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3,010,811
ZINC SALT DEICERS

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3 Claims. (Cl. 44—68)

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 warmup 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 it 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 warmup 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 10 percent. The most critical conditions are temperatures of 35–40° 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 40° 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 buildup 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 restarted when the heat from the exhaust manifold melts the ice sufficiently. However, stalling will continue until the engine is completely warmed up.

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. In modern engine operation, however, control of stalling by means of decreased volatility is not feasible, because other performance characteristics are affected.

It has now been found that stalling during engine warmup can be overcome simply and economically. It has been discovered that small amounts of certain zinc salts of partial esters of phosphoric acid or thiophosphoric 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 warmup in cool, humid weather. A specific object is to provide an antistall gasoline containing the zinc salt of certain mixed partial esters of phosphoric acid or thiophosphoric 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 the zinc salt of mixed partial esters of phosphoric acid or of thiophosphoric acid, and particularly the zinc salt of mixed mono(lower-alkyl penyl) and di(lower-alkyl phenyl) esters of phosphoric acid.

The zinc salts contemplated herein are readily prepared by methods known in the art. The salt can be prepared from any mixed ester of phosphoric acid or of thiophosphoric acid. Esters of phosphoric acid can be prepared by methods known in the art. A typical procedure involves reacting P_2O_5 with straight or branched chain alcohols having 1 to 18 carbon atoms, such as methanol, propanol, butanol, octanol, 2-ethylhexanol, dodecanol, and oleyl alcohol; or with alkylphenols, such as cresol, octylphenol, diamylphenol, and waxphenol. The preferred class of mixed partial esters includes the mixed mono(lower-alkyl phenyl) and di-(lower-alkyl phenyl) ester of orthophosphoric acid. These esters are prepared, suitably, by reacting lower-alkyl phenols (e.g., cresol, amylphenol, diamylphenol, butylphenol) with P_2O_5 in a molar ratio of 3:1, respectively. The conditions and method of carrying out this reaction are clearly described, as for example, in United States Letters Patents Numbers 2,638,447 and 2,790,767.

The mixed partial esters of thiophosphoric acid corresponding to the aforedescribed phosphoric acid mixed esters are prepared by reacting P_2S_5 with the alcohols or alkylphenols. Typical methods are set forth, for example, in United States Letters Patent Number 2,410,650.

The zinc salt is prepared by reacting the sodium salt of the mixed partial esters of phosphoric acid with an aqueous or alcoholic solution of zinc chloride. Another procedure is to react the partial esters directly with zinc acetate or zinc carbonate. It will be understood that the salt can be made by any method for producing neutral salts and that this invention is not to be limited to the aforementioned methods.

The amount of zinc salt of mixed alkylphenyl partial esters of phosphoric acid that is added to the motor gasoline will vary between about 0.0001 percent and about one percent, by weight, of the gasoline. In preferred practice, amounts varying between about 0.001 percent and about 0.1 percent, by weight, are used.

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, anti-knock agents, preignition inhibitors, anti-rust agents, metal-deactivators, dyes, antioxidants, detergents, etc., may be present in the gasoline. Also, the gasoline may contain a small amount, from about 0.01 percent to about 1 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 diester oils, polyalkylene glycols, silicones, phosphate esters, polyphenyl ethers, polypropylenes, polybutylenes and the like, may also be used.

The following examples are for the purpose of illustrating the additives of this invention and demonstrating the effectiveness thereof. This invention is not to be limited to the specific composition set forth in the example 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.

EXAMPLE 1

Three moles of diamylphenol (702 grams) are placed

in a 3 liter, 3-neck flask equipped with stirrer, thermometer and reflux condenser and heated to 100° C. One mole of P_2O_5 (142 grams) is added in small portions over a three hour period. The temperature is then raised to 150° C. and held for three hours. The mixture is cooled and filtered through a layer of Hi-flo clay. The acid has a neutralization number of 165.

Fifty grams of this acid are dissolved in 100 grams of mineral oil having a viscosity at 100° F. of 100 S.U.S. To this is added 11.6 grams of $ZnCO_3$ (25% exess). The mixture is heated at 160–170° C. for about two hours, cooled and filtered through a layer of Hi-flo clay.

Final blend contains 35.5% of the zinc salt.

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

A standard Chevrolet engine, equipped with a Holley single downdraft carburetor, was mounted in a "cold" room refrigerated to 45° F. A thermocouple was attached to the throttle plate shaft to record the plate temperature. A ½-inch insulating gasket was placed between the carburetor and manifold to prevent heat conduction. An asbestos sheet covered the entire manifold system to shield the carburetor from convection and radiation. A spray chamber and an ice tower was used to saturate the incoming air with moisture and to cool the air to about 35° F. before it entered the carburetor.

In conducting a test, the engine was first run for about 10 minutes at 2000 r.p.m. to bring the engine temperature to equilibrium. The engine was then shut off. When the throttle shaft 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 20 to 40 seconds. Run-time means the time that the engine was run at 2000 r.p.m. before returning to idle.

All the runs were started when the throttle shaft reached 40° F. At the instant of starting, the throttle arm was moved to the 2000 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 at each run-time and averaged.

In evaluating an additive, the base fuel was first tested followed by several concentrations of the additive. The system was flushed between tests with 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 gasoline used to test the additives contemplated herein was a blend of, by volume, 70 percent catalytically cracked gasoline and 30 percent natural gasoline. It had an A.S.T.M. boiling range of 98° F. to 387° F., with a mid-boiling point of 194° F.

Using this test gasoline, the salt of Example 1 was

subjected to the aforedescribed stalling test. The pertinent data and test results are set forth in Table I.

Table I

Compound added	Conc'n, weight percent	Run-time to 10 sec. stall time (sec.)
None (blank fuel)	0.0	30
Example 1	0.01	90

It will be apparent from the data of Table I, that the zinc salts described herein are effective antistall additives for gasoline. Most show an increase in run-time of 50–100 percent over the blank fuel. The material of Example 1 increases run-time by 200 percent.

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 a small amount, sufficient to inhibit stalling, of the zinc salt of mixed mono-(lower alkyl phenyl) phosphoric acid and di(lower alkyl phenyl) phosphoric acid.

2. A motor gasoline containing between about 0.0001 percent and about 1 percent, by weight of the gasoline, of the zinc salt of mixed mono(lower alkyl phenyl) phosphoric acid and di(lower alkyl phenyl) phosphoric acid.

3. A motor gasoline containing between about 0.001 percent and about 0.1 percent, by weight of the gasoline, of a zinc salt of mixed mono (diamylphenyl) phosphoric acid and di(diamylphenyl) phosphoric acid.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 3,010,811 November 28, 1961

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 33, for "10 percent" read -- 100 percent --; column 2, line 7, for "penyl" read -- phenyl --.

Signed and sealed this 24th day of April 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents