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# **EUROPEAN PATENT APPLICATION**

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- (5) Anti-fouling fuel composition.
- © A fuel composition for reducing and/or preventing carburetor or fuel injector fouling in an internal combustion engine is described. The fuel delivered to the carburetor or fuel injector means comprises gasoline and an effective amount of a condensation product of a branched C<sub>12</sub>-C<sub>30</sub> carboxylic acid and an alkylene amine.

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#### **ANTI-FOULING FUEL COMPOSITION**

#### BACKGROUND OF THE INVENTION

This invention is directed to an anti-fouling fuel composition and to a method for using same. More specifically, the present invention is directed at a fuel composition having particular applicability in minimizing and/or preventing fouling in gasoline engines equipped with carburetors or with electronically controlled multiport fuel injectors.

The use of detergents to prevent and/or minimize carbonaceous deposits in internal combustion engines is well-known. The need for improved carburetor detergents has been accentuated by recent changes to engines particularly for environmental considerations. In conventional carburetor-equipped vehicles detergents have been added to the fuel to minimize deposits, particularly on the throttle plate and throttle bore. Deposits in these areas may lead to poor performance, rough idling, stalling, higher hydrocarbon emissions and poor fuel economy.

One of the most significant improvements which has been made to automobile engines in recent years has been the widespread use of fuel injection to improve the performance and fuel economy of internal combustion engines. While carburetor-equipped internal combustion engines admix the air and fuel for distribution through a manifold to all of the cylinders, in a multi-port fuel injected engine the fuel is injected into the manifold close to the intake valve of each cylinder for combustion. Fuel injection systems are of two basic types, mechanically controlled and electronically controlled. The early fuel injected engines were 20 controlled mechanically, i.e., the operation of each cylinder was controlled by fuel pressure. Recently, however, the use of electronically controlled fuel injection engines has become increasingly widespread. In an electronically controlled fuel injection system sensors disposed in the exhaust are employed to maintain the air to fuel ratio within narrow limits. Electronically controlled fuel injection systems offer the same performance and fuel economy benefits that would be achieved with mechanically controlled fuel injection systems and also serve to more closely regulate fuel-air mixtures to thereby enable the catalytic converter to oxidize carbon monoxide and hydrocarbons to carbon dioxide and simultaneously to reduce nitrogen oxides and thus meet emissions control legislation. Such legislation, imposing as it did strict control of exhaust pollutants, utimately led to the development and widespread application of new technologies.such as electronic fuel injection.

It has been found that the electronically controlled fuel injector systems have small port openings which are prone to fouling by deposits. These deposits are believed to occur, at least in part, by gasoline and oil vapor, which is present in close proximity to the injector tip, becoming baked onto the hot surfaces of the injector pintle and on the surfaces of the annulus surrounding the pintle when the engine is shut off. These deposits restrict the fuel flow to that particular cylinder. This, in turn, causes a sensor disposed in the exhaust to detect a higher than desired oxygen to fuel ratio. The sensor will attempt to correct this condition by increasing the amount of fuel injected into all of the cylinders. This, in turn, will result in a lower than desired oxygen to fuel ratio in the exhaust. The sensor then will attempt to correct this by decreasing the amount of fuel injected in to each cylinder. This cyclical adjustment of the oxygen to fuel ratio ranging between too lean a mixture and too rich a mixture can at times result in poor operating performance of the vehicle. In addition, close tolerances in this new type of injector and concurrently higher underhood temperature also tend to enhance deposit formation resulting in poor vehicle driveability and exhaust pollutant levels which exceed limits set by emissions control legislation.

It has been found that conventional gasoline detergents, which have proven effective in preventing and/or eliminating carburetor deposits are not particularly effective in removing and/or preventing deposit build-up that may occur in electronically controlled fuel injection systems. Presently available methods for removing deposits from fuel injector orifices typically comprise either mechanically cleaning the injectors or the addition to the fuel of relatively large quantities, of particular additives. Mechanical cleaning, which may involve either the complete removal of the injector for manual deposit removal or the use of polar solvents for flushing the deposits free, is not desired because of the relatively high cost and inconvenience. Currently available additives are not particularly desirable because product recommendations indicate they must be used at relatively high concentrations, i.e. about two to about four thousand pounds per thousand barrels of fuel.

