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DETERGENT MOTOR FUEL

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U.S. Cl. 44—66 **17 Claims**

ABSTRACT OF THE DISCLOSURE

Detergent motor fuel compositions are disclosed and claimed which are particularly useful in spark-ignition, internal combustion engines. The detergent compositions of the present invention contain certain additives which either substantially eliminate or maintain at a low level deposits which would otherwise form in the carburetor and in the intake valves and ports. Such carburetor and intake system deposits are to be avoided since they tend to restrict the flow of air through the carburetor especially at idle and at low speeds and/or cause improper valve closing and sluggish valve action. These conditions produce rough engine idling, stalling and can also result in excessive hydrocarbon and carbon monoxide exhaust emissions.

A suitable detergent composition comprises the combination of (1) a tertiary alkyl branched chain primary amine having a total of about 6 to 24 carbon atoms, (2) a surface active ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer hydrocarbon acid; and (3) a hydrocarbon-soluble polybutene having a number average molecular weight of about 700 to 3000.

This invention relates to motor fuel compositions for spark ignition, internal combustion engines. More particularly, this invention relates to a detergent motor fuel containing additives which reduce or prevent the formation of deposits in the carburetor. Thus, the formulations of the present invention are particularly effective as carburetor detergents to clean up and maintain the cleanliness of the carburetor. Other additives may also be present to reduce or prevent deposits in the induction system such as the areas around the ports and valves. This invention also relates to the mixture or combination of additives.

Modern internal combustion engine design is undergoing and has undergone important changes to meet stricter standards for engine and exhaust gas emissions. A major change in engine design is the feeding or recycling of blowby gases from the crankcase of the engine into the intake air supply to the carburetor rather than the venting of these gases to the atmosphere, as in the past. The blow-by gases contain substantial amounts of deposit-forming substances and are known to form deposits in and around the throttle plate area of the carburetor. These deposits restrict the flow of air through the carburetor at idle and at low speeds so that an overrich fuel mixture results. This condition produces rough engine idling, stalling and also results in excessive hydrocarbon and carbon monoxide exhaust emissions being emitted to the atmosphere.

In addition to the changes that have already been made, it is anticipated that additional burdens and demands will be placed on present day internal combustion engines and their fuels with the advent of new emission control devices, such as exhaust gas recirculation systems and exhaust catalytic mufflers. Also, the use of certain fuel additives such as the alkyl ammonium phosphate detergents may have to be restricted or eliminated because catalytic exhaust mufflers which utilize metal catalysts will be poisoned by phosphorus-containing compounds.

It is an object of the present invention to provide a

detergent motor fuel which will have certain carburetor detergent properties and which will clean up and maintain the cleanliness of the carburetor and optionally the remainder of the fuel induction system such as the valves and ports. It is another object of the present invention to provide a detergent fuel which will maintain a low level of hydrocarbon and carbon monoxide exhaust gas emissions and which will avoid the use of phosphorus-containing additives. It is still a further object of the present invention to provide a detergent fuel which has other desirable properties such as rust and corrosion protection, water demulsibility properties, anti-icing properties, etc. It is a further object of the present invention to provide multi-functional gasoline additives which are effective in inhibiting the formation of intake valve deposits in addition to being effective as carburetor detergents, and which can be used at relatively low concentrations (and thus at relatively low cost) for example at a treating level of about 1000 parts per million (p.p.m. on a weight basis in the gasoline), or less, and more preferably 600 p.p.m. or less, and even more preferably 400 p.p.m. or less.

There are, of course, other detergent motor fuel compositions available today, but they generally suffer from one or more deficiencies. Either they are used at very high concentrations, for example, something of the order of 4000 p.p.m.; or if used at the use levels in which we are interested, the available formulations suffer from one or more defects.

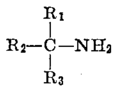
We have discovered that the combination of (1) selected tertiary alkyl primary amines having branched backbones and a total of about 6 to 24 carbon atoms, and more preferably, a total of 12 to 22 carbon atoms; (2) a surface active ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer acid; and (3) a hydrocarbon-soluble polyisobutylene (or polybutene) having a number average molecular weight ($\overline{\mathrm{Mn}}$) of from about 700 to about 3000 and a viscosity of from about 9000 to 900,000 SUS at 100° F. and of from about 300 to 20,000 SUS at 210° F., are effective in reducing or preventing the formation of carburetor and other induction system deposits.

According to the present invention, therefore, we provide a normally liquid, multi-functional additive composition for addition to a leaded, low lead, or unleaded gasoline, i.e., to a distillate hydrocarbon fuel comprising a major proportion of a hydrocarbon base fuel distilling within the gasoline distillation range. The three component composition ranging from a total of about 180 to about 1000 parts, on a weight basis, is comprised of about 20 to about 250 parts, and more preferably, about 50 to 100 parts by weight of (1) a tertiary alkyl branched chain primary amine, as above described; about 10 to about 100 parts and, more preferably, about 25 to about 50 parts by weight of (2) a surface active alkyl ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer acid, as above described; and about 150 to about 650 parts by weight and, more preferably, about 200 to 400 parts by weight of (3) a hydrocarbon-soluble polybutene, as above described. In an alternative embodiment of the invention and where carburetor detergency and rust inhibition, per se, are primarily desired, then the polybutene component (3) can be omitted, and a two component additive composition can be utilized, which, on a total weight basis of about 30 to about 350 parts, is comprised of about 20 to 250 parts and, more preferably, 50 to 100 parts by weight (1) the tertiary alkyl branched chain primary amine, above-noted; and about 10 to about 100 parts and, more preferably, about 25 to 50 parts by weight of (2) the surface active salt-ester, above-noted. Thus, a preferred two component additive composition comprises about 50 to about 100 parts of (1) and about 25 to 50 of (2) in a total of about 75 parts to about 150 parts, all parts being on a weight basis.

On a treating level basis, i.e., on a level related to the gasoline, the three component additive composition should be added to or used in the gasoline at a total level of about 180 to about 1000 p.p.m. (weight basis) and, on an individual or component basis, in an amount of from about 20 to 250 p.p.m., and more preferably 50 to 100 p.p.m. of (1); 10 to 100 p.p.m., more preferably 25 to 50 p.p.m. of (2); and 150 to 650 p.p.m., more preferably 200 to 400 p.p.m. of (3). On a pounds per barrel of gasoline basis this is 5 to 62.5, more preferably 12.5 to 25 lbs./1000 barrels (bbls.) of gasoline of (1); 2.5 to 25, more preferably 6.25 to 12.5 lbs./1000 bbls. of gasoline of (2); and 37.5 to 162.5, more preferably 50 to 100 lbs./1000 bbls. of gasoline of (3).

For the two component additive composition, the pounds per barrel of gasoline treating level is the same as noted for components (1) and (2) above.

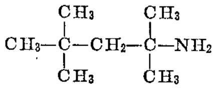
The tertiary (tert.) or t-alkyl primary amine, having at least one branched chain, may be represented by the general Formula I



$$R_2-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{\overset{|}{\underset{|}{C}}}}-NH_2 \qquad \text{(I)}$$

in which R_1, R_2 and R_3 are alkyl groups whose total carbon atom content ranges franm 6 to 24. It is preferred that two of the R groups, for example, the R_1 and R_3 of the t-alkyl primary amine be methyl groups.

The t-alkyl primary amines, having a branched chain, which may be used in the compositions of the present invention include, for example, t-octylamine, t-nonylamine, t-dodecylamine, t-tetradecylamine, t-octadecylamine, t-docosylamine, t-tetracosylamine and mixtures of two or more of such amines. These amines are commonly prepared by reactions known to those skilled in the art such as the reaction of nitriles with alkenes or secondary or tertiary alcohols in strongly acidic media. Commercially available t-alkyl primary amines are often mixtures. t-Octylamine having a branched structure has the formula



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-NH_2$$

and the alkyl group of this amine will hereinafter be referred to as t-octyl. One form of t-nonylamine is prepared as a mixture containing

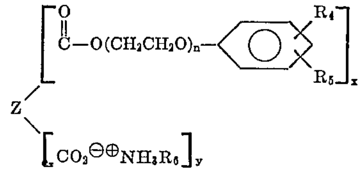
$$C_6H_{13}C(CH_3)_2NH_2$$

and

$$C_7H_{15}C(CH_3)_2NH_2$$

and has a neutral equivalent of about 142. A commercial preparation which is useful in the present invention is available under the trademark Primene 81-R which is mixture of t-dodecyl-, t-tridecyl- and t-tetradecylamines or principally a mixture of t-$C_{12}H_{25}NH_2$ to t-$C_{14}H_{29}NH_2$ amines having a neutral equivalent of about 191. Another commercial preparation which is useful in the present invention is available under the trademark Primene JM-T which is principally a mixture of t-$C_{18}H_{37}NH_2$ to t-$C_{22}H_{45}NH_2$ and which has a neutral equivalent of about 315. The important consideration is that in a t-alkyl primary amine, the NH_2 group is always attached to a carbon atom containing no hydrogen atoms and in the present invention at least one of the alkyl groups is branched.

The alkyl ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer acid which is added or included, primarily to provide rust and corrosion protection although there is also some modest carburetor detergency activity, has the following Formula II



(II)

wherein *n* is an average number from 1.5 to 12.5 and more preferably from about 3 to 10; and in the case of a salt-ester derived from a trimer acid

x is 1 or 2, and
y is 1 or 2, the sum of *x* and *y* being 3;

and in the case of the salt-ester derived from a dimer acid, both *x* and *y* are each 1;

R_4 is an alkyl group containing 4 to 12 carbon atoms;
R_5 is H or an alkyl group containing 4 to 12 carbon atoms;
R_6 is an alkyl group containing 2 to 24 carbon atoms which may be straight or branched chain or an amine substituted alkyl group of 2 to 24 carbon atoms. Preferably, R_6 contains 12 to 22 carbon atoms; and
Z is a saturated or unsaturated hydrocarbon residue of the acid, said hydrocarbon residue having 34 to 51 carbon atoms.

The alkyl ammonium carboxylate salt-ester, i.e., component (2), may be used as all trimer acid derivative or all dimer acid derivative, or any mixture of the dimer and trimer acid derivatives may be used in the present invention.

Also, the presence of some monocarboxylic C_{18} acids or the like in the ester or salt form, or mixtures of both ester and salt form, may be tolerated in minor amounts, about 5% or less.

TABLE I

	n	R	X	Y
Alkyl ammonium carboxylate salt-ester:				
A	1.5	t-C_{12-14}	1	2
B	1.5	t-C_{12-14}	2	1
C	3	t-C_{12-14}	1	2
D	3	t-C_{12-14}	2	1
E	5	t-C_{12-14}	1	2
F	7.5	t-C_{12-14}	1	2
G	9.5	t-C_{12-14}	1	2
H	9.5	t-C_{12-14}	2	1
I	12.5	t-C_{12-14}	1	2
J	3	$CH_2CH_2NH_2$	2	1
K	3	$(CH_2CH_2NH)_2H$	2	1
L	3	$(CH_2CH_2NH)_3H$	2	1
M	1.5	t-C_{12-14}	1	1
N	3	t-C_{12-14}	1	1
O	9.5	t-C_{12-14}	1	1

The polybutene component of this invention consists essentially of polyisobutenes (i.e., polybutenes wherein each monomer unit in the polymer chain is

$$—C(CH_3)_2CH_2—$$

derived from isobutene), or polybutenes wherein the butylene units are derived from 1-butene or 2-butene, or co-polymers of the various butenes, provided the polybutene is liquid at ordinary temperatures and has a molecular weight and viscosity as previously defined. For reasons of availability and overall characteristics the polyisobutenes are preferred. The term polyisobutene (or the equivalent term polyisobutylene) as used herein is meant to include polymers which may have incorporated in the polymer chain minor amounts of 1-butene and

2-butene units. The polyisobutenes are conveniently obtained by polymerizing isobutene or mixtures of isobutene with small amounts of 1-butene and/or 2-butene, according to known methods. Polybutenes which may be used in this invention are commercially available. Further examples of and descriptive material relating to useful polybutenes may be found in British Pat. 1,258,549.

