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MOTOR FUEL MULTIPURPOSE AGENTS

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Int. Cl. A23j 7/00

U.S. Cl. 260—403 4 Claims

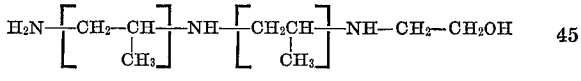
ABSTRACT OF THE DISCLOSURE

Monoethoxylated or monopropoxylated derivatives of dialkylene triamines or trialkylene tetramines and lecithin mixtures with and derivatives of said triamines or tetramines are advantageous motor fuel multipurpose agents.

This application is a division of Serial Number 544,840 filed Apr. 25, 1966 now Pat. No. 3,497,333.

This invention relates to multipurpose additives for motor fuels, to motor fuel compositions containing a minor proportion of said additives, and to methods for improving operation of gasoline burning engines by utilizing said compositions. The gasoline additives of the present invention perform three primary functions in gasoline including (1) reducing wear of cast iron piston rings in a gasoline-burning engine, (2) reducing the tendency of gasoline to clog a fuel filter element, and (3) performing a carburetor gum detergency function to inhibit or remove carburetor-type gum formations.

The additives of the present invention comprise monoethoxylated or monopropoxylated derivatives of dialkylene triamines or trialkylene tetramines and lecithin mixtures with and derivatives of said triamines or tetramines. A preferred gasoline additive of the present invention is monoethoxylated dipropylene triamine having the formula



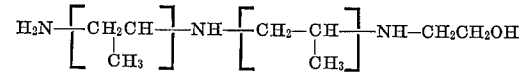
and the lecithin derivative thereof. Brackets are utilized in the structural formula to signify that the propylene can be either a 1-methylethylene or a 2-methylethylene substituent.

In the absence of lecithin, the alkoxylated triamines or tetramines of this invention impart antiwear characteristics to gasoline as evidenced by reduction in loss of metallic iron from cast iron piston rings. However, lecithin mixtures with and lecithin derivatives of the alkoxylated triamines or tetramines of this invention exert an additional highly beneficial effect in gasoline, i.e., they reduce the tendency of the gasoline to clog the fuel filter

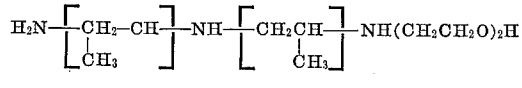
through which it passes in its flow to an engine. In addition, the lecithin derivatives perform a carburetor detergency function by inhibiting or reducing formation of gummy carburetor deposits. It is shown below that the derivative of lecithin and an alkoxylated triamine of this invention far excelled a large number of closely related compounds in ability to inhibit or reduce formation of gummy carburetor-type deposits.

The observed reduction in fuel filter clogging with the lecithin-containing additives of this invention signifies that these additives cause dispersed solids in gasoline to be either completely dissolved or partially dissolved and reduced in size. This indicates that the antiwear and antifilter-clogging characteristics of the additives of this invention cooperate to reduce engine wear because the presence of solid particles in gasoline, especially relatively large particles, in itself tends to increase wear of piston rings by abrasion. The antiwear and antifilter-clogging characteristics of the additives of this invention therefore cooperate to reduce engine wear with the antiwear function contributing directly to piston ring wear rate reduction and the antifilter-clogging function contributing indirectly to reduction of engine wear by completely dissolving or partially dissolving and reducing the size of abrasive solid particles in gasoline, thereby permitting easier removal by filtration of any remaining relatively small but still potentially abrasive solids.

It is significant that compounds differing only slightly from the additives of the present invention do not exhibit the advantageous characteristics in gasoline of the compounds of this invention. For example, while lecithin with monoethoxylated dipropylene triamine having the formula

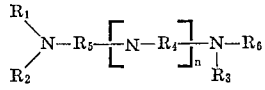


is a highly advantageous compound of the present invention, it is shown below that lecithin with dipropylene triamine plus two mols of ethylene oxide having the formula

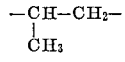


and/or a methyl isomer thereof, or a corresponding triamine having two separate hydroxyethyl groups attached to a terminal nitrogen, does not exhibit corresponding advantageous characteristics in gasoline. Furthermore, it was found that lecithin derivatives of monoamines such as isooctylamine and diisooctylamine, and lecithin derivatives of diamines, such as Duomeen compounds, do not exhibit the advantageous characteristics in gasoline of compounds of this invention.

