United States Patent Office

3,014,792

Patented Dec. 26, 1961

3,014,792

SYNERGISTIC ADDITIVE COMBINATION FOR ANTISTALL GASOLINE

Julius Capowski and William L. Wascher, Jr., Pitman, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

No Drawing. Filed Sept. 19, 1960, Ser. No. 56,651
3 Claims. (Cl. 44—63)

This invention relates to gasoline compositions adapted to improve the operation of internal combustion engines. It is more particularly concerned with motor fuels that provide improved engine operation under cool, humid weather conditions.

As is well known to those skilled in the art, frequent stalling of automobile engines, especially during the warm-up period, has been a common occurrence. This difficulty is most pronounced in postwar cars having automatic transmissions and a consequent limit on the maximum permissible idle speed, although icing also occurs in cars without automatic transmissions. Stalling of this type, of course, is a definite safety hazard, as well as a decided inconvenience in frequent restarting of the engine.

It is now recognized that stalling during the warm-up period is attributable to the formation of ice on the throttle plate and the carburetor barrel near it. The water which forms the ice does not come from the gasoline, i.e. as entrained water, but from the air that enters the carburetor. As has been mentioned hereinbefore, stalling generally occurs in cool, humid weather, when the temperatures are above about 30° F. and below about 60° F. and the relative humidity is about 65 percent and higher, up to 100 percent. The most critical conditions are temperatures of 35–45° F. and 100 percent relative humidity.

As the gasoline evaporates in the carburetor, it reduces the temperature of the surrounding metal by as much as 50° F. Moisture in the incoming air comes in contact with these parts and begins to build up ice on the throttle plate and in the carburetor barrel. The more moist this air is, the greater the build-up of ice. Then, when the engine is idled, the throttle plate closes and the ice chokes off the normal small flow of air through the small clearance between the throttle plate and the carburetor wall. This causes the engine to stall. The engine can usually be re-started when the heat from the exhaust manifold melts the ice sufficiently. However, stalling will continue until the engine is completely warmed up.

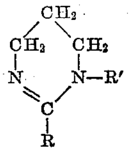
Carburetor icing occurs in many vehicles when cruising at speeds of 30–60 m.p.h. Such icing is a pronounced problem in the case of certain trucks and in cars equipped with carburetors having Venturi-type fuel-air mixing tubes (emulsion tubes). Such carburetors are found in many European cars. The ice builds up on the tube and restricts the flow of air, thereby enriching the fuel mixture and reducing efficiency. Eventually the engine may stall.

Gasoline is a mixture of hydrocarbons having an initial boiling point falling between about 75° F. and about 135° F. and an end-boiling point falling between about 250° F. and about 450° F. The boiling range of the gasoline, of course, reflects on its volatility. Thus, a higher boiling gasoline will be less volatile and give less stalling difficulty. It has been proposed in the art that a gasoline having an ASTM mid-boiling (50%) point of 310° F. or higher will not be subject to stalling. Although this may be the case for a given series of gasolines, however, it is not the sole and controlling factor. Gasolines of higher mid-boiling point but a low initial boiling point (e.g. full boiling range gasolines) can induce stalling when the aforementioned stall-inducing atmospheric conditions are prevalent. Thus, any gasoline will give difficulty in damp, cool weather. In modern engine operation, however, control of stalling by means of volatility is not feasible, because other performance characteristics are affected.

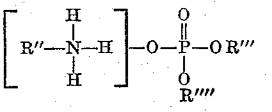
It has now been found that stalling during engine warm-up can be overcome simply and economically. It has been discovered that small amounts of a synergistic combination of certain substituted tetrahydropyrimidines and certain amine salts of partial alkyl esters of orthophosphoric acid, when added to motor gasoline, will overcome stalling difficulties attributable to carburetor icing.

Accordingly, it is an object of this invention to provide an improved motor fuel. Another object is to provide a motor fuel adapted to prevent stalling during engine warm up in cool, humid weather. A specific object is to provide an antistall gasoline containing a synergistic combination of certain substituted tetrahydropyrimidines and certain amine salts of partial alkyl esters of orthophosphoric acid. 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 stalling, of synergistic combination of a tetrahydropyrimidine having the structure:



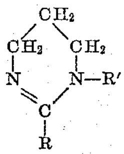
wherein R is naphthenyl and R′ is an aliphatic hydrocarbon radical having 8 to 18 carbon atoms, and an amine phosphate having the structure:



$$\left[R''-\underset{H}{\overset{H}{N}}-H\right]-O-\underset{\underset{R''''}{O}}{\overset{\overset{O}{\|}}{P}}-OR'''$$

wherein R″ is an aliphatic hydrocarbon radical of 6 to 18 carbon atoms, R‴ is an alkyl radical having 6 to 18 carbon atoms, and R⁗ is hydrogen or R‴.

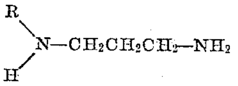
The tetrahydropyrimidines that form part of the synergistic combination of this invention have been proposed as carburetor detergents in copending application Serial Number 757,457, filed August 27, 1958, and now Patent No. 2,961,308. Although effective carburetor detergents, the tetrahydropyrimidines, at the concentrations used, have little effectiveness by themselves as antistalling additives. The tetrahydropyrimidines contemplated herein have the structure:



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

These tetrahydropyrimidines are 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 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; an acid number of 178; about 5 percent unsaponifiables; and distils, at a pressure of 2 mm. Hg, over the range 315–485° F.

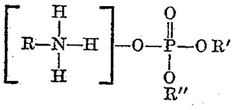
The diamine reactant used to make the additives contemplated herein is N-aliphatic hydrocarbon substituted propylene diamine having the formula,



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 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.

The amine salt components of the synergistic combination of this invention are salts of mono- and/or di-esters of orthophosphoric acid having the structure:



$$\left[R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-H\right]-O-\overset{\overset{O}{\|}}{\underset{\underset{R''}{\underset{|}{O}}}{P}}-OR'$$

wherein R is an aliphatic hydrocarbon radical having between about 6 carbon atoms and about 18 carbon atoms, R′ is an alkyl radical having between about 6 carbon atoms and about 18 carbon atoms, and R″ is hydrogen or R′.

The phosphate ester portion of the amine phosphate component is a mono-ester of orthorphosphoric acid, a di-ester of orthorphosphoric, or a mixture of mono-ester and di-ester. The ester groups of the phosphate ester are alkyl radicals having between about 6 and about 18 carbon atoms, preferably between about 6 and about 10 carbon atoms. The mono- and/or di-esters are suitably prepared by reacting an alcohol with phosphorus pentoxide in molar proportions of alcohol to phosphorus pentoxide varying between 2 and 4. The esterification reaction is generally carried out at temperatures from 60° to 212° F. with active stirring for a time needed to complete the reaction as evidenced by complete solution of the phosphorus pentoxide. An especially preferred phosphate ester amine salt is the octylamine salt of a mixture of mono- and di-octyl phosphate.

The components of the synergistic additive combinations are each used in the gasoline at concentrations varying between about 0.001 percent and about 0.03 percent, by weight of the gasoline. The weight ratio of phosphate ester amine salt to tetrahydropyrimidine will vary between about 5:1 and about 1:1, respectively. Preferably, the weight ratio of ester salt to tetrahydropyrimidine will be about 3:1, respectively.

The antistall additives of the invention may be used in the gasoline along with other antistall addition agents or other additives designed to impart other improved properties thereto. Thus, antiknock agents, preignition inhibitors, anti-rust agents, metal-deactivators, dyes, antioxidants, etc., may be present in the gasoline. Also, the gasoline may contain a small amount, from about 0.01 percent to about one percent, by weight, of a solvent oil or upperlube. Suitable oils, for example, include coastal and mid-continent distillate oils having viscosities within the range of from about 50 to about 500 S.U.S. at 100° F. Synthetic oils, such as di-ester oils, polyalkylene glycols, silicones, phosphate esters, polypropylenes, polybutylenes, and the like, may also be used.

The following examples are for the purpose of illustrating this invention and demonstrating the effectiveness thereof. This invention is not to be limited to the specific composition set forth in the examples or to the operations and manipulations involved. Other materials and formulations as described hereinbefore can be used, as those skilled in the art will readily understand.

The ability of an additive to inhibit stalling is demonstrated in the following test:

HILLMAN-MINX ENGINE TEST

A standard Hillman-Minx engine, equipped with a Crosley single downdraft carburetor, was used in this test. A thermocouple was attached to the throttle body to record the throttle body temperature. An eight inch long water-cooled standpipe was placed between the carburetor and manifold to prevent heat conduction. A spray chamber and an ice tower were used to saturate the incoming air with moisture and to cool the air to about 40° F. before it entered the carburetor.

In conducting a test, the engine was first run for about 10 minutes at 2750 r.p.m. to bring the engine temperature to equilibrium. The engine was then shut off. When the throttle body temperature rose to 40° F., the engine was restarted with the idle speed set at 450 r.p.m. so that the base fuel stalled at idle in 10 seconds or less after a run-time of 50 to 70 seconds. Run-time means the time that the engine was run at 2750 r.p.m. before returning to idle.

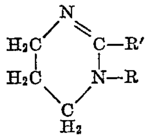
All the runs were started when the throttle body reached 40° F. At the instant of starting, the throttle arm was moved to the 2750 r.p.m. position and a stop watch started. At the end of the selected run-time, the throttle arm was moved to the idle position. The time required to stall was recorded. Several tests were made for each fuel and the run-times were averaged.

In evaluating an additive, the base fuel was first tested followed by the base fuel containing several concentrations of the additive. The system was flushed between tests with a solvent mixture of acetone, methanol, benzene and the fuel to be run next. Any improvement caused by the additive was reflected in a longer run-time (as compared to the base fuel) to cause stalling in 10 seconds or less when the engine was idled. The more effective the additive, the longer the run-time.

The base gasoline used to evaluate the antistall additives was a blend, by volume, of 78 percent platinum reformate gasoline, 16 percent natural gasoline, and 6 percent butane, having an API gravity of 58.1°. It had an ASTM boiling range of 78° F. to 396° F., with a mid-boiling point of 200° F.

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 base gasoline and a blend of the additive of this example in the base gasoline were each subjected to the Hillman-Minx engine test. Pertinent data are set forth in Table I.

Example 2

There was obtained a commercially available phosphate ester amine salt, the octylamine salt of mixed mono- and di-octyl phosphate, having the composition—

Constituent:	Wt. percent
Carbon	59.14
Hydrogen	11.58
Phosphorus	8.06
Nitrogen	3.62
Oxygen	17.60

This material was blended in the base gasoline and the blend was subjected to the Hillman-Minx engine test. Pertinent data are set forth in Table I.

Example 3

A blend in the base gasoline of the additive of Example 2 and that of Example 1, in a weight ratio of 3:1, respectively, was subjected to the Hillman-Minx engine test. Pertinent data are set forth in Table I.

TABLE I

Fuel	Additive	Conc., lb./M b.[1]	Run Time to 10 Sec. Stall Time (Sec.)
Base gasoline	None		58
Do	Example 1	5	50
Do	Example 2	15	121
Do	Example 1 Example 2	5 15	>300

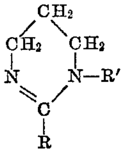
[1] Pounds per thousand barrels of gasoline.

It will be noted that the tetrahydropyrimidine (Example 1) was not an effective antistall additive. The amine salt of phosphate ester (Example 2) was somewhat effective. However, the combination of the two additives (Example 3) had a synergistic effect and gave results considerably more than mere additive effect of the two addition agents.

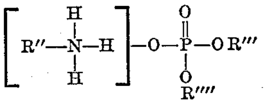
Although the present invention has been described with preferred embodiments it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications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

What is claimed is:

1. A motor gasoline containing between about 0.001 percent and about 0.03 percent, by weight of the gasoline, of a synergistic combination of a tetrahydropyrimidine having the structure:



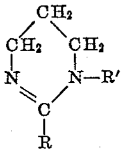
wherein R is naphthenyl and R′ is an aliphatic hydrocarbon radical having between about 8 and about 18 carbon atoms, and an amine phosphate having the structure:



$$\left[R''-\underset{H}{\overset{H}{N}}-H\right]-O-\underset{\underset{R''''}{O}}{\overset{\overset{O}{\|}}{P}}-OR'''$$

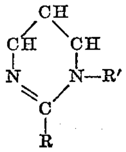
wherein R″ is an aliphatic hydrocarbon radical having between about 6 and about 18 carbon atoms, R‴ is an alkyl radical having between about 6 and about 18 carbon atoms, and R⁗ is selected from the group consisting of hydrogen and R‴; the weight ratio of said amine phosphate to said tetrahydropyrimidine in said synergistic combination being between about 5:1 and about 1:1.

2. A motor gasoline containing between about 0.001 percent and about 0.03 percent, by weight of the gasoline, of a synergistic combination of a tetrahydropyrimidine having the structure:



wherein R is naphthenyl and R′ is an aliphatic hydrocarbon radical having between about 8 and about 18 carbon atoms, and the octylamine salt of a mixture of mono- and di-octyl phosphate; the weight ratio of said octylamine salt to said tetrahydropyrimidine in said synergistic combination being between about 5:1 and about 1:1.

3. A motor gasoline containing between about 0.001 percent and about 0.03 percent, by weight of the gasoline, of a synergistic combination of a tetrahydropyrimidine having the structure:



wherein R is naphthenyl and R′ is a mixture of aliphatic radicals of which 2 percent are tetradecyl, about 24 percent are hexadecyl, about 28 percent are octadecyl, and about 46 percent are octadecenyl, and the octylamine salt of a mixture of mono- and di-octyl phosphate; the weight ratio of said octylamine salt to said tetrahydropyrimidine in said synergistic combination being between about 5:1 and about 1:1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,863,742	Cantrell et al.	Dec. 9, 1958
2,863,904	Cantrell et al.	Dec. 9, 1958
2,915,528	Raifsnider	Dec. 1, 1959
2,919,684	Carr	Jan. 5, 1960
2,961,308	Andress	Nov. 22, 1960