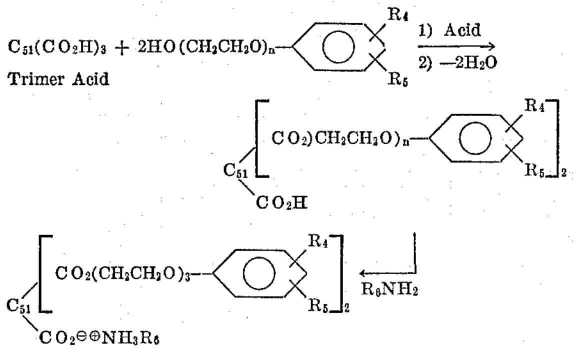
The molecular weights referred to hereinabove are number average molecular weights determined by vapor pressure isomery according to ASTM D–2503. Thus the polybutene component of this invention having molecular weights in the range 700 to 3000 are mixtures of polybutene molecules averaging from about 12 to about 54 C_4H_8 units in the polymer chain, with each molecule containing an olefinic double bond, analyzable by titration with bromine according to standard methods, such as ASTM D–1159.

The molecular weight and molecular weight distribution among the polybutene molecules in these mixtures are such that the viscosities of these normally liquid materials range from about 9000 SUS at 100° F. and from about 300 SUS at 210° F. for the low (700) molecular weight polymers to about 900,000 SUS at 100° F. and about 20,000 SUS at 210° F. for the high (3000) molecular weight polymers, the viscosities being determined according to ASTM D–445 and 446.

Preferred polybutenes useful in the present invention have molecular weights in the range of 950 to 1400 and viscosities in the range 1050 to 2990 SUS at 210° F. and in the range of 40,000 to 123,000 SUS at 100° F. Preferably, the polybutene is primarily (80% or more) polyisobutylene or polyisobutene. Mixtures of two or more of the various polybutenes may be used if desired.

The polybutenes are the preferred additive for induction system deposit (ISD) control. However, the polybutene may be replaced in whole or in part by mineral oil for ISD control; or the polybutene or mineral oil may be omitted entirely where ISD control is not considered necessary or where other additives may be used for ISD control.

The alkyl ammonium carboxylate salt ester can be made in known fashion, by the acid catalyzed esterification of a suitable trimer or dimer acid; for example, in the case of the diester-monosalt, with two moles of a suitable ethoxylated alkyl phenol followed by conversion of the remaining carboxylic acid function to an alkyl ammonium carboxylate salt with the addition of a suitable amine. The trimer acid may be the product derived from the trimerization reaction of a C_{18} unsaturated fatty acid; an example of a suitable trimer acid is that available under the trademark Empol 1041. A generalized reaction scheme for the preparation of an alkyl ammonium carboxylate salt-ester is shown below.



where *n*, R_4, R_5 and R_6 have the values given previously, and C_{51} is the carbon atom content of the hydrocarbon residue.

In the following examples which illustrate this invention, all parts and percentages are by weight, unless otherwise stated. The ability of the additive combinations of this invention to clean up and maintain the cleanliness of the carburetor of an internal combustion engine is illustrated by the carburetor detergency engine tests described below. The gasoline fuel for Tables II and III (an MS–08 gasoline) has the following properties.

Gravity, API, sp. gr. at 60° F.	59.7
ASTM D–86 distillation, ° F.:	
IBP	93
10%	123
50%	205
90%	348
E. P.	405
Percent recovered	98
Percent residue	1
Percent loss	1
Percent sulfur	0.11
Lead, gm./gal.	3.08
FIA composition (percent):	
Aromatics	23.1
Olefins	20.0
Saturates	56.9
Oxidation stability, minutes	600+
ASTM gum (unwashed), mg./100 ml.	1.0
Research octane number	95.5
Percent H	13.10
Percent C	86.61
H/C	1.80

ENGINE TEST EVALUATION OF MULTIPURPOSE CARBURETOR DETERGENTS

(A) Blowby Carburetor Detergency Keep Clean Engine Test

(1) Engine Test Procedure: The Blowby Carburetor Detergency Keep Clean Engine Test (BBCDT-Keep Clean) measures the ability of a gasoline additive to keep clean the carburetor throttle body area, and is run in a 1970 Ford 351 CID V–8 engine equipped by means of a special Y intake manifold with two one-barrel carburetors, which can be independently adjusted and activated. With this arrangement, a separate test fuel can be evaluated by each carburetor which feeds four of the eight cylinders via the non-interconnected intake manifold. The carburetors are modified with removable aluminum sleeves in order to facilitate weighing of the deposits which accumulate in the throttle body area. The severity of the test is adjusted to an appropriate level by recycling the entire amount of blowby gases, approximately 90–110 c.f.h., to the top of the air cleaner so that each carburetor receives an equal volume of these gases. Equal intake mixture flow through each carburetor is adjusted during the first hour of operation by means of intake manifold differential pressure and CO exhaust gas analysis. The following test cycle and operating conditions are employed:

