(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 376 578 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89313238.1**

(51) Int. Cl.5: **C10L 1/14**

(22) Date of filing: **18.12.89**

(30) Priority: **30.12.88 US 292139**

(43) Date of publication of application:
04.07.90 Bulletin 90/27

(84) Designated Contracting States:
BE DE FR GB IT NL

(71) Applicant: **MOBIL OIL CORPORATION**
150 East 42nd Street
New York New York 10017(US)

(72) Inventor: **Abramo, Guy Paul**
215 Loring Court
Sewell New Jersey 08080(US)
Inventor: **Trewella, Jeffrey Charles**
8 Morgan Road
Flemington New Jersey 08822(US)

(74) Representative: **Colmer, Stephen Gary et al**
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

(54) Polyalkylene succinimide deposit control additives and fuel compositions containing same.

(57) Deposits on intake valves in gasoline internal combustion engines are reduced by an additive for fuel compositions comprising a mixture of (1) a polyalkylene succinimide, (2) a polyalkylene and (3) a mineral oil. A fuel composition containing such an additive and a method for removing and/or preventing engine deposits which adversely affect the performance of gasoline powered engines using such additve.

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POLYALKYLENE SUCCINIMIDE DEPOSIT CONTROL ADDITIVES AND FUEL COMPOSITIONS CONTAINING SAME

This invention relates to additives for controlling or preventing engine deposits and to fuel compositions containing these additives.

Hydrocarbyl succinimides, such as those derived from poly-alkylene polyamines, are known materials which have been widely used as fuel detergents. For example. U.S. Patent No. 4,240,803 describes the use of alkenyl succinimides in gasoline to reduce engine deposits. U.S. Patent No. 4,482,357 discloses additive mixtures for diesel fuels which include a hydrocarbyl succinimide or succinamide and the reduction of coke deposition by the use of these additive mixtures.

This invention provides an additive composition for reducing carbon deposits in internal combustion engines comprising:

(a) a polyalkylene succinimide prepared by reacting a polyalkylenesuccinic acid or anhydride, wherein the polyalkylene is derived from a C_2 C_3, or C_4 olefin or mixture thereof, with a polyalkylene polyamine of the formula

$NH_2—(RNH)_{\overline{n}}R—NH_2$

in which R is an alkylene radical having from 1 to 5 carbon atoms and n is from 0 to 10,

(b) a polyalkylene, and

(c) a mineral oil.

This invention also provides a liquid fuel composition comprising a major amount of a liquid fuel and a minor amount of an additive composition for reducing carbon deposits in internal combustion engines comprising:

(a) a polyalkylene succinimide prepared by reacting a polyalklyenesuccinic acid or anhydride, wherein the polyalkylene is derived from a C_2, C_3, or C_4 olefin or mixture thereof with a polyalkylene polyamine of the formula

$NH_2—(RNH)_n\text{-}R—NH_2$

in which R is an alkylene radical having from 1 to 5 carbon atoms and

n is from 0 to 10,

(b) a polyalkylene, and

(c) a mineral oil.

This invention further provides a method for cleaning a gasoline internal combustion engine with fuel injectors having deposits from fuel decomposition which noticeably affect performance comprising running the engine for a period of time sufficient to improve performance with a fuel containing greater than 80 pounds per thousand barrels of an additive composition for reducing carbon deposits in internal combustion engines comprising from 22 to 28 parts of a polyalkylene succinimide, between 40 to 50 parts of a polyalkylene, and between about 27 to 33 parts of a mineral oil.

The polyalkylenesuccinimide utilized to make the additive composition of this invention is prepared by reacting a polyalkylenesuccinic acid or anhydride, wherein the polyalkylene is derived from a C_2, C_3 or C_4 olefin, or mixtures thereof, with a polyalkylene polyamine of the formula

$NH_2—(RNH)_n\text{-}R—NH_2$

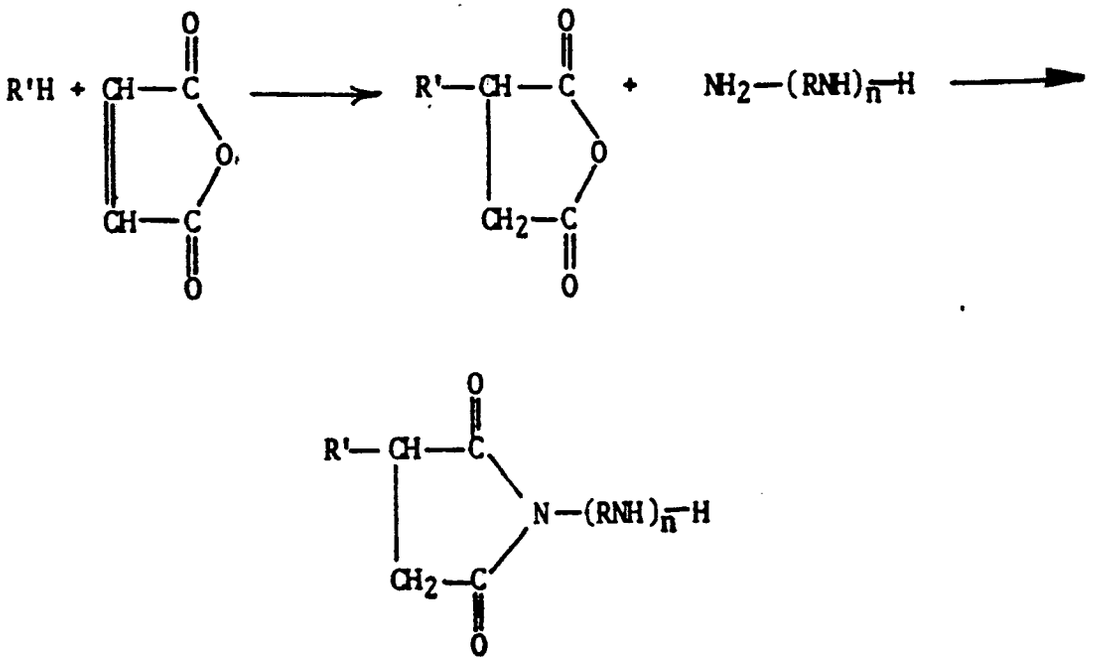
in which R is an alkylene radical having from 1 to 5 carbon atoms and "n" is from 0 to 10.

The polyalkylenesuccinic anhydride can be made in accordance with a prior art process involving the thermal condensation of a polyalkylene or polyalkylene mixture with maleic anhydride. This is conveniently carried out at from 150 $^{\circ}$ C to 250 $^{\circ}$ C, preferably 175 $^{\circ}$ C to 225 $^{\circ}$ C.

Particularly preferred is the succinic acid or anhydride derived from a polyalkylene such as isobutylene.

Suitable polyamines include methylene diamine, ethylene diamine, diethylene triamine, dipropylene triamine, triethylene tetramine, tetraethylene pentamine, pentamethylene hexamine, hexaethylene heptamine and undecaethylene dodecamine.

One series of reactions, showing one possible product, is as follows:



In the formula above, R′ is polyalkylene containing 12 to 500 carbons, R is alkylene containing 1 to 5 carbon atoms and n is from 0 to 10.

The reaction mixture may contain from 1 mole of the anhydride per mole of the amine, or it may have an amount of anhydride equivalent to the total NH functions in the amine, i.e., up to 14 moles of anhydride per mole of amine.

The polyalkylene component of the additive composition preferably is a liquid polyalkylene where the average number of carbon atoms per molecule is between 12 and 500. Preferably, the polyalkylene is a polymer of ethylene or propylene and, even more preferably, is polyisobutylene wherein the average number of carbon atoms per molecule is between 12 and 500.

The mineral oil can be characterized as one having a viscosity from 100 to 800 SUS at 100° F, and a minimum viscosity index of 90, more typically 91.

The three-component additive composition is formulated by mixing the components in the following broad and preferred proportions:

	Parts by Weight	
	Range	Preferred Range
Polyalkylene succinimide	20 to 30	22 to 28
Polyalkylene	35 to 55	40 to 50
Mineral Oil (100 SUS)	24 to 36	27 to 33
or		
Mineral Oil (700 SUS)	32 to 42	35 to 39

In general, the invention contemplates the use of the additive in a fuel composition in a concentration of from 80 lbs. to 400 lbs. per 1,000 barrels of fuel, and most preferably, from 120 lbs. to 250 lbs. per 1,000 barrels, the base gasoline containing less than 0.1 weight percent sulfur. Since sulfur and olefins are believed to contribute to gum formation, their reduction is advantageous in obtaining good cleanliness performance. The gasoline can also contain conventional additives such as antioxidants, metal deactivators, lead alkyls, lead scavengers, and corrosion inhibitors.

EXAMPLE 1

Premium unleaded gasoline containing various quantities of a polyisobutylene succinimide, polyalkylene, and a mineral oil mixed in the ratios shown below were evaluated in a single cylinder CIR engine using a 10W-30 mineral oil lubricant. After 40 hours of operation at 1100 rpm and 10 to 12 inches manifold vacuum, the intake valve was removed, its combustion chamber side cleaned and the gross weight determined. Deposits were then removed mechanically and the valve's tare weight was measured in order to calculate the net weight of deposits.

The table below presents the results for several runs with premium unleaded gasoline containing various additive package components alone and in specific combinations. As indicated, use of polyisobutylenesuccinimide alone at 50 pounds per 1000 barrels (Run B) increased ITV deposits 171% compared to Run A in which no additives were present in the fuel. The use of 60 pounds of mineral oil per 1000 barrels (Run D) also increased ITV deposits, but only slightly. Polyalkylene alone at 100 pounds per thousand barrels (Run C) did reduce intake valve deposits to 37% of Rune A. However, significant further reductions in deposits were obtained when packages of the type described herein were used (Runs E and F).

Table 1

CLR Intake Valve Cleanliness Test Results						
Pkg.	Concentration Pounds Per 1000 Barrels of Fuel				Intake Valve Deposits	
	PIB-Succinimide	Polyalkylene	100 SUS Mineral Oil	700 SUS Mineral Oil	Weight, Mgs.	Percent of Base
A	-	-	-	-	298[1]	-
B	50	-	-	-	511	171
C	-	100	-	-	109	37
D	-	-	60	-	351	117
E	50	90	60	-	54	18
F	56	133	-	111	10	3

[1] Average of 8 runs

Premium unleaded gasoline, for example, Phillips J alone and containing additive packages C and E were evaluated in the standard CRC carburetor cleanliness test. After 20 hours of operation with the standard cycle, the tared carburetor sleeve was removed and weighed to determine the weight of deposits thereon. Table II below presents the results of several runs. Use of a polyalkylene package C provided no carburetor keep-clean performance. The package E embodying this invention provided significant improvements in carburetor cleanliness.

Table II

Carburetor Cleanliness Test Results					
Pkg.	Concentration Pounds Per 1000 Barrels of Fuel			Carburetor Sleeve Deposits	
	PIB-Succinimide	Polyalkylene	Light Mineral Oil	Weight, Mgs.	Percent of Base
A	-	-	-	24	-
C	-	100	-	23	96
E	50	90	60	2	8

Claims

1. An additive composition for reducing carbon deposits in internal combustion engines comprising:

(a) a polyalkylene succinimide prepared by reacting a polyalkylenesuccinic acid or anhydride, wherein the polyalkylene is derived from a C_2, C_3, or C_4 olefin or mixture thereof, with a polyalkylene polyamine of the formula

$NH_2—(RNH)_n—R—NH_2$

in which R is an alkylene radical having from 1 to 5 carbon atoms and n is from 0 to 10,

(b) a polyalkylene, and

(c) a mineral oil.

2. The additive composition of claim 1 wherein the polyalkylene succinic acid or anhydride is derived from isobutylene.

3. The additive composition of claim 1 or 2 wherein the polyalkylene succinimide is prepared from a polyamine selected from methylene diamine, ethylene diamine, diethylene triamine, dipropylene triamine, triethylene tetramine, tetraethylene pentamine, pentamethylene hexamine, hexaethylene heptamine, and undecaethylene dodecamine.

4. The additive composition of any one claims 1 to 3 wherein the polyalkylene is a liquid polyalkylene wherein the average number of carbon atoms per molecule is between 12 and 500.

5. The additive composition of claim 1 wherein the polyalkylene is preponderantly polyethylene or polypropylene or polyisobutylene.

6. The additive composition of any one of claims 1 to 5 wherein the mineral oil has a viscosity of from 100 SUS to 800 SUS at 100° F, and a minimum viscosity index of 90.

7. The additive composition of claim 6 wherein the mineral oil has a viscosity of from 105 to 115 SUS at 100° F, and a minimum viscosity index of 95.

8. The additive composition of any one of claims 1 to 6 wherein the mineral oil has a minimum viscosity index of 91.

9. The additive composition of any one of claims 1 to 8 comprising from 20 to 30 parts by weight of a polyalkylene succinimide, from 35 to 55 parts of a polyalkylene, and from 24 to 36 parts of a mineral oil.

10. The additive composition of claim 9 comprising from 22 to 28 parts by weight of a polyalkylene succinimide, from 40 to 50 parts of a polyalkylene, and from 27 to 33 parts of a mineral oil.

