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(54) Improved fuel composition for multi-port fuel injection systems, and additive concentrates therefor.

(57) An additive package, a fuel composition including the additive package and a method for reducing and/or preventing injector fouling in a multi-port fuel injection means utilizing the fuel composition are described. The additive package comprises a particularly described amine and a particularly described demulsifier. A particularly preferred composition comprises an amine, an amine oxide and a demulsifier. The fuel composition prevents and/or reduces fouling of the fuel injector means.

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IMPROVED FUEL COMPOSITION FOR MULTI-PORT FUEL INJECTION SYSTEMS, AND ADDITIVE CONCENTRATES THEREFOR.

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 injector fouling in gasoline engines equipped with electronically controlled multiport fuel injectors.

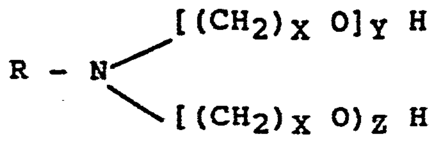
Over the past several years, improvements have been made in the performance of internal combustion engines. One of the most significant improvements which has been made has been the widespread use of fuel injection to improve the performance and fuel economy of internal combustion engines. While carburetor-equipped internal combustion engines admix the air and fuel for distribution through a manifold to all of the cylinders, in a 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 controlled mechanically, i.e., the operation of each injector was controlled by 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 richer than desired fuel to air ratio in the exhaust. The sensor then will attempt to correct this by decreasing the amount of fuel injected into each cylinder. This cyclical adjustment of the fuel to air 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 exceeding exhaust pollutant levels 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 one to about two tons per thousand barrels of fuel.

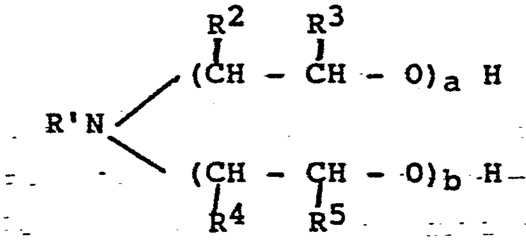
To be useful commercially a gasoline additive for reducing and/or preventing injector port fouling must be effective at low concentration, must not significantly affect the combustion characteristics of the fuel and must not foul the catalytic converter catalyst.

Additives have been added to gasoline to improve certain properties of the fuel. U.S. Patent No. 3,115,400 discloses the use of compounds of the structure



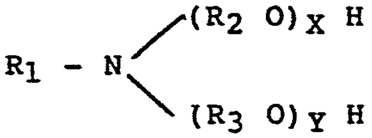
where R is a C_6-C_{22} aliphatic hydrocarbon radical, X is an integer from 2 to 4, Y is an integer of at least 1, and Z is an integer of at least 1, for use in motor fuel to prevent or reduce carburetor icing.

U.S. Patent No. 4,409,000 discloses combination of hydroxy amines and hydrocarbon-soluble carboxylic dispersants as engine and carburetor detergents for normally liquid fuels. Among the hydroxy amines disclosed are compounds of the formula



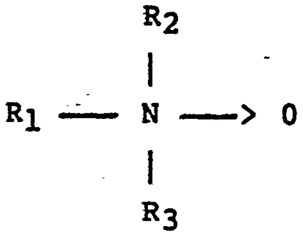
where R' may be an alkyl radical containing from about 8 to about 30 carbon atoms, where R^2, R^3, R^4 and R^5 each may be hydrogen and where a and b may be integers from 1 to 75.

U.S. Patent No. 4,231,883 discloses the use of a compound of the formula



where R_1 is a C_{12}-C_{36} aliphatic hydrocarbon group, R_2 and R_3 are divalent hydrocarbon radicals containing 2-4 carbon atoms and X and Y are integers from 1-4, for friction reduction in lube oils. Preferred compounds comprise N,N-bis (2-hydroxyethyl) hydrocarbylamines.

U.S. Patent No. 3,387,953 is directed at the use of organo-substituted nitrogen oxides, particularly amine oxides for rust inhibition and as anti-icing agents in gasoline. Several representative formulas for amine oxides are given including the following:



$$R_1 - \overset{\displaystyle R_2}{\underset{\displaystyle R_3}{\overset{|}{\underset{|}{N}}}} \longrightarrow O$$

where: R_1 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; and R_2 and R_3 are the same or different and are C_1-C_{24} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic or heterocylic. R_2 and R_3 preferably comprise hydroxy substituted alkyls. These compounds typically are added to gasoline in a concentration within the range of about 2.0 to about 100 pounds of amine oxide per 1,000 barrels of gasoline (ptb). Among the most preferred additives is bis(2-hydroxy ethyl) cocoamine oxide.

U.S. Patent No. 3,594,139 is directed at a rust-inhibitor concentrate that can be blended with gasoline year-round. This patent also discloses the use of amine oxides having the aforementioned formula for use as gasoline additives for rust prevention. This patent also discloses a particularly preferred concentrate comprising bis(2-hydroxy ethyl) cocoamine oxide.

The amine oxides described above have been typically used to inhibit rust and carburetor icing, although these amines also were known as carburetor detergents.

It has been discovered that use of hydroxy substituted amine oxides can result in additive losses because of high water solubility and adsorption on polar surfaces.

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.

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.

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

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

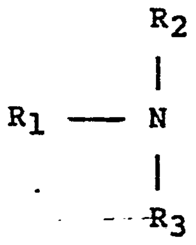
It also would be desirable to provide a gasoline additive package which could be easily added to the finished gasoline at any point during the storage and/or distribution system.

SUMMARY OF THE INVENTION

The present invention is directed at a fuel composition for minimizing and/or preventing injector fouling in a multiport electronically controlled fuel injected engine. The composition comprises:

A. fuel (e.g., gasoline)

B. an anti-fouling agent having the formula:



$$R_1 - \underset{\displaystyle R_3}{\overset{\displaystyle R_2}{N}}$$

where: R_1 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; and R_2 and R_3 independently are C_1-C_{24} substituted alkyl, aryl, cycloaliphatic or heterocylic; and,

C. a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;
and mixtures thereof.

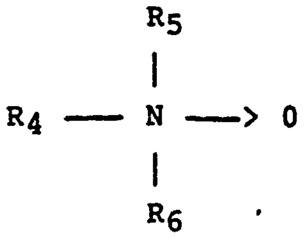
In this composition R_1 preferably is C_6-C_{20} alkyl, or alkylated aryl, and R_2 and R_3 independently are C_1-C_{12} hydroxy substituted alkyl. In a more preferred composition R_1, comprises C_8-C_{18} substituents derived from fatty acid. The additive preferably is selected from the group consisting of bis(2-hydroxy ethyl) cocoamine, bis(2-hydroxy ethyl) tallow amine, bis(2-hydroxy ethyl) stearyl-amine, bis(2-hydroxy ethyl) oleyl amine and mixtures thereof. A particularly preferred additive is bis(2-hydroxy ethyl) cocoamine. The anti-fouling agent concentration in the fuel typically may range between about 2 to about 200 ppm, (parts per million by weight based on the total weight of the fuel composition) preferably between about 20 to about 80 ppm. The active concentration of the demulsifying agent may range between about 0.1 and about 20 ppm, preferably between about 1.0 and about 8 ppm. A preferred demulsifier is selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl phenol-formaldehyde resins and polyglycols; and,

iii. oxyalkylated alkylphenol-formaldehyde resin; and mixtures thereof.

The fuel additive also may include a second, amine oxide anti-fouling agent having the following structural formula:



$$R_4 - \overset{\displaystyle R_5}{\underset{\displaystyle R_6}{N}} \rightarrow O$$

where R_4 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl, substituted aryl; R_5 and R_6 independently are C_1-C_{24} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic, heterocyclic, and mixtures thereof; and,

Preferred amine oxide anti-fouling agents include compounds wherein: R_4 is C_6-C_{20} alkyl, or alkylated aryl; and R_5 and R_6 independently are hydroxy substituted C_1-C_{12} alkyl. Particularly preferred compounds are compounds wherein R_1 comprises a C_8-C_{18} substituent. The amine oxide additive preferably is selected from the group consisting of bis (2-hydroxy ethyl) cocoamine oxide, bis(2-hydroxy ethyl) stearylamine oxide, dimethylcocoamine oxide dimethyl hydrogenated tallow amine oxide, dimethylhexadecylamine oxide , and mixtures thereof. A particularly preferred amine oxide anti-fouling agent is bis(2-hydroxy ethyl) cocoamine oxide.

A fuel composition such as gasoline, typically may further comprise:

A. about 2 to about 200 ppm bis(2-hydroxy ethyl) cocoamine; and,

B. about 0.1 to about 20 ppm of a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof.

The fuel composition more preferably comprises:

A. about 20 to about 120 ppm bis(2-hydroxy ethyl) cocoamine; and,

B. about 1 to about 12 ppm of a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof.

The preferred fuel composition also may comprise about 4 to about 40 ppm bis(2-hydroxy ethyl) cocoamine oxide.

A preferred fuel additive concentrate for internal combustion engines comprises:

A. about 5 to about 60 wt.% bis(2-hydroxy ethyl) cocoamine;

B. about 0.25 to about 10 wt.% of a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

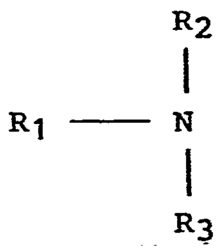
and mixtures thereof.

C. about 40 to about 95 wt.% solvent.

The fuel additive concentrate also may comprise about 1 to about 15 wt.% bis(2-hydroxy ethyl) cocoamine oxide.

The solvent preferably comprises an alkyl aromatic hydrocarbon solvent, such as xylene, and a C_4+ alcohol, preferably a C_4-C_{12} alcohol, more preferably a C_8 alcohol and most preferably a C_8 oxo alcohol. Where the ratio of the concentration of water relative to amine oxide exceeds about 0.05, a highly water and hydrocarbon soluble alcohol, preferably isopropanol, also should be added.

The present invention also is directed at a method for reducing and/or preventing fouling in a multi-port electronically controlled fuel injection system for an internal combustion engine, said method comprising delivering to said fuel injection system a fuel comprised of an effective amount of an additive comprising



$$R_1 - \overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}}$$

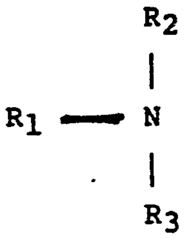
where: R_1 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; R_2 and R_3 independently C_1 to C_{24} substituted alkyl, aryl, cycloaliphatic or heterocyclic. The R_2 and R_3 preferably are hydroxyl substituted.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed at a fuel composition, a fuel (e.g. gasoline) additive package, and a method for delivering the fuel composition to a fuel injection system in which the composition has been found to be particularly effective in reducing and/or eliminating injector fouling. The present invention is directed at a fuel comprising:

A. fuel (e.g., gasoline);

B. an anti-fouling agent having the following structural formula:



$$R_1 - \underset{\substack{| \\ R_3}}{\overset{\substack{R_2 \\ |}}{N}}$$

where R_1 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl, substituted aryl; R_2 and R_3 independently are C_1-C_{24} substituted alkyl or aryl, cycloaliphatic, heterocyclic, and mixtures thereof; and,

C. a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

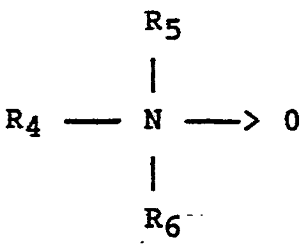
iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof.

Preferred anti-fouling agents include compounds wherein: R_1 is C_6-C_{20} alkyl, or alkylated aryl; and R_2 and R_3 independently are hydroxy substituted C_1-C_{12} alkyl. Particularly preferred compounds are compounds wherein R_1 comprises a C_8-C_{18} substituent. The additive preferably is selected from the group consisting of bis (2-hydroxy ethyl) cocoamine, bis(2-hydroxy ethyl) stearylamine, bis(2-hydroxyethyl) oleyl amine and mixtures thereof. These additives are prepared in accordance with known techniques, such as disclosed in U.S. Patent 2,541,678 the disclosure of which is incorporated herein by reference. A particularly preferred anti-fouling agent is bis(2-hydroxy ethyl) cocoamine.

Amine oxides also have been found to be effective as anti-fouling agents. While these compounds may be extracted to varying degrees into any water present, these compounds also provide anti-rust properties to the fuels. These compounds have the following structural formula:



$$R_4 - \overset{\displaystyle R_5}{\underset{\displaystyle R_6}{\overset{|}{\underset{|}{N}}}} \longrightarrow O$$

where R_4 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl, substituted aryl; R_5 and R_6 independently are C_1-C_{24} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic, heterocyclic and mixtures thereof.

Therefore, the use of these amine oxides compounds in combination with the previously described amines may provide an effective anti-fouling composition also providing anti-rust properties. These amine oxides may be prepared by well-known techniques, such as disclosed in U.S. Patent No. 3,387,953.

Where amine and amine oxides are used in combination as the anti-fouling agent, the concentration of the amine typically will range between about 2 and about 200 ppm, preferably between about 16 and about 100 ppm, while the amine oxide concentration will range between about 2 and about 80 ppm, preferably between about 4 and about 40 ppm.

The amine oxide typically has water present from the manufacturing process. While it is possible to remove most of the water, removal of the water to relatively low levels, i.e. a ratio of about 0.02 to about 0.04 of water to amine oxide, adds complexity to the manufacturing process. Therefore, the amine oxide is commercially available as a solution comprising water and a solvent, which typically is isopropyl alcohol. It has been found that when a concentrate comprising the above amine oxide solution and a solvent containing demulsifiers was admixed with gasoline and terminal tank water bottoms a three phase system resulted, two organic phases and a water phase.

Formation of two organic layers is not desirable, since this was found to result in uneven distribution of the amine oxide between layers. In addition, the second organic layer, which has a much higher amine oxide concentration, tends to adhere to surfaces, resulting in additive loss and potential contamination of subsequent hydrocarbon products that might contact these surfaces. It has been found that replacement of a portion of the isopropanol by a higher alcohol, preferably a C_4-C_{12} alcohol, more preferably a C_8 oxo alcohol, decreases the likelihood of forming a two organic layer system. While the admixture of the amine with the amine oxide may also decrease the formation of two organic phases, it is preferred that the solvent comprise a C_4-C_{12} alcohol as described above to further decrease the possibility of two organic phase formation.

A concentrate utilizing both the amine and amine oxide typically also comprises about 40 to about 95 wt.% solvent. A preferred composition range is as follows:

Component	Wt.% Range
Amine	8-32
Amine Oxide	2-8
Solvent	
Xylene	30-80
C_4-C_{12} alcohol	2-20
Isopropanol	2-16
Water	0.2-1.5
Demulsifier	1-4

The following Comparative Examples and Examples demonstrate the utility of the anti-fouling agent in reducing and/or eliminating fuel injector fouling. In the following Comparative Examples and Examples, the octane rating of the fuel utilized is the posted octane rating which is defined as:

$$\frac{\text{Research Octane + Motor Octane}}{2}$$

COMPARATIVE EXAMPLE I

In this test three 1985 Oldsmobile 98's having electronically controlled, fuel injected, 3.8 liter, six cylinder engines were driven on a commercial, unleaded, 87 octane reference fuel having a detergent concentration of about 32 ppm by weight of the fuel for approximately 3500 miles under the following driving cycle: 0.5 hours city-type driving, 0.5 hour engine off, 0.5 hour highway driving, 0.5 hour engine off. Driveability on all four vehicles became poor to very poor. The vehicles then were driven for 300 miles with a commercial premium grade 92 octane unleaded fuel containing 2.5 times the detergent used in the above reference fuel. Driveability remained unchanged. The data in Table I below show that there was still a marked reduction in fuel flow indicating that a high level of deposit was unaffected by the detergent even at the high treat rate. The percent fuel flow reduction was determined by measuring the volume of a mineral spirit that flowed through the injector under predetermined standardized conditions, including fuel pressure, pulse width and duty cycle. The percent reduction is calculated using the formula:

$$\% \text{ Reduction} = \frac{V_{clean} - V_{dirty}}{V_{clean}} \times 100\%$$

where V_{clean} and V_{dirty} are the measured volumes of mineral spirit passed through the clean and dirty fuel injectors.

TABLE I

% FLOW REDUCTION THROUGH INJECTOR PORTS

Cyl #	1	2	3	4	5	6
Car A	11	12	35	30	7	10
Car B	7	9	12	38	9	14
Car C	22	11	28	4	11	10
Typical New Injectors	2	2	0	0	2	1

From Table I it can be seen that this conventional, known carburetor detergent was ineffective in removing deposits from injector ports and in fact permitted deposits to form.

COMPARATIVE EXAMPLE II

A 1985 Chrysler LeBaron equipped with a 2.2 liter turbocharged engine having electronically controlled fuel injection was driven for 2858 miles on a mileage accumulation dynamometer using a typical regular grade, 87 octane, unleaded, detergent-free gasoline. The driving was based on repetition of the following cycle: 30 minutes city driving, 30 minutes engine off, 30 minutes highway driving, 30 minutes engine off. The driveability became very poor as typified by rough idle, severe hesitation, backfire and roughness during acceleration. The hydrocarbon emissions measured before the catalytic converter were 804 ppm at engine idle and 725 ppm at 2500 rpm. The injector fouling also was measured using a pressure differential test. In this test the fuel rail is pressurized to 49 psig and an injector is pulsed for 0.5 seconds. The difference in the pressure drop between the 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, the greater the injector fouling. A summary of the results at 2585 miles on the detergent-free fuel are set forth in Table II as the measurements at 0 miles after HECA addition.

EXAMPLE I

Following the test set forth in Comparative Example II, the vehicle was refueled with the same fuel except that the fuel also contained 80 ppm of bis(2-hydroxy ethyl) cocoamine (HECA). The vehicle then was driven on the following cycle: 15 minutes city driving, 30 minutes highway driving, 15 minutes city driving, 2 hours engine off. This test continued until 308 miles were accumulated on the vehicle. At the end of this test period the driveability was very good. The hydrocarbon emissions at idle before the catalytic converter were reduced to 65 ppm and to 16 ppm at 2500 rpm. The emissions before the catalytic converter at idle and at 2500, rpm and the pressure differentials measured at various intervals during the clean-up driving are summarized in Table II. The injector flow reduction measurements are summarized in Table III.

From the data of Example I and Tables II and III, it can be seen that the use of a relatively low concentration of HECA was able to produce a significant improvement in driveability. The idle emissions were significantly reduced and the pressure differential and percent flow reduction of the flow injectors were returned to "as new" conditions after a relatively few miles of driving.

TABLE II

MILES AFTER ADDITION OF HECA	EMISSIONS BEFORE CATALYTIC CONVERTER					Δ P LEAKDOWN, PSI			
	IDLE		2500 RPM						
	HC, PPM	CO%	HC, PPM	CO%	CYL #	1	2	3	4
0	804	0.68	725	0.31		17	18	20	21
73	813	1.78	188	1.99		17	17	19	22
140	375	0.95	35	1.10		17.5	18.5	19	20.5
219	95	0.70	30	0.75		19	19	19.5	25
308	65	0.67	16	0.69		23	24	24	25

TABLE III

PORT INJECTOR FLOW REDUCTION

MILES DRIVEN AFTER HECA ADDITION	INJECTOR NO.	1	2	3	4
308	% FLOW REDUCTION	0	0	0	1

COMPARATIVE EXAMPLE III

A second 1985 Chrysler LeBaron equipped with a 2.2 liter turbocharged engine was driven on a mileage accumulation dynamometer using a regular grade 87 octane unleaded, detergent-free gasoline from a different batch from that of Comparative Example II and Example I. The same driving cycle was used in this Comparative Example as was used in Comparative Example I. The engine was judged to be fouled and the driveability poor after 4016 miles.

The emissions before the catalytic converter and the pressure differential across each injector were measured and are presented in Table IV as the measurements at 0 miles after HECA addition.

EXAMPLE II

Approximately 60 ppm of bis(2-hydroxyethyl) cocoamine was added to the fuel of Comparative Example III and the vehicle of Comparative Example III was driven on the same driving cycle described in Example I. Measurements of the emissions before the catalytic converter and the pressure differential across each injector were measured as previously described. These results are presented in Table IV. Driveability was judged to be good after only 357 miles of driving. At the termination of the test the injectors were removed and flow tested as previously described. These results are presented in Table V.

TABLE IV

MILES AFTER ADDITION OF HECA	EMMISIONS BEFORE CATALYTIC CONVERTER					ΔP LEAKDOWN, PSI			
	IDLE		2500 RPM						
	HC, PPM	CO%	HC, PPM	CO%	CYL #	1	2	3	4
0	148	2.17	126	2.21		11.0	10.0	12.5	10.0
188	190	2.6	125	3.2		15.0	16.0	19.0	21.0
359	112	0.94	53	1.12		15.5	16.0	16.0	16.5

TABLE V

PORT INJECTOR FLOW REDUCTION

MILES DRIVEN AFTER HECA ADDITION	INJECTOR NO.	1	2	3	4
359	% FLOW REDUCTION	5	2	1	0

From a review of Tables II-V it can be seen that the use of relatively low concentrations of HECA was able to reduce the injector tip deposits in a relatively short period of time. By comparison, the use of a conventional carburetor detergent was unable to prevent a relatively rapid deposit buildup of injector tip deposits.

While the data presented above has demonstrated the utility of the anti-fouling agent in gasoline, the anti-fouling agent also may be of utility in other fuels, such as diesel fuel.

While the presently described anti-fouling agent may be used alone, it also may be desirable to utilize the present invention in combination with a demulsifying agent to facilitate the separation of the gasoline from any foreign substances which may be present in the distribution system, such as water and sediment.

The water, if any, typically has a pH ranging from about 7 to about 13. Thus, a demulsifying agent for use with the anti-fouling agent preferably should be effective over this pH range. The following Comparative Examples and Examples demonstrate the utility of various demulsifying agents.

COMPARATIVE EXAMPLE IV

In this Comparative Example the effectiveness of various commercially available demulsifying agents were tested in a 90 wt.% fuel - 10 wt.% water system. The fuel contained an additive package comprising approximately 60 ppm HECA and 2 ppm of the various additives noted below. The effectiveness of the various demulsifying agents was determined using a modified Multiple Contact Emulsion Test. In this test 10 ml of terminal water bottoms having a pH of approximately 10 was added to separate half-pint bottles. To each bottle was added 100 ml of gasoline. The bottles were capped, placed on their sides in a mechanical shaker and agitated at approximately 180 cycles per minute for ten minutes. The bottles then were placed upright and allowed to stand for 1 hour. The mixture then was rated considering the gasoline layer, the water layer and the interface using the rating scale set forth in Table VI below. After the ratings were completed, the gasoline level was sucked down to a level about 1/4 inch above the interface or emulsion layer without disturbing the interface or water layer. The withdrawn fuel was discarded and 100 ml of fresh gasoline was added to each bottle. The mixture was then shaken and the test repeated for the indicated number of times with the worst rating noted. The trade names of the commercially available additives utilized, the worst ratings of each mixture and the number of times the test was run are set forth in Table VII below.

TABLE VI

RATING SCALE FOR REPORTING EMULSION TEST REUSLTS

RATING	DESCRIPTION OF EMULSION
0	No skin or interface
1	Slight skin on interface - not completely continuous
2	Thicker skin on interface - usually completely continous
3	Incipient emulsion 1/8 as thick as water layer
4	Emulsion 1/4 as thick as water layer
5	Emulsion 3/8 as thick as water layer
6	Emulsion 1/2 as thick as water layer
7	Emulsion 5/8 as thick as water layer
8	Emulsion 3/4 as thick as water layer
9	Emulsion 7/8 as thick as water layer
10	Emulsion completely filling water layer Emulsion of maximum severity

TABLE VII

EMULSION TEST RESULTS

DEMULSIFIER DESCRIPTION	WORST RATING	NO. OF TIMES TEST RUN
Tolad T-292	3	2
Tolad T-347	3	2
Tolad T-370	4	1
Nalco 5450	4	1
Nalco 5451	3	4
Nalco 5452	3-4	4
Nalco 5453	4	1
Nalco 85BD-194	4	1
Nalco 3BD-829	4	1

EXAMPLE III

A 100 ml gasoline sample containing 60 ppm of HECA was admixed with 10 ml of the terminal water bottoms of Comparative Example IV. However, in place of the demulsifiers listed in Table VII the following demulsifiers were utilized individually: Tolad T-500; Tolad T-284; Tolad T-286; Tolad T-326; and Nalco 5455. The modified Multiple Contact Emulsion Test previously described was utilized to determine the effectiveness of each demulsifier. These test results are summarized in Table VIII below. A description of each additive is presented in Table IX below.

TABLE VIII

EMULSION TEST RESULTS

DEMULSIFIER DESCRIPTION	WORST RATING	NO. OF TIMES TEST RUN
Tolad T-284	2	4
Tolad T-286	1-2	4
Tolad T-326	2	2
Tolad T-500	2	4
Nalco 5455	2	4

TABLE IX

DEMULSIFIER DESCRIPTIONS

Demulsifier	Description
Tolad T-284*	Solution of acylated polyglycols in aromatic hydrocarbons
Tolad T-286*	Alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins in aromatic hydrocarbons and isopropyl alcohol
Tolad T-326*	Oxyalkylated alkylphenol-formaldehyde resins and polyglycols in aromatic naphtha
Tolad T-500*	Oxyalkylated alkylphenol-formaldehyde resins in aromatic hydrocarbons and alkanols
Nalco 5455**	Oxyalkylated alkyl phenol-formaldehyde resin in aromatic solvent

* Manufactured by Tretolite Division of Petrolite Corporation, St. Louis, Missouri.

** Manufactured by Nalco Chemical Company, Oak Brook, Illinois.

COMPARATIVE EXAMPLE V

A 1985 Chrysler LeBaron equipped with a 2.2 liter turbocharged engine was driven on a mileage accumulation dynamometer using a regular grade 87 octane unleaded detergent-free fuel. The driving cycle to foul the injectors was 30 minutes city-type driving, 30 minutes soak, 30 minutes highway driving, 30 minutes soak. The engine was judged to be fouled after 2,300 miles.

The emissions before the catalytic converter and the pressure differential across each injector were measured and are presented in Table X as the measurement at 0 miles after additive addition.

EXAMPLE IV

This Example demonstrates the utility of using an additive comprising the combination of an amine and an amine oxide in cleaning up fouled injectors in the vehicle of Comparative Example V. The fuel utilized was similar to that of Comparative Example V, but further comprised 80 ppm of bis(2-hydroxy ethyl) cocoamine and 10 ppm of bis(2-hydroxy ethyl) cocoamine oxide. The driving cycle was the same as that of Example I. After 301 miles of driving the driveability went from very poor to good.

The measurements of the emissions before the catalytic converter and the pressure differential across each injector also were measured as previously described. These results also are presented in Table X. At the termination of the test the injectors were removed and flow tested as previously described. These results are presented in Table XI.

Based on these results, it can be seen that the use of an additive comprising the amine and amine oxide in combination cleaned fouled injectors. Additional tests were run on other test vehicles. In almost all cases it has been found that this combination of amine and amine oxide cleaned fouled injectors in a relatively short period.

TABLE X

MILES AFTER ADDITIVE ADDITION	EMISSIONS BEFORE CATALYTIC CONVERTER					ΔP LEAKDOWN, PSI				MAX ΔP DIFFERENCE	Driveability
	IDLE		2500 RPM								
	HC, PPM	CO%	HC, PPM	CO%	CYL #	1	2	3	4		
0	491	1.66	175	1.32		14	16	21	19	5	Very Poor
151	1,112	2.22	140	2.43		17	19	19	24	7	Very Poor
301	128	0.77	61	1.06		18	19	18	19	1	Good

TABLE XI

PORT INJECTOR FLOW REDUCTION

MILES AFTER ADDITIVE ADDITION	INJECTOR NO.	1	2	3	4
301	% FLOW REDUCTION	2	1	4	2

Where the presently described invention is used as a gasoline additive, the additive package may be added to the gasoline at any point after the gasoline has been refined, i.e., the additive package can be added at the refinery or in the distribution system.

In this patent specification, the following conversions of units are employed:

1 ton = 1.016 tonne
1 pound = 0.4536 kg
1 barrel = 159.0 litre
1 pint = 473.2 ml
1 mile = 1.60935 km
1 inch = 25.4 mm
1 psig or psi = 6.895 kPa gauge or 6.895 kPa

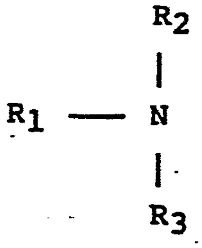
"Oldsmobile", "Chrysler" and "Le Baron" are trade marks.

CLAIMS:

1. A fuel composition for an internal combustion engine, said fuel composition comprising:

A. fuel (e.g., gasoline);

B. an antifouling agent having the formula



$$R_1 - \overset{\displaystyle R_2}{\underset{\displaystyle R_3}{N}}$$

wherein: R_1 is C_6 to C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; R_2 and R_3 independently are C_1 to C_{24} substituted alkyl, aryl, cycloaliphatic or heterocyclic; and

C. a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof.

2. The fuel composition of claim 1 wherein R_1 is C_6 to C_{20} alkyl, or alkylated aryl; and, R_2 and R_3 independently are hydroxy substituted C_1 to C_{12} alkyl.

