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GASOLINE COMPOSITION

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U.S. Cl. 44—63 5 Claims

ABSTRACT OF THE DISCLOSURE

Fuel composition comprising a major portion of a liquid hydrocarbon boiling in the gasoline boiling range and in an amount sufficient to inhibit deposit formation, a mono- or bis-alkenyl succinimide of a bis- or tris-polymethylene polyamine wherein the alkenyl groups of the succinate moieties contain from about 50 to 250 carbon atoms and wherein the polyamine is of the formula:

$$(NH_2—R\rightarrow_s N\leftarrow H)_t$$

in which R is a polymethylene radical of 4 to 9 carbon atoms, s is 2 to 3, t is 0 to 1, and the sum of $s+t=3$.

This invention concerns gasoline-type fuels having incorporated therein metal-free detergent additives. More particularly, it relates to fuel compositions inhibited from deposit formation and to certain alkenyl succinimides useful as detergents in said fuel compositions and in lubricants.

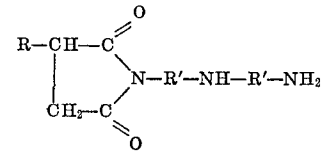
In recent years spark-ignition internal combustion engines have been designed and built by the industry with great emphasis being placed upon higher compression ratios, larger engines and high volumetric efficiency at high speeds. The volumetric efficiency is dependent upon such factors as unhindered flow of fuel-air mixtures through the valves and ports and the maintenance of high compression by efficient valve closure and by proper timing maintenance. However, most fuels in use today, when employed in these engines, undergo deterioration and leave hard carbonaceous deposits upon the intake valves, underheads and stems and in the valve ports. These deposits interfere with proper valve seating, resulting in a loss of power and thus requiring frequent maintenance in order that the engines may develop their maximum efficiency as to power and fuel consumption. These deposits result in part from "puffback" of decomposition products from the compression chamber and also in part from the decomposition of the crankcase oil entering by way of the valve stems. The deposits may also contain lead compounds that result from the decomposition of lead-containing octane improvers. Such deposits attach firmly to the valve and ports, and detergents that are in current use in fuels have little or no effect in either reducing deposits previously formed or preventing formation of new harmful deposits.

Therefore, it is highly desirable that fuels be supplied which, due to the presence of certain additives, result in lowered deposition in the engines in which they are used and also reduce deposits which are already present due to prior operation with fuels which have formed heavy deposits.

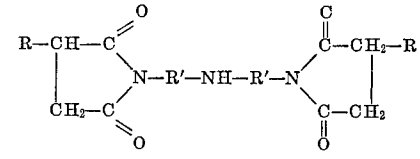
It has now been found that superior gasoline-type fuel compositions, resistant to harmful deposit formation, result from the addition to gasoline-type fuel compositions of minor amounts of a mono-, bis- or tris-alkenyl succinimide of a bis- or tris-polymethylene polyamine of the formula $(NH_2—R\rightarrow_s N\leftarrow H)_t$ wherein R is a polymethylene radical of 4 to 9 carbon atoms, s is 2 to 3, t is 0 to 1 and $s+t=3$, and wherein the alkenyl radicals contain from about 50 to 240 carbon atoms.

Examples of the additives of this invention may be represented by the following formulae wherein R in each case is an alkenyl group of 50 to 250 carbon atoms and R′ is a polymethylene group of 4 to 9 carbon atoms:

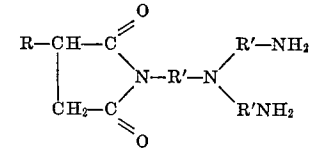
Monosuccinimide of bis-(polymethylene triamine)



Bis-succinimide of bis-(polymethylene triaminie)



Monosuccinimide of tris-(polymethylene tetramine)



The bis and tris derivatives of tris-(polymethylene tetramine) are also effective.

The additives of this invention are preferably prepared by reacting a suitable alkenyl succinic anhydride with a multi-polymethylene polyamine. The reaction is commonly effected by mixing the reactant and heating and by removing one mol of water per each mole of product formed.

The alkenyl succinic anhydrides mentioned above can be prepared by reacting maleic anhydride with a suitable polyolefin, preferably a polyolefin derived from olefins containing from 2 to 5 carbon atoms. Examples of suitable olefins are ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures of said olefins. Preferred polyolefins are polyisobutenes having molecular weights of from about 700 to 3500 and more preferably from 800 to 3200.

As previously mentioned, the polymethylene polyamines used include those having from 8 to 27 carbon atoms, e.g., ranging from bis-tetramethylenetriamine to tris-nonamethylenetetramine. The preferred amine is the bis-hexamethylenetriamine, which is a by-product in the production of nylon and is available commercially.

In addition to the deposit-suppressing and detergent qualities of the alkenyl succinimides of this invention, they also display highly desirable non-emulsifying properties in fuel compositions. A disadvantage, common to many surface-active additives, is the property of forming undesirable emulsions of water with the hydrocarbon stocks in which they are used. The alkenyl succinimides of this invention show very low emulsifying propensities in hydrocarbon fuels.

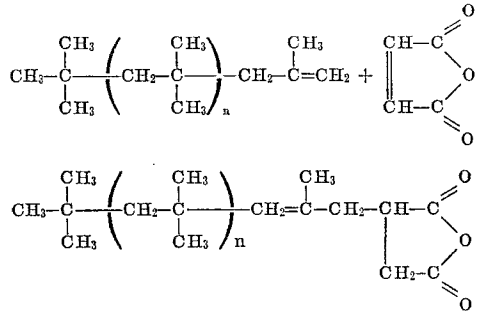
The effective amount of the additives that must be added to impart the desired anti-deposit characteristics will vary according to the use and nature of each particular base fuel, however, in general, amounts of from 10 to 1,000 p.p.m. are sufficient, and under most circumstances an amount of from 50 to 500 p.p.m. is preferred.

The addition to the fuel compositions of a minor portion of a light petroleum oil in addition to the above-described compound further enhances the deposit-suppressing effects and makes it possible to reduce the

amount in the composition and achieve a like desirable reduction of deposit formation. The light petroleum oil may be any low viscosity petroleum oil fraction, preferred examples being neutral oils in the range of from 50 to 480 SSU at 100° F. A specific example of a specially preferred material is an oil having a viscosity of 60 SSU at 100° F. The use of these oils in minor proportions, from 5,000 to 15,000 p.p.m., is effective, a preferred amount being in the range of from 5,000 to 10,000 p.p.m.

The substituted succinic anhydrides which are used in preparing the additives of this invention are prepared by reactions well known in the art. The polymerization of olefins is especially well known. The method employed has no effect upon the compounds described herein, and thus any available process may be used for this step.

The aforementioned reaction of α-polyolefin and maleic anhydride to produce an alkenyl succinic anhydride can be described by the following formulae, using a polyisobutene as an example:



in which n is an integer from about 10 to about 60.

The reaction can be carried out using molar ratios of polyolefin to anhydride of from 1:1 to 1:10 and preferably from 1:1 to 1:5. The reaction temperature may vary from 300 to 500° F.; a range from about 425° to about 475° F. is preferred because of the high yields obtained.

The polymethylene amines which are employed in reacting with the succinic anhydride may be described as bis- and tris-polymethylene amines. These compounds are represented by the following structures:

$$NH_2—R—NH—R—NH_2$$

$$NH_2—R—\underset{\displaystyle R—NH_2}{\underset{|}{N}}—R—NH_2$$

R represents an alkylene radical of 4 to 9 carbon atoms.

The following examples illustrate the preparation of the additives of this invention. The examples are intended to be only illustrative and not limiting. The amounts of materials used are on a weight basis unless otherwise specified.

Example 1.—Preparation of Polyisobutenyl succinic anhydrides

One mol of polyisobutene having an average molecular weight of 1,000, was placed in a 3-neck, 2-liter flash equipped with a thermometer, mechanical stirrer, and reflux condenser. The material was heated to 240° C., at which point molten maleic anhydride was added dropwise at such a rate that the temperature of 240° C. was maintained without further heating. Two mols of maleic anhydride were added over the course of six hours. The excess maleic anhydride was then stripped from the reaction mixture under vacuum. The reaction product was diluted with a solvent/refined 150 neutral oil and filtered through diatomaceous earth to remove the small amount of by-product. The yield of anhydride was 860 g. or 80% of theoretical based upon polyisobutene.

Example 2.—Preparation of Monoimide of polyisobutenyl succinic acid and bis-hexamethylenetriamine

One mol of polyisobutenyl succinic anhydride prepared by the method described in Example 1 and having a molecular weight of 1,000 was dissolved in an equal volume of toluene and heated in a vessel equipped with thermometer and an overhead water trap to reflux. To this material was added 1.1 mol of bis-hexamethylenetriamine. The mixture was heated, and refluxing was continued until 1 mol of water was isolated in the overhead condensate. Excess amine was removed from the mixture by water-washing. The yield of product was 95% based upon polyisobutenyl succinic anhydride. Based upon the recovery of unreacted amine, the product constituted a mixture of 85% monosuccinimide and 15% bis-succinimide.

Tests which were employed to demonstrate the detergent effect of the succinimide of this invention were a simulated Urban-Suburban Laboratory Engine Test, a modified Glass Throttle-Body Test, and an Automobile Engine Field Test.

A modification of the Glass Throttle-Body Test, previously described in U. S. Patent No. 2,839,372 and No. 2,974,022, is designated as the Glass Throttle-Body Deposit Removal Test. In the modification, a six-cylinder Plymouth automobile engine is set up in the laboratory and is provided with a conventional carburetor, modified as described in the above-mentioned U.S. patent by the introduction of a similar removable glass throttle-body section between the carburetor body and the original cast-iron throttle body. This glass throttle-body is a section of glass tubing ¼" thick of approximately 1¾" outside diameter and about 1¾" long. An automatic cycler or timer, which consists of a constant speed electric motor and a magnetic clutch, is provided for insuring cyclic operation of the engine with 7.5 minute idle periods followed by 5 accelerations to 2,000 r.p.m. Crankcase fumes are vented to the carburetor air inlet, since these fumes are now known to be responsible for the larger portion of the deposits. The engine is started up, using leaded gasoline containing a conventional amount of tetraethyl lead (1.5 ml./gal.), but no surface-active additives of any kind. It is run for one hour with the blowby fumes being drawn in at the air intake. The engine is then stopped, the glass body is removed, and both sides of it are photographed. Thereupon, the dirty glass body is again installed on the engine and run for four hours on the same leaded base gasoline compound with the detergent-action succinimide. This time the blowby fumes are not piped to the carburetor. After the run is completed, the glass throttle-body is again photographed, and the effectiveness of the succinimide containing gasoline (the percentage of cleanup of deposits) is visually estimated.

The following table shows results of this test performed upon gasolines containing (A) the substituted succinimide of Example 2, (B) a monoimide of 1, 6-hexamethylenediamine produced by a similar reaction and (C) a corresponding succinimide of tetraethylenepentamine.

TABLE I.—CARBURETOR CLEANUP TEST

Compound	Conc., p.p.m.	Cleanup, percent
A	50	80
	100	95
B	30	16
	100	25
C	100	30

The results of these tests show that the succinimide of hexamethylenetriamine is remarkably more effective in reducing carburetor deposits than the imide of the monohexamethylenediamine and the imide of tetraethylenepentamine, a material which is known in the prior art to be remarkably effective as a lubricating oil detergent.

The simulated Urban-Suburban Engine Test mentioned above shows the effect of detergent on engine valves and ports and is specifically designed to duplicate the conditions encountered in everyday stop-and-start driving. The engine used was an F–956 Chevrolet V–8 of 283 cubic inch displacement. The engine was cycled in a pattern under the following running conditions.

Time, seconds	Speed, r.p.m.	Vacuum, inches of Hg
6	700	[1] 21
6	1,775	13
6	1,775	8.5
6	1,775	17
6	1,775	13
6	1,775	17
12	700	[1] 21
12	1,775	13
12	1,775	17
12	1,775	13
6	1,775	8.5

[1] Idle.

Each cycle was repeated eight times, after which the engine was shut down for three minutes, restarted and the cycles repeated. The complete test was 150 hours.

At the end of the test, the engine was dismantled, and the intake valves and ports were visually inspected for deposits. A rating scale of 0 to 10 was used, a rating of "0" indicating a perfectly clean valve or port and "10" indicating very heavy deposits. The deposit from each valve was also weighed.

The gasoline used in the test was of premium grade and contained 2.06 ml. per gallon of tetramethyl lead. The engine in this test was set up with four dirty and four clean valves. This allowed a simultaneous determination of deposit removal and deposit prevention activity. The dirty valves were obtained from commercial garages and has been removed from automobiles operating under normal service conditions. They were inspected before assembly in the test engine. Thus, deposit removal was determined by weighing the dirty valves, including deposits, before the test, weighing them after the test, removing the deposits and determining the weight of the clean valve and thus determining the initial deposit, and the final deposit, and calculating from these data the percent improvement. Deposit prevention was calculated by comparing the aforementioned ratings of the initially clean valve after the test was run with fuel containing the inhibitor and the ratings obtained when the test was run without the inhibitor. The additive used was the succinimide of Example II.

TABLE II.—URBAN-SUBURBAN CYCLE ENGINE TEST

[Gasoline containing alkenyl succinimide of bis-hexamethylenetriamine]

Type of test	Concentration, p.p.m.	Valve condition: Start, Numerical rating	Start, Wt. of deposits (g.)	Finish, Numerical rating	Finish, Wt. of deposits (g.)	Improvement, percent
Deposit	0	0		4.5		
Prevention	100	0		1.3		70
Deposit	100		2.20		0.90	55
Removal	47		3.28		1.74	50

TABLE III.—DEPOSIT SUPPRESSION AND REDUCTION IN TEST AUTOMOBILES USING A COMMERCIAL PREMIUM GRADE GASOLINE+500 P.P.M. ADDITIVE

Compound	Deposit levels: Initial rating, Valves	Initial rating, Ports	Final rating, Valves	Final rating, Ports	Deposit reduction, percent: Valves	Deposit reduction, percent: Ports	Deposit increase, percent: Valves	Deposit increase, percent: Ports	Deposit on clean valves: Before cleaning	Deposit on clean valves: After test	Deposit suppression, percent
Monosuccinimide of bis-hexamethylenetriamine	7.5	3.8	7.3	2.8	2.7	26			7.5	2.2	70
Monosuccinimide of tetraethylenepentamine	3.0	3.1	3.4	3.0		3		13	2.8	2.5	11

It is apparent from the above data that the imides of this invention impart surprising deposit-suppressing and deposit-removing characteristics to spark-ignition engine fuels or gasolines in which they are employed.

In order to further demonstrate the detergent and deposit-suppressing characteristics of these additives, fuel compositions containing the additives and related compounds were evaluated under field test conditions in privately owned (employed) automobile engines. In the test, standard American automobiles were employed. Three cars were used for testing each additive. The cars had been driven approximately 30,000 miles each and had developed substantial deposits in the valves and ports. At the beginning of each test, each automobile had thus been driven a sufficient length of time to accumulate an equilibrium deposit in the intake manifold and upon the intake valves. The equilibrium deposit is the amount of deposit that is normally accumulated after extended operations with similar fuels. When this amount is deposited, it has been found that further operation under normal conditions results in essentially no further buildup of carbonaceous material. Prior to the test, each automobile had been operated on a high-grade leaded fuel representative of generally available commercial gasolines.

In the test procedure adopted, each engine was disassembled, and each intake valve and port was visually rated for the amount of deposit on a scale from 0 to 10 with 0 representing a completely clean port and 10 representing a very heavy deposit. Two valves were removed from each engine, cleaned, and the total weight of deposit was determined. This figure represented the equilibrium deposit for the engine. The engines were reassembled, and each automobile was then driven for approximately 5,000 miles under urban-suburban operating conditions with a fuel composition consisting of gasoline of the same type previously employed in the automobile and 500 p.p.m. of the additive being tested, plus 7,000 p.p.m. of a neutral oil having a viscosity of about 60 SSU at 100° F. At the end of the test period, each engine was disassembled; and the valves which had been removed at the beginning of the test were visually rated and cleaned. The deposit from this valve was weighed. The difference between this weight of deposit and the previously determined equilibrium deposit is expressed in the terms of equilibrium deposit in Table III as "Deposit Prevention." "Deposit Increase," if any, is shown in a separate column. The undisturbed valves which had been previously rated by inspection were re-rated, and the difference between the two deposit ratings, is expressed in Table III as "Deposit Reduction."

This test thus shows that the additives of this invention are highly effective in both preventing the deposit formation in the intake valve and port of the test automobiles and in reducing the amount of deposits previously formed. The comparison shows that the succinimide of hexamethylenetriamine is decidedly superior to the succinimide of tetraethylenepentamine, a material which is disclosed in U.S. Patent No. 3,172,892 as being a highly effective lubricating oil detergent.

The fuels which are contemplated for use in the compositions of this invention are fuels in the gasoline boiling

range, including hydrocarbon base fuels boiling substantially in the range of from about 100° F. to about 400° F. These fuels may be leaded fuels, i.e., fuels containing lead alkyl additives such as tetraethyl lead, tetramethyl lead and like compounds which are introduced into the compositions to prevent pre-ignition and engine "knock."

In addition to the additives of this invention, the use of other conventional fuel additives is contemplated. Thus, the fuel compositions may also contain surface-ignition suppressants, such as phosphorus-containing compounds, dyes, gum inhibitors, and oxidation inhibitors, etc.

The alkenyl succinimides which have been heretofore described are also useful as detergent additives in lubricants. As such they may be used in a wide variety of lubricating oils, such as naphthenic-base, paraffin-base and mixed-base lubricating oils and in other synthetic oils, e.g., alkylene polymer and alkylene oxide-type polymers, etc.

We claim:

1. A spark-ignition fuel comprising a major portion of liquid hydrocarbon boiling in the gasoline boiling range and a minor portion sufficient to inhibit deposit formation of a monoalkenyl succinimide of a bis- or tris-polymethylene polyamine wherein the alkenyl groups contain

from about 50 to 250 carbon atoms and wherein the polyamine is of the formula:

$$(NH_2—(CH_2)_6)_sN(H)_t$$

in which s is 2 to 3, t is 0 to 1, and the sum of $s+t=3$.

2. The composition of claim **1** in which s is 2 and t is 1.

3. The composition of claim **2** in which the alkenyl group of the succinimide contains about 50 carbon atoms.

4. The composition of claim **3** wherein the succinimide is present in the amount of from 10 to 1,000 p.p.m.

5. The composition of claim **4** wherein the succinimide is present in the amount of from 50 to 500 p.p.m.

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