To be useful commercially a gasoline additive for reducing and/or preventing carburetor and/or injector port fouling must be effective at low concen tration, must not significantly affect the combustion characteristics of the fuel and must not foul the catalytic converter catalyst.

The use of fatty acid polyamides in 2-cycle gasoline engines and in lubricants is known. U.S. Patent No. 3,169,980 discloses the use of polyamides as detergent compositions for two cycle engines where the polyamide comprises

R<sup>2</sup>
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H<sub>2</sub>N[R<sub>1</sub>N]<sub>n</sub> R<sub>1</sub>-NH<sub>2</sub>

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where R, contains 2 to 4 carbon atoms;

R<sub>2</sub> is hydrogen or an acyl group derived from a mixture of about 5 to about 30 mole percent of straight-chain fatty acid and about 70 to about 95 mole percent of branched-chain fatty acid, where the fatty acid contains from about I2 to about 30 carbon atoms and n is an integer of from I to 5. The examples disclose the preparation of the polyamide of tetraethylene pentamine utilizing a mixture of stearic acid and methyl branched stearic acid. While the use of these compounds would be useful in keeping the carburetor clean, there usually is not a concern about carburetor fouling, since the screws regulating the air to fuel ratio are not sealed on a two cycle engine. In addition, two cycle engines typically are not designed for high mileage-type applications. These additives typically are added to the fuel at a rate of about 500 pounds per thousand barrels (ptb). However, use of this high additive level in four cycle engines would not be desirable based on economic and operational considerations.

- U.S. Patent No. 3,II0,673 discloses the use of the above-noted fatty acid polyamide as a pour point depressant and as a detergent for lubricating oils.
- U.S. Patent No. 3,897,224 is directed at an ashless dispersant for gasoline which comprises an amide derived from an aliphatic polyamine and a high molecular weight monocarboxylic acid. The monocarboxylic acid utilized has a molecular weight ranging between about 600 and 3,000.
- U.S. Patent No. 3,231,348 is directed at the use of alkyl-and alkenyl-substituted diethylene triamines to reduce or eliminate the formation of deposits in the fuel induction system of an engine.
- It is believed the use of fatty acid polyamides in gasoline at effective levels may emulsify any water present unless a demulsifier is added.

Accordingly, it would be desirable to provide an additive package for gasoline which will be effective in reducing and/or eliminating fouling without appreciable additive losses or emulsification.

It also would be desirable to provide an additive package having a demulsifying agent which is effective in the presence of both neutral and basic waters.

It also would be desirable to provide a gasoline additive package which is relatively inexpensive and effective at low concentrations to reduce and/or eliminate carburetor and/or injector fouling.

It also would be desirable to provide a gasoline additive package which is non-corrosive, non-deleterious to the emissions catalyst, and does not affect the combustion characteristics of the fuel.

It also would be desirable to provide a gasoline additive package which could be easily added to the finished gasoline at any point during the storage and/or distribution system.

#### SUMMARY OF THE INVENTION

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The present invention is directed at a fuel composition for minimizing and/or preventing carburetor or injector fouling in a four cycle combustion engine. The composition comprises:

A. gasoline

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B. an anti-fouling agent having the formula:

R<sup>2</sup>
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| H<sub>2</sub>N[R<sub>1</sub>N]<sub>n</sub> R<sub>1</sub>-NH<sub>2</sub>

wherein: R<sub>1</sub> is C<sub>2</sub>-C<sub>4</sub>

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 $R_z$  is hydrogen or  $R_s$  -  $\ddot{C}$  where  $R_s$  is hydrogen, alkyl, aryl, alkaryl or aralkyl; and n is an integer of I to 5.

The present invention also is directed at a method for reducing and/or preventing fouling of internal combustion engines, said method comprises delivering to said engine a fuel comprised of an effective amount of an additive comprising

5 wherein: R, is C2-C4

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 $R_2$  is hydrogen or  $R_3$  -  $\ddot{C}$  where  $R_3$  is hydrogen, alkyl, aryl, alkaryl or aralkyl; and n is an integer of l to 5.

The composition preferably further comprises a demulsifying agent. The anti-fouling agent preferably is the condensation product of a fatty acid and an alkylene amine where alkylene amine is selected from the group consisiting of diethylene triamine, triethylene tetramine, tetraethylene pentamine, heptaethyleneoctamine, tetrapropylene pentamine and hexabutylene heptamine. A particularly preferred composition comprises the reaction product of methyl-branched or aromatic-branched stearic acid and tetraethylene pentamine.

**DETAILED DESCRIPTION OF THE INVENTION** 

The present invention is directed at a fuel composition including an anti-fouling agent and a method for using same for reducing and/or preventing fouling of internal combustion engines. The anti-fouling agent comprises an effective amount of a compound having the formula

R2
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H2N[R1N]n R1-NH2

wherein: R<sub>1</sub> is C<sub>2</sub>-C<sub>4</sub>

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 $R_2$  is hydrogen or  $R_3$  - C where  $R_3$  is hydrogen, alkyl, aryl, alkaryl or aralkyl; and n is an integer of I to 5.  $R_3$  preferably is alkyl and more preferably is a substituted stearic acid.

Preferred anti-fouling agents comprise the condensation products of fatty acids and polyamines where the fatty acids comprise  $C_{12}$ - $C_{30}$  fatty acids and the amines comprise polyalkyleneamines, preferably where the alkylene groups are  $C_2$  to  $C_4$ . Preferred fatty acids comprise fatty acids with  $C_1$ - $C_3$  branches with  $C_1$  to  $C_4$  branches being particularly preferred. Particularly preferred fatty acids are methyl-branched stearic acid, aryl branched stearic acid and alkaryl-branched stearic acid. A particularly preferred fatty acid is methyl-branched stearic acid. As used herein the term "methyl-branched stearic acid" refers to a  $C_{17}$  straight chain fatty acid having a methyl side chain. The terms aryl-branched stearic acid and "alkaryl-branched stearic acid" refer to  $C_{18}$  straight chain fatty acids having aryl or alkaryl pendant groups, respectively. Preferred polyalkylene amines comprise diethylene triamine, triethylene tetramine, tetraethylene pentamine, hexaethylene heptamine, heptaethylene octamine, tetrapropylene pentamine, and tetrabutylene heptamine. A particularly preferred anti-fouling agent comprises the condensation product of methyl-branched stearic acid and tetraethylene pentamine.

The ratio of the fatty acid to the amine typically may range between a mole ratio of about 1:1 and about 4:1. A particularly preferred mole ratio when the reactants comprise methyl-branched stearic acid and tetraethylene pentamine is about 3:1.

The concentration of the fatty acid polyamide may range between about 5 and about 50 ptb, preferably between about 10 and about 30 ptb, more preferably between about 15 and about 25 ptb.

The condensation reaction of stearic acid and tetraethylene pentamine at a mole ratio of 3:l may be represented as follows:

As used hereinafter, the term "isostearic acid" refers to-stearic acid which has a pendant alkyl group irrespective of the exact position of the pendant group. A particularly preferred stearic acid is a methyl-branched stearic acid, preferably branched at the 9 or 10 carbon atom. To prepare this condensation product, initially half of the isostearic acid was charged to the reactor in order to obtain a level sufficient to permit agitation and heat transfer. The tetraethylene pentamine then was added slowly at 110°C and the remaining acid was added. Then, the batch temperature was raised slowly to drive the condensation reaction. Water of condensation was removed through an overhead vapor removal system assisted by a nitrogen sparge. At a temperature of approximately 160°C when most of the water had been removed, vacuum stripping was applied and the reactor temperature was raised to 200°C to drive the condensation reaction to completion. After the reaction had been driven to completion, the product was cooled to 120°C and a small amount of water, i.e. about 2% by weight of the original charge, was added to hydrolyze any resin lactone impurity in the isostearic acid. This hydrolysis step also shifted the equilibrium to remove or eliminate any unreacted primary amine. The excess water then was removed by nitrogen stripping at 120°C.

Bench scale and on-the-road tests were conducted to evaluate the effectiveness of the subject fatty acid polyamides in reducing and/or removing carburetor deposits in internal combustion engines.

## **COMPARATIVE EXAMPLE I**

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In this Comparative Example, commercially available detergents were added to gasoline to determine if the detergents were effective in preventing carburetor deposits. The test procedures utilized are set forth in the CRC "Research Technique for the Study of Carburetor Cleanliness of Gasoline" SAE technical paper 831708, by J. J. Malakar, et al., the disclosure of which is incorporated herein by reference. In this test a 300 CID Ford six cylinder engine was specially tuned to accelerate carburetor deposits. The engine was fitted with a carburetor with removable throttle plate and throttle bore sleeves. The throttle plate and throttle bore sleeves were cleaned and weighed at the start of the test. The engine was run for a total of 20 hours, cycling between idle and middle cruise speed, utilizing a standard reference gasoline without any detergent. Following this run, the throttle plate bore and sleeves were weighed, rated and cleaned. The average values for the deposits and ratings of the throttle plate and sleeve are presented in Table I. Additional tests indicated as tests A-E were conducted utilizing various concentrations of commercially available additives utilizing the same test procedure. At the end of the test, the throttle plate and throttle bore sleeve were removed, rated and weighed. The rating of the sleeve and throttle plates was determined by the method described the report "Carburetor Cleanliness Test Procedure State of the Art Summary Report"; 1973-1981 Report No. 529 Coordinating Research Council, Appendix C, April 1983, the disclosure of which is incorporated herein by reference. Utilizing this procedure, the sleeve and throttle plate were rated on a scale of 0-i0 where a rating of I0 denoted a completely clean surface. The results of these tests also are set forth in Table I.

## **EXAMPLE I**

Varying concentrations of the fatty acid polyamide of isostearic acid and tetraethylene pentamine (ISAT) were added to the base gasoline of Comparative Example I. The ISAT was added as concentrate which also included a conventional corrosion inhibitor, a demulsifier and solvent. The demulsifier comprised an alkylphenol-formaldehyde resin and ethylene oxide-propylene oxide, where the alkylphenol was a nonylphenol. The solvent comprised 5.68 wt.% 2-ethyl hexanol with the balance being Solvesso 100, an aromatic hydrocarbon solvent. A summary of the composition of the adpack utilized was as follows:

10	Component ·	Wt.%
	Detergent .	42.61
	Corrosion Inhibitor	2.84
15	Demulsifier	1.71
	Solvents	52.84

The same engine test procedures were utilized as set forth in Comparative Example I. A summary of the engine test results for varying concentrations of this additive also are set forth in Table I. From these test results it can be seen that the use of the polyamide was effective in preventing carburetor deposits.

50 55	40 45	35	30	25	20	15	10	5
	-	٠	TABLE	<b>⊢i</b>			٠	
	EFFECTIVEN	ENESS OF DETER	DETERGENTS IN	KEEPING	ARBURE	CARBURETOR CLEAN		
ADDITIVE IDENTIFICATION	ADDITIVE CONC. (ptb)	SLEEVE (1	VE (mg)	THROTTLE PLATE DEPOSIT (mo	LE (mg)	SLEEVE	THROTTLE PLATE RATI	TTLE
None	0.0	33.3	en en	12.6		5.30	4.31	
<b>4</b> -	7.0	11.7	.7	7.1		86.9	5.78	78
<b>M</b>	8.0	6.2	7	4.1		7.09	6.75	75
υ	0.8	ř	й• й•	4.0		8.02	6.30	30
U	7.0	5.4	₹.	1.2		7.07	7.05	55
۵	15.0	4.7	7	3.0	-	7.60	6.45	5
<b>Q</b>	7.3	7.7	7.	1.0		7.07	6.72	72
N	15.0	1.0	0	0.4		8.33	7.50	0:0
E	. 7.3	5.6	. 9	1.1		7.56	7.50	09
Ħ	4.9	14.5	د	10.4		6.21	4.90	06
ISAT	19.9	2.7		1.1		7.56	7.81	31
ISAT	19.9	3.6	9	0.7		.7.09	7.25	25
ISAT	10.1	5.6	9	0.8		29.9	6.82	

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## **COMPARATIVE EXAMPLE 2**

These test procedures were designed to determine the effectiveness of various additives in cleaning up fouled carburetors. The engine utilized was the same engine as Comparative Example I. The carburetor throttle plate and the throttle bore sleeves were cleaned at the start of the test. The engine was run for 20 hours on a detergent-free gasoline, cycling between idle and medium cruise speed. At the end of this period, the carburetor parts were visually rated and weighed. Then various commercially available additives were added to the fuel. The test procedure then was repeated with 20 hours of driving, cycling between idle and medium cruise speed at the end of the test, the throttle plate and throttle bore were again removed, rated and weighed. The results of these tests are presented in Table II.