11. A liquid fuel composition comprising a major amount of a liquid fuel and a minor amount of an additive composition for reducing carbon deposits in internal combustion engines comprising:

(a) a polyalkylene succinimide prepared by reacting a polyalkylenesuccinic acid or anhydride, wherein the polyalkylene is derived from a C_2, C_3, or C_4 olefin or mixture thereof with a polyalkylene polyamine of the formula

$NH_2—(RNH)_n-R—NH_2$

in which R is an alkylene radical having from 1 to 5 carbon atoms and

n is from 0 to 10,

(b) a polyalkylene, and

(c) a mineral oil.

12. The liquid fuel composition of claim 11 wherein the polyalkylene succinic acid or anhydride is derived from isobutylene.

13. The liquid fuel composition of claim 11 wherein the polyalkylene succinimide is prepared from a polyamine selected from methylene diamine, ethylene diamine, diethylene triamine, dipropylene triamine, triethylene tetramine, tetraethylene pentamine, pentamethylene hexamine, hexaethylene heptamine, and undecaethylene dodecamine.

14. The liquid fuel composition of claim 11 wherein the polyalkylene is a liquid polyalkylene wherein the average number of carbon atoms per molecule is between 12 and 500.

15. The liquid fuel composition of claim 11 wherein the polyalkylene is preponderantly polyethylene or polypropylene or polyisobutylene.

16. The liquid fuel composition of any one of claims 11 to 15 wherein the minderal oil has a viscosity of from 100 to 800 SUS at 100° F, and a minimum viscosity index of 90.

17. The additive composition of claim 11 wherein said mineral oil has a viscosity of from 105 to 115 SUS at 100° F, and a minimum viscosity index of 95.

18. The liquid fuel composition of any one of claims 11 to 16 wherein the mineral oil has a minimum viscosity index of 91.

19. The liquid fuel composition of any one of claims 11 to 18 wherein the additive comprises from 20 to 30 parts by weight of a polyalkylene succinimide, from 35 to 55 parts of a polyalkylene, and from 24 to 36 parts of a mineral oil.

20. The liquid fuel composition of claim 19 wherein the additive comprises from 22 to 28 parts by

weight of a polyalkylene succinimide, from 40 to 50 parts of polyalkylene, and from 27 to 33 parts of a mineral oil.

21. The liquid fuel composition of any one of claims 11 to 20 wherein the liquid fuel component is gasoline or diesel fuel.

22. The liquid fuel composition of claim 11 wherein the additive comprises from 22 to 28 parts by weight of a polybutylene succinimide, from 40 to 50 parts of polybutylene, and form 27 to 33 parts of a mineral oil having a viscosity of from 100 SUS to 800 SUS at 100° F, and a minimum viscosity index of 90 and the liquid fuel component is gasoline.

23. A method for cleaning a gasoline internal combustion engine with fuel injectors having deposits from fuel decomposition which noticeably effect performance comprising running the engine for a period of time sufficient to improve performance with a fuel containing greater than 80 pounds per thousand barrels of an additive composition for reducing carbon deposits in internal combustion enginese comprising from 22 to 28 parts of a polyalkylene succinimide bvetween 40 to 50 parts of a polyalkylene, and between about 27 to 33 parts of a mineral oil.

24. The method of claim 23 wherein the additive comprises from 22 to 28 parts by weight of a polybutylene succinimide, from 40 to 50 parts of polybutylene, and from 27 to 33 parts of a mineral oil having a viscosity of from 100 SUS to 800 SUS at 100° F, and a minimum viscosity index of 90 and the liquid fuel component is gasoline.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 3238

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y	GB-A-1 486 144 (CITIES SERVICE OIL CO.) * Whole document *	1-6,8-16,18-22 7,17,23,24	C 10 L 1/14
Y	GB-A- 419 690 (STANDARD OIL) * Whole document, in particular page 3, line 91 - page 4, line 20 *	7,17	
D,Y	US-A-4 482 357 (HANLON) * Whole document *	23,24	
A	US-A-3 717 446 (HOWLAND et al.) * Whole document *	1-24	
A	US-A-4 325 708 (BAGNETTO) * Whole document *	1-24	
A	FR-A-1 382 910 (ESSO) * Whole document *	1-24	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 173 456 (SCHEULE et al.) * Whole document *	1-24	C 10 L
A	US-A-4 022 589 (ALQUIST et al.) * Whole document *	1-24	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-03-1990	DE LA MORINERIE B.M.S.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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