

[54] LUBRICANT AND FUEL COMPOSITIONS

[75] Inventors: **Franklin H. Robinson**, North Brunswick; **Marvin S. Rakow**, East Brunswick; **Paul M. Kerschner**, Trenton, all of N.J.

[73] Assignee: **Cities Service Oil Company**, Tulsa, Okla.

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Primary Examiner—Patrick P. Garvin

Assistant Examiner—I. Vaughn

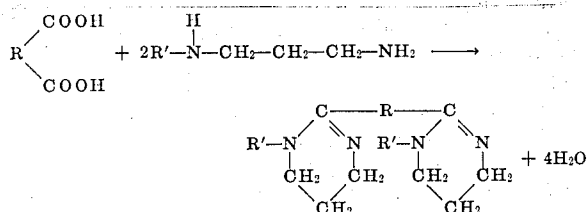
Attorney, Agent, or Firm—J. W. Carpenter; G. L. Rushton; E. T. Yates

[57] **ABSTRACT**

Hydrocarbyl acid phosphate salts of ditetrahydropyrimidines and petroleum hydrocarbon compositions containing the same. The salts are formed by neutralizing with a hydrocarbyl acid orthophosphate at least 25 percent of the basic nitrogens of the ditetrahydropyrimidine. Petroleum hydrocarbon compositions containing these salts exhibit desirable properties such as enhanced corrosion resistance and improved detergency. Gasoline compositions containing the salts are also characterized by improved carburetor anti-icing characteristics.

3 Claims, No Drawings

R and R' are as defined above. In the case where a dicarboxylic acid is used, 4 moles of water are eliminated:



Again, R and R' are as defined above.

The dicarboxylic acid or dicarboxylic acid anhydride which is used in the preparation of the ditetrahydropyrimidine has a hydrocarbylene group R that contains about 2 to 34 carbons and preferably about 2 to 10 carbons. R may be aliphatic, aromatic or naphthenic, or it may contain various mixtures of aliphatic, aromatic and naphthenic segments. Aliphatic and naphthenic segments may be either saturated or unsaturated. Examples of suitable dicarboxylic acids and dicarboxylic acid anhydrides are maleic anhydride, maleic acid; succinic acid; succinic anhydride; glutaric acid; glutaric anhydride; adipic acid; terephthalic acid; 1,4-cyclohexanedicarboxylic acid; 1,10-dicarboxydecane; 1,18-dicarboxyoctadecane; 1,8-dicarboxyoctane; and a dimer acid produced by the dimerization of a polyunsaturated C₁₈ monocarboxylic fatty acid to produce an unsaturated C₃₆ dicarboxylic acid wherein R contains 34 carbons. It is preferred that the ditetrahydropyrimidine be prepared from maleic anhydride or maleic acid in which case R is vinylene.

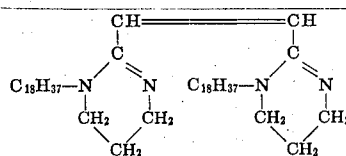
The N-hydrocarbyl-1,3-propylenediamine which is condensed with the dicarboxylic acid or dicarboxylic acid anhydride to form the ditetrahydropyrimidine has a hydrocarbyl group R' that contains about 6 to 30 carbons and preferably about 10 to 25 carbons. R' may be aliphatic, aromatic or naphthenic, or it may contain various mixtures of aliphatic, aromatic and naphthenic segments. Aliphatic and naphthenic segments may be either saturated or unsaturated. Examples of suitable R' groups are hexyl, cyclohexyl, phenyl, p-tolyl, tricontyl, tricosyl, eicosyl, decyl, dodecyl, 4-butylcyclohexyl, stearyl, oleyl, and cyclooctenyl. The preferred hydrocarbyl group R' is tallowyl, hence the preferred propylenediamine is N-tallowyl-1,3-propylenediamine.

The hydrocarbyl acid orthophosphate which is reacted with the ditetrahydropyrimidine to form a salt may be a dihydrocarbyl acid orthophosphate, a hydrocarbyl diacid orthophosphate or preferably a mixture of a dihydrocarbyl acid orthophosphate and a hydrocarbyl diacid orthophosphate. The hydrocarbyl portions contain from about 1 to about 15 carbons and preferably from about 3 to about 10 carbons. In the case of dihydrocarbyl acid orthophosphates and mixtures of dihydrocarbyl acid orthophosphates and hydrocarbyl diacid orthophosphates, the hydrocarbyl groups may be the same or different. The hydrocarbyl portions may be aliphatic, aromatic or naphthenic or they may contain various mixtures of aliphatic, aromatic and naphthenic segments. Aliphatic and naphthenic segments may be either saturated or unsaturated. It is preferred that the hydrocarbyl portions be aliphatic.

The ratio of hydrocarbyl acid orthophosphate to the ditetrahydropyrimidine is such at least about 25 percent of the basic nitrogens of the ditetrahydropyrimidine are converted to the hydrocarbyl acid orthophosphate salt. While about 25 percent to about 100 percent of the basic nitrogens may be converted to the hydrocarbyl acid orthophosphate salt, it is preferred that about 50 percent to about 90 percent of the basic nitrogens be converted to the salt. However, an excess of hydrocarbyl acid orthophosphate may be present in the case where 100 percent of the basic nitrogens are converted to the salt.

Examples of hydrocarbyl acid orthophosphates are cyclohexyl diacid orthophosphate, diphenyl acid orthophosphate, methyldecyl acid orthophosphate, pentadecyl diacid orthophosphate, dipropyl acid orthophosphate, heptyl diacid orthophosphate, isooctyl diacid orthophosphate, and diisooctyl acid orthophosphate. The preferred hydrocarbyl acid orthophosphate is a mixture of isooctyl diacid orthophosphate and diisooctyl acid orthophosphate. Most preferred is a mixture of about 65 weight percent diisooctyl acid orthophosphate and about 35 weight percent of isooctyl diacid orthophosphate.

A particularly preferred hydrocarbyl acid orthophosphate salt of a ditetrahydropyrimidine is thus the salt of a ditetrahydropyrimidine prepared by the condensation of 1 mole of maleic acid or maleic anhydride with 2 moles of N-tallowyl-1,3-propylenediamine and having the structural formula



wherein about 50 to 90 percent of the basic nitrogens contained therein are converted to a salt by reaction with a mixture of about 65 weight percent diisooctyl acid orthophosphate and about 35 weight percent isooctyl diacid orthophosphate.

While the concentration of the hydrocarbyl acid orthophosphate salt of the ditetrahydropyrimidine additive of this invention in petroleum hydrocarbon products, such as fuels and lubricating oils, may be varied over a broad range, petroleum hydrocarbon compositions containing about 1 to 250 pounds of additive per thousand barrels (PTB) of the composition are generally used. However, hydrocarbon fuel and lubricating oil compositions containing from about 3 to 100 PTB of additive are preferred.

The efficacy of the additives of this invention in petroleum hydrocarbon product compositions is determined by subjecting said compositions to one or more of the following tests. The test procedures are as follows.

CARBURETOR DETERGENCY TEST:

Engine blow-by contaminants are generated in an engine and collected in a flask. At the end of the collecting period the water phase is separated from the fuel phase, the latter being discarded. The water phase of the contaminants is used for the carburetor detergency evaluations.

The carburetor detergency test is run on a Cooperative Lubricants Research (CLR) engine, a single cylin-

der research engine manufactured by Laboratory Equipment Company. The contaminants are injected into the carburetor throttle body of a CLR engine running with a rich mixture and on which the throttle plate has been removed and a 200 mesh stainless steel specimen screen installed at the entrance to the intake manifold. The amount of deposits accumulated on the screen after 3 hours of engine operation indicates the detergency performance of the fuel. Experimental fuels and reference fuels are tested with the same batch of contaminants.

At the conclusion of the 3 hour run, the 200 mesh screen is removed and evaluated for contaminant accumulation. The reflectance of the screen, determined by means of a reflectance meter, is a measure of the amount of deposits accumulated on the screen. The higher the reflectance, the cleaner the screen, i.e., the lower the accumulation of deposits.

The effectiveness of an additive is represented as the ratio, expressed as a percentage, of the average screen reflectance for the fuel containing the additive to the average screen reflectance for a reference fuel containing a commercially available carburetor detergent additive at a concentration of 15 pounds per thousand (PTB). Thus, a fuel composition containing an experimental additive that equals the performance of the reference fuel will have an effectiveness of 100 percent, an experimental fuel that performs at a lower level than the reference fuel will have an effectiveness of less than 100 percent, and an experimental fuel that performs at a higher level than the reference fuel will have an effectiveness of greater than 100 percent.

CARBURETOR ANTI-ICING TEST:

The test is run on a CLR single cylinder engine coupled to a speed control dynamometer. The engine is fitted with a special, thermally-isolated carburetor with external float bowls; no idle fuel system is used. The carburetor has an adjustable main jet and the throttle body is constructed of glass or clear plastic so icing can be confirmed by visual inspection. A temperature and humidity control system supplies inlet air to the carburetor at the desired conditions and also to a glass or clear plastic box enclosing the carburetor.

All anti-icing additives are evaluated in a blended base fuel composed of 25 volume percent of ASTM isooctane and 75 volume percent of precipitation naphtha and containing 1.5 ml./gal. of tetraethyl lead. Also present are a scavenger, metal deactivator, and an antioxidant. A non-icing purge fuel consisting of the base fuel containing 5.5 percent of isopropyl alcohol is used in the test. The anti-icing properties of fuel compositions containing additives of this invention are compared to those of the base fuel containing no anti-icing additive.

Ice formation on the throttle plate of the carburetor is measured by an increase in manifold vacuum caused by a choking of the engine by the ice formation. The time in seconds for the manifold vacuum to increase 2.0 inches of mercury is recorded as time to ice with the fuel which is being evaluated. An increase in manifold vacuum of 2.0 inches of mercury is defined as severe ice.

Engine operating conditions are set so as to cause a reference fuel, i.e., a base fuel containing a reference anti-icing additive, to ice sufficiently to cause a 2.0 inch manifold vacuum increase in 40 to 50 seconds. When

these conditions are set, the base fuel containing no anti-icing additive will ice to the same extent in 18 to 20 seconds. Once these operating conditions have been achieved, the anti-icing characteristics of base fuel containing the experimental additives can be evaluated.

In running the test on a fuel composition containing an experimental additive, once ice severe enough to raise the manifold vacuum 2.0 inches of mercury has formed, the carburetor is switched to the purge fuel which removes the ice. After 50 seconds to allow for ice removal and engine stabilization, the carburetor is switched back to the experimental fuel. The above procedure is repeated until five runs on the experimental fuel have been made, the times for a manifold vacuum increase of 2.0 inches of mercury being noted. The times of the five runs are then averaged. Either a base fuel or a reference fuel is run after every two experimental additive runs.

In addition to the foregoing, the rust inhibition properties of the inventive additives are determined by the ASTM D-665 and the Mil-25017-B procedures.

The invention will be further illustrated by the following specific examples.

EXAMPLE I

In a flask fitted with a stirrer, thermometer, reflux condenser, and Dean-Stark trap and containing toluene as diluent are placed 148 g. of a dimer acid which is produced by the dimerization of a polyunsaturated C_{18} monocarboxylic fatty acid to produce an unsaturated C_{36} dicarboxylic acid and 180.8 g. of N-tallowyl-1,3-propylenediamine. The reaction mixture is stirred under reflux at 175°C and water of condensation collected in the Dean-Stark trap. The amount of water collected is 20 ml.; the theoretical amount of water for the formation of the ditetrahydropyrimidine is 22.3 ml. The toluene is then removed by distillation to leave a residue of the ditetrahydropyrimidine.

The hydrocarbyl acid orthophosphate salt of the above ditetrahydropyrimidine is prepared by adding to 6.75 g. of said ditetrahydropyrimidine 3.25 g. of a mixture comprising about 65 weight percent diisooctyl acid orthophosphate and about 35 weight percent isooctyl diacid orthophosphate. The pH of the salt is 7.0, corresponding to 90 percent of the basic nitrogens of the ditetrahydropyrimidine being converted to the salt. This salt is designated additive a.

EXAMPLE II

Using the procedure of Example I, 15.9 g. of maleic anhydride are condensed with 110.5 g. of N-tallowyl-1,3-propylenediamine. The collected water of condensation amounts to 12.8 ml.; the theoretical amount of water for the formation of the ditetrahydropyrimidine is 12.9 ml. of water. Removal of toluene by distillation leaves a residue of the ditetrahydropyrimidine.

To 6.34 g. of the ditetrahydropyrimidine prepared by the above reaction are added 3.66 g. of the mixed isooctyl acid orthophosphates described in Example I. The pH of the salt is 7.0, corresponding to 82 percent of the basic nitrogens of the ditetrahydropyrimidine being converted to the salt. This salt is designated additive b.

To 6.94 g. of the ditetrahydropyrimidine prepared by the above reaction are added 3.06 g. of the same mixture of isooctyl acid orthophosphates as are used above. The pH of the resultant salt is 7.5, correspond-

ing to 63 percent of the basic nitrogens of the ditetrahydropyrimidine being converted to the salt. This salt is designated additive c.

EXAMPLE III

Gasoline compositions are prepared by dissolving the hydrocarbyl acid orthophosphate salts or ditetrahydropyrimidines designated additives a and b in a base gasoline containing 3 ml. of TEL/gal. and the compositions are subjected to the carburetor detergency test. For comparison purposes, a base leaded gasoline containing no other additive than 3 ml. of TEL/gal. and a leaded (3 ml. of TEL/gal.) gasoline composition containing a commercially available multi-functional additive, i.e., DMA-4 manufactured by the Du Pont Company and containing 80 percent of active ingredient and 20 percent kerosene are also subjected to the carburetor detergency test. The make-up of each gasoline composition and its screen reflectance as well as its percent effectiveness as determined by the average screen reflectance are given in Table I. The gasoline composition containing 15 PTB of DMA-4 has been assigned an effectiveness of 100 percent and all results are relative to this reference. Each result is the average of a number of determinations.

TABLE I

Additive	Concentration PTB	Screen Reflectance	% Effectiveness
—	—	5.1	60
DMA-4	15	8.5	100
a	15	17.4	205
b	15	27.2	320

It is seen from Table I that gasoline compositions containing additives of this invention have excellent carburetor detergency properties.

EXAMPLE IV

A fuel composition is prepared by dissolving additive c in a high volatility fuel comprising a blend of isooctane and precipitation naphtha containing 1.5 ml. of TEL/gal. and the composition is subjected to the carburetor anti-icing test. For comparison purposes, a base fuel containing no other additive than 1.5 ml. of TEL/gal. and base fuel containing the commercial multi-functional additive DMA-4 are also subjected to the carburetor anti-icing test. The make-up of each fuel composition and its percent effectiveness are given in Table II. The percent effectiveness of each composition is determined by comparing the average time for a 2.0 inch manifold vacuum increase to the average time for a 2.0 inch manifold vacuum increase for a fuel composition containing 15 PTB of DMA-4 which has been assigned an effectiveness of 100 percent.

TABLE II

Additive	Concentration, PTB	% Effectiveness
—	—	60
DMA-4	15	100
c	12	98

The data in Table II show that fuel compositions containing an additive of this invention have improved carburetor anti-icing properties compared to a base fuel and compare favorably to a fuel composition contain-

ing a commercially available additive.

EXAMPLE V

Fuel compositions are prepared by dissolving additives of this invention in leaded (3 ml. of TEL/gal.) gasoline and in isooctane, and the compositions are subjected to the ASTM D-665 and the Mil-25017-B rust tests. Also subjected to the rust tests are base leaded gasoline and isooctane containing no rust inhibitor. The make-up of each fuel composition and the results of the rust tests are set forth in Table III. The results of the rust tests are expressed in the percent of the surface of a steel test specimen that is covered by rust; each result is the average of two or more determinations.

TABLE III

Additive	Concentration, PTB	ASTM D-665	Mil-25017-B	
		Leaded Gasoline	Leaded Gasoline	Isooctane
—	—	53	55	100
a	15	0	<0.5	—
b	12	—	—	<0.5
b	15	0	2.5	—
c	12	—	—	10.5

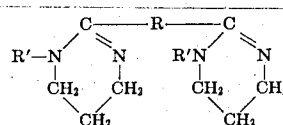
The data in Table III illustrate the excellent rust inhibiting properties imparted to fuel compositions by the incorporation therein of additives of this invention.

In addition to the petroleum hydrocarbon fuels exemplified above, the additives of this invention, when incorporated in fuels such as diesel fuel, jet fuel and burner fuel, yield fuel compositions characterized by enhanced corrosion resistance and improved detergency properties. By the same token, when the additives of the instant invention are incorporated in lubricating oils the resultant compositions exhibit improved detergency and corrosion resistance characteristics.

While the invention has been described above with respect to certain preferred embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention.

We claim:

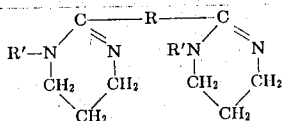
1. A normally liquid petroleum hydrocarbon composition comprising a major proportion of a normally liquid petroleum hydrocarbon selected from the group consisting of gasoline, diesel fuel, jet fuel, burner fuel, and lubricating oil and about 1 to 250 pounds per thousand barrels of a hydrocarbyl acid orthophosphate salt of a ditetrahydropyrimidine having the formula



wherein the hydrocarbyl portions of said hydrocarbyl acid orthophosphate each contains from 1 to about 15 carbons, R is a hydrocarbylene group of about 2 to 34 carbons, R' is a hydrocarbyl group of about 6 to 30 carbons, and at least about 25 percent of the basic nitrogens of the ditetrahydropyrimidine are converted to the hydrocarbyl acid orthophosphate salt.

2. A gasoline composition comprising a major proportion of gasoline and about 3 to 100 pounds per thousand barrels of a hydrocarbyl acid orthophosphate salt of a ditetrahydropyrimidine having the formula

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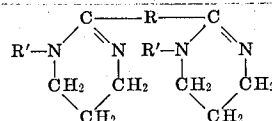


wherein the hydrocarbyl portion of the salt-forming hydrocarbyl acid orthophosphate is aliphatic, R is a hydrocarbylene group of about 2 to 10 carbons, R' is a hydrocarbyl group of about 10 to 25 carbons, and about 50 to about 90 percent of the basic nitrogens of the ditetrahydropyrimidine are converted to the hydrocarbyl acid orthophosphate salt.

3. A gasoline composition comprising a major proportion of gasoline and about 3 to 100 pounds per

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thousand barrels of a hydrocarbyl acid orthophosphate salt of a ditetrahydropyrimidine having the formula



wherein the salt-forming hydrocarbyl acid orthophosphate is a mixture of diisooctyl acid orthophosphate and isooctyl diacid orthophosphate, R is vinylene, R' is tallowyl, and about 50 to about 90 percent of the basic nitrogens of the ditetrahydropyrimidine are converted to the hydrocarbyl acid orthophosphate salt.

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