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(54) **Method for reducing and/or preventing fouling in multiport electronically-controlled fuel injection systems.**

(57) A method for reducing and/or preventing injector fouling in a multiport electronically-controlled fuel injection means is described. The method comprises delivering to the fuel injection means a fuel (e.g., gasoline or diesel fuel) comprised of an effective amount of one or more particularly described amine oxides, such as bis (2-hydroxyethyl) cocoamine oxide.

EP 0 232 069 A1

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BACKGROUND OF THE INVENTION

This invention is directed to an anti-fouling composition for fuel injection systems. More specifically, the present invention is directed at a method for 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 cyclinder 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 ultimately 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 oxygen to fuel 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 air 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, closer tolerances in this new type of injector and concurrently higher underhood temperatures 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. 3,387,953 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:

$$\begin{array}{ccccc} & & R_2 & & \\ & & | & & \\ R_1 & — & N & \longrightarrow & O \\ & & | & & \\ & & R_3 & & \end{array}$$

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. 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. While these compounds were used commercially during the late 1960's and early 1970's, their use was discontinued as more effective additives were found. The use of these compounds had been discontinued well before the development of electronically controlled, fuel injected engines.

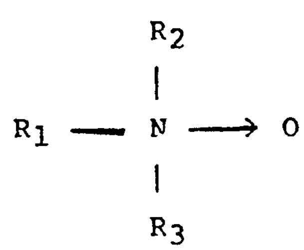
Accordingly, it would be desirable to provide a gasoline additive which is relatively inexpensive and effective at low concentrations to reduce and/or eliminate injector fouling.

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

It also would be desirable to provide a gasoline additive 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 method for minimizing and/or preventing injector fouling in a multiport electronically controlled fuel injected engine. The method comprises delivering to said fuel injection system a fuel comprised of an effective amount of an additive comprising:



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} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic or heterocylic. R_1 preferably is C_9-C_{20} alkyl, or alkylated aryl, and R_2 and R_3 independently are C_1-C_{12} alkyl. In a more preferred composition R_1, R_2 and R_3 independently are C_8-C_{18} groups derived from fatty acid. The additive preferably is selected from the group consisting of bis(2-hydroxy ethyl) cocoamine oxide, bis(2-hydroxy ethyl) tallow amine oxide, bis(2-hydroxy ethyl) stearyl-amine oxide, dimethylcocoamine oxide, dimethyl hydrogenated tallow amine oxide, dimethylhexadecylamine oxide and mixtures thereof. A particularly preferred additive is bis(2-hydroxy ethyl) cocoamine oxide. The additive concentration in the fuel typically may range between about 0.5 and about 50 ptb, preferably between about 5 and about 10 ptb. The additive may be used alone or may be added to the fuel with an effective amount of a demulsifier.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed at a fuel additive which has been found to be particularly effective to reduce and/or eliminate injector fouling. The present invention comprises adding to the fuel an effective amount of an additive comprising

$$\begin{array}{ccccc} & & R_2 & & \\ & & | & & \\ R_1 & — & N & \longrightarrow & O \\ & & | & & \\ & & R_3 & & \end{array}$$

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} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic, heterocyclic, and mixtures thereof. Preferred compounds include compounds wherein: R_1 is C_9-C_{20} alkyl, or alkylated aryl; and R_2 and R_3 independently are C_1-C_{12} alkyl. Particularly preferred compounds are compounds wherein R_1, R_2 and R_3 independently are C_8-C_{18} groups. The 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. These additives are prepared in accordance with known techniques, such as disclosed in U.S. Patent 3,387,953, the disclosure of which is incorporated herein by reference. A particularly preferred additive is bis(2-hydroxy ethyl) cocoamine oxide.

The following Comparative Examples and Examples demonstrate the utility of the present invention 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 8.5 ptb 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 1300 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 and severe hesitation. The hydrocarbon emissions measured before the catalytic converter were 321 ppm at engine idle. The injector fouling 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 pressure drop, or leakdown ΔP, is indicative of how readily the fuel flows, i.e., the higher the number, the less the injector is obstructed. In this vehicle the pressure differential for a clean injector under these conditions is 19-22 psig. This data is set forth below in Table II.

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 10 ptb of bis(2-hydroxy ethyl) cocoamine oxide (HECO). 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 270 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 200 ppm. The percent injector flow reduction and the pressure differential were significantly improved as set forth in Table II.

From the data of Example I and Table II it can be seen that the use of a relatively low concentration of HECO 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

PORT INJECTOR FOULING

HECO ADDITIVE CONCENTRATION (ptb)	MILES DRIVEN	% INJECTOR FLOW REDUCTION INJECTOR NO. 1	2	3	4	LEAKDOWN P INJECTOR NO. 1	2	3	4
None	1300	Not run*				13	13	13	12
10	270	0	1	0	0	19	19	19	19

* Test not run to avoid disturbing deposit formation before end of test.

As shown by the following Comparative Examples and Example, bis (2-hydroxy ethyl) cocoamine oxide also was effective in preventing the build-up of fuel injector tip deposits.

COMPARATIVE EXAMPLE III

In this Comparative Example, four 1985 Chrysler LeBarons equipped with four cylinder, electronically controlled, fuel injected, turbocharged, 2.2 liter engines were driven on mileage accumulation dynamometers under the following conditions: 0.5 hour city-type driving, 0.5 hour engine off, 0.5 hour highway type driving and 0.5 hour engine off for 4,000 miles. The control cars ran on a regular grade, 87 octane, detergent-free, unleaded fuel. Following the test, the percent flow reduction was measured using the procedures previously set forth hereinabove. The tests were repeated in four different cars (same make and model). The results of these tests are set forth in Table III below.

EXAMPLE II

A 1985 Chrysler LeBaron, similar to that set forth in Comparative Example III was used in this test which was conducted under the same conditions set forth in that Comparative Example. The gasoline used during this test was the same at that used in the control cars, but with the further addition of 10 ptb of bis(2-hydroxy ethyl) cocoamine oxide (HECO). The results of these tests are also set forth in Table III below. From a review of these tests it can be seen that the addition of a relatively low concentration of HECO was able to prevent a significant reduction in the fuel injector flow rate.

TABLE III

HECO ADDITION PREVENTS SIGNIFICANT INJECTOR PORT FOULING

	Initial Test						Repeat Test	
Comp. Example III	Driveability	% Flow Reduction #1	#2	#3	#4	Avg.	Driveability	Avg. % Flow Reduction
Control Car No.								
1	Undriveable	35	25	24	24	24	Undriveable	26
2	Undriveable	39	13	14	16	20	Undriveable	19
3	No problems	13	23	13	14	16	Undriveable	19
4	Undriveable	3	21	11	14	12	Undriveable	11
Example II								
Car with HECO in fuel	No problems	0	0	0	0	0	No problems	<1.0*

*Car ran 5000 miles

COMPARATIVE EXAMPLE IV

In this test a 1985 Chrysler LeBaron having a four cylinder, turbocharged, 2.2 liter engine with electronically controlled fuel injection was operated for 2,002 miles on a mileage accumulation dynamometer simulating alternating driving and engine-off cycles. The fuel utilized was typical of a regular grade, 87 octane, unleaded fuel containing 8.5 ptb of the same detergent used in Comparative Example I. Following the completion of this test, the percent flow reduction through the fuel injector ports was measured by the method previously described herein. As shown in Table IV below the use of this conventional carburetor detergent was ineffective in preventing injector fouling.

EXAMPLE III

A vehicle similar to that utilized in Comparative Example IV was utilized in this Example under the same operating conditions. The fuel utilized was similar but with the replacement of the conventional carburetor detergent by 10 ptb of bis(2-hydroxyl ethyl) cocoamine oxide. The vehicle was driven for 9,600 miles under the same sequence set forth in Comparative Example IV. The bis(2-hydroxy ethyl) cocoamine oxide was able to prevent any significant flow reduction in the fuel injectors as shown by data presented in Table IV.

TABLE IV

COMPARISON OF HECO AND CONVENTIONAL CARBURETOR DETERGENT IN PREVENTING INJECTOR PORT FOULING

ADDITIVE	CONCENTRATION, ptb	MILES DRIVEN	% FLOW REDUCTION CYL # 1	2	3	4
Conventional Carburetor Detergent	8.5	2,002	4	8	1	16
HECO	10	9,600	0	1	0	0

From this Table it can be seen that the use of a relatively low concentration of HECO was able to prevent any significant buildup of injector tip deposits. By comparison, the use of a conventional carburetor detergent at approximately the same rate was unable to prevent a relatively rapid deposit buildup of injector tip deposits.

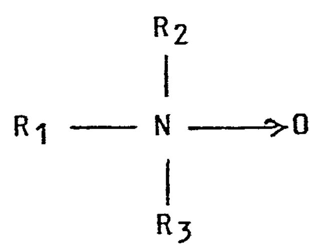
While the data presented above has demonstrated the utility of the present invention in gasoline, the present invention also may be of utility in other fuels, such as diesel fuel. Where the presently described invention is used as a gasoline additive, the additive may be added to the gasoline at any point after the gasoline has been refined, i.e., the additive can be added at the refinery or in the distribution system. While the presently described additive may be used alone, it also may be desirable to utilize the present invention in combination with a demulsifier to facilitate the separation of the gasoline from any foreign substances which may be present in the distribution system. Other additives conventionally employed in gasolines may also be used in combination with the additives of the present invention.

In this patent specification;

- The words "Oldsmobile", "Chrysler" and "Lebaron" are Trade Marks.
- Weight in ton is converted to tonne by multiplying by 1.016.
- Weight in pounds is converted to kg by multiplying by 0.4536.
- 1 Barrel is 159.0 liters.
- 1 mile is 1.60935 km.
- 1 pound per square inch (gauge), psig is 6.895 kPa gauge.
- # denotes "number".

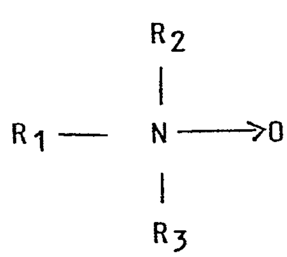
CLAIMS:

1. A method for reducing and/or preventing fouling in a multiport, 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



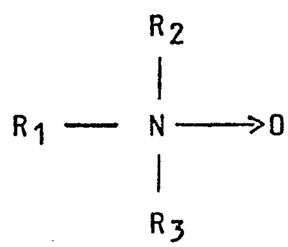
wherein: R_1 is C_6 to C_{24} alkyl, aryl, cycloaliphatic, heterocyclic, substituted alkyl or substituted aryl; R_2 and R_3 independently are C_1 to C_{24} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic or heterocyclic.

2. A method for combusting fuel in an internal combustion engine wherein fuel is delivered to the combustion zone of the engine by means of a multiport, electronically-controlled fuel injection system, the method comprising combusting a fuel comprising an effective amount of an additive having the formula:



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

3. A method of operating an internal combustion engine having a multiport, electronically-controlled fuel injection system, the method comprising delivering to said fuel injection system a fuel comprising an effective amount of an additive comprising:



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} alkyl, aryl, substituted alkyl or aryl, cycloaliphatic or heterocyclic.

4. The method of any of claims 1 to 3 wherein: R_1 is C_9 to C_{20} alkyl, or alkylated aryl; and, R_2 and R_3 independently are C_1 to C_{12} alkyl.

5. The method of any one of claims 1 to 4 wherein the additive is selected from the group consisting of bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallow amine oxide, bis(2-hydroxyethyl) stearylamine oxide, dimethylcocoamine oxide, dimethyl hydrogenated tallow amine oxide, dimethylhexadecylamine oxide and mixtures thereof.

6. The method of any one of claims 1 to 5 wherein the additive is bis(2-hydroxyethyl) cocoamine oxide.

7. The method of any one of claims 1 to 6 in which the concentration of the additive is in the range of from 0.5 to 50 pounds per thousand barrels of fuel (0.23 to 22.68 kg per 159000 liters of fuel).

8. The method of any one of claims 1 to 7 in which the concentration of the additive is in the range of from 5 to 10 pounds per thousand barrels of fuel (2.27 to 4.54 kg per 159000 liters of fuel).

9. The method of any one of claims 1 to 8 in which the fuel is gasoline.

10. The method of any one of claims 1 to 9 in which the air to fuel ratio of the engine is regulated in accordance with the oxygen concentration of the exhaust gas as sensed by sensor means responsive to oxygen concentration in the exhaust gas.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 30 0514

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.4)
A	US-A-3 007 784 (EBNER) * Whole document *	1-10	C 10 L 10/00 C 10 L 1/22 F 02 B 77/04
D,A	US-A-3 594 139 (BOUFFARD) * Claims *	1-10	
D,A	FR-A-1 521 990 (ESSO) * Abstract; page 1 *	1-10	
A	US-A-4 482 356 (HANLON) * Claims; column 1 *	1-3	
A	US-A-4 398 505 (CAHILL) * Whole document *	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 L
F 02 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-05-1987	DE LA MORINERIE B.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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