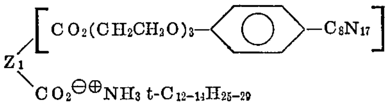
Test cycle:	
Phase I	650 engine r.p.m., 8 min.
Phase II	3000 engine r.p.m., 1 min.
Test duration, hrs.	10.
Intake air, ° C.	135±10.
Jacket water, ° C.	190±10.
Engine oil-sump, ° F.	210±10.
Percent CO in exhaust	3.0±0.2.
Blowby, c.f.h.	90–110.

The weight (mgs.) of deposits accumulated on the aluminum sleeve is measured, and the average value of four tests per additive or additive mixture is reported.

TABLE II.—BLOWBY CARBURETOR DETERGENCY ENGINE TEST—KEEP CLEAN

Example	Additive	Treated level, p.p.m. (in gasoline)	Deposit wgt., mg. (avg. of 4 tests)
Control	Untreated gasoline		15.9
1	I/II [1]	50/25	2.3
2	I	50	1.7
3	II	50	8.6
4	I/II/III	50/25/440	2.6
5	IV	50	3.3

[1] Additive component I is a tert. C^{12}–C^{14} alkyl amine with a highly branched backbone, a molecular weight principally in the 185–213 range, and a neutral equivalent of 191; additive component II is essentially an an alkyl ammonium carboxylate salt-ester of Formula III:


(III)

where Z_1 is the hydrocarbon residue of the product of trimerization of an unsaturated C_{18} fatty acid, the trimer acid as for example being Empol 1041 (Emery Industries Inc.). It is understood that Empol 1041 is a mixture of about 90% trimer acid (C_{54}) and about 10% dimer acid (C_{36}). Additive component III is a hydrocarbon-soluble polyisobutylene having a number average molecular weight ($\bar{M}_n$) of about 1,000; additive component IV is a tert. C_{18-22} alkyl amine with a highly branched backbone, a molecular weight principally in the 269–325 range and a neutral equivalent of 315.

It is apparent from Table II that the additive combination or mixture of Example I, which contains 50 parts of component I in admixture with 25 parts of component II, is an effective carburetor detergent, as is the combination or mixture of Example 4. The effectiveness of the carburetor detergency is shown by the weight of the deposits, the less the deposit weight, the more effective the carburetor detergent. Thus, the untreated MS–08 gasoline gave a deposit weight of 15.9 mg. in the keep clean test, whereas the combination of Example I gave only 2.3 mg., and the combination of Example 4 gave only a 2.6 mg. weight deposit, both of which are significantly lower than the untreated gasoline. It is also apparent from Table II that component II has carburetor detergent properties, in addition to its rust inhibition properties, as shown hereinafter.

(B) Blowby Carburetor Detergency Clean Up Engine Test

The Blowby Carburetor Detergency Clean Up Engine Test (BBCDT-Clean Up) is run to measure the ability of a gasoline additive to clean up carburetor throttle body area deposits. The procedure is similar to that of the BBCDT-Keep Clean procedure except that the carburetor aluminum sleeves are dirtied up first by running untreated MS–08 gasoline, then cleaned up by running additive treated gasoline. Test results are recorded as weight (mgs.) of deposits accumulated and removed from the sleeves, and reported as percent clean up.

TABLE III.—BLOWBY CARBURETOR DETERGENCY ENGINE TEST—CLEAN UP

Example	Additive component(s)	Treating level, p.p.m.	Percent clean up (avg. of 4 tests)
6	I/II [1]	50/25	19.5
7	I	50	16.3
8	I/II/III	50/25/300	19.6
9	IV	50	23.9

[1] Additive components, I, II, III and IV are the same as given previously. In the "clean up" test, the higher the percentage clean up, the more effective the additive combinations or mixtures. Thus, it is apparent from Table III that Examples 6 and 8 produce significant clean up. The untreated MS–08 gasoline, i.e., without the additives, gave a value of minus (—)22.3% clean up, i.e., additional dirtying of 22.3%.

(C) Slave Engine Carburetor Detergency Engine Test

The Slave Engine Carburetor Detergency Engine Test (SECDT) is similar to the BBCDT except that the severity is adjusted to an appropriate level by feeding a portion of the exhaust gases from Labeco "slave engine" into the top of the air cleaner of the Ford carburetor detergency engine. This is intended to simulate the use of exhaust gas recirculation (EGR) systems such as those being developed by the automotive industry to help control exhaust pollutants.

TABLE IV.—SLAVE ENGINE CARBURETOR DETERGENCY ENGINE TEST—KEEP CLEAN

Example	Additive component(s)	Treating level, p.p.m. (in gasoline)	Deposits wt., mg.
Control	Untreated gasoline [1]		10.0
10	I/II	50/25	1.9
11	I	50	2.4
12	II [2]	25	4.1

[1] The gasoline used in the test reported in Table IV is unleaded gasoline having the following properties.

Research octane No. (RON)	91.2–91.0
Distillation, ° F.:	
IBP	88–90
10 percent	126–130
50 percent	214–224
90 percent	343–347
E.P	385–414
FIA:	
Percent aromatics	23.9–25.9
Percent olefins	18.7–15.8
Percent saturates	57.4–58.3
Sulfur—natural wt. percent	0.088–0.084
Gum (washed), mg	0.8
Lead, p.p.m	0.8–1.8

[2] Additive components I and II are the same as given previously

An inspection of Table IV shows that the combination or admixture of components I and II give the lowest mg. deposit in this keep clean test.

(D) Induction System Deposit Engine Test

(1) Engine test procedure: The Induction System Deposit Test (ISDT) which is used to evaluate the ability of gasoline additives or mixtures of additives to control induction system deposits, is run using a new-air-cooled, single cylinder, 4 cycle, 2.5 H.P. Briggs and Stratton engine for each test. The engine is run for 150 hours at 3000 r.p.m. and 4.2 ft. lbs. load, with a 1 hour shutdown every 10 hours to check the oil level. Carbon monoxide exhaust emission measurements are made each hour to insure that a constant air to fuel (A/F) ratio is being maintained.

Upon completion of a test run, the engine is partially disassembled, and the intake valve and port are rated and valve and port deposits are collected and weighed.

TABLE V.—INDUCTION SYSTEM DEPOSIT ENGINE TEST

Example	Additive	Treating level, p.p.m. (in gasoline)	Valve and port deposits, mg.
13	Untreated gasoline [1]		475
14	I/II	250/25	977
15	I/II/III [2]	250/25/300	446

[1] The untreated gasoline was the same as used for the test reported in Table IV. Example 15, comprising the combination of components I, II and III exhibits improved induction system deposit control, keeping in mind that components I and II need be added for carburetor detergency and rust inhibition performance.

[2] Additive components I, II and III same as given before.

TABLE VI.—RUST INHIBITION TEST (ASTM-D-665)

Example	Additive	Treating level, p.p.m.	Percent area rusted
16	Isooctane (control)		80
17	I/II	250/20	1
18	I	250	65
19	II	20	2

NOTE.—Additive components I and II are the same as identified previously.

The above Table VI shows that the combination of I and II gives good rust inhibition and exhibits a very marked improvement over the component I, i.e., only 1% area rusted vs. 65% area rusted in the above-identified ASTM test.

As noted previously, the polyisobutylene (or polybutene) component may be omitted entirely (where induction system deposit control is not deemed necessary) or it may be replaced in whole or part with mineral oil to control induction system deposits. Where mineral oil is used, however, it generally has to be used at a higher treating level for ISD control, for example at a level of about 2 to 5 times as high as the polybutene component.

Other additives may be included in or within the two or three component additive composition of the present invention. Also, it is sometimes desirable to include a minor amount of an alcohol such as n-butanol, for example, about 5–15 weight percent, with the three component additive composition to form a non-separating solution of the three component package to improve handling characteristics.

While the above disclosure refers to component (2) as an "ethoxylated" ester, it will be understood that the equivalent propoxylated analogues may also be used. Also, in the claims where reference is made to the alkyl ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer acid, it will be understood that mixtures of such trimer and dimer acid salt-esters are also embraced and included.

We claim:

1. A multi-functional additive composition suitable for addition to distillate hydrocarbon fuels having a major proportion of a hydrocarbon base fuel distilling within the gasoline distillation range, the additive composition comprising a mixture of

(1) about 20 to about 250 parts by weight of a tertiary alkyl primary amine having a branched backbone and a total of 6 to 24 carbon atoms;

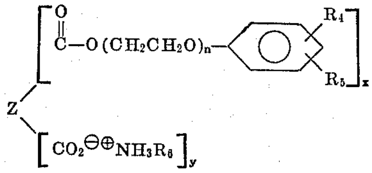
(2) about 10 to 100 parts by weight of a surface active alkyl ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer hydrocarbon acid;

(3) about 150 to 650 parts by weight of a hydrocarbon-soluble polybutene having a number average molecular weight of from about 700 to about 3000.

2. A multi-functional additive composition suitable for addition to gasoline, said additive composition comprising a mixture of

(1) about 20 to about 250 parts by weight of a tertiary alkyl primary amine having a branched backbone and a total of 6 to 24 carbon atoms;

(2) about 10 to 100 parts by weight of a surface active alkyl ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer acid of the formula



where n is an average number from 1.5 to 12.5; and wherein is the case of the salt-ester derived from a trimer acid

x is 1 or 2, and

y is 1 or 2, the sum of x and y being 3;

and in the case of the salt-ester derived from a dimer acid, both x and y are each 1;

R_4 is an alkyl group containing 4 to 12 carbon atoms;

R_5 is H or an alkyl group containing 4 to 12 carbon atoms.

R_6 is an alkyl group containing 2 to 24 carbon atoms which may be straight or branched chain or an amine substituted alkyl group of 2 to 24 carbon atoms; and

Z is a saturated or unsaturated hydrocarbon residue of the acid, said hydrocarbon residue having 34 to 51 carbon atoms; and

(3) about 150 to about 650 parts by weight of a hydrocarbon-soluble polybutene having a number average molecular weight of from about 700 to about 3000.

3. A composition according to claim **2** wherein the tertiary alkyl primary amine has a carbon atom content of 12 to 22 carbon atoms.

4. A composition according to claim **3** wherein the tertiary alkyl primary amine is present in an amount of from about 50 to 100 parts by weight.

5. A composition according to claim **2** wherein the polybutene is essentially all polyisobutylene having a number average molecular weight of about 950 to about 1400.

6. A composition according to claim **2** wherein in the formula of component (2), n is 3 to 10, x is 2, y is 1 and Z is a hydrocarbon acid residue having about or an average number of 51 carbon atoms.

7. A composition according to claim **6** wherein n is 3.

8. A composition according to claim **2** wherein component (1) is present in an amount of about 50 to about 100 parts by weight, component (2) is present in an amount of about 25 to about 50 parts by weight, and component (3) is present in an amount of about 200 to about 400 parts by weight.

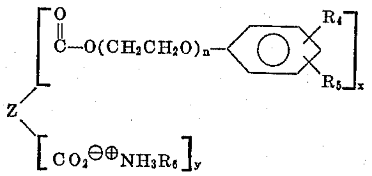
9. An improved detergent motor fuel composition comprising (A) a major proportion of a hydrocarbon base fuel boiling in the gasoline boiling or distillation range and (B) about 180 to about 1000 p.p.m. of the additive composition of claim **2**.

10. An improved detergent motor fuel composition comprising (A) a major proportion of a hydrocarbon base fuel boiling in the gasoline boiling or distillation range and (B) about 275 to about 550 p.p.m. of the additive composition of claim **2**.

11. A detergent additive composition suitable for addition to gasoline comprising a mixture of

(1) about 20 to about 250 parts by weight of a tertiary alkyl primary amine having a branched backbone and a total of 6 to 25 carbon atoms;

(2) about 10 to about 100 parts by weight of a surface active alkyl ammonium carboxylate salt-ethoxylated alkyl phenol ester of a trimer or dimer acid of the formula



where n is an average number from 1.5 to 12.5; in the case of a salt-ester derived from a trimer acid

x is 1 or 2, and

y is 1 or 2, the sum of x and y being 3;

and in the case of the salt-ester derived from a dimer acid, both x and y are each 1;

R_4 is an alkyl group containing 4 to 12 carbon atoms;

R_5 is H or an alkyl group containing 4 to 12 carbon atoms;

R_6 is an alkyl group containing 2 to 24 carbon atoms which may be straight or branched chain or an amine substituted alkyl group of 2 to 24 carbon atoms; and

Z is a saturated or unsaturated hydrocarbon residue of the acid, said hydrocarbon residue having 34 to 51 carbon atoms.

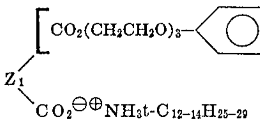
12. A composition according to claim **11** wherein component (1) is present in an amount of about 50 to about 100 parts by weight and component (2) is present in an amount of about 25 to about 50 parts by weight

13. A composition according to claim **11** wherein (1) the tertiary alkyl primary amine has a carbon atom content of 12 to 22 carbon atoms and wherein the formula of component (2), n is 3 to 10, x is 2, y is 1 and Z is a hydrocarbon acid residue having about 51 carbon atoms.

14. An improved detergent motor fuel composition comprising (A) a major proportion of a hydrocarbon base fuel boiling in the gasoline boiling or distillation range and (B) about 30 to about 350 p.p.m. of the additive composition of claim **11**.

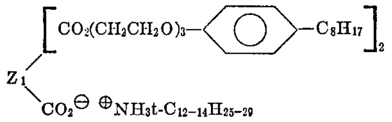
15. An improved detergent motor fuel composition comprising (A) a major proportion of a hydrocarbon base fuel boiling in the gasoline boiling or distillation range and (B) about 75 to about 150 p.p.m. of the additive composition of claim **11**.

16. A composition according to claim **1** wherein (1) the tertiary alkyl primary amine has a total carbon atom content of 12 to 14 carbon atoms, and (2) wherein the surface active ammonium carboxylate salt-ethoxylated alkyl phenol ester is an alkyl ammonium carboxylate salt ester of the formula



where Z_1 is the hydrocarbon residue of the product of trimerization of an unsaturated C_{18} fatty acid.

17. A composition according to claim **11** wherein (1) the tertiary alkyl primary amine has a total of 12 to 14 carbon atoms, and (2) wherein the surface active ammonium carboxylate salt-ethoxylated alkyl phenol ester is an alkyl ammonium carboxylate salt ester of the formula



where Z_1 is the hydrocarbon residue of the product of trimerization of an unsaturated C_{18} fatty acid.

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A. H. METZ, Assistant Examiner

U.S. Cl. X.R.

44—71

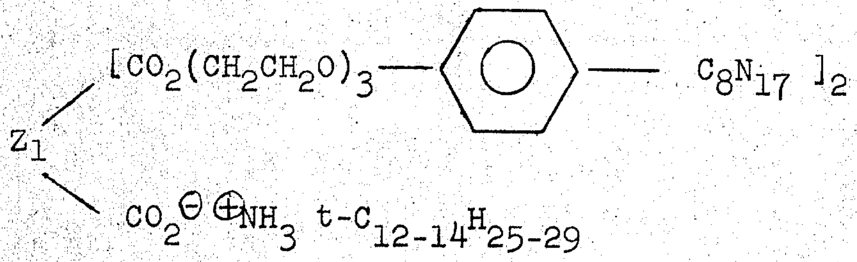
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,782,912 Dated January 1, 1974

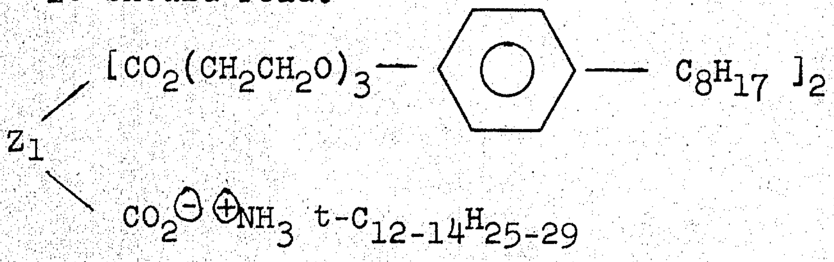
Inventor(s) Warren H. Machleder and Robert R. Kuhn

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

In Column 7, Formula III, it reads:



It should read:



In Claim 11, line 5, "6 to 25 carbon atoms" should read "6 to 24 carbon atoms".

Signed and sealed this 20th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents