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CHEMICAL COMPOSITION

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Int. Cl. C10l *1/26, 1/22*

U.S. Cl. 44—72 6 Claims

ABSTRACT OF THE DISCLOSURE

Alkanol amine salts of alkyl acid orthophosphates are used as anti-stalling agents for gasoline.

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a division of copending application Ser. No. 425,329, filed Jan. 13, 1965, now Pat. No. 3,428,713 which is a continuation-in-part of application Ser. No. 375,357, filed June 15, 1964, now abandoned.

This invention is directed to novel alkanol amine salts of alkyl acid phosphates and to improved gasoline compositions containing alkanol amine salts of alkyl acid phosphates as additives.

A common occurrence in the operation of an internal combustion engine is frequent engine stalling in climates where high humidity is common with temperatures between about 30° F. and 60° F. This stalling is attributed to the formation of ice particles in the carburetor, especially on the throttle plate and surrounding body walls. The formation of ice in the carburetor, known as "carburetor icing," is caused by a temperature reduction in the metal parts of the carburetor as the fuel vaporizes. This lower metal temperature in turn causes the moisture in the air coming into the carburetor to condense and freeze at the edge of the throttle plate and on the air bleeds of the carburetor. Ice formation at the edge of the throttle plate reduces the flow of air to the engine thereby causing the engine to stall. On the other hand, ice formation on the air bleeds or venturi causes the engine to stall from excessively rich mixtures of gasoline.

Ice formation also occurs in the emulsion tube type carburetor which is used extensively in foreign-make cars. This type of carburetor comprises an emulsion tube in which the air and gasoline are mixed, metered and then carbureted. Ice initially forms at the air correction inlet of the emulsion tube and eventually causes the engine to stall.

Frequent engine stalling also results from operating conditions existing in heavy stop-and-go traffic when the engine is often operating at idling speeds. The reason for the engine to stall in such traffic is due mainly to accumulation of foreign materials on the walls of the carburetor throttle body which is below the closed portion of the throttle plate. Foreign materials are able to enter the carburetor at idling speeds because the air filter at such speeds is relatively ineffective. Most contaminants or foreign materials which enter the carburetor at idling speeds are those thrown out of the engine through the crankcase blowby. These contaminants remain trapped under the hood while the car is stopped and easily enter the carburetor while the engine is idling. Other sources of contaminants are exhaust fumes from the car ahead and the normal smoke and dust which accumulate in the air as a result of heavy traffic conditions. A common remedy used to eliminate this problem is the adjustment

of the engine to higher idling speeds. This action, however, is uneconomical since it wastes gasoline.

It is, therefore, an object of the present invention to provide novel alkanol amine salts of alkyl acid phosphates.

It is another object of the present invention to provide an improved distillate fuel composition which reduces engine stalling by preventing ice formation in the carburetor and by maintaining a clean carburetor free from carbonaceous deposit.

More specifically, the present invention is directed to novel salts of primary alkyl acid orthophosphates wherein each esterifying alkyl group contains 8 to 16 carbon atoms and an alkanol amine having either the structure

(A) $$RR'NCH_2\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

wherein R and R′ may be hydrogen, alkyl, cycloalkyl, phenyl and alkyl phenyl wherein R and R′ have a sum total of from 8 to 24 carbon atoms, or

(B) $$R''N(R''')_2$$

wherein R″ is an alkyl, cycloalkyl, phenyl, or aralkyl hydrocarbon radical of from 6 to 25 carbon atoms and R‴ is either a hydroxy ethyl or hydroxy propyl radical.

The present invention is also directed to a normally liquid hydrocarbon distillate fuel containing as an anti-stall additive an effective amount of the hereinbefore described alkanol amine salt.

