

[54] **ALKYLDIAMINOAMIDS OF FATTY ACIDS  
AS GASOLINE ADDITIVES**

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[51] **Int. Cl.<sup>2</sup>** ..... **C01L 1/22**

[58] **Field of Search**..... **44/66, 71, 72**

[56] **References Cited**

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[57]

**ABSTRACT**

Gasoline fuel compositions containing a dual additive comprising a composition having the general formula  $R-NHCH_2CH_2CH_2NHCO-R'$  is improved by incorporation therewith of a second additive having the general formula  $R''OCH_2CH_2CH_2NHCH_2CH_2-CH_2NHCOR'$  in which R is an aliphatic hydrocarbon radical having 10–20 carbon atoms; R' is an aliphatic hydrocarbon radical having 9–19 carbon atoms and R'' is an aliphatic hydrocarbon radical having 10–15 carbon atoms. The carburization systems of internal combustion engines operating on gasolines containing these additives remain low in harmful deposits of varnish scale which normally results from untreated fuel.

**4 Claims, No Drawings**

## ALKYLDIAMINOAMIDS OF FATTY ACIDS AS GASOLINE ADDITIVES

This invention relates to an improved gasoline composition for internal combustion engines. Particularly, the invention relates to the discovery that the incorporation of a combination of additives in gasoline produces a lower formation of deposits in the upper portion of the induction system, including the carburetor bore area, than that found for gasolines containing a single additive selected from the combination.

Modern internal combustion engine design is undergoing important changes to meet certain standards concerning engine and exhaust gas emissions. A major change in the engine design presently being widely adopted is the feeding of blow-by gasses from the crank case out of the engine into the intake air supply to the carburetor rather than venting these gases to the atmosphere as in the past. These blow-by gases contain substantial amounts of deposit forming substances, and it has been observed that some of the substances in the blow-by gases form deposits in and around the throttle plate area of the carburetor. These deposits restrict the flow of air through the carburetor and idle in low speed so that an over-rich fuel mixture results. This condition produces rough idling, engine stalling, and also results in excessive hydrocarbon exhaust emissions to the atmosphere. In addition to overcoming the foregoing problem, it is felt that the incorporation of these additives will provide corrosion inhibition and anti-icing.

The use of amine derivatives such as amides, imides, amines, imidazolines, triazines, pyrimidines, polyamids, low molecular weight polymers, organophosphates, and amine phosphates as well as ordinary ammonium salts of such materials are well known fuel additives which in part increase the operating efficiency of the carburetor system. Representative of U.S. patents teaching the use of alkyl substituted diaminoamid derivatives are U.S. Pat. Nos. 2,805,135; 2,922,707; 2,996,365; 3,251,853; 3,313,607; 3,589,877; 3,653,853; 3,704,109; 3,707,361; and 3,813,228.

The deposits which are formed in the carburetor system may be due in part to the make up of the motor fuel which is used; but it is believed that deposits are due to a greater extent, at least to foreign matter introduced into the carburetor, through the air intake system since air cleaners are not completely effective. Major contributors to air contamination are crank case vapors formed from the crank case, exhaust vapors, dust, smoke and the like. The problem with respect to carburetor deposits resulting from air contamination is further aggravated by the positive crank case ventilating system which is employed in many of the recently introduced automatic engines. In engines equipped with a positive crank case ventilating system, fumes and vapors from the crank case are passed through a metering valve into the air intake system of the engine. While this system helps to cut down on the fumes escaping to the atmosphere, the system adds the problem of deposits formed in the carburetor. Deposits are encountered not only in the carburetor, but also in the components of the metering valve employed in connection with the positive crank case ventilating system.

Another source of carburetion deposit is derived from the composition and history of the fuel. Trace contaminants in the fuel which result from its process of manufacture, storage and geographical origin are

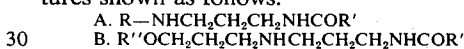
thought to be responsible for the high molecular varnishes and gums which are deposited over long periods of use.

Many commercially available gasolines and fuel oils contain additives which are used to either keep the intake system free from additional deposits ("stay clean") and/or to clean off existing deposits ("clean up") and thereafter keep the system clean. Clean up detergency requires much higher dosages of additives than are needed for stay clean detergency.

It is a major objective of this invention to provide a fuel such as gasoline which contains a minor amount of an additive combination which performs as a detergent to keep the intake system of an internal combustion engine free from additional deposits or to clean off existing deposits and thereafter keep the system relatively clean.

Another objective of the invention is to provide gasoline compositions comprising hydrocarbons boiling in the gasoline boiling range with a combination of detergents comprising alkoxy substituted derivatives of propylamides and alkylamine substituted derivatives of propylamides.

These and other objectives of the invention are accomplished by introducing into a hydrocarbon fuel a by-component detergent composition comprising a blend of monoamides A and B having the general structures shown as follows:



The first component (A) of the blend is a propylene diamine derivative wherein R' and R is a C<sub>9</sub>-C<sub>19</sub> fatty aliphatic hydrocarbon radical.

The second component (B) of the blend is a propylene diamine derivative wherein R' is a C<sub>9</sub>-C<sub>19</sub> fatty aliphatic hydrocarbon radical and R'' is a hydrocarbon radical having 10-15 carbon atoms.

The first detergent component referred to above can be made by reacting a monoalkyl N-substituted propylenediamine derivative with monocarboxylic acids to form the N,N' amide derivative. Specific examples of such N-aliphatic substituted propylene diamines are N-nonyl propylenediamine, N-tetradecylpropylenediamine, N-tetradecenylpropylenediamine, N-hexadecylpropylenediamine, N-eicosylpropylenediamine, N-eicosenylpropylenediamine, N-docosylpropylenediamine, and N-docosenylpropylenediamine. Preferably those in which the aliphatic N- substituent is an alkyl or alkenyl group containing at least 12 and preferably 16-20 carbon atoms are considered to be most effective. Examples of the N-aliphatic substituted propylenediamines which are considered to form especially effective materials are the N-dodecyl, N-hexadecyl, propylenediamines, and especially the 18 carbon alkyl-, alkenyl- and the alkydienyl-substituted propylenediamines such as the N-octadecyl-, N-octadecenyl, and N-octadecadienyl propylenediamine. Mixtures of N-aliphatic substituted propylenediamine such as are formed when the aliphatic N- substituent is derived from mixed fatty acids obtained from naturally occurring fats and oils, form highly effective materials for use in the composition of the invention. In such instances the aliphatic N- substituent is a straight chain, monovalent and hydrocarbon radical containing from 10-20 carbon atoms. Examples of such mixtures of N-aliphatic substituted propylenediamines are N-"tallow" propylenediamine, N-"soya" propylenediamine and N-"coco"

propylenediamine where the respective N- substituents are mixed alkyl and unsaturated alkyl groups derived from animal tallow (C<sub>14</sub>-C<sub>18</sub>) fatty acids, soybean (C<sub>16</sub>-C<sub>20</sub>) fatty acids and coconut (C<sub>8</sub>-C<sub>18</sub>) fatty acids.

These N- aliphatic substituted propylenediamines can be prepared by converting commercially available fatty acids to their corresponding nitriles and thereafter reducing the nitriles with hydrogen to form the primary amine. This primary amine is then treated with acrylonitrile to obtain the corresponding cyanopropyl aliphatic amine which is then hydrogenated to obtain the alkyl substituted propylenediamine. Exemplary commercially available N-aliphatic substituted propylenediamines are Duomeen-T and Duomeen-S (products of Armour and Company) which have general formulas RNHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> wherein R is derived from "tallow" fatty acid and soya fatty acid respectively.

The monocarboxylic acid amine of the alkyl substituted diamine is prepared by mixing the acid with the diamine in equal molar portions. Specific examples of preferred acids are 2-ethylhexanoic, oleic, stearic, capric, decylenic, undecylenic, lauric, myristic, palmitic, ricinoleic, lineoleic, arachidic, behenic, erucic, octacosic and mixtures thereof obtained from coconut oil, tallow, and soybean oil.

Specific examples of these amide derivatives are as follows: N-hexadecyl propylenediaminemonooxide, N-octadecylpropylenediaminemonooxide, N-octadecylpropylenediaminestearate, N-"tallow" propylenediaminemonooxide, N-"soya" propylenediaminemonooxide, and N-"coco" propylenediaminestearate.

A preferred detergent derivative representative of the above described is prepared by reacting 1 mol of oleic acid which is commercially available and sold under the trademark ACINTOL F.A. No. 1 with 1 mol of N-"tallow" propylenediamine sold under the trademark KEMAMINE D-974 at a temperature ranging between 50° and 105°C. until the removal of 1 mol of water is accomplished.

The second detergent component of the blend is made by reacting compounds having the general formula:



wherein R'' is an aliphatic hydrocarbon radical having 10-15 carbon atoms with a monocarboxylic acid having 10-20 carbon atoms selected from those described above. Such starting materials are readily commercially available and can be reacted together at temperatures up to about 105°C. in equal molar quantities to eliminate 1 mol of water. A preferred material is prepared by reacting 1 mol of oleic acid (Acintol F.A. No. 1) with N-tridecyloxypropylethylenediamine (Adogen 583).

The detergent compositions of the invention can also be made by simultaneously reacting in one vessel equal molar portions of the N-alkyl substituted propylenediamine compounds along with the N-alkoxypropylpropylenediamine derivatives with 2 equivalents of the monocarboxylic acid to form a mixture of the detergent combination. In making the combined detergents, it is preferred that the A and B diamine derivatives be present in the final combination in weight ratios of 1:9 to 9:1. Of course, the individually prepared detergents can be mixed together in these weight ratios for addition to the gasoline such that the total detergent blend is present in concentrations ranging from 0.003-0.15

percent by weight of the fuel. Of course each individual detergent can be added directly to the gasoline in the appropriate weight ratios and concentrations.

The advantages offered by the invention can be more readily understood by reference to the following examples which are designed to indicate the improved results offered by the addition of the second detergent component to the first. Unexpectedly it was found that the combination of the detergents produced results superior to that found for the exclusive use of either one in similar fuels carbonized under similar conditions.

#### EXAMPLE 1

In a test device called an Induction System Deposit (ISD) bench apparatus, the performance of the detergent blends was measured in a gasoline designed specifically for lube oil engine tests. The bench test apparatus was designed specifically for military and commercial organizations and is described in detail in a publication entitled "A Bench Technique for Evaluating the Induction System Deposit Tendencies of Motor Gasolines" by A. A. Johnston and E. Dimitroff, *SAE Transactions*, Vol. 75 (1967), paper No. 660783. The test operates by impinging a stream of air propelled fuel onto a pre-weighed heated deposit-collecting tube made of aluminum tubing. As the gasoline impinges on the tube, thin film, flash evaporation occurs and varying amounts of deposits remain, depending upon the fuel's deposition tendencies.

To demonstrate this synergistic effect of one component upon the other for increasing their individual effectiveness as an antideposition detergent, varying concentrations of N-"tallow" propylenediaminemonooxide, designated Component A, and N-(3-tridecyloxypropyl)-propylenediaminemonooxide, designated Component B, were run in the above-described bench test in gasoline having the analysis described in Table I.

In Table II, the results of the bench test employing a blend of the detergents indicate a deposition rate substantially lower than that found for either component additive used singly.

#### EXAMPLE 2

The effectiveness of the additive blend is more realistically demonstrated by comparing their effectiveness as a detergent in maintaining valves and carburetor cleanliness in a standard operating V-8 automobile engine modified slightly such that two gasolines may be compared simultaneously. Removable aluminum sleeves are placed in the throttle bores of two test carburetors and the weight of deposit accumulated on these sleeves is a measure of fuel additive performance. The results of a 24 hr. test are indicated in Table III using low lead gas as described in Table I. The results obtained in Table III for the performance test suggests that Additive A is improved by a factor of about 10 percent while Additive B is improved by a factor of 20 percent.

TABLE I

	Test Gasoline Characteristics	
	MSO8	Fuel Low Lead
Gravity, °API	59.7	60.0
Tetraethyl Lead	3.08g/gallon	0.50g/gallon
RVP	8.4	9.8
Composition		
% Aromatics	23.1	23.0
% Olefins	20.0	6.1
% Saturates	56.9	70.9

TABLE I-continued

Test Gasoline Characteristics	Fuel	
	MSO8	Low Lead
Distillation Range		
IBP	93°F	92°F
10%	123°F	124°F
50%	205°F	220°F
90%	348°F	346°F
E.P.	405°F	420°F
Research Octane No.	95.5	94.0

TABLE II

ISD bench test data showing the deposit weights (mg) obtained for the individual amides and amide blend.					
Detergent Additive	Fuel	"Stay Clean"		"Clean Up"	
		at 16ptb	at 100ptb	at 16ptb	at 100ptb
A*	MSO8+0.15% used oil	6.1***	3.3***	19.6***	1.8***
B**	MSO8+0.15% used oil	1.5,2.2	0.3,0.3	3.7,5.3	1.9,1.4
20%A:80%B	MSO8+0.15% used oil	0.2,0.1	—	0.2,0.3	—
30%A:70%B	MSO8+0.15% used oil	0.1,0.2	—	0.1,0.2	—
None	MSO8+0.15% used oil	7.5 to 9.0		21 to 24	

ptb is pounds of additive per thousand barrels of fuel  
\*A is Acintol F.A. No. 1 amide of Kemamine D-974  
\*\*B is Acintol F.A. No. 1 amide of Adogen 583  
\*\*\*Avg. of two determinations

TABLE III

Comparative engine test data for amides and amide blend/run.			
Compound	Active ptb	Fuel	% Carburetor Deposit Reduction
A	50	Low Lead	32
B	50	Low Lead	15
15 ptb A + 35 ptb B	50	Low Lead	36

What is claimed is:

1. A gasoline fuel composition comprising from 0.003 to 0.15 percent by weight of a dual additive com-

bination consisting of at least one compound having the general formula A:  $RNHCH_2CH_2CH_2NHCOR'$  and at least one compound of the general formula B:  $R'\lambda'OCH_2CH_2CH_2NHCH_2CH_2CH_2-NHCOR'$ , wherein R is an aliphatic hydrocarbon radical having 10-20 carbon atoms; R' is an aliphatic hydrocarbon radical having 9-19 carbon atoms; and R'' is an aliphatic hydrocarbon radical having 10-15 carbon atoms in said formulas.

2. A gasoline fuel of claim 1 wherein the weight ratio of additive formula A to additive formula B ranges from 1:9 to 9:1.

3. A gasoline fuel of claim 1 wherein the additive of formula A is N-"tallow" propylenediaminemonooleate and the additive of formula B is N-(3-tridecyloxypropyl)propylenediaminemonooleate.

4. A dual additive comprising the simultaneous reaction product of a monocarboxylic having 10-20 carbon atoms with a mixture of an N-alkyl substituted propylenediamine derivative wherein said alkyl substituent is an aliphatic group having 10-20 carbon atoms, with N-(3-tridecyloxypropyl)propylenediamine such that the molar ratio of the monocarboxylic acid present in the reaction mix to each of the propylenediamine derivatives is 2:1.

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