3. A fuel additive concentrate for internal combustion engines, said additive concentrate comprising:

A. about 5 to about 60 wt.% bis(2-hydroxy ethyl) cocoamine;

B. about 0.25 to about 10 wt. % of a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof; and,

C. about 40 to about 95 wt.% solvent.

4. The fuel additive concentrate of claim 3 further comprising about 1 to about 15 wt.% bis(2-hydroxy ethyl) cocoamine oxide.

5. A fuel additive concentrate for internal combustion engines, said additive concentrate comprising:

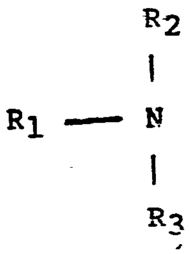
A. about 8 to about 32 wt.% amine;

B. about 2 to about 8 wt.% amine oxide;

C. about 40 to about 95 wt.% solvent; and,

D. about 1 to about 4 wt.% demulsifier.

6. A method for reducing and/or preventing fouling in a multi-port, electronically controlled fuel injection system for an internal combustion engine, said method comprising delivering to said fuel injection system a fuel comprised of an effective amount of an anti-fouling agent comprising



$$R_1 - \underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{N}}$$

wherein: R_1 is C_6 to C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; R_2 and R_3 independently are C_1 to C_{24} substituted alkyl, aryl, cycloaliphatic or heterocyclic.

7. The method of claim 6 wherein R_1 is C_6 to C_{24} alkyl, or alkylated aryl; and, R_2 and R_3 independently are hydroxy substituted C_1 to C_{12} alkyl.

or alkylated aryl; and, R_2 and R_3 independently are hydroxy substituted C_1 to C_{12} alkyl.

8. A method for reducing and/or preventing fouling in a multi-port fuel injection system having a sensor means disposed in the exhaust adapted to regulate the air to fuel ratio, said method comprising delivering to the fuel injection system a fuel comprising:

A. fuel (e.g., unleaded gasoline);

B. an anti-fouling agent selected from the group consisting of bis(2-hydroxy ethyl) cocoamine, bis(2-hydroxy ethyl) tallow amine, bis(2-hydroxy ethyl) stearylamine, bis(2-hydroxy ethyl) oleyl amine and mixtures thereof; and

C. a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof.

9. A method for combusting a fuel (e.g. gasoline) in an internal combustion engine wherein fuel is delivered to the combustion zone of the engine by means of a multi-port, electronically controlled fuel injection system, the method comprising combusting fuel (e.g., a gasoline) including:

A. an effective amount of an anti-fouling agent selected from the group consisting of bis(2-hydroxy ethyl) cocoamine, bis (2-hydroxy ethyl) tallow amine, bis(2-hydroxy ethyl) stearylamine, bis(2-hydroxy ethyl) oleyl amine and mixtures thereof; and,

B. a demulsifying agent selected from the group consisting of:

i. acylated polyglycols;

ii. alkyl aryl sulfonates, polyglycols, oxyalkylated alkylphenol-formaldehyde resins;

iii. oxyalkylated alkylphenol-formaldehyde resins and polyglycols; and,

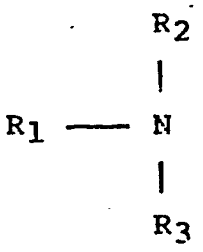
iv. oxyalkylated alkylphenol-formaldehyde resins;

and mixtures thereof.

10. A fuel composition for an internal combustion engine said engine composition comprising:

A. fuel (e.g., gasoline);

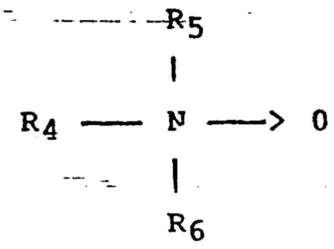
B. an amine anti-fouling agent having the formula:



$$R_1 - \overset{\displaystyle R_2}{\underset{\displaystyle R_3}{N}}$$

wherein: R_1 is C_6 to C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; R_2 and R_3 independently are C_1 to C_{24} substituted alkyl, aryl, cycloaliphatic or heterocyclic; and,

C. an amine oxide anti-fouling agent having the following structural formula:



$$R_4 - \overset{\displaystyle R_5}{\underset{\displaystyle R_6}{N}} \longrightarrow O$$

where R_4 is C_6-C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl, substituted aryl; R_5 and R_6 independently are C_1-C_{24} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic, heterocyclic and mixtures thereof.