# **EXAMPLE 2**

The test procedures utilized in this example were similar to those of Comparative Example 2 with the exception that the additive utilized was the condensation product of isostearic acid and tetraethylene pentamine. The results of these tests also are set forth in Table II.

5		ITS	THROTTLE PLATE RATING	4.31	4.90	5.07	4.82	6.37	5.65	4.87	4.92	5.27	6.97	6.25
15		CARBURETOR DEPOSITS	SLEEVE	5.30	5.64	5.72	5.93	5.81	6.10	6.18	5.47	5.68	6.85	6.93
20	II	CLEANING-UP CARBU	THROTTLE PLATE DEPOSIT (mg)	12.6	13.0	10.1	14.2	6.1	. 7.2	8.2	12.0	11.4	1.6	6.3
<i>30</i>	TABLE	DETERGENTS IN CL	SLEEVE DEPOSIT (mg)	33.3	37.6	31.0	36.7	39.1	27.0	18.4	43.4	31.3	4.4	. 8.4
40		EFFECTIVENESS OF	ADDITIVE CONC. (ptb)	0.0	10.5	10.5	7.0	10.6	14.7	10.5	10.1	15.0	19.9	19.9
<b>4</b> 5		日日	ADDITIVE IDENTIFICATION	None	<b>V</b>	æ	. <b>U</b> -	<b>U</b> :	Ω-	<b>L</b> .,	ISAT	ISAT	ISAT	ISAT

From a review of the data of Tables I and II, it can be seen that the fatty acid polyamide was effective in preventing and/or cleaning up carburetor deposits.

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Fleet tests also were run to determine the utility of various detergents in preventing and/or reducing carburetor deposits. In these tests, two techniques were used to assess the performance of the carburetor detergents. Visual determinations were made of the amount of deposits on each of the carburetors. In addition, emission measurements prior to the catalytic converter, also were taken. Prior to the start of the tests, each of the 24 vehicles to be utilized was driven an average of approximately 5,434 kilometers on a detergent-free base fuel, which had an RON of 94.6 and a MON of 85.4. To this fuel were added 20 ptb of a standard detergent. These cars were run on this fuel to provide a recent driving history on a common fuel. The carburetors of each vehicle then were inspected and the emissions prior to the catalyst were measured. The fleet was divided into four groups of six cars each to provide each group with a representative range of degrees of carburetor fouling.

#### **COMPARATIVE EXAMPLE 3**

In this test, the vehicles were fueled with base fuel to which had been added either 7 ptb of Additive A or 20 ptb of Additive B, both commercially available detergent additives. Additive A comprised an amineamide carboxylate manufactured by DuPont and sold under the trade name DMA-54. Additive B comprised another commercially available detergent comprising a succinimide. The vehicles then were driven for 10,000 kilometers over a 160 kilometer route that included about 33% city driving, 4% highway driving and 20 63% suburban driving. The carburetors were removed, visually inspected and rated at the end of the test. The emissions prior to the catalyst were measured at the start of the test and also at the end of the test. These results are summarized in Table III.

#### **EXAMPLE 3** 25

In this test, two six car fleets generally similar to those of Comparative Example 3 were utilized. The same detergent-free base fuel of Comparative Example 3 was used. To the fuel of one six car fleet was added I0 ptb of the previous described fatty acid polyamide and to the fuel of the other fleet was added 20 ptb of the fatty acid polyamide. The vehicles were driven over the same route as in Comparative Example 3 for the same total driving distance. The degree of carburetor fouling was noted and the emissions prior to the catalytic converter were measured. These results also are set forth in Table III. From this table it also can be seen that the ISAT at 20 ptb improved overall carburetor ratings and also decreased emissions.

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			0.90	2.04	0.87	1.51		
5		₩ 20(1) 800	1.05	0.82	0.45	1.60		ling.
10		EMISSIONS PRIOR TO CATALYTIC CONVERTER  IDLE (2) CO(1) CO(2) HC(1) HC(2) CO (VOI. %)	273	139	184	1,18		ional fou
15	EMISSIONS	ATALYTIC HC(1)	171	109	222	136		es addit:
20		ONS PRIOR TO C CO(1) CO(2)	2.55	0.73	1.19	2.24		cest.
<b>2</b> 5	III RATINGS AND	SSIONS PI	1.49	1.20	0.57	2.39		at start of test. at 10,000 KM, at end of test. vement; a negative number ind
	TABLE	$\frac{\text{EMISSION}}{\text{IDLE}}$ $\text{HC}(1)  \text{HC}(2)  \text{CC}$	231	. 178	291	209		at start of test. at 10,000 KM, at ovement; a negative
30	RAGE CAR			171	299	245		it start at 10,000 rement;
35	TABLE FLEET AVERAGE CARBURETOR	CHANGE IN CARBURETOR RATING**	+0.13	-0.44	+0.05	+0.41	-	Denotes measurements and ratings at start of test. Denotes measurements and ratings at 10,000 KM, at end of test. A positive number indicates improvement; a negative number indicates additional fouling.
40		CARBURETOR OVERALL AVERAGE RATING (1)* (2)*		5.44	5.82	6,33	 	ents an ents an c indic
			5.37	5.89	5.77	5.92		sureme sureme sumbes
<b>4</b> 5		ADDI- TIVE CONC. (PTB)	10	50	10	70		Denotes measurements Denotes measurements A positive number in
50	·	ADDITIVE	Additive A	Additive B	ISAT	ISAT		(1) Denote (2) Denote ** A posi

From a comparison of the data in Table III it can be seen that the fatty acid polyamide at 20 ptb was particularly effective in cleaning up most areas of the carburetors.

## **COMPARATIVE EXAMPLE 4**

In this Comparative Example, one of the two six car test fleets from Comparative Example 3 was utilized with a conventional detergent at 7 ptb in the base fuel of Comparative Example 3. The vehicle was driven for 5,000 kilometers over the same I60 kilometer route of Comparative Example 3. The results are presented in Table IV.

#### **EXAMPLE 4**

In this Example the same four six-car test fleets previously used were utilized in this Example. The base fuel used in Comparative Example 3 and Comparative Example 4 was utilized here but with the addition of various additives. To one six car test fleet was added 20 ptb of the fatty acid polyamide. To another six car test fleet was added 20 ptb of the fatty acid polyamide and 7 ptb of the amine-amide carboxylate. To the third six car test fleet was added 20 ptb of the fatty acid polyamide and 20 ptb of a succinimide. At the end of the test the carburetor ratings were determined and the emissions prior to the catalytic converter were measured. The results of these measurements are set forth in Table IV. From a review of data in Table IV, it can be seen that the combination of 20 ptb of the fatty acid polyamide alone or in combination with other carburetor detergents was effective in cleaning up carburetor deposits.

5				1) co(2) (vor %)	1.18	1.01	1.10	0.56	
			糕	$\sim$	06.0	1.51	0.87	1.74	ling.
10			CONVERT	1500 RPM HC(2) CO (PPM)	302	86	. 66	192	onal fou
15		CONS	WALYTIC	HC(1) (PI	273	118	184	183	s additi
20		ND EMISS	TOR TO CA	1) CO(2) (VOL 8)	1.68	1.65	1.63	0.81	st. indicate
25	ы	ATINGS A	EMISSIONS PRIOR TO CATALYTIC CONVERTER	. 8	2.55	2.24	1.19	0.73	t of test. 5,000 KM end of test. a negative number indicates additional fouling.
20	TABLE IV	JRETOR R	EMIS	IDLE HC(2) (M)	152	211.	189	. 183	start of test. the 5,000 KM er ent; a negative
30		GE CARBU		HC(1) HC(2) (PPM)	231	209	291	178	start o the 5,0 ment; a
35		FLEET AVERAGE CARBURETOR RATINGS AND EMISSIONS		CHANGE IN CARBURETOR RATING**	80*0-	+0,31	+0.52	+0.49	Denotes measurements and ratings at start of test. Denotes measurements and ratings at the 5,000 KM end of test. A positive number indicates improvement; a negative number in
40			CARBURETOR	OVERALL AVERAGE RATING 1)* (2)*	5.42	6.64	6.37	5.93	ents and ents and r indice
				_	5.50	6.33	5.85	5.44	surem surem numben
<b>4</b> 5			ADDI-	(PTB)	7	20	20 <del>+</del>	20+ 20	s mea s mea tive
50			ADDITIVE		Additive A	ISAT	ISAT + Additive A	ISAT + Additive B	(1) Denote (2) Denote ** A posi

While the data described above discloses a utility of fatty acid polyamides as carburetor detergents, these additives also are effective in preventing and/or reducing deposits in multi-port fuel injection systems.

## **COMPARATIVE EXAMPLE 5**

In this Comparative Example, a multi-port fuel injected 1985 Buick Somerset Regal equipped with a 3 liter, 6 cylinder engine was used. The car was driven for approximately 1,019 miles using a regular grade 87 octane, detergent-free unleaded fuel with a new set of injectors. The driving cycle employed to foul the injectors was normal commuter use. Following the test, the injector fouling was measured by measuring the emissions before the catalytic converter and by a pressure differential test. In this test, the fuel rail was pressurized to 49 psig and each injector is pulsed individually for 0.5 seconds. The difference in the pressure drop or leakdown between injectors is a rough measure of the degree to which the injectors are obstructed, i.e. the greater the numerical difference between the highest and lowest values, denoted as  $\Delta$  P difference, the greater the driveability problem. A summary of the results periodically up to 1,019 miles is set forth in Table V. Driveability of the vehicle was poor with emissions and leakdown data confirming fouled injectors. A conventional carburetor detergent then was added to the fuel at the 40 ptb level. The vehicle then was run for 371 miles in normal commuter use. The emissions and the pressure differential during the test are also presented in Table V. Throughout this period the driveability remained poor, with emissions and leakdown data confirming fouled injectors. From a review of this data, it can be seen that this conventional carburetor detergent did not clean-up the fouled injectors.

## 20 EXAMPLE 5

In this Example, 20 ptb of the previously described fatty acid polyamide were added to the same base fuel. The car of Comparative Example 5 having fouled injectors then was driven for an additional 762 miles in normal commuter use. The emissions prior to the catalytic converter and the pressure differential were measured periodically As shown by the data presented in Table V, the use of the fatty acid polyamide detergent resulted in a significant decrease in emissions over a relatively few miles of driving. After 552 miles, the driveability improved to the point where the emissions, pressure differential test and driveability all indicated that the injectors had been returned substantially to "as new" condition. Generally confirmatory data also were obtained at 762 miles. The difference between the highest and lowest values of the pressure differentials also decreased, indicating decreased injector fouling.

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5		Δ P DIFFERENCE	2.0	2.0	0.9	0 <b>.</b> 8	5.5	5.5	4.0	1.5	1.0	0.5	1.5
10		9	16.5	13	11	15	10.5	10.5	12.0	10.5	8.5	9.5	11.0
		5	14.5	12	10.5	14	10.5	10.5	12.0	11.0	8.5	9.5	11.0
15	ICLE	ম। ক	14.5	13	11	14	10.5	10.5	12.0	10.5	8.5	9.5	11.0
	PED VEH	INJECTOR AP TESTS AP FOR CYLINDER #	14.5	13	11	14	10.5	10.5	12.0	11.0	8.0	9.5	11.0
20	INJECT	ECTOR AP TEST FOR CYLINDER	14.5	13	11	14	11	10.5	12.0	11.0	8.5	10.0	11.5
25	N FUEL	INJE AP	14.5	11	ß	7	5.5	5.0	8.0	9.5	. 7.5	9.0	10.0
30	TABLE V PRESSURE O	RPM CO(VOL%)	0.71	0.75	2.44	2.15	2.54	2.22	1.33	0.70	1.42	0.73	0.62
35	T ERENTIAL P	EMISSIONS 2500 OL8) HC(PPM)	154	9	1158	1207	1231	1137	262	18	465	63	73
	TABLE VEMISSIONS AND DIFFERENTIAL PRESSURE ON FUEL INJECTED VEHICLE	≥	0.59	08.0	1.99	1.87	2.48	1.76	1.64	0.73	1.12	08.0	0.78
40	MISSIONS	IDLE HC(PPM) CO	188	170	1422	1418	1091	1394	196	136	471	154	186
<b>4</b> 5	-1	TEST	0	367	954	1019/0	153	371/0	140	301	366	552	762
50		ADDITIVE CONC (PTB)	0	<b>o</b> .	0	0/40	40	20	20	20	20	20	20
55		ADDITIVE	None		-	Comm. Carb. Det.	٠	ISAT	<sub>-</sub>				

## **COMPARATIVE EXAMPLE 6**

In this Comparative Example three vehicles, two I986 Chrysler LeBarons (Vehicles I and 2) with 2.2 liter turbocharged 4 cylinder fuel injected engines and one I985 Buick Park Avenue (Vehicle 3) equipped with a 3.8 liter 6 cylinder fuel injected engine were tested. The emissions prior to the catalytic converter were measured after which the cars were run on a detergent-free unleaded gasoline on a cycle designed to promote injector fouling. The hydrocarbons prior to the catalytic converter again were measured when the vehicles were judged to exhibit poor driveability. The vehicles were judged to have CRC driveabilities of 400 + by a modified CRC Intermediate Temperature Durability Test, Test No. 5I2, the disclosure of which is incorporated herein by reference. In this test a new car typically has driveability ratings of below about 40 while ratings above, I00 typically indicate severe driveability problems. This data is presented in Table VI.

#### **EXAMPLE 6**

The three vehicles of Comparative Example 6 then were refueled with the same fuel of Comparative 6, but with the further addition of about 25 ptb of ISAT. The vehicles then were driven on the same driving cycle of Comparative Example 6 for the indicated miles at which time the CRC driveability of each car had improved significantly. The results also are tabulated in Table VI.

<b>4</b> 5	40	35	· 30	25	20	10 15	5
			TABLE	E VI			
		FUEL	INJECTED	VEHICLE	TESTS		
			•				
			Antı- Fouling	Agent Conc.			
			Agent	(ptb)	Vehicle 1	Vehicle 2	Vehicle 3
Hydrocarbon Emissions (Injectors Clean)	(mďď) s	-	· 		1600	1800	2700
Miles to Foul Injectors Hydrocarbon Emissions ( CRC Driveability	ors s (ppm)		None	0	1576 8500 400+	2057 9000	3673 9000 4004
Miles to Clean Injectors Hydrocarbon Emissions (ppm CRC Driveability	tors s (ppm)		ISAT	25	441 9000 30	443 1200 23	451 ** 34
	•		•				
* Not measured.							

Typical fuels will comprise several additives including a demulsifier to minimize any water pick-up, antirust agents, etc. A particularly preferred demulsifier comprises a alkylphenol-formaldehyde resin ethylene oxide-propylene oxide.

#### 0 240 255

The anti-fouling agent discussed hereinabove may be added to the fuel at any point in the manufacturing or distribution process.

In this patent specification:

1 pound = 453.6 g

1 barrel = 159.0 liter 1 mile = 1.60935 km.

Gauge pressure in pounds per square inch gauge (psig) is converted to kPa equivalent by multiplying by 6.895.

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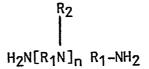
#### Claims

1. A fuel composition for a four cycle internal combustion engine, said fuel composition comprising:

A. gasoline:

B. an anti-fouling agent which has the formula

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wherein: R<sub>1</sub> is C<sub>2</sub>-C<sub>4</sub>

R<sub>2</sub> is hydrogen or R<sub>3</sub>- C where R<sub>3</sub> is hydrogen, alkyl, aryl, alkaryl or aralkyl; and n is an integer of 1 to 5, or which is a condensation product of a branched C12 to C30 carboxylic acid and an alkylene amine.

- 2. The fuel composition of claim 1 wherein R<sub>3</sub> comprises an alkyl.
- 3. The composition of claim 2 wherein R₃ or the branched carboxylic acid is stearic acid or substituted stearic acid.
  - 4. The composition of any one of claims 1 to 3 comprising demulsifier.
- 5. The fuel composition of any one of claims 1 to 4 wherein the alkylene amine is selected from diethylene, triamine, triethylene tetramine, tetraethylene pentamine, hexaethylene heptamine heptaethylene octamine, tetrapropylene pentamine and hexabutylene heptamine.
  - 6. The fuel composition of claim 5 wherein the alkyleneamine comprises tetraethylene pentamine.
- 7. A method for reducing and/or preventing fouling of an internal combustion engine, said method comprising delivering to said engine a fuel composition according to any one of claims 1 to 6.
  - 8. A method as in claim 7 wherein the engine comprises a multi-port, electronically controlled fuel injection system.
    - 9. A method as in claim 7 wherein the engine comprises a carburetor.

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