; and when R^1 and R^2 are taken together $-\text{O}-$;

- b) at least one polyhydroxyl alcohol selected from the group consisting of:

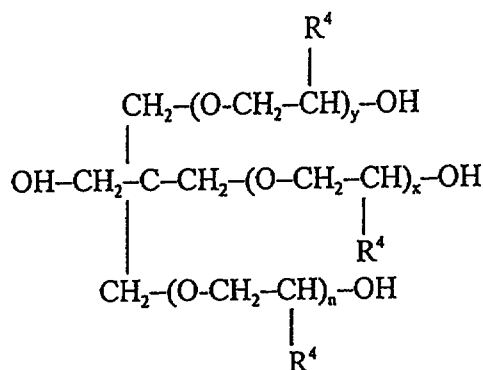


wherein x is an integer of 2 or more and R^3 is a hydrocarbyl group of 1 to 20 carbon atoms;



wherein y is an integer of 1 to 10 carbon atoms and z is an integer of 1 to 100; and

iii)



wherein each R^4 can be independently H or $-\text{CH}_3$; and x, y and n can each independently range from 1 to 20; and



iv) mixtures thereof; and

c) at least one phosphorus-containing compound.

30. A method of stabilizing a fuel, wherein said method comprises adding to a fuel to be stabilized the additive fluid concentrate of claim 29.

