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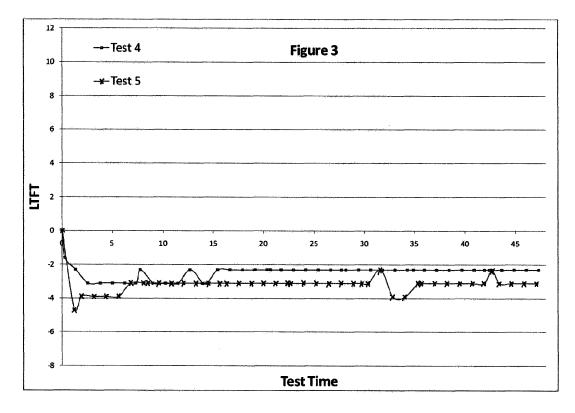
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(54) Fuel additives and gasoline containing the additives

(57) The present disclosure relates to a gasoline additive concentrate including a reaction product of (a) 1,8-naphthalic anhydride; and (b) a reaction product of a hy-

drocarbyl-substituted succinic anhydride with a polyamine. Fuel compositions containing the additive concentrate are also disclosed. Method of reducing greenhouse gas emissions is also disclosed.



Description

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DESCRIPTION OF THE DISCLOSURE

5 Field of the Disclosure

[0001] The present disclosure relates in one embodiment a gasoline additive concentrate comprising the product of combining a 1,8-naphthalic anhydride and a reaction product of a hydrocarbyl-substituted succinic anhydride with a polyamine. A fuel composition comprising the gasoline concentrate is also disclosed. Moreover, there is also disclosed a method for reducing greenhouse gas emissions comprising adding to a gasoline the disclosed additive and combusting the fuel composition in an engine.

[0002] This invention materially enhances the quality of the environment by contributing to the restoration or maintenance of the basic life-sustaining natural elements. In particular, this invention materially contributes to greenhouse gas emission reduction.

Background of the Disclosure

[0003] Gasoline fuel requires additives to maintain optimal performance for machineries that use gasoline fuel. Common fuel additives include a reaction product of hydrocarbyl phenol with formaldehyde and amines, which are generally known as Mannich base products or dispersant/detergents. Additives could also include hydrocarbons and alkyl polyols, which are commonly known as carrier fluids. One critical performance requirement of machinery such as automobile engines is maintaining a clean fuel delivery system. Additives mentioned above could mitigate the problem of fouling fuel delivery system. Yet there is always a need for additives that could afford better performance.

[0004] Over the years considerable work has been devoted to additives for controlling (preventing or reducing) deposit formation in the fuel induction systems of spark-ignition internal combustion engines. In particular, additives that can effectively control fuel injector deposits, intake valve deposits and combustion chamber deposits represent the focal point of considerable research activities in the field and despite these efforts, further improvements are desired.

[0005] In addition, more sophisticated engines are being developed to increase automobile performance including increasing fuel economy, reducing emission. An example is direct injection gasoline (DIG) engine. These newer engines demand more effective additives to keep the fuel delivery systems from being clogged and to clean up the clogged fuel delivery systems. However, direct injection gasoline engines can encounter problems different from those of the conventional engines due to the direct injection of gasoline into the combustion chamber.

[0006] Current generation DIG technologies have experienced deposit problems. Areas of concern are fuel rails, injectors, combustion chamber (CCD), crankcase soot loadings, and intake valves (IVD). Deposits in the intake manifold come in through the pressure control valve and exhaust gas recirculation (EGR). Because there is no liquid fuel wetting the back of the intake valves, these deposits build up quite quickly.

[0007] The additives which work well as detergents in multi-port injection engines will not necessarily work well in DIG engines, and as such additional detergents prepared especially for DIG engines may be required as a "top-treat" type additive or as an after-market fuel supplement.

[0008] One approach to reducing deposits has been to introduce a small amount of the reaction product of hydrocarbyl succinic anhydride (HSA) with polyamines (PAM) of about one to one molar ratio. However there is still a need for additives that offer improved performance.

[0009] It has been known to combine certain aromatic anhydrides and ethylene carbonate post-treated dispersants to improve dispersancy in an engine oil. In particular, the post reaction of polyisobutylene succinimide (PIBSI) with a so-called capping agent is common in engine oil additives. Many capping agents, including maleic anhydride, succinic anhydride, phthalic anhydride, 1,8-naphthalic anhydride, and boric acid are known. It has been known to formulate an oil-soluble lubricating oil additive with a naphthalic anhydride post-treated mono-succinimide derived from a 2300 MW polyisobutylene succhinic anhydride (PIBSA) and a heavy polyamine. However, the ratio of the naphthalic anhydride capping agent to the PIBSA was 0.60:1 and this compound was used in an engine oil containing known engine oil additives. One of ordinary skill in the art would know that engine oils contain additives that are not suitable for use in fuels, such as zinc dialkyldithiophosphate. Further, it is known to further treat with a cyclic carbonate, which is not required by the present invention.

[0010] It has also been known to prepare fuel compositions comprising additives prepared by acylation of alkyl or alkenyl succinimides with the polyether half-esters of dicarboxylic acids, such as phthalic acid or 1,8-naphthalic acid. To be clear, the polyether half-esters of dicarboxylic acids are grafted onto the polyamine moiety of alkyl or alkenyl succinimides by reacting the succinimide and the half-ester under conditions to form an amide group. The succinimides and the polyamines are present in a ratio of 2:1, thereby forming a bis compound.

[0011] Capping by other materials in diesel can be detrimental to keeping injectors clean and contradictory to common

sense. In particular, when compounds made by reacting terminal amine moieties with anhydrides are used in fuels, such as diesel, they generally have a negative effect on the fuels performance. For this reason, such compounds have not been used.

[0012] It has been surprisingly found that a class of material when mixed into the additized gasoline fuels containing typical Mannich base product or detergent and carrier fluid could enhance the ability of the additized fuel in keeping a clean fuel delivery system for advanced automotive engines.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate certain embodiments of the invention and together with the description, serve to explain the principles of the invention. In the figures:

[0014] Figure 1 is a graph of the Long Term Fuel Trim (LTFT) of a conventional additized gasoline fuel comprising Mannich and carrier fluid.

[0015] Figure 2 is a graph of the LTFT for various comparative compositions.

[0016] Figure 3 is a graph of the LTFT of various inventive compositions.

SUMMARY OF THE DISCLOSURE

20 [0017] In accordance with the disclosure, there is disclosed a gasoline additive concentrate comprising the product of combining (a) a 1,8-naphthalic anhydride; and (b) a reaction product of a hydrocarbyl-substituted succinic anhydride with a polyamine.

[0018] In another aspect, there is disclosed a method to reduce the amount of deposits in direct injection gasoline engines, the method comprising adding to a gasoline to be combusted in the direct injection gasoline engine a gasoline additive concentrate to form a gasoline composition, then combusting the gasoline composition.

[0019] Moreover, there is disclosed a method to reduce greenhouse gas emissions, the method comprising adding to a gasoline to be combusted in the direct injection gasoline engine a gasoline additive concentrate to form a gasoline composition, then combusting the gasoline composition.

30 DESCRIPTION OF THE EMBODIMENTS

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[0020] The present disclosure relates in one embodiment to a gasoline additive concentrate comprising a product of combining (a) a 1,8-naphthalic anhydride; and (b) a reaction product of a hydrocarbyl-substituted succinic anhydride with a polyamine. It is believed, without being limited to any particular theory, that the reaction product forms an imide. The molar ratio of (a) to (b) is about 1:1, for example ranging from about 0.95:0.05 to about 0.05:0.95, and as a further example from about 0.8:0.2 to about 0.2:0.8. In an aspect, the molar ratio is from about 0.5:1 to about 1:0.5.

[0021] The prior art teaches using a reaction product of PIBSA and various amines in fuel and lubricant compositions, but an improvement herein lies in top treating a gasoline composition with a gasoline additive concentrate comprising a product of combining (a) a 1,8-naphthalic anhydride; and (b) a reaction product of a hydrocarbyl-substituted succinic anhydride with a polyamine.

[0022] There is disclosed (b) a reaction products obtained by reacting a hydrocarbyl-substituted succinic anhydride, acid, acid-ester or lower alkyl ester with an amine containing at least two amino groups, such as a polyamine. Representative non-limiting examples are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,219,666; 3,272,746, 3,254,025, 3,216,936, 4,234,435; and 5,575,823. The hydrocarbyl-substituted succinic anhydride may be prepared readily by heating a mixture of olefin and maleic anhydride to about 180-220° C. The hydrocarbyl is, in an embodiment, a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like. In another embodiment, the source of alkenyl group is from polyisobutene having a molecular weight up to 10,000 or higher. In another embodiment, the alkenyl is a polyisobutene group having a molecular weight of about 200-5,000, for example about 500-2,000, and as a further example form about 700-1000. In another aspect, the polyisobutene group has a molecular weight less than about 1000, such as about 950.

[0023] In an aspect, the hydrocarbyl substituent of the hydrocarbyl-substituted succinic anhydride is a polyisobutylene. [0024] Amines which may be employed include any that have at least two amino groups which can react to form an imide group. A few representative examples are: N-dodecyl propanediamine, N-aminopropyl piperazine ethanolamine, N-ethanol ethylene diamine and the like. Preferred amines include the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)-triamine, tetra-(1,2-propylene)pentaamine.

[0025] In one embodiment the amines are the ethylene polyamines that have the formula $H_2N(CH_2CH_2NH)_nH$ wherein n is an integer from one to ten. These ethylene polyamines include ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexaamine, and the like, including mixtures thereof in which case

n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. A heavy polyamine can also be used. In an embodiment, the polyamine is tetraethylene pentamine.

[0026] The molar ratio of the hydrocarbyl-substituted succinic anhydride to the polyamine is about 1:1, but may include other ratios such as 5:1-1:5, and ranges in between.

[0027] Thus the reaction product (b) for use in the present invention can also include the products of reaction of a polyethylenepolyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, such as polyisobutene, having a molecular weight of 250 to 5,000, for example 500 to 2000, and as a further example less than about 1000, with an unsaturated polycarboxylic acid or anhydride, e.g. maleic anhydride.

[0028] The gasoline additive concentrate can be used to top treat a gasoline composition in any amount effective to reduce intake valve deposits. In particular, the additive concentrate can be used in a gasoline composition in an amount of 0.1 ptb to about 10 ptb, such as 0.4 ptb to about 7 ptb, as a further example 1 ptb to about 6 ptb, and as a further example, 2 ptb to about 5.5 ptb.

[0029] The fuel compositions disclosed herein comprise a minor amount of the disclosed gasoline additive concentrate and a major amount of a hydrocarbon fuel in the gasoline boiling range. As used herein "minor amount" means less than about 50% by weight of the total weight of the fuel composition. As used herein, "major amount" means greater than or equal to about 50% by weight of the total weight of the fuel composition.

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[0030] The fuel utilized in the practice of this disclosure can be traditional blends or mixtures of hydrocarbons in the gasoline boiling range, or they can contain oxygenated blending components such as alcohols and/or ethers having suitable boiling temperatures and appropriate fuel solubility, such as methanol, ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), and mixed oxygen-containing products formed by "oxygenating" gasolines and/or olefinic hydrocarbons falling in the gasoline boiling range. Thus this disclosure involves use of gasolines, including the so-called reformulated gasolines which are designed to satisfy various governmental regulations concerning composition of the base fuel itself, componentry used in the fuel, performance criteria, toxicological considerations and/or environmental considerations. The amounts of oxygenated components, detergents, antioxidants, demulsifiers, and the like that are used in the fuels can thus be varied to satisfy any applicable government regulations, provided that in so doing the amounts used do not materially impair the improved ignition performance made possible by the practice of this invention.

[0031] When formulating the fuel compositions of this invention, the gasoline additive concentrate is employed in amounts sufficient to reduce or eliminate injector deposits. Thus, the fuels will comprise minor amounts of the gasoline additive, i.e., the reaction product of (a) an aromatic anhydride or derivative thereof, and (b) a hydrocarbyl amine or alcohol proportioned so as to prevent or reduce formation of engine deposits, especially fuel injector deposits, and most especially intake valve deposits.

[0032] The gasoline additive concentrate or fuel composition further comprises other additives, such as a Mannich base detergent such as those disclosed in U.S. Patent No. 7,491,248. The Mannich base detergents useful in embodiments of the present invention are the reaction products of an alkyl-substituted hydroxy aromatic compound, aldehydes and amines. The alkyl-substituted hydroxyaromatic compound, aldehydes and amines used in making the Mannich reaction products of the present invention may be any such compounds known and applied in the art, such as those disclosed in U.S. Patent No. 7,491,248.

[0033] In another embodiment, the gasoline additive concentrate or fuel composition further comprises a liquid carrier or induction aid such as those disclosed in U.S. Patent No. 7,491,248. Such carriers can be of various types, such as for example liquid poly-alpha-olefin oligomers, mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, polyalkenes, liquid esters, and similar liquid carriers. Mixtures of two or more such carriers can be employed.

[0034] Liquid carriers can include but is not limited to 1) a mineral oil or a blend of mineral oils that have a viscosity index of less than about 120, 2) one or more poly-alpha-olefin oligomers, 3) one or more poly(oxyalkylene) compounds having an average molecular weight in the range of about 500 to about 3000, 4) polyalkenes, 5) polyalkyl-substituted hydroxyaromatic compounds or 6) mixtures thereof.

[0035] The fuel compositions of the present invention may contain supplemental additives in addition to the detergent (s), and carrier fluids described above. Said supplemental additives include additional dispersants/detergents, antioxidants, carrier fluids, metal deactivators, dyes, markers, corrosion inhibitors, biocides, antistatic additives, drag reducing agents, demulsifiers, dehazers, anti-icing additives, antiknock additives, anti-valve-seat recession additives, lubricity additives and combustion improvers.

[0036] The additives used in formulating the preferred fuels of the present invention can be blended into the base fuel individually or in various sub-combinations. However, it is preferable to blend all of the components concurrently using an additive concentrate as this takes advantage of the mutual compatibility afforded by the combination of ingredients when in the form of an additive concentrate. Also use of a concentrate reduces blending time and lessens the possibility of blending errors.

[0037] Other aspects of the present invention include a method to reduce the amount of deposits in direct injection gasoline engines, the method comprising adding to a gasoline to be combusted in the direct injection gasoline engine a gasoline additive concentrate to form a gasoline composition, then combusting the gasoline composition.

[0038] Moreover, there is disclosed a method to reduce greenhouse gas emissions, the method comprising adding to a gasoline to be combusted in the direct injection gasoline engine a gasoline additive concentrate to form a gasoline composition, then combusting the gasoline composition.

[0039] EXAMPLES

[0040] The following examples further illustrate aspects of the present disclosure but do not limit the present disclosure.

[0041] Example A - synthesis of comparative additive (PIBSI)

[0042] An additive was produced from the reaction of polyisobutylenesuccnic anhydride (PIBSA, from Afton Chemical) with polyamine (PAM, in this case PAM is tetraethylenepentamine, TEPA) in a molar ratio of PIBSA/PAM = 1/1. A modified procedure of US 5752989 was used. PIBSA (551g) was diluted in solvent aromatic 150 (200g) under nitrogen atmosphere. The mixture was heated to 115C. 112 g of TEPA was then added through an addition funnel. The addition funnel was rinsed with additional solvent aromatic 150 (50g). The mixture was heated to 180° C for about 2hr under a slow nitrogen sweep. Water was collected in a Dean-Stark trap. Product was obtained as a brownish oil. The FTIR peak absorptions were at 1772 cm⁻¹ and 1703 cm⁻¹.

Example B - synthesis of inventive additive-PIBSA-TEPA-NA

1,8-naphthalic anhydride (27.7g, 0.14 mol) was added to a PIBSI (950 MW PIB), a reaction product of PIBSA with TEPA in about 1 to 1 molar ratio with a method disclosed in US 5752989 (180.9g, 0.164 mol). Solvent aromatic 150 (128g) was added. The mixture was heated to 175° C for 1.5 hr under a slow nitrogen sweep. It was then filtered via celite 512 to afford product as a brown oil. The FTIR peak absorptions were at 1702 cm⁻¹ and 1664 cm⁻¹. DIG test - An engine test measuring fuel injector deposit is performed following a procedure disclosed in Society of Automotive Engineer (SAE) International publication 2009-01-2641"Test and Control of Fuel Injector Deposits in Direct Injected Spark Ignition Vehicles". A mathematical value of Long Term Fuel Trim (LTFT) is used to gauge the ability of the additive to keep deposits from accumulating in the injectors, or keep the injector clean. The higher the LTFT, the more deposit in the injectors, the less effective the additive is in keeping the injector clean. A 2008 General Motors Pontiac Solstice GXP equipped with a DISI 2.0 liter turbocharged 1-4 was used in the test.

Table 1. Injector Cleanliness as determined by Long Term Fuel Trim (LTFT).

(2.1.1)							
TEST#	additives	LTFT					
1	no top treat, reference run	17.2%					
2	PIBSA-TEPA 1.5 ptb	11.7%					
3	PIBSA-TEPA 2 ptb	4.7%					
4	PIBSA-TEPA-NA 2 ptb	0.8%					
5	PIBSA-TEPA-NA 1 ptb	2.4%					

40 [0045] Comparative example 1 - DIG test with conventional additized gasoline fuel containing Mannich and carrier fluid. No additional additive was used. The treat rate of the Mannich and carrier fluid was 38.4 pound additive per thousand barrel of gasoline fuel (ptb). The LTFT was measured at 17.2%. Comparative example 2 - PIBSI from Example A was used at a treat rate of 1.5 ptb. The LTFT was measured at 11.7%.

[0046] Comparative example 3 - Same as comparative example 2 except that 2.0 ptb of active PIBSI from example A was mixed into the fuel. The LTFT was measured at 4.7%.

[0047] Inventive example 4 - 2 ptb of active material from Example B was used. The LTFT was measured at 0.8%.

[0048] Inventive example 5 - Same as inventive example 4 except that the amount of additive was reduced to 1 ptb. The LTFT was measured at 2.4%.

[0049] The smaller the LTFT, the cleaner the fuel injector. So, the data in Table 1 shows that inventive compositions 4-5 have a smaller LTFT, i.e., cleaner injectors, as compared to comparative composition 1-3. This demonstrates the unexpected and superior performance of the PIBSA-TEPA NA in a fuel composition.

[0050] Ford 2.3-IVD test. Another test (a modified ASTM D620) was conducted to determine the intake valve depositforming tendency of gasoline using a Ford 2.3-Liter engine (short for Ford 2.3-IVD test). The additive was mixed into gasoline to control the amount of deposit in the intake valve. For this test, a 1994 Ford 2.3-L dual spark plug engine on a dynamometer test stand was used. The test cycle consists of:

[0051] 2,000 rpm and 230-mm Hg manifold absolute pressure for 4 minutes

[0052] 30-second ramp to 2,800 rpm

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[0053] 2,800 rpm and 540 Hg manifold absolute pressure for 8 minutes

[0054] 30-second ramp back to 2,000 rpm

[0055] The cycle was repeated for 100 hours. Intake valve deposit weights were reported

Table 2. Reduction in Intake Valve Deposit of Port Fuel Injection Engine.

TEST	Valve 1	Valve 2	Valve 3	Valve 4	Avg IVD(mg)	
8	106.4	159.7	85.4	123.8	118.8	ref
9	136.5	89.9	114.5	62.1	100.8	ref
10	76.8	82.9	101.4	27.3	72.1	2ptb PIBSA-TEPA-NA

[0056] The compositions in Table 2 were run in a test cycle CRC for 100 hours. Inventive composition 10 exhibited a reduction in intake valve deposits as compared to Comparative compositions 8-9. The additives in tests 8 and 9 were 28 ptb of a mixture of a typical Mannich base and a typical carrier fluid.

[0057] Comparative example 8 - Ford 2.3-IVD test with conventional additive Mannich and carrier fluid. The average intake valve deposit (IVD) was at 118.8 mg.

[0058] Comparative example 9 - Repeat of comparative example 8. The average IVD was 100.8 mg.

[0059] Inventive example 10 - Same as comparative example 8 except that material from example B was added at a treat rate of 2.0 ptb. The average IVD was 72.1 mg. The less the amount of deposit, the more effective the additive was in reducing intake valve deposit. This also demonstrates the unexpected and superior performance of the PIBSA-TEPA NA in a fuel composition.

Table 3. Dirty, 2006 Buick Lacrosse with artificially plugged injector, LTFT 4.7%

CO2	Run No.		FTP B1 (hot)	FTP B2	FTP B3	HwFET	US06 city	US06 Hwy
g/mi		1	387.8023633	440.731	390.3925	262.904	564.6301	321.0167
		2	393.8057617	444.8809	391.3243	263.9494	563.2401	319.5851
		3	393.6697355	448.6128	391.0601	262.5692	566.2071	310.4464
	Avg		391.759	444.742	390.926	263.141	564.692	317.016
			-2.42%	-1.76%	-2.40%	-3.08%	-2.27%	-3,44%

	Run No.		FTP B1 (hot)	FTP B2	FTP B3	HwFET	US06 city	US06 Hwy
Fuei						· · · · · · · · · · · · · · · · · · ·		
Economy		1	22.9279614	20.2136	22.7966	33.86581	15.65253	27.68976
mi/gal		2	22.5957295	20.01766	22.74065	33.70907	15.74413	27.80583
_		3	22.59947057	19.84532	22.75711	33.89471	15.68088	28.63305
	Avg		22.708	20.026	22.765	33.823	15.693	28.043
			2.59%	1.91%	2.50%	3.23%	2.91%	3.65%

[0060] As can be seen from the data in Table 3, there is about a 1 to 3% reduction in CO₂ emission in gasoline powered vehicles directly resulting from injector keep clean or clean up. The emissions reduction can be measured and quantified in units of grams/mile, and it is sustainable, so long as injectors are kept clean with the inventive gasoline additive concentrate. Fuel economy of the vehicle is improved by an equivalent amount, so reduced gasoline consumption is yet another benefit.

[0061] At numerous places throughout this specification, reference has been made to a number of U.S. patents, published foreign patent applications and published technical papers. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0062] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter

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should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0063] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to "an antioxidant" includes two or more different antioxidants. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0064] It is to be understood that the reactants and components referred to by chemical name anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., base fuel, solvent, etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together either in performing a desired chemical reaction (such as a Mannich condensation reaction) or in forming a desired composition (such as an additive concentrate or additized fuel blend). It will also be recognized that the additive components can be added or blended into or with the base fuels individually per se and/or as components used in forming preformed additive combinations and/or subcombinations. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, components or ingredient as it existed at the time just before it was first blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that the substance, components or ingredient may have lost its original identity through a chemical reaction or transformation during the course of such blending or mixing operations is thus wholly immaterial for an accurate understanding and appreciation of this disclosure and the claims thereof.

[0065] As used herein the term "fuel-soluble" or "gasoline-soluble" means that the substance under discussion should be sufficiently soluble at 20° C in the base fuel selected for use to reach at least the minimum concentration required to enable the substance to serve its intended function. Preferably, the substance will have a substantially greater solubility in the base fuel than this. However, the substance need not dissolve in the base fuel in all proportions.

[0066] At numerous places throughout this specification, reference has been made to a number of U.S. Patents and published foreign patent applications. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein. This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

[0067] Applicant does not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part of the invention under the doctrine of equivalents.

Claims

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1. A gasoline additive concentrate comprising:

the product of combining:

- (a) a 1,8-naphthalic anhydride; and
- (b) a reaction product of a hydrocarbyl-substituted succinic anhydride with a polyamine.
- 2. The concentrate of claim 1, wherein the polyamine is selected from the group consisting of N-dodecyl propanediamine, N-aminopropyl piperazine ethanolamine, N-ethanol ethylene diamine, propylene diamine, dipropylene triamine, di-(1,2-butylene)-triamine, tetra-(1,2-propylene)pentaamine, ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexaamine, heavy polyamine, and mixtures thereof.
- 3. The concentrate of claim 1, wherein the polyamine is tetraethylene pentamine.
- 55 **4.** The concentrate of any of claims 1 to 3, wherein the hydrocarbyl substituent is polyisobutylene.
 - 5. The concentrate of claim 4, wherein the polyisobutylene has a molecular weight ranging from about 200 to about 5000.

- **6.** The concentrate of claim 1, wherein the concentrate is a reaction product of 1,8-naphthalic anhydride and a polyisobutylene succinic anhydride tetraethylene pentamine.
- 7. The concentrate of any of claims 1 to 6, wherein the 1,8-naphthalic anhydride and the reaction product of a hydrocarbyl-substituted succinic anhydride with a polyamine are present in a molar ratio of about 0.5:1 to about 1:0.5.
 - **8.** The concentrate of any of claims 1 to 7, wherein the hydrocarbyl-substituted succinic anhydride and the polyamine are present in a molar ratio of about 1:1.
- 10 9. The concentrate of any of claims 1 to 8, further comprising at least one of a Mannich base detergent and a carrier fluid.
 - **10.** A fuel composition comprising:

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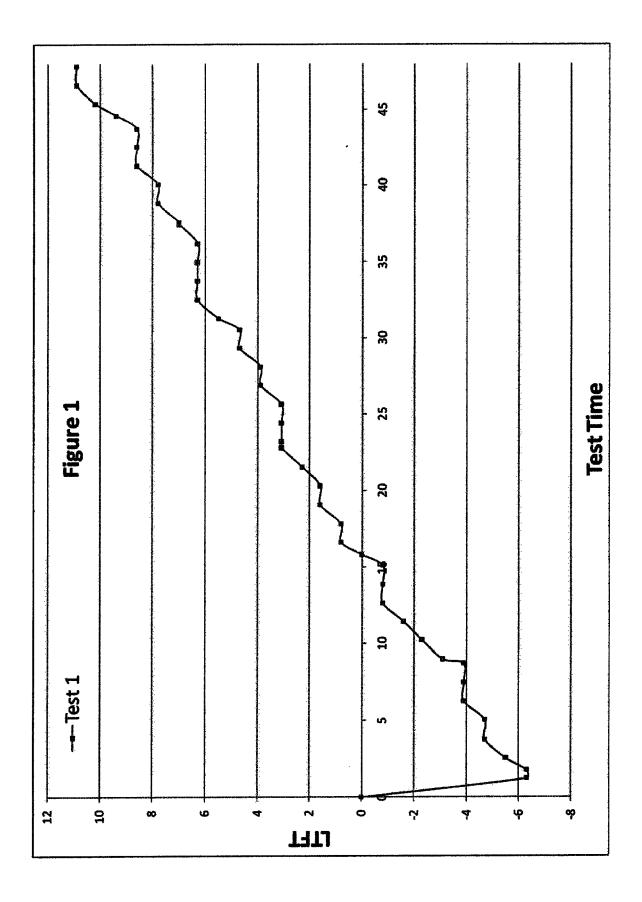
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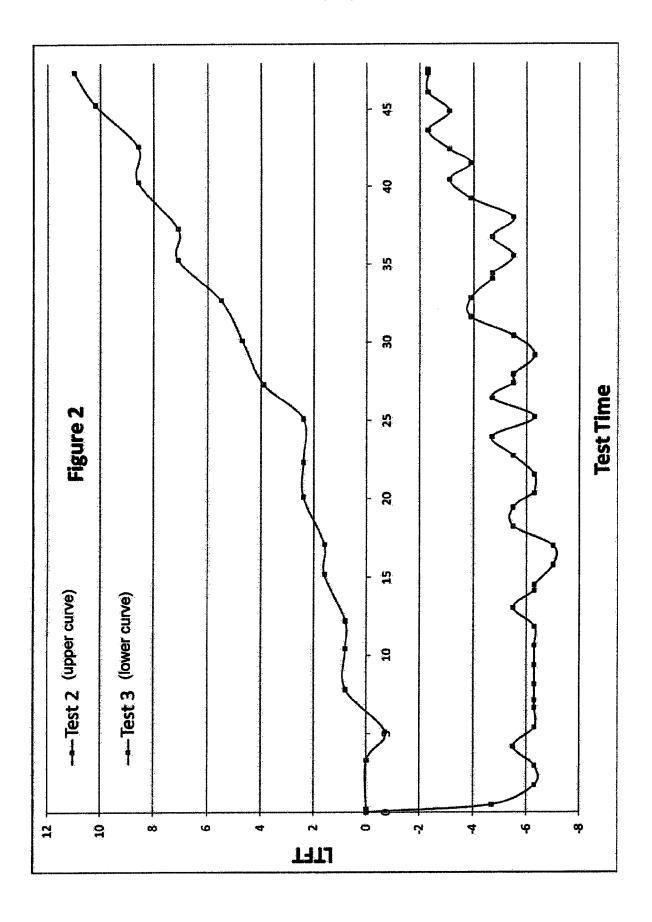
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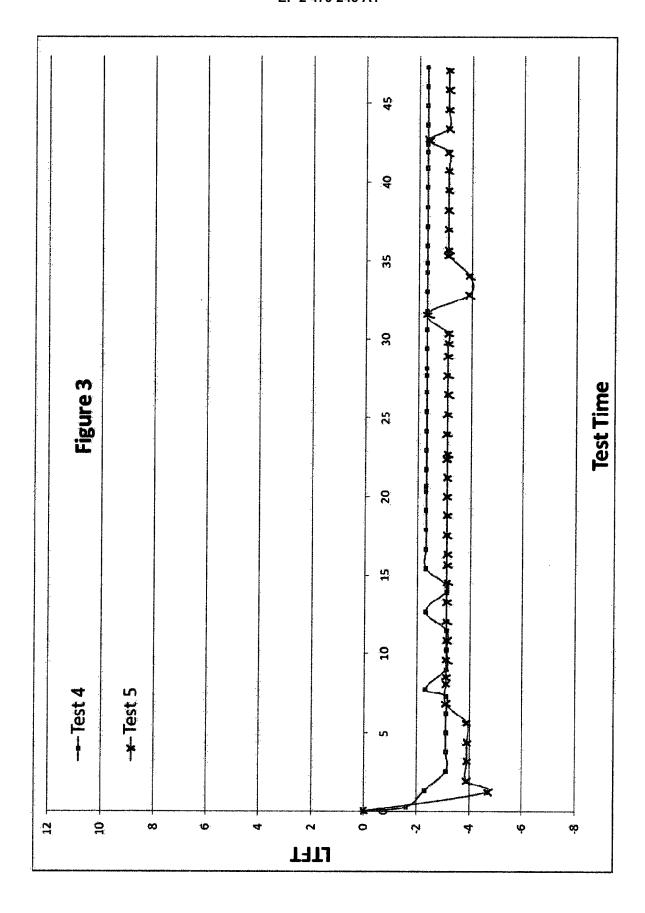
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- (1) a minor amount of the gasoline additive concentrate of any of claims 1 to 9; and
- (2) a major amount of a hydrocarbon fuel boiling in the gasoline range.
- 11. The composition of claim 10, wherein the additive concentrate can be used in the gasoline composition in an amount of 0.1 ptb to about 10 ptb.
- **12.** A method to reduce the amount of deposits in direct injection gasoline engines, said method comprising: adding to a gasoline to be combusted in the direct injection gasoline engine a gasoline additive concentrate of any of claims 1 to 9 to form a gasoline composition, then combusting said gasoline composition.
- 25 **13.** A method for reducing greenhouse gas emissions, said method comprising: adding to a gasoline to be combusted in the direct injection gasoline engine a gasoline additive concentrate of any of claims 1 to 9 to form a gasoline composition, then combusting said gasoline composition.
- **14.** Use of a gasoline additive concentrate of any of claims 1 to 9 in a gasoline to reduce the amount of deposits when said gasoline is combusted in a direct injection gasoline engine.
 - **15.** Use of a gasoline additive concentrate of any of claims 1 to 9 in a gasoline to reduce greenhouse gas emissions when said gasoline is combusted in a direct injection gasoline engine.

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