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GASOLINE CONTAINING A TETRAHYDROPYRIMIDINE TO REDUCE CARBURETOR DEPOSITS

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This invention relates to improved motor fuel. It is more particularly concerned with motor gasoline containing additives that inhibit the formation of deposits in carburetors of gasoline engines.

During the operation of spark-ignited internal combustion engines, deposits build up in the throttle body area of the carburetor. These deposits are attributable to foreign matter introduced into the carburetor through the air intake and not to the components of the gasoline itself. The major contributors are blowby and crankcase fumes which emit from the crackcase vent, collect under the hood, and are pulled into the air intake. Another factor contributing to deposits is air pollution. This can be because of general contaminants in the atmosphere, such as industrial wastes, or it can be because of exhaust gases, particularly in "stop and go" driving in heavy traffic.

As they accumulate, these deposits cause rough idling and necessitate frequent adjustment of the idle air bleed screw. Eventually the engine will fail to idle and the carburetor must be removed and cleaned. In extreme cases, it may even be necessary to replace the carburetor. The formation of heavy carburetor deposits is most pronounced in vehicles that are operated at idle speeds for a large portion of the time, such as taxicabs, local door-to-door delivery trucks, and passenger cars used in congested areas in stop-and-go traffic. Although the problem of carburetor deposits is rather widespread, the nature of the deposits vary in different localities. Thus, smog appears to accelerate the formation of deposits, that are tacky and less carbonaceous. On the other hand, in relatively smog-free areas, the deposits will be dry, hard, and carbonaceous. Whatever the type of deposit, however, the build-up of deposits in the carburetor adversely affects engine performance. Particularly in the case of commercial fleet operation, carburetor deposits greatly increase maintenance costs. Accordingly, it is highly desirable to provide a means of inhibiting the formation of carburetor deposits.

It has now been found that the formation of carburetor deposits can be inhibited simply and economically. It has been discovered that certain tetrahydropyrimidines, when added to the gasoline in small amounts, effectively reduce carburetor deposits.

Accordingly, it is a broad object of this invention to provide a stable gasoline composition. Another object is to provide a gasoline adapted to reduce the formation of carburetor deposits. A further object is to effectively reduce carburetor deposits in spark-ignited internal combustion engines. A specific object is to provide a motor gasoline containing small amounts of certain tetrahydropyrimidines. Other objects and advantages of this invention will become apparent to those skilled in the art, from the following detailed description.

In general, this invention provides a motor gasoline containing a small amount, sufficient to inhibit the formation of carburetor deposits, of a tetrahydropyrimidine resulting from the condensation of naphthenic acid with an

aliphatic hydrocarbon substituted propylene-diamine having the formula:

$$\underset{H}{\overset{R}{>}}N-CH_2CH_2CH_2-NH_2$$

wherein R is an aliphatic hydrocarbon group containing between about 8 carbon atoms and about 18 carbon atoms.

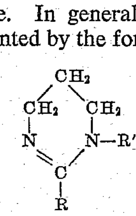
The addition agents contemplated herein are tetrahydropyrimidines, i.e., condensation products of naphthenic acids with certain aliphatic hydrocarbon-substituted propylene diamines, described hereinafter. The naphthenic acids, as is well known to those familiar with the art, are monocarboxylic acids found in crude petroleum and in petroleum distillates. They are obtained as mixtures rather than as pure compounds. Particularly utilizable herein are naphthenic acids containing between about 10 and about 30 carbon atoms. Such acids can have an acid number (mg. KOH per gram) varying between about 120 and about 220, corresponding to an average molecular weight of between about 420 and about 275. A particularly useful naphthenic acid, acid X, has an average molecular formula, $C_{19}H_{34}O_2$; an average molecular weight of 297; and acid number of 178; about 5 percent unsaponifiables; and distils, at a pressure of 2 mm. Hg, over the range 315–485° F.

The diamine reactant used to make the additives contemplated herein is N-aliphatic hydrocarbon substituted propylene diamine having the formula,

$$\underset{H}{\overset{R}{>}}N-CH_2CH_2CH_2-NH_2$$

wherein R is an aliphatic hydrocarbon group containing between about 8 carbon atoms and about 18 carbon atoms. The diamine reactant can be a pure compound, but, in practice, it will often be a mixture of pure diamines. Several mixtures of diamine reactants are available on a commercial scale. "Amine A" is a mixture of N-substituted propylene diamines of the formula set forth hereinbefore, wherein about 20 percent of the R groups are hexadecyl, about 17 percent are octadecyl, about 26 percent are octadecenyl, and about 37 percent are octadecadienyl. "Amine B" is a similar mixture wherein 8 percent of the R groups are octyl, about 9 percent are decyl, about 47 percent are dodecyl, about 18 percent are tetradecyl, about 8 percent are hexadecyl, about 5 percent are octadecyl, and about 5 percent are octadecenyl. In another mixture, "amine C," about 2 percent of the R groups are tetradecyl, about 24 percent are hexadecyl, about 28 percent are octadecyl, and about 46 percent are octadecenyl. Amine C is particularly preferred.

The tetrahydropyrimidines utilizable herein are condensation products of the naphthenic acid and the propylene diamine reacted in a 1:1 molar ratio. As water is a by-product of the reaction, provision is made for water removal. Thus, as is well known, temperatures of 130–275° C. can be used for periods of time until evolution of water ceases, usually 4–16 hours. Other means of facilitating water removal can be employed, such as, for example, azeotropic distillation and operation under subatmospheric pressure. In general, the tetrahydropyrimidines can be represented by the formula:



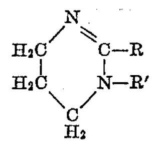
wherein R is naphthenyl and R' is an aliphatic hydrocarbon radical having 8 to 18 carbon atoms. Because, however, most products will be made from mixtures of diamines and of naphthenic acids, as a general rule, they can more accurately be defined by a process definition reciting the reactant mixtures.

The amount of tetrahydropyrimidine added to the motor gasoline will vary between about one pound per thousand barrels (1 lb./M b.) and about 200 lbs./M b., and preferably between about 5 lbs./M b. and about 20 lbs./M b. The motor gasoline can, also, contain small amounts of other addition agents, such as, antiknock agents, scavengers, preignition additives, gum inhibitors, and the like.

The following examples are for the purpose of illustrating the addition agents of this invention and of demonstrating the effectiveness thereof as gasoline detergents. It is to be understood that this invention is not to be limited to the particular components set forth therein. Other components, as described hereinbefore, can be used, as those skilled in the art will readily appreciate.

EXAMPLE 1

A mixture of 400 parts of naphthenic acid X and 510 parts of amine C was refluxed in xylene solution for 8 hours. The reaction mixture was slowly heated to 265° C. and held at that temperature until the evolution of water had ceased. Thirty-six parts (2 moles) water were obtained. The xylene solvent was removed, leaving a substituted tetrahydropyrimidine having a formula;



wherein R is naphthenyl and R' is 2 percent tetradecyl, 24 percent hexadecyl, 28 percent octadecyl, and 46 percent octadecenyl.

The deposit-forming tendencies of a fuel are determined in the 40-hour engine test. This accelerated test, when run on fuels that contain no detergents, produces an amount of deposit equivalent to the amount observed in 20,000 miles of operation in field tests on taxicab fleets. A six-cylinder Chevrolet engine is equipped with notched rings to increase the amount of blowby. The engine is operated for forty hours, using the fuel under test, at alternate idle and running cycles. In the idle cycle, the engine is run at idling speed of 400 r.p.m. with no load, for five minutes. Then, for one minute, the engine is run at a speed of 2500 r.p.m., under a load of 30 B.H.P. and at 9.4 in. mercury manifold pressure. During the running cycle, the blowby and part of the exhaust are collected in a balloon. Then, the collected gases are released into the carburetor air intake during the idling cycle. After 40 hours' operation at alternate run and idle, the carburetor is examined and rated as to the amount of deposit in the throttle throat. In the rating scale, a rating of 0 (zero) indicates a clean carburetor; 1=trace deposits; 2=light deposits; 3=medium deposits; and 4=heavy deposits.

This 40-hour engine test has been found to correlate well with results obtained in long-term field tests on fleets of taxicabs and local delivery trucks. In actual practice, about one-tenth of the amount of detergent required for the accelerated test is found to be needed in fleet operation.

Three gasoline formulations were used in testing the carburetor detergent of this invention. Gasoline "A" contained 1.9 cc./gal. lead tetraethyl; 2.5 pounds per thousand barrels gasoline (lbs./M b.) of phenylene diamine (antioxidant); and 0.4 lb./M b. of N,N'-disalicylidene-1,2 propanediamine. Gasoline B contained 2.2 cc./gal. lead tetraethyl; 5 lbs./M b. of 2,6-di-t-butyl-4-methyl phenol (antioxidant); one lb./M b. of N,N'-disalicylidene-1,2 propanediamine; and 43 lbs./M b. of cresyl diphenyl phosphate (preignition additive). Gasoline "C" contained 3 cc./gal. lead tetraethyl; one lb./M b. of N,N'-disalicylidene-1,2 propanediamine; 10 lbs./M b. of 2,6-di-t-butyl-4-methyl phenol (antioxidant); 64 lbs./M b. of cresyl diphenyl phosphate; and 25 lbs./M b. of glyceryl monooleate (de-icer).

EXAMPLE 2

Into portions of each of the aforedescribed gasolines, were blended 50 pounds per thousand barrels of the tetrahydropyrimidine of Example 1. The resultant blends were then subjected to the 40-hour engine test. The gasolines without tetrahydropyrimidine were also tested. Pertinent data and test results are set forth in Table I.

Table I

Gasoline	Compound of Example 1, lbs./M b.	Engine Rating	Percent Reduction in Deposits
A	0	2.5	
A	50	1.0	60
B	0	3.0	
B	50	1.5	50
C	0	3.5	
C	50	1.5	57
C	150	1.0	72

From the data in Table I, it will be noted that carburetor deposits were highly reduced when the test gasoline contained a carburetor detergent of this invention. The use of the detergent not only reduces build-up of deposits, but also will remove deposits and tend to clean up dirty carburetor throat bodies. This is shown in the following example:

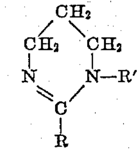
EXAMPLE 3

A gasoline blend (D) containing 3 cc./gal. lead tetraethyl, one lb./M b. N,N'-disalicylidene-1,2 propanediamine, and 10 lbs./M b. of 2,6-di-t-butyl-4-methylphenol was run on the 40-hour engine test. The carburetor was inspected and was found to have a rating of 4. Then, 100 lbs./M b. of the tetrahydropyrimidine of Example 1 was added to the gasoline blend (D) and run on the engine test for 70 hours, using the same dirty carburetor that had a rating of 4. At the end of the run, the carburetor had become cleaner and had a rating of 3.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understood. Such variations and modifications are considered to be within the purview and scope of the appended claims.

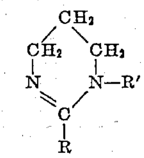
What is claimed is:

1. A motor gasoline containing between about 1 pound and about 200 pounds per 1000 barrels of gasoline of a tetrahydropyrimidine having the structure:



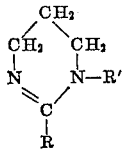
wherein R is naphthenyl and R' is an aliphatic hydrocarbon radical having 8 to 18 carbon atoms.

2. A motor gasoline containing between about 5 pounds and about 20 pounds per 1000 barrels of gasoline of a tetrahydropyrimidine having the structure:



wherein R is naphthenyl and R' is an aliphatic hydrocarbon radical having 8 to 18 carbon atoms.

3. A motor gasoline containing between about 5 pounds and about 20 pounds per 1000 barrels of gasoline of a tetrahydropyrimidine having the structure:



wherein R is naphthenyl and R' is a mixture of aliphatic radicals of which about 2 percent are tetradecyl, about 24 percent are hexadecyl, about 28 percent are octadecyl and about 46 percent are octadecenyl.

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