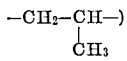
The triamine and tetramine compounds of the present invention have the general formula



wherein R_1, R_2 and R_3 are either hydrogen or a methyl or ethyl radical, preferably hydrogen; R_4 and R_5 are an ethylene, trimethylene (—CH_2—CH—CH_2—), or propylene (either



or



group, R_6 is a —C_2H_4OH or —C_3H_6OH group, and n is 1 or 2.

Examples of amine compounds of this invention include the monoethoxylate and monopropoxylate of diethylene triamine, dipropylene triamine, ditrimethylene triamine, triethylene tetramine, tripropylene tetramine, N-aminomethylethylenediamine, N-aminoethyl-N'-aminopropyltrimethylene diamine, N-methyltripropylene tetramine and N-methylaminoethyldiethylene triamine.

Any lecithin can be utilized in accordance with this invention, such as lecithin derived from soybean oil, corn oil, egg yolk or linseed oil. A suitable commercial lecithin to be reacted with an ethoxylated or propoxylated triamine or tetramine compound of this invention is a neutral oil solution of a filtered soybean lecithin with a moisture value less than 0.75 percent, an acetone-insoluble value of 70 percent and a viscosity of 3046 centipoises. According to one method of preparation of the lecithin derivative of the ethoxylated or propoxylated triamine or tetramine, base lecithin is reacted with the triamine or tetramine at 55–80° C. for 19 to 55 hours while stirring the reaction mixture. The reaction conditions of the base lecithin with the ethoxylated or propoxylated triamine or tetramine of this invention are not critical. In general, the reaction can occur at a temperature between 40° and 100° C. for a time duration of 5 to 100 hours.

The concentration in gasoline of the additives of this invention is not critical. For example, the additives of this invention can be present in gasoline in a general concentration range of 0.1 to 100 pounds per 1000 barrels, or a preferable concentration range of 1 to 25 pounds per 1000 barrels. In terms of weight percentage, the additives can be present in gasoline in a general range of .00004 to .04 percent and a preferable range of .0004 to .01 percent. If the additive to gasoline comprises an unreacted mixture of lecithin and ethoxylated or propoxylated triamine or tetramine, the components of the mixture can be preesnt over a wide ratio range. For example, the ratio of components in the mixture can range from substantially no lecithin to from about 1:100 to about 20:1 weight ratio of lecithin to amine.

The gasoline compositions of this invention contain as the hydrocarbon portion thereof any of the known gasoline hydrocarbons, such as, for example, hydrocarbons boiling between about 90° and 400° or 425° F. The hydrocarbon portion of the gasoline compositions can contain normal, branched-chain, and cyclic hydrocarbons having from 4 to 12 carbon atoms. The hydrocarbon portion of the gasoline compositions can comprise products prepared in the chemical conversion of hydrocarbons to produce gasoline such as the products prepared by isomerization, alkylation, polymerization, cracking, disproportionation, hydrogenation, dehydrogenation, and combinations of such processes. A common gasoline composition contains a major proportion of the gasoline hydrocarbons prepared by fluid catalytic cracking and a minor proportion of an alkylate prepared from isobutane and C_3 and/or C_4 olefins. The base fuel can comprise about 80 percent of gasoline from the fluid catalytic cracking process, and about 20 percent of the aforementioned alkylate.

EXAMPLE 1

A radioactive piston ring wear test was performed to demonstrate the high antiwear characteristics of a gasoline containing a compound of this invention. Following is a description of the procedure employed in the radioactive piston ring wear test.

Test procedure

The radioactive ring wear test was performed with a laboratory test, 4-stroke, single cylinder internal combustion engine equipped with a cast iron top compression ring which prior to use had been rendered radioactive by insertion into the pile of an atomic reactor. The engine provided with the radioactive ring was operated at constant speed for 10 hours under the following test conditions:

Speed: r.p.m.	2000.
Load: BHP	5.
Spark	15° before top center.
Air-fuel ratio	13.7/1.0.
Cylinder wall temp. ° F.	112.
Sump oil temp. ° F.	125.
Carburetor: intake air temp. ° F.	85.

During the test the motor oil accumulated particles of the radioactive metal lost by the radioactive piston ring through year. The radioactive metal content of the motor oil was continuously counted by means of a Geiger counter and recorded. At intervals oil samples were taken and the amount of dilution of oil by fuel was determined. Since dilution of oil by fuel tends to depress the radioactivity measurement, the amount of wear was calculated on the basis of radioactivity counts corrected by a factor corresponding to amount of dilution of the motor oil with fuel.

Table 1 shows the result of the radioactive piston ring wear test.

TABLE 1.—RADIOACTIVE PISTON RING WEAR TEST

Additive	Additive concentration, grams per gallon of gasoline	Percent change in piston ring wear rate compared to reference gasoline
Dipropylene triamine plus 1 mol of ethylene oxide	0.140	−15

As shown in Table 1, the antiwear agent of this invention reduced the piston ring wear rate 15 percent as compared to a reference gasoline.

EXAMPLE 2

Tests were conducted to illustrate the improvement imparted to gasoline by lecithin mixtures with an ethoxylated triamine of this invention and by lecithin derivatives of an ethoxylated triamine of this invention in regard to (1) reducing the tendency of gasoline to clog a fuel filter element and in regard to (2) performance of a carburetor gum detergency function to inhibit formation of or remove gummy carburetor deposits. In order to illustrate the especially high utility of the lecithin derivatives of this invention in regard to reduction of carburetor-type gum deposits, comparative tests were also conducted employing lecithin mixtures with and reaction products of closely related compounds. The results of these tests are presented in Table 2.

TABLE 2

Gasoline additives:									
Lecithin[a]	X								
Reaction product of lecithin[a] and the reaction product of long chain fatty acids and diethylene triamine[b].		X							
Mixture of lecithin[a] and the reaction product of long chain fatty acids and diethylene triamine[b]			X						
Reaction product of lecithin[a] and the reaction product of long chain fatty acids and dipropylene triamine plus 2 mols of ethylene oxide[c].				X					
Mixture of lecithin[a] and the reaction product of long chain fatty acids and dipropylene triamine plus 2 mols of ethylene oxide[c]					X				
Reaction product of lecithin[a] and the the reaction product of dipropylene triamine and 2 mols of ethylene oxide[d].						X			
Mixture of lecithin[a] and the reaction product of dipropylene triamine 2 mols of ethylene oxide[d].							X		
Reaction product of lecithin[a] plus plus the reaction product of dipropylene triamine and 1 mol of ethylene oxide[c].								X	
Mixture of lecithin[a] plus the reaction product of dipropylene triamine and 1 mol of ethylene oxide[c].									X
Gasoline tests:									
Gasoline Circulation Test[f], percent reduction in flow rate at stated fuel throughput in gallons (more than 50 percent reduction in flow rate at 20 gallons fuel throughput is unsatisfactory), gals.	50%, 10–15	25%, 20	22%, 20	35%, 20	20%, 20	45%, 20	54%, 20	35%, 20	38%, 20
Intake System Deposit Test[g], percent reduction in carburetor-type gum deposits.	46	48	61	58	59	20	49	83	33

[a] A commercial neutral oil solution of a filtered soybean lecithin with moisture value less than 0.75 percent by weight, an acetone-insoluble value of 70 percent by weight and a viscosity of 3,046 centipoises.

[b] A commercial mixture comprising about 90 to 95 percent by weight of 1-(2-aminoethyl)-2-heptadecenylimidazoline; $(C_{17})-C(=N-CH_2CH_2NH_2)-N(CH_2)-CH_2$

[c] A mixture comprising in major proportion $(C_{17})-C(=N-CH_2-CHNH(CH_2CH_2O)_2H)-N(CH_2)-CH(CH_3)$ and/or methyl isomers thereof, or corresponding imidazolines having two separate hydroxyethyl groups attached to the side chain nitrogen.

[d] Diethoxylated dipropylene triamine $NH_2-CH(CH_3)-CH_2-NH-CH_2-CH(CH_3)-NH(CH_2CH_2O)_2H$ and/or methyl isomers thereof, or corresponding triamines having two separate hydroxyethyl groups attached to a terminal nitrogen.

[e] Monoethoxylated dipropylene triamine $NH_2-CH(CH_3)-CH_2-NH-CH_2-CH(CH_3)-NHCH_2CH_2OH$ and/or methyl isomers thereof.

[f] For the Gasoline Circulation Tests additive concentrations were 15 lbs. per 1,000 barrels of gasoline plus 0.5 percent by volume solvent oil. Gasoline Circulation Test procedure is described in SAE Reprint No. 610 B, G. E. Gaston and J. J. Thomas, "Contribution of Sediment and Additives in Gasoline to Clogging of Filters in Automotive Fuel Systems", presented at Philadelphia, Pa., Meetings, Oct. 29–Nov. 2, 1962.

[g] For the Intake System Deposit Tests the concentration of additives was 15 lbs. per 1,000 barrels of gasoline. The test simulates deposition of gum carried by gasoline in a carburetor and involves forming a gum deposit in a test apparatus by evaporating additive-containing, high gum content fuel flowing countercurrent to a stream of heated air. At the end of the test, the weight of the adhering gum is determined and compared to a reference run without additive for an appraisal of the additive's detergency action. The test employs the same apparatus described by J. L. Keller and F. S. Liggett "Induction System Gum-Engine Versus Bench Test", symposium on Vapor Phase Oxidation of Gasoline, ASTM Special Technical Publication No. 202, pp. 21–40 (1956), but a somewhat different procedure is employed in order to appraise detergency action of additives. A gum deposit is formed on the walls of a steam-jacketed glass U-tube by evaporating two liters of gasoline distillate admitted to the system, countercurrent to a stream of preheated air. The U-tube is then washed with a number of portions of naphtha until a final wash shows no discoloration. The amount of gum adhering to the apparatus is then determined by extracting with C. P. acetone and evaporating the acetone extract with filtered, heated air to obtain a gum residue which is heated in an oven for one-half hour at 100–105° C., cooled and weighed. Results of runs using the same gasoline with and without additives are compared to determine detergency action.

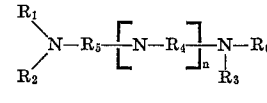
Table 2 shows that while lecithin alone reduced carburetor-type gum deposits 46 percent, the reaction product of lecithin and dipropylene triamine plus 1 mol of ethylene oxide produced an exceptional 83 percent reduction in carburetor-type gum deposits. Table 2 also shows that none of the other lecithin derivatives or mixtures tested were capable of imparting to gasoline a comparable ability to reduce carburetor-type gum deposits.

It is also shown in Table 2 that the gasoline sample containing lecithin without amine showed unsatisfactory filter-clogging characteristics. The lecithin mixture with and the lecithin derivative of diethoxylated dipropylene triamine somewhat improved gasoline filter-clogging characteristics. However, the compounds of this invention which improved gasoline most significantly in regard to filter-clogging characteristics were the lecithin mixture with and the lecithin derivative of monoethoxylated dipropylene triamine.

Various changes and modifications can be made without departing from the spirit of this invention or the scope thereof as defined in the following claims.

I claim:

1. A lecithin derivative of a compound having the formula



wherein

R_1, R_2 and R_3 are selected from the group consisting of hydrogen, methyl and ethyl radicals,

R_4 and R_5 are selected from the group consisting of ethylene, trimethylene and propylene substituents,

R_6 is a $-C_2H_4OH$ or $-C_3H_6OH$ substituent, and n is 1 or 2.

2. The lecithin derivative of dipropylene triamine ethoxylate.

3. The lecithin derivative of dipropylene triamine propoxylate.

4. The lecithin derivative of a compound selected from the group consisting of the ethoxylates and propoxylates of diethylene triamine, ditrimethylene triamine, triethylene tetramine, and tripropylene tetramine.

References Cited

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ELBERT L. ROBERTS, Primary Examiner

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44—57, 72, 73; 260—584