The amine salts of the present invention may be prepared according to any of the methods known to the art. For instance, the amine salt may be prepared by neutralizing the alkyl acid phosphate with the amine. Normally a molecule of amine is used for each molecule of the phosphate to produce a salt exerting a substantially neutral pH. The preferred salt of this invention is the bis(2-hydroxyethyl) n-dodecyl amine salt of an approximately equimolar mixture of di-oxo-tridecyl hydrogen phosphate and mono-oxo-tridecyl dihydrogen phosphate which is commonly referred to as the C_{12} alkyl diethanolamine salt of the mixed mono- and di-tridecyl acid phosphate. Other preferred salts of the present invention are the N-(2,3-dihydroxypropyl) tert.-dodecylamine salt of an approximately equimolar mixture of di-oxo-tridecyl hydrogen phosphate and mono-oxo-tridecyl dihydrogen phosphate, the bis(2-hydroxyethyl) cocoa amine salt of an approximately equimolar mixture of di-oxo-actyl hydrogen phosphate and mono-oxo-octyl dihydrogen phosphate, and the bis(2-hydroxyethyl) cocoa amine salt of an approximately equimolar mixture of di-oxo-tridecyl hydrogen phosphate and mono-oxo-tridecyl dihydrogen phosphate.

The primary alkyl acid esters of orthophosphoric acid (acid phosphates) will be understood to be those esters in which only 1 or 2 of the three acidic hydrogen atoms of orthophosphoric acid have been replaced by alkyl groups, i.e., the monoalkyl dihydrogen phosphates and the dialkyl hydrogen phosphates. Such esters may be obtained according to the general methods of the art which involve reacting an alcohol with phosphorus pentoxide (P_2O_5). From about 2 to about 4 moles of the alcohol may be used per mole of P_2O_5. Preferably, about 3 moles of the alcohol per mole of P_2O_5 will be used to yield approximately equimolar mixtures of the mono- and dialkyl esters of orthophosphoric acid, that is, from about 40 to about 60 mole percent of the monoalkyl esters and the remainder of the dialkyl esters. These mixtures of mono- and dialkyl esters are preferred for reasons of economy, but other mixtures, as well as the monoalkyl esters and dialkyl esters individually, may also be used in forming the amine salts of this invention. The esters

can be separated from the mixtures in which they are prepared by conventional means known in the art.

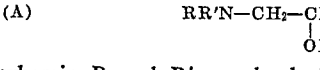
For the preparation of these primary alkyl acid phosphates, the alcohol is a branched or straight-chain primary alkanol having 8 to 16 carbon atoms or a mixture of two or more straight or branched chains or mixtures of straight and branched chain alkanols. The branched chain alkanols are preferably those made by the well-known Oxo-process from CO, H_2 and a branched chain olefin such as the C_7–C_{15} monoolefinic polymers and interpolymers of propylene and butylene, as described, for example, in U.S. Patents 2,824,836 and 2,884,379. Examples of preferred Oxo-alcohols that may be used are isooctyl alcohol from the propylene-butylene dimer, branched tridecyl primary alcohols from triisobutylene and from tetrapropylene, and the branched hexadecyl primary alcohols from pentapropylene. Other branched chain primary alkanols that can be used are those that may be prepared by alkaline condensation of two primary alkanols, having the structure RCH_2CH_2OH wherein R is an alkyl of from 2 to 6 carbon atoms, to produce primary alkanols branched in the 2-position such as $RCH_2CH_2CHRCH_2OH$. For example, 2-hexyldecanol-1 is produced by heating n-octanol with caustic and zinc dust, and similarly, 2-ethylhexanol-1 is prepared from butanol-1, as more fully described in U.S. Patent 2,457,-866. Other alcohols that may be prepared by the latter method and other methods known in the art and used to prepare phosphates according to the present invention are of the formula RCH_2CH_2—CHR—CH_2OH wherein R is the same or different alkyl group, each alkyl group having from 2 to 6 carbon atoms. The branched alcohols may also be prepared by the conventional aldolization of suitable aldehydes followed by hydrogenation. In this way, the well-known Oxo-octaldehyde, which is obtained from heptene-1, CO and H_2 and which is a mixture consisting very largely of dimethylhexaldehydes, ethylhexaldehydes, and methylheptaldehydes containing the grouping —CH_2CH=O, is converted into "2-hexyldecanol," $R'CHRCH_2OH$, wherein R stands for C_6 alkyl groups, such as dimethylbutyl, methylpentyl and ethylbutyl, and R' stands for C_8 alkyl groups such as dimethylhexyl, ethylhexyl and trimethylpentyl groups. The straight-chain primary alkanols are readily available commercially. Examples of such straight-chain alcohols are octanol, nonanol, decanol, dodecanol, tridecanol, tetradecanol and hexadecanol.

The preferred alkyl acid phosphates utilized in this invention are the mono- and dialkyl acid phosphates wherein the alkyl group is either isooctyl, 2-ethylhexyl, tridecyl or hexadecyl.

The amines which are utilized to produce the novel salts of the alkyl acid phosphates of this invention are alkanol amines of two different classifications.

The first class, designated as (A), has the following structural formula

(A)



wherein R and R' can be hydrogen, alkyl, cycloalkyl, phenyl, or alkylphenyl. The total number of carbon atoms present in the R and R' substituents must be from 8 to 24. Representative examples of the alkyl and cycloalkyl radicals are ethyl, butyl, hexyl, n-octyl, tert.-octyl, no-dodecyl, tert.-dodecyl, hexadecyl, the mixed C_{18} to S_{24} tertiary-alkyl fractions, cyclohexyl, cyclooctyl and cyclodecyl. Examples of the alkylphenyl radicals are p-octylphenyl, p-decylphenyl, and p-dodecylphenyl. The alkanol amines of this class may be obtained by any of the methods known in the art. For example, they are easily obtained by the reaction of the appropriate amine, RR'NH, with 3-chloropropanediol-1,2,

[Cl—CH_2—CH(OH)—CH_2OH]

The preferred amines of this class are the amines wherein R is hydrogen and R' is n-dodecyl, tert.-dodecyl, and tert.-C_{18}–C_{22} alkyl, or wherein both R and R' are butyl radicals.

The second class of amines, designated as class (B), has the following structural formula

(B) $R''N(R''')_2$

wherein R'' is an alkyl, cycloalkyl, phenyl, or aralkyl hydrocarbon radical of from 6 to 25 carbon atoms such as octyl, isooctyl, decyl, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl, the mixed C_8 to C_{16} alkyl fractions from cocoa amines, cyclohexyl, cyclodecyl, cyclooctadecyl, phenyl, or octylbenzyl, hexylbenzyl, decylbenzyl and octadecylbenzyl. R''' is either a hydroxy ethyl radical or hydroxy propyl radical. This class of alkanol amines is easily prepared by the reaction of one mole of the appropriate amine, $R''NH_2$, with 2 moles of ethylene oxide or propylene oxide. Another route for the preparation of this class of amines, wherein R''' is hydroxy ethyl, is the reaction of the alkyl or aralkyl chloride, R''Cl, with diethanol amine [$HN(CH_2CH_2OH)_2$]. The preferred amines of this class are of the formula wherein R'' is n-dodecyl, octadecyl, cyclohexyl, octadecylbenzyl or derived from a naturally occurring fatty oil having 8 to 18 carbon atoms such as coconut oil.

In the improved distillate fuels of this invention the amount of the alkanol amine salt of the alkyl ester phosphate added to the gasoline is not critical as long as the amount is sufficient to improve the anti-stalling characteristics of the gasoline. The preferred amount of the salt added to the gasoline is from about 0.0003% to about 0.02% by weight based on the weight of the distillate fuel.

Naturally, the gasoline compositions of this invention may contain all the additives incorporated in modern gasoline in addition to the subject alkanol amine phosphate salts. Such additives as anti-knock agents, anti-oxidant, dyes, and metal deactivators do not affect the performance of the salts of this invention and are compatible in gasolines with the subject anti-stalling additive.

When the salt is to be used as an anti-stalling additive in gasoline, it is preferred to dissolve the salt in a solvent such as methanol, kerosene, or xylene in sufficient concentration to make a 50 to 80% by weight solution of the salt. Such a concentrate provides a convenient means for handling the salt and facilitates the blending of the salt composition into the base gasoline.

For a clearer understanding of the present invention, the following specific examples are given. These examples are intended to be illustrative of the present invention and not in limitation thereof in any respect. All parts are by weight unless otherwise specified.

EXAMPLE I

Preparation of alkanol amine phosphate salts

(A) Preparation of the alkyl acid phosphate.—Phosphorous pentoxide (P_2O_5), in the amount of 142 grams (1 mole), was gradually stirred into 600 grams (3 moles) of Oxo-tridecyl alcohol. During the addition of the P_2O_5, the temperature was allowed to rise to about 65° C. The reaction mass was thereafter maintained at about 65° C. by external cooling. After the P_2O_5 had been added, the reaction mass was stirred at a temperature of about 65° C. for 12 hours.

(B) Neutralization of acid phosphate with the amine component.—N-(2,3-dihydroxypropyl) tert.-dodecylamine, i.e., tert.-dodecyl NH—$CH_2CHOHCH_2OH$, in an amount of 518 grams (2 moles) was added dropwise to the reaction mixture prepared by procedure A while the temperature was maintained between 60 and 70° C. The mixture was stirred for a few hours at 60–70° C., completing the mixing and neutralizing reactions, thereby forming the N-(2,3-dihydroxypropyl) tert.-dodecylamine salt of an approximately equimolar mixture of di-oxo-tridecyl hydro-

gen phosphate and mono-oxo-tridecyl dihydrogen phosphate.

The reaction mass was diluted with kerosene to provide an 80% by weight solution of said neutralized product. Alternatively, a lower alcohol such as methanol may be employed as diluent to provide a highly fluid additive for distillate fuels.

In another procedure to form the subject amine salts, the amine may be added in the neutralization step as a kerosene or methanol solution, whereby the above salt product is obtained directly as a freely mobile solution, e.g., 80% by weight in the diluent.

Since the method used to prepare the alkyl acid phosphates of this invention results in a mixture of the mono- and dihydrogen phosphates, it is most preferred commercially to use this mixture in the preparation of the amine salts. The resulting alkanol amine salt mixture can then be used directly as a gasoline additive.

However, if specific alkanol amine salts of this invention are desired instead of the mixture, they are prepared by first separating the monohydrogen phosphate from the dihydrogen phosphate, and thereatfer reacting the isolated acid phosphate with a specific alkanol amine. The separation of the monohydrogen phosphate from the dihydrogen phosphate is accomplished by conventional techniques. For example, the di-oxo-tridecyl hydrogen phosphate is separated and recovered from the mono-oxo-tridecyl hydrogen phosphate of this example by techniques used and described in U.S. Patents 2,818,421 and 2,854,-468. The separated di-oxo-tridecyl hydrogen phosphate is then reacted with N-(2,3-dihydroxypropyl) tert.-dodecylamine to form the corresponding amine salt free from significant amounts of the amine salt of the dihydrogen phosphate. The amine salt of the dihydrogen phosphate is similarly prepared by reacting the mono-oxo-tridecyl dihydrogen phosphate with N-(2,3-dihydroxypropyl) tert.-dodecylamine.

Repeating the above procedures A and B with other dihydroxyl alkyl substituted amines and other alkyl acid phosphates as tabulated below in Table I, the corresponding salt additives of this invention were prepared.

TABLE I.—DIHYDROXYALKYL AMINE SALT COMPONENTS

Alkanol Amine (A) $RR'N—CH_2—CH(OH)CH_2OH$		
R	R′	Acid Phosphates [1]
H	Tert.-dodecyl	Tridecyl. [2]
H	2,4-dimethylphenyl	Do.
H	n-Dodecyl	Do.
Cyclohexyl	Cyclohexyl	Do.
H	p-Dodecylphenyl	Do.
Ethyl	Cyclohexyl	Do.
H	Tert.-C_{18}–C_{24} alkyl mixed fraction	Do.
Ethyl	Phenyl	Do.
n-Butyl	n-Butyl	Do.
H	Tert.-dodecyl	Isooctyl. [2]
H	do	Hexadecyl.
(B) $R''N(R''')_2$		
R″	R‴	
n-Dodecyl	CH_2CH_2OH	Tridecyl.
Phenyl	CH_2CH_2OH	Do.
n-Octadecyl	CH_2CH_2OH	Do.
Alkyl from tallow	CH_2CH_2OH	Do.
n-Octadecyl benzyl	CH_2CH_2OH	Do.
Cyclohexyl	CH_2CH_2OH	Do.
n-Dodecyl benzyl	CH_2CH_2OH	Do.
n-Dodecyl	CH_2CH_2OH	Isodecyl.
Alkyl from cocoa	CH_2CH_2OH	Isooctyl.
Do	CH_2CH_2OH	C_{12}–C_{16} alkyl mixed fraction.
Do	CH_2CH_2OH	Di-(2-ethylhexyl)
Do	DH_2CH_2OH	Hexadecyl.
Do	CH_2CH_2OH	Tridecyl.
Cyclohexyl	$CH_2CH(CH_3)OH$	Do.
Phenyl	$CH_2CH(CH_3)OH$	Do.
n-Dodecyl	$CH_2CH(CH_3)OH$	Do.
n-Dodecyl benzyl	$CH_2CH(CH_3)OH$	Do.

[1] Unless otherwise stated, a mixture of the mono- and diester.
[2] Tridecyl and isooctyl in this table refer to those groups present in oxo-tridecyl and oxo-octyl alcohols.

EXAMPLE II

Gasoline samples containing the alkanol amine phosphate salts of the present invention were prepared for testing in an internal combustion engine. The tests were made to determine the effect of the additives of the present invention in improving the characteristics of gasolines in repect to their abilities to prevent carburetor icing and carburetor contaminant deposits. The samples were prepared by adding to the gasoline small amounts of the subject alkanol amine phosphate salts, as more fully described in Tables II, III, and IV below.

The gasoline used in the tests was commercially available and had the following inspection data:

Reid vapor pressure ---------- p.s.i.	13.0
ASTM Distillation (D86), ° F.:	
Initial Boiling Point ----------	75
10% ----------	105
50% ----------	195
90% ----------	339
End Point ----------	406

The following is a brief discussion of the test procedures and equipment used to evaluate these samples.

Anti-icing test

The anti-stalling properties of the alkanol amine phosphate salts of the present invention were demonstrated in a 6-cylinder Chevrolet engine having a horsepower rating of 86 at 3400 r.p.m. and a displacement of 216.5 cu. in. Two types of carburetors were employed in the tests, (a) a throttle plate carburetor and (b) an emulsion tube type. The test conditions were as follows:

	Carburetor Type	
	Throttle plate	Emulsion tube
Intake air, ° F	38–40	34–36
Relative humidity, percent	98–100	98–100
Engine load, horsepower	10	15
Engine speed, r.p.m.	[1] 1,500	[2] 1,500
Idle speed, r.p.m.	350	----------
Fuel temp. to carburetor, ° F	50–55	50–55

[1] At high speed.
[2] Initially.

(a) Throttle plate carburetor.—The operating time of the engine was varied at the conditions described above, using the time required for stalling as a measure of the

fuel's tendency to cause or prevent stalling due to carburetor icing. All runs were started after soaking the throttle plate with methanol for 0.5 minute at a temperature of 40° F. The operating time selected for the engine depended on the ice-forming tendencies of the fuel. Operating times at the 1500 r.p.m. engine speed were usually in the 0.5–1.5 minute range for uninhibited base fuels. At the end of the 1500 r.p.m. portion of the operating cycle, the throttle was cut back to idle position. If no stall occurred within 30 seconds at idle, the run was repeated for a longer period at 1500 r.p.m. until a time was found when the engine stalled within 30 seconds after converting back to idle. The anti-stall rating or "stall time" of a gasoline was defined as the longest 1500 r.p.m. run (to the nearest 0.25 minute) followed by a complete 30 second idle period without stalling. A stall time of 3 or more minutes was considered excellent performance.

(b) Emulsion tube carburetor.—A Solex, Model No. 32 PBICA, single barrel down draft carburetor adapted to 12" extension of 1½" pipe on intake manifold was substituted for the throttle plate carburetor described above and the engine was operated under the conditions listed above. Under these conditions, using the emulsion type carburetor, the engine does not stall completely. The engine is operated for 20 minutes at an initial speed of 1500 r.p.m., and the reduction in engine speed is taken as a measure of the effectiveness of the anti-icing agent. A reduction of not more than 50 r.p.m. on operating for 20 minutes is considered excellent anti-icing performance.

For the purposes of demonstrating the effectiveness of the subject additives, tests were made on gasolines both with and without the additive. Tests with the base fuel without an additive resulted in a stall time of 0.25 minute using the throttle plate carburetor, and a reduction in engine r.p.m. after 20 minutes to 900 r.p.m. using the emulsion tube carburetor. The results of tests where the gasoline contained effective anti-stalling amounts of the alkanol amine salts of the present invention are listed below in Table II.

TABLE II.—ANTI-ICING TESTS

Additive (80% solution by weight in kerosene)			Wt. percent additive in fuel	Throttle plate carburetor	Emulsion tube carburetor
(A) $RR'N\text{-}CH_2\text{-}CH(OH)CH_2OH$				Stall time in minutes	Engine speed final r.p.m.
R	R′	Acid phosphate [1]			
H	Tert.-dodecyl	Tridecyl	0.002	3.00	
			0.004		1,250
			0.008		1,400
			0.012		1.450
H	2,4-dimethylphenyl	do	0.006		1,375
H	n-Dodecyl	do	0.006	3.00	
Cyclohexyl	Cyclohexyl	do	0.006		1,400
H	p-Dodecylphenyl	do	0.004	2.75	
			0.012		1,400
Ethyl	Cyclohexyl	do	0.006		1,400
H	Tert.-C_{18}-C_{24} alkyl mixed fraction	do	0.006	>3.00	
			0.016		1,300
Ethyl	Phenyl	do	0.006		1,000
n-Butyl	n-Butyl	do	0.003	3.00	
			0.004	>3.00	
H	Tert.-dodecyl	Isooctyl	0.004		1,475
			0.002		1,200
H	do	Hexadecyl	0.004		1,450
			0.004		1,150
			0.016		1,000
(B) $R''N(R''')_2$					
R″	R‴				
n-Dodecyl	CH_2CH_2OH	Tridecyl	0.001		1,350
			0.002	2.25	1,475
			0.003	3.00	
			0.004		1,500
Phenyl	CH_2CH_2OH	do	0.006		1,150
n-Octadecyl	CH_2CH_2OH	do	0.004	1.00	
			0.016	2.50	
Alkyl from tallow	CH_2CH_2OH	do	0.008		1,350
n-Octadecylhexyl	CH_2CH_2OH	do	0.006	2.25	
Cyclohexyl	CH_2CH_2OH	do	0.002		1,375
			0.004		1,475
			0.004		1,475
			0.004		1,300
n-Dodecylbenzyl	CH_2CH_2OH	do	0.012		1,430
			0.016		1,500
n-Dodecyl	CH_2CH_2OH	Isodecyl	0.006		1,500
Alkyl from cocoa	CH_2CH_2OH	Isooctyl	0.002		1,375
			0.004		1,450
Do	CH_2CH_2OH	C_{12}-C_{16} alkyl mixed fraction	0.004		1,250
			0.012		1,450
Do	CH_2CH_2OH	di-(2-ethylhexyl)	0.004		1,300
			0.008		1,475
Do	CH_2CH_2OH	Hexadecyl	0.002		1,400
Do	CH_2CH_2OH	Tridecyl	0.004	3.00	1,500
Cyclohexyl	$CH_2CH(CH_3)OH$	do	0.001	1.25	
			0.002	>3.00	1,400
			0.004		1,500
n-Decyl	$CH_2CH(CH_3)OH$	do	0.002	2.50	
			0.003	>2.75	
			0.004	>3.00	
			0.008		1,500

[1] Unless otherwise stated, a mixture of the mono and diester.

In addition to possessing the unique property of preventing stalling in engines having an emulsion tube carburetor, the novel alkanol amine salts of the present invention are also very effective in use with the conventional throttle plate carburetor. It has been known that compounds which are effective in one type of carburetor are not necessarily effective in another. For instance, unsubstituted amine salts of acid phosphates are known anti-icing agents for use in a throttle plate carburetor. However, they range from only slightly effective to ineffective in the emulsion tube carburetor.

Comparison tests under the same operating conditions as described above were made to illustrate the effect of

various unsubstituted amine phosphate salts on engine stalling. The results are set forth in Table III below.

TABLE III.—ANTI-ICING TESTS

Additive (80% solution by weight in solvent)		Wt. percent additive in fuel	Emulsion tube carburetor: Engine speed, final r.p.m.
Amine	Phosphate [1]		
2-ethyl hexyl	Tridecyl	0.004	900
		0.008	900
Do	Isooctyl	0.004	1,150
		0.008	625
N-tallow-1,3-diamino propane	do	0.004	950
		0.008	1,150
C_{12-15}-tert.-alkyl	do	0.004	1,100
		0.016	750
Di-2-ethyl hexyl	C_{8-18}-alkyl from coconut oil	0.004	1,150
		0.016	775
Do	Di-2-ethyl hexyl	0.004	1,025
		0.016	950

[1] Mixture of mono- and diesters unless indicated otherwise.

It can be seen from the above Table III that there is a considerable loss in r.p.m. when unsubstituted amine phosphate salts are used in contrast to the alkanol amine phosphate salts of Table II. This effect is in most cases intensified with greater amount of additive used.

In addition, the alkanol amine salts of the present invention have shown superiority over the unsubstituted amine salts in tests with the conventional throttle plate carburetor. For example, using a commercial gasoline having a mid-boiling point of 231° F. as the base fuel, a stall time of 3 minutes in the throttle plate carburetor was reached by using 0.008 wt. percent (80% active ingredient) of the 2-ethyl hexylamine salt of tridecyl acid phosphate, while only 0.0016 wt. percent (80% active ingredient) of the n-dodecyldiethanol amine salt of tridecyl acid phosphate was required to obtain the same stall time of 3 minutes in the throttle plate carburetor.

The alkanol amine salts of the present invention also exhibit excellent carburetor detergency properties. Although the detergency test, as described below, was carried out with a throttle plate carburetor, it is also applicable to an engine with an emulsion tube carburetor.

Carburetor detergency test

The carburetor detergency properties of the alkanol amine phosphate salts of the present invention may be demonstrated using a Lausen test engine equipped with a Tillotsen carburetor modified by inserting removable leaflets around the throttle plate. Throughout the test, a portion of the exhaust gases of a second single cylinder engine running at a constant 2500 r.p.m. was introduced into the test carburetor. The test engine was cycled one minute at open throttle under dynamometer load and then for two minutes at idle of 1100±100 r.p.m. for a period of two hours. At the conclusion of the test the leaflets were removed and rated on the scale from 1 to 10 where 10 represented bright and shiny and 0 represented very heavy black deposits. The base fuel used was the same as that used for the anti-icing tests described above.

Comparative inspection of the leaflets from the carburetor after the engine was operated on the base gasoline with those leaflets from the carburetor after the engine was operated on gasoline containing an additive of the present invention demonstrates the effective cleaning power of the subject additives. Results of these comparative tests are shown in Table IV below.

TABLE IV.—CARBURETOR DETERGENCY

			Wt. percent additive in fuel	Carburetor detergency rating
Base gasoline				5.6
Additive (80% Soln. by Wt. in Kerosene)				
(A) $RR'N-CH_2-CH(OH)CH_2OH$				
R	R'	Acid phosphate [1]		
H	Tert.-dodecyl	Tridecyl	0.004	9.5
H	Tert.-C_{18}-C_{24} alkyl mixed fraction	do	0.004	8.4
			0.006	9.0
H	n-Dodecyl	do	0.004	9.1
H	p-Dodecylphenyl	do	0.004	7.8
			0.006	9.7
H	Octadecyl	do	0.004	9.5
			0.006	9.9
Butyl	Butyl	do	0.004	9.3
			0.006	10.0
(B) $R''N(R''')_2$				
R''	R'''			
Octadecyl benzyl	CH_2CH_2OH	do	0.004	9.0
n-Dodecyl	CH_2CH_2OH	do	0.002	9.3
			0.003	9.9
Octadecyl	CH_2CH_2OH	do	0.004	9.2
Alkyl derived from tallow	CH_2CH_2OH	do	0.004	9.8
Cyclohexyl	$CH_2CH(CH_3)OH$	do	0.006	8.0
			0.008	9.8
n-Dodecyl	$CH_2CH(CH_3)OH$	do	0.012	9.6

[1] Mixture of mono- and diesters of tridecyl acid phosphate.

It can be seen from the foregoing table that high carburetor detergency ratings were obtained with very small amounts of the alkanol amine phosphate salt additive present in the gasoline.

It is to be understood that the preceding examples are representative and that said examples may be varied within the scope of the total specification, as understood by one skilled in the art, to produce essentially the same results.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed, are defined as follows:

1. An improved distillate fuel containing a normally liquid hydrocarbon distillate fuel and a salt of a primary alkyl acid orthophosphate wherein each esterifying alkyl group contains from 8 to 16 carbon atoms and an alkanol amine selected from the group consisting of

(A) $RR'NCH_2CH(OH)CH_2OH$

and

(B) $R''N(R''')_2$

wherein R and R' are individually selected from the group consisting of hydrogen, alkyl, cycloalkyl, phenyl, and alkyl phenyl, with the proviso that R and R' have a total of from 8 to 24 carbon atoms, and wherein R'' is a hydrocarbon radical of from 6 to 25 carbon atoms selected from the group consisting of alkyl, cycloalkyl, phenyl, and aralkyl and R''' is selected from the group consisting of a hydroxy ethyl radical and a hydroxy propyl radical, said salt being present in an amount sufficient to impart antistalling properties to said improved distillate fuel.

2. The improved distillate fuel of claim 1 in which the salt is a salt of a tridecyl acid orthophosphate and N-(2,3-dihydroxypropyl) tert.-dodecylamine.

3. The improved distillate fuel of claim 1 in which the salt is a salt of a tridecyl acid orthophosphate and bis (2-hydroxyethyl) n-dodecyl amine.

4. The improved distillate fuel of claim 1 in which the salt is a salt of an octyl acid orthophosphate and bis-(2-hydroxyethyl) cocoa amine.

5. The improved distillate fuel of claim 1 in which the salt is a salt of an octyl acid orthophosphate and bis-(2-hydroxyethyl) cocoa amine.

6. An anti-stalling additive for distillate fuels comprising a salt of a primary alkyl acid orthophosphate wherein each esterifying alkyl group contains from 8 to 16 carbon atoms and an alkanol amine selected from the group consisting of

(A) $RR'NCH_2CH(OH)CH_2OH$

and

(B) $R''N(R''')_2$

wherein R and R' are individually selected from the group consisting of hydrogen, alkyl, cycloalkyl, phenyl, and alkyl phenyl, with the proviso that R and R' have a total of from 8 to 24 carbon atoms, and wherein R'' is a hydrocarbon radical of from 6 to 25 carbon atoms selected from the group consisting of alkyl, cycloalkyl, phenyl, and aralkyl and R''' is selected from the group consisting of a hydroxy ethyl radical and a hydroxy propyl radical and a solvent selected from the group consisting of methanol, xylene and kerosene, said alkanol amine phosphate salt being in sufficient quantities to make a 50 to 80% by weight solution of the salt.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,505,044 Dated April 7, 1970

Inventor(s) Philip Lee Bartlett and Charles Bedford Biswell

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11, line 35, "an octyl" should read

-- a tridecyl --.

SIGNED AND
SEALED
AUG 25 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents