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POLYCARBOXYLIC ACID SALTS OF ALKYLENE NITROGEN
COMPOUNDS AS FUEL DETERGENTS
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3,565,592

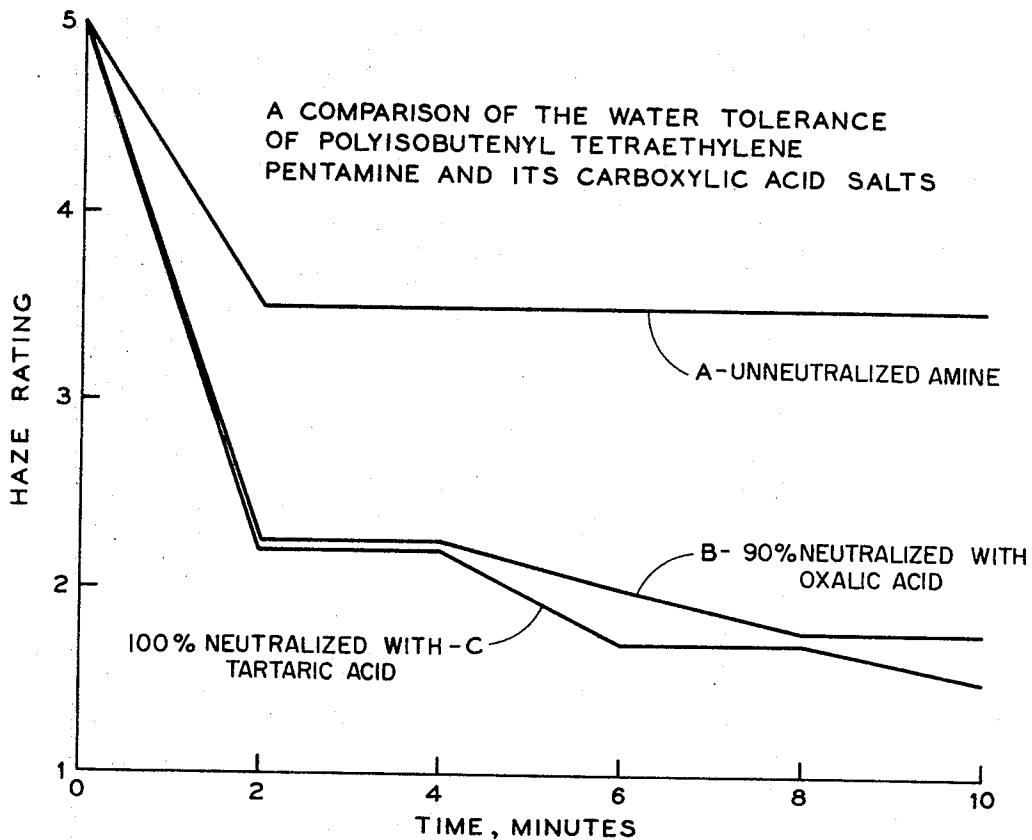


FIG. 1

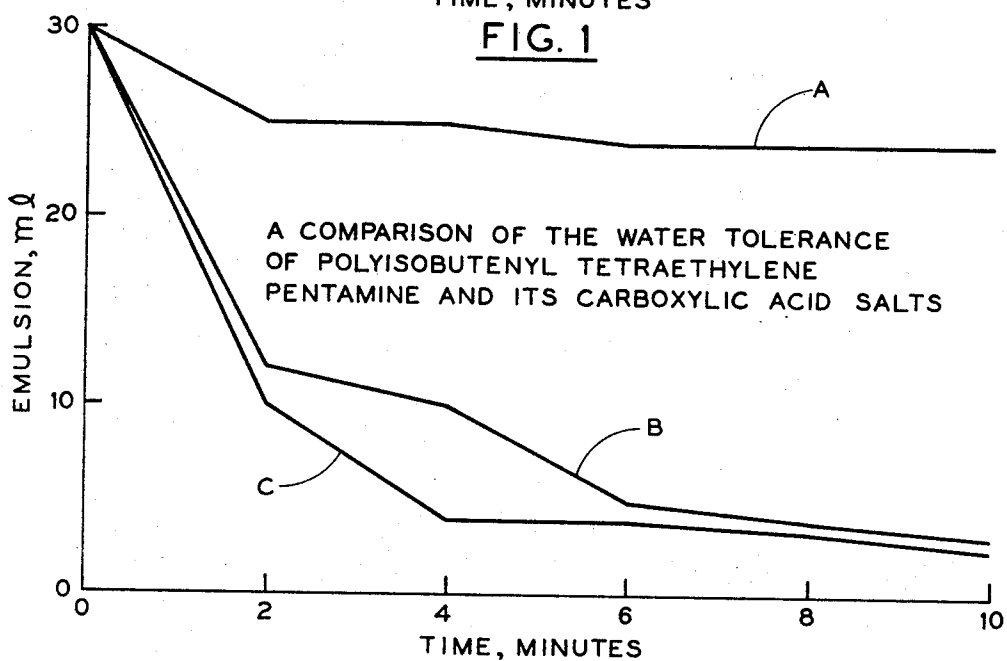


FIG. 2

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3,565,592 POLYCARBOXYLIC ACID SALTS OF ALKYLENE NITROGEN COMPOUNDS AS FUEL DETERGENTS

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U.S. Cl. 44-63

13 Claims

ABSTRACT OF THE DISCLOSURE

Aliphatic polycarboxylic acid salts of amine nitrogen containing compounds find use as fuel detergents having improved water tolerance.

BACKGROUND OF THE INVENTION

Field of the invention

Deposits resulting from polymeric materials in fuels remain a continuing problem in the smooth operation of internal combustion engines. Recently, a number of basic amine nitrogen containing fuel detergent additives have been incorporated into fuels to reduce deposit formation. These additives help by maintaining various parts of the engine in clean condition, and by reducing incomplete combustion. Thus the additives contribute to longer engine life, improved fuel performance and reduction of the production of smog-producing exhaust problems.

These additives, for the most part, have one or more long chain aliphatic hydrocarbon groups bonded to a polyamine either directly or through a nonoxo carbonyl group forming amides, amic acids, imidazolines or imides.

Because these detergents are frequently excellent emulsifiers, it is found that when the fuels containing the detergents are shaken with water, the separation of the fuel from the water and the clarity of the fuel phase are not as good as desired. That is, a relatively large cuff forms which is quite stable and significant water is retained in the fuel phase so as to cause a haze. This phenomenon referred to as water tolerance varies, depending on the particular composition of the fuel detergent.

The problem of water tolerance can be acute with fuels which come in contact with water. In many storage tanks, the housekeeping is fairly poor and water collects at the bottom of the tank. When fuel is introduced into the tank or withdrawn, significant agitation may occur. If the fuel and water do not separate quickly, significant amounts of water may be withdrawn with the fuel. Or, a cuff results, which means loss of fuel. If water is retained in the fuel phase, the fuel appears hazy and is unacceptable.

Also transferring by means of a centrifugal pump can result in "homogenization" of water and fuel, if a water phase is present in the holding tank. Rapid separation of the water from the fuel is essential, if the fuel is to be in condition for use.

Description of the prior art

U.S. Pats. Nos. 2,945,749, 3,050,043, and 3,231,348 disclose relatively low molecular weight amine derivatives as fuel detergents.

U.S. Pats. Nos. 2,905,542, 3,007,782, 3,118,745 and 3,228,758 disclose amine salts as deicing agents and anti-corrosion agents in fuels.

U.S. Pats. Nos. 3,219,666 and 3,275,554 disclose basic amine nitrogen containing lubricating oil detergents, which have since been reported to be useful in fuels.

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SUMMARY OF THE INVENTION

Aliphatic polycarboxylic acid salts of amine nitrogen containing fuel detergents, having at least one aliphatic hydrocarbon chain of at least 30 carbon atoms, are provided as fuel detergents having greatly improved water tolerance. The polycarboxylic acids are of from 2 to 8 carbon atoms and are free of substituents other than hydroxyl.

Brief description of the drawing

FIG. 1 is a graph of haze rating versus time for water tolerance determinations according to a modified version of ASTM D 1094-57 having polyisobutenyl tetraethylene pentamine neutralized with oxalic acid and tartaric acid.

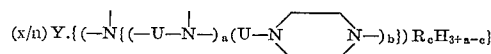
FIG. 2 is a graph of the emulsion volume versus time for the same compositions employed for FIG. 1 and under the same test conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions of this invention will, for the most part, fall into one of three categories. The compositions of this invention will be organic polycarboxylic acid salts of (1) aliphatic hydrocarbon substituted alkylene polyamines; (2) alkyl or alkenyl succinimides of alkylene polyamines; and (3) aliphatic carboxamides or imidazolines of alkylene polyamines.

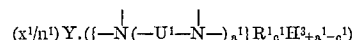
Aliphatic hydrocarbon substituted alkylene polyamines

The compositions within the first group will, for the most part, have the following formula:



wherein U is alkylene of from 2 to 6 carbon atoms, more usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms. R is substantially aliphatic hydrocarbon radical of from about 420 to 5,000 average molecular weight, more usually of from 450 to 3000 molecular weight, usually having at least one branch of from 1 to 6 carbon atoms per six carbon atoms along the chain. a is an integer of from 0 to 5; b is an integer of from 0 to 1; a+2b is an integer of from 1 to 5. c is an integer of from 1 to 3 and is on the average in the range of about 1 to 2. x is in the range of from .75 to 1 times the titratable amine nitrogen. n is the number of carboxylic acid groups of the carboxylic acid Y. And, Y is an aliphatic polycarboxylic acid of from 2 to 3 carboxyl groups and of from 2 to 8 carbon atoms, which is free of substituents other than hydroxyl, and the unsubstituted polybasic acids are incapable of forming unimolecular cyclic anhydrides of from 5 to 6 annular members.

Preferred aliphatic hydrocarbon substituted alkylene polyamines will have the following formula:

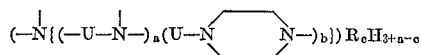


wherein R¹ is an oil soluble branched chain aliphatic hydrocarbon radical of from about 450 to 5,000 average molecular weight, more usually 450 to 3,000 molecular weight, usually having at least one branch of from 1 to 2 carbon atoms per 4 carbon atoms along the chain, and preferably polypropylene or polyisobutylene; U¹ is alkylene of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms; Y is as defined previously; a¹ is an integer of from 1 to 4; c¹ is an integer of from 1 to 3; x¹ is at least 0.75 times and usually in the range from 0.8 to 1 times the number of titratable amine nitrogen atoms and n¹ is the number of carboxylic acid groups of the organic acid Y.

The alkylene polyamines which find use in preparing

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the organic acid salts of this invention have the following formula:

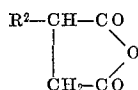


wherein all the symbols have been defined previously when defining the salt.

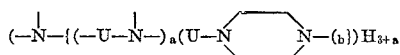
Succinimides

The next group of compositions are the reaction products of alkyl or alkenyl succinic anhydrides and alkylene polyamines. The products are prepared by reacting the anhydride and the amine under dehydrating conditions, wherein imides are formed, as well as some amic acid and diamide. Also, depending on the ratio of reactants, one or more of the anhydrides may react to form the various possible products. If more than 2 anhydrides are used per mole of alkylene polyamine, clearly, the third anhydride cannot form an imide. Therefore, the compositions are best described by treating them as a product by process. (See U.S. Pat. No. 3,219,666.)

The compositions are prepared by reacting under dehydrating conditions (85°–250° C.) an aliphatic hydrocarbon substituted succinic anhydride of the following formula:



wherein R² is alkyl or alkenyl of from 30 to 200 carbon atoms having at least one branch of from 1 to 2 carbon atoms per 4 carbon atoms along the chain, and preferably polypropylene or polyisobutylene, with an alkylene polyamine of the following formula:

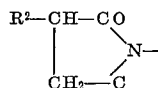


wherein the symbols have been defined previously. The mole ratio of anhydride to alkylene polyamine will generally be from 1 to 3, more usually of from 1 to 2.

With only 2 moles of anhydride, and more likely with only 1 mole of anhydride per mole of alkylene polyamine the major product will be succinimides. Therefore, as a good approximation the compositions may be described by the formula of the succinimide as follows:



where at least 1 of the X's is:

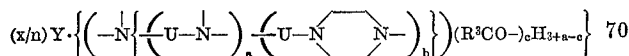


R² being defined previously, the other X being the same or amino; U is alkylene of from 2 to 6 carbon atoms, more usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms; l is 1 to 5.

The anhydride-alkylene polyamine reaction product will have at least .75 times, and usually 0.8 to 1 times the amount of titratable amine nitrogen neutralized with the organic polycarboxylic acids previously described. Therefore, the formula as the salt would have (x/n)Y included therein, the symbols being previously described.

Carboxamides of alkylene polyamines

The third category of compositions are the carboxamides which, for the most part, are included in the following formula:



wherein X, N, a, b, c, U and Y have all been defined previously, and R³ is an aliphatic hydrocarbon group of from 30 to 200 carbon atoms, either alkyl or alkenyl, usually having at least 1 branch of from 1 to 2 carbon atoms per

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4 carbon atoms along the chain, and preferably polyisobutylene or polypropylene.

The carboxamide compositions will, depending on the conditions of preparation and the particular compound used, frequently form the imidazoline. There is a dynamic equilibrium with the carboxamide and imidazoline, depending on the conditions which are present. Therefore, for the purposes of this invention the two will be considered equivalent.

The preparation of carboxamides is described in U.S. 3,298,955.

Reactants

The alkylene polyamines, which when combined with a long chain hydrocarbon group find use in this invention, are those of from 3 to 6 amine nitrogen atoms and of from 6 to 30 carbon atoms, more usually of from 6 to 15 carbon atoms.

Illustrative alkylene polyamines which may be substituted with a hydrocarbon radical, either directly or through an acyl (nonoxo carbonyl) group, are illustrated by diethylene triamine, tetraethylene pentamine, 2-aminoethyl piperazine, dipropylene triamine, ditetramethylene triamine, dihexamethylene triamine, tris-aminoethyl amine, etc.

In many instances, a single compound is not used as a reactant in the preparation of the hydrocarbon substituted amine. That is, mixtures will be used, wherein one or 2 compounds will predominate and the average composition or molecular weight is indicated. For example, tetraethylene pentamine prepared by the polymerization of aziridine or reaction of dichloroethylene and ammonia will have both lower and higher member, e.g., triethylene tetramine and pentaethylene hexamine. But, the composition will be mainly tetraethylene pentamine and the empirical formula of the total composition will closely approximate that of tetraethylene pentamine.

Similarly, the molecular weight reported for the long chain aliphatic hydrocarbon group is an average for a mixture which is sharply peaked when graphing the number average molecular weight distribution. That is, at least 80 weight percent of the composition will be within 20 weight percent of the average molecular weight reported.

Also, as the formulas suggest, the particular position of the substituting group is frequently not known and may be on any of the nitrogens. Therefore, when preparing the compositions, mixtures are inherently prepared.

The long chain hydrocarbon group bonded to the amine nitrogen, either directly or through an acyl group, is preferably a branched aliphatic hydrocarbon, substantially free of aromatic unsaturation, having 0 to 1 site of olefinic unsaturation. These compositions are readily prepared by the polymerization of low molecular weight olefins, although other sources may be found and used. The group should be fuel solubilizing and therefore preferably branched, having about 1 branch per 6 carbon atoms along the chain, preferably per 4 carbon atoms, usually of from 1 to 2 carbon atoms and more usually methyl. Illustrative hydrocarbon chains are polypropylene, polyisobutylene, copolymers of ethylene and propylene or ethylene and isobutylene, etc.

As already indicated, the organic acids are polycarboxylic acids having from 2 to 3 carboxylic acid groups and of from 2 to 8 carbon atoms. They are free of substitution other than hydroxyl. There may be from 1 to 3 hydroxyl groups. Usually, there will be not more than 1 site of aliphatic unsaturation, e.g., ethylenic or acetylenic. The unsubstituted polycarboxylic acids are restricted to those which cannot on heating form a cyclic anhydride of from 5 to 6 annular members.

Illustrative polycarboxylic acids include malic acid, citric acid, fumaric acid, trans-pentene-dioic acid, oxalic

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acid, malonic acid, tartaric acid, acetylene dicarboxylic acid, etc.

The salts employed in this invention are readily prepared by combining in a suitable medium the carboxylic acid and hydrocarbon substituted amine in the appropriate proportions. (The method for determining the titre of the amine will be described subsequently.) Useful mediums include alcohols, mixtures of alcohols and hydrocarbons, e.g., tert.-butyl alcohol and toluene. These volatile materials may then be removed and the product isolated, if desired. By suitable choice of solvent, the product may be obtained directly as a concentrate for use in combining with fuels.

The preparation of the substituted amines has appeared in copending application Ser. No. 647,611, filed June 21, 1967, and now U.S. 3,438,757.

The detergent will generally be employed in a hydrocarbon base liquid fuel. The detergent additive may be formulated as a concentrate, using a suitable hydrocarbon alcohol solvent boiling in the range of about 150° to 400° F. Preferably, an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the detergent additive. In the concentrate, the amount of the additive will be ordinarily at least 10 percent by weight and generally not exceed 70 percent by weight.

The amount of the detergent used in the fuel will generally be at least 50 and more usually from about 100 to 1,000 p.p.m.

In gasoline fuels, other fuel additives may also be included such as antiknock agents, e.g., tetramethyl lead or tetraethyl lead. Also included may be lead scavengers such as aryl halides, e.g., dichlorobenzene or alkyl halides, e.g., ethylene dibromide.

A nonvolatile lubricating mineral oil, e.g., petroleum spray oil, particularly a refined naphthenic lubricating oil having a viscosity at 100° F. of 1,000 to 2,000 SUS, is a suitable additive for the gasoline compositions having the detergents of this invention and its use is preferred. These oils are believed to act as a carrier for the detergent and assist in moving and preventing deposits. They are employed in amounts from about 0.05 to 0.5 percent by volume, based on the final gasoline composition.

EXAMPLES

The illustrative preparation of the tartrate salt of polyisobutenyl tetraethylene pentamine will suffice to exemplify the method of preparation for all the salts prepared.

Example I

A 50 weight percent solution in a C₉ aromatic solvent of polyisobutenyl tetraethylene pentamine (polyisobutenyl of about 1,000 molecular weight) was titrated as follows. Approximately 0.5 g. of the above solution was dissolved in a solution having 20 volumes of benzene, 75 volumes of isopropyl alcohol and 5 volumes of distilled water. The solution was potentiometrically titrated with approximately 0.1 Normal HCl, graphing the course of the titration. The mid-point of the curve (pH of about 5.3) determines the amount of titratable nitrogen. By this titration, the equivalent of the solution was found to be 682. Tartaric acid was obtained as 99.9 weight percent pure and was presumed to have 2 equivalents per mole.

The tartaric acid (75 g.) was dissolved in tert.-butyl alcohol in a beaker on a hot plate. To the beaker was added with stirring, 682 g. of the solution described above. Stirring was continued until the solution appeared homogeneous. The solution was then transferred to a distilling flask and the tert.-butyl alcohol distilled off. Toluene was then added to the residue to obtain a final weight of 832 g.

Salts of numerous other polybasic carboxylic acids were

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prepared similarly. In order to demonstrate the excellent water tolerance of the various salt mixtures employed in this invention, the test procedure of modified ASTM D-1049-57 was employed. The following table indicates the results obtained after 10 minutes, using distilled water. The results are reported for those salts which demonstrated significant improvement in water tolerance over the base fuel containing polyisobutenyl tetraethylene pentamine, as well as for some which did not. Significant improvement is evidenced by the increasing rate at which the water and fuel layer separate and the haze of the fuel layer drops. (The fuel used is a commercially-available gasoline free of additives.)

TABLE I

Composition 1:	Rating ²
Citric acid -----	+
Tartaric acid -----	+
Oxalic acid -----	+
Malic acid -----	+
Adipic acid ³ -----	+
Malonic acid -----	±
Fumaric acid -----	+
Maleic acid -----	—
Lactic acid -----	—
Terephthalic acid -----	—
Succinic acid -----	—

¹ The salts are 100% neutralized polyisobutenyl tetraethylene pentamine. The method of preparation and amine are described in Example I. A concentration of 250 p.p.m. was used.

² + significant improvement in water tolerance; ± some improvement in water tolerance; — no improvement in water tolerance.

³ 90% neutralized.

Also tested were the oxalate and tartrate salts of a polyisobutenyl succinimide of tetraethylene pentamine (polyisobutenyl of about 1,000 molecular weight.)

The results are evaluated as follows: The haze rating is a rating based on a rating of 1 to 5; the cylinder is observed against a flat vertical plate of diffused white light. Horizontal black strips are fixed to the surface of the plate. The graduated cylinder is placed in front of the plate and the haze rating determined by the degree of diffuseness of the black strips. A sharp appearance is rated as 1; an almost totally obscured strip is rated as 5. Also reported are the milliliters of emulsion that are present at the end of the 10 minutes.

TABLE II

Composition 1	Haze	Emulsion, ml.
Succinimide -----	1.7	24
90% neutralized oxalate salt -----	1.2	15
100% neutralized tartrate salt -----	1.1	9

¹ Succinimide is polyisobutenyl succinimide of tetraethylene pentamine (polyisobutenyl of about 1,000 average molecular weight). Concentration in fuel is 250 p.p.m.

To further demonstrate the excellent water tolerance of the salts of this invention, the accompanying figures indicate the significant improvement of the oxalate and tartrate salts as compared to the base polyisobutenyl tetraethylene pentamine (polyisobutenyl of about 1000 molecular weight, about 1:1 mole ratio of polyisobutenyl to tetraethylene pentamine) at concentrations of 250 p.p.m. While the base fuel containing the base amine at 10 minutes has a haze rating of about 3.5, both of the fuels containing salts have a haze rating of less than 2. Furthermore, the base amine containing fuel has 24 ml. of emulsion at the end of 10 minutes as compared to about 3 ml. of emulsion at the end of 10 minutes for either of the fuels containing the salts.

To demonstrate that the compositions of this invention still are effective as fuel detergents, the following test was carried out. A base fuel having a boiling range of 102° to 414° F.; 58 percent paraffins, 22 percent aromatics, and 20 percent olefins (by volume) and a vapor pressure (Reid) of 7.4 was employed. The additive was incorporated at a concentration of 250 p.p.m. and included

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in the fuel is 1,750 p.p.m. of a petroleum spray oil Ze-
rolene 9).

The test is carried out with a single cylinder CFR
engine equipped with throttle. The operating conditions
for the test are: jacket temperature, 212° F.; oil tempera-
ture, 150°-180° F.; intake air temperature, 95° F.; ig-
nition timing, 15° BTC; intake manifold vacuum, 15
in. Hg; fuel/air ratio, 0.07; speed, 1,800 r.p.m. The dura-
tion of the test is 12 hrs.

The intake valve is weighed at the end of the test,
cleaned and tared. The intake port is washed with hexane,
then fitted with a receiver, and the deposits removed
mechanically with the aid of chloroform. The chloro-
form is evaporated at about 250° F. and the deposits
weighed.

The following table indicates the results:

TABLE III

Additive ¹	Deposits ²	
	Ports, mg.	Valves, mg.
None	38	214
A-90% oxalate	14(2)	9(2)
A-100% tartrate	17	40
B-90% oxalate	33(2)	15(2)
B-100% tartrate	8	17

¹ A—polyisobutenyl tetraethylene pentamine (polyisobutenyl of about
1,000 average molecular weight; about one polyisobutenyl group per
tetraethylene pentamine); B—polyisobutenyl succinimide of tetra-
ethylene pentamine (polyisobutenyl of about 1,000 average molecular
weight).

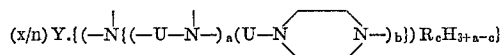
² The number in parentheses indicates the number of runs averaged
for the reported result.

It is evident from the above results that not only do
the salts greatly improve the water tolerance of the fuel
containing the base compositions, but the salts are still
excellent detergents. Therefore, the resulting salt com-
position can find wide acceptance as detergents in fuels,
even where problems of contact with water exist.

I claim:

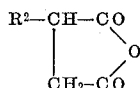
1. A liquid hydrocarbon fuel composition having a
major amount of a liquid hydrocarbon fuel and from
50 p.p.m. to 1000 p.p.m. as a fuel detergent of one of
the following:

(1) a salt of the formula:

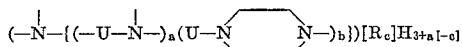


wherein R is a substantially aliphatic hydrocarbon
radical of from about 420 to 5,000 average molecu-
lar weight;

(2) the reaction product of from 1 to 3 moles of an
aliphatic hydrocarbon substituted succinic anhy-
dride of the formula:

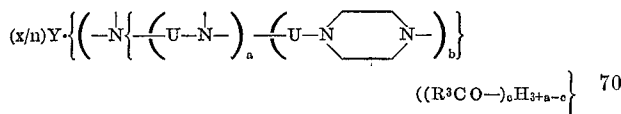


wherein R² is alkyl or alkenyl of from 30 to 200
carbon atoms and an alkylene polyamine of the
formula:



neutralized to from .75 to 1 times the amount of
titratable amine nitrogen with the organic polycar-
boxylic acid Y; and

(3) a salt of the formula:



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wherein R³ is an aliphatic hydrocarbon group of
from 30 to 200 carbon atoms and

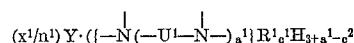
wherein in all the formulas, U is alkylene of
from 2 to 6 carbon atoms; a is an integer of
from 0 to 5; b is an integer of from 0 to 1;
a+2b is an integer of from 1 to 5; c is an
integer of from 1 to 3; x is in the range of .75
to 1 times the titratable amine nitrogen; n is
the number of carboxylic acids of the carboxyl-
ic acid Y and Y is an aliphatic polycarboxylic
acid of from 2 to 3 carboxyl groups and of
from 2 to 8 carbon atoms, having from 0 to 3
hydroxyl substituents, and the unsubstituted
polycarboxylic acids are incapable of forming
unimolecular cyclic anhydrides of from 5 to 6
annular members.

2. A composition according to claim 1 wherein U is
alkylene of from 2 to 3 carbon atoms and R, R² and
R³ are polyisobutene.

3. A composition according to claim 1 wherein Y is
oxalic acid.

4. A composition according to claim 1 wherein Y is
tartaric acid.

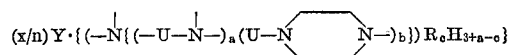
5. A composition according to claim 1 wherein said
fuel detergent is of the formula:



wherein R¹ is an oil soluble branched chain aliphatic
hydrocarbon radical of from about 450 to 5,000 aver-
age molecular weight; U¹ is alkylene of from 2 to 3
carbon atoms; Y is an aliphatic carboxylic acid of from
2 to 3 carboxyl groups and of from 2 to 3 carbon atoms,
having from 0 to 3 hydroxyl groups, and the unsub-
stituted polybasic acids are incapable of forming unimo-
lecular cyclic anhydrides of from 5 to 6 annular mem-
bers; α¹ is an integer of from 1 to 4; c¹ is an integer of
1 to 3; x¹ is in the range from 0.8 to 1 times the num-
ber of titratable amine nitrogen atoms and n¹ is the
number of carboxyl groups of the organic acid Y.

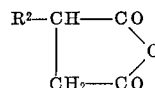
6. A salt useful as a fuel detergent and having en-
hanced water tolerance comprising a member of the
group consisting of:

(1) a salt of the formula:

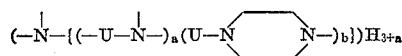


wherein R is a substantially aliphatic hydrocarbon
radical of from about 420 to 5,000 average molecu-
lar weight;

(2) the reaction product of from 1 to 3 moles of an
aliphatic hydrocarbon substituted succinic anhy-
dride of the formula:

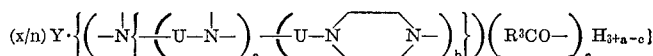


wherein R² is alkyl or alkenyl of from 30 to 200
carbon atoms and an alkylene polyamine of the
formula:



neutralized to from .75 to 1 times the amount of
titratable amine nitrogen with the organic poly-
carboxylic acid Y; and,

(3) a salt of the formula



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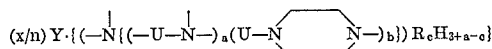
wherein R³ is an aliphatic hydrocarbon group of from 30 to 200 carbon atoms, and

wherein in all the formulas, U is alkylene of from 2 to 6 carbon atoms; *a* is an integer of from 0 to 5; *b* is an integer of from 0 to 1; *a*+2*b* is an integer of from 1 to 5; *c* is an integer of from 1 to 3; *x* is in the range of .75 to 1 times the titratable amine nitrogen; *n* is the number of carboxylic acids of the carboxylic acid Y and Y is an aliphatic polycarboxylic acid of from 2 to 3 carboxyl groups and of from 2 to 8 carbon atoms, having from 0 to 3 hydroxyl substituents, and the unsubstituted polybasic acids are incapable of forming unimolecular cyclic anhydrides of from 5 to 6 annular members.

7. A salt according to claim 6 wherein Y is oxalic or tartaric acid.

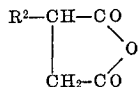
8. A salt according to claim 6 wherein U is alkylene of from 2 to 3 carbon atoms.

9. A salt according to claim 6 wherein said salt is the formula:



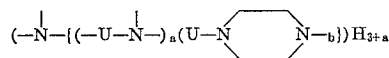
wherein R is polypropylene or polyisobutylene of from 450 to 3,000 molecular weight; U is alkylene of from 2 to 3 carbon atoms; *a* is an integer of from 0 to 5; *b* is an integer of from 0 to 1; *a*+2*b* is an integer of from 1 to 5; *c* is an integer of from 1 to 3; *x* is in the range of .75 to 1 times the titratable amine nitrogen; *n* is 2 and Y is oxalic or tartaric acid.

10. A salt according to claim 6 wherein said salt is the reaction product of from 1 to 3 moles of an aliphatic substituted succinic anhydride of the formula:



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wherein R² is polypropenyl or polyisobutenyl of from 30 to 200 carbon atoms and an alkylene polyamine of the formula:



wherein U is alkylene of from 2 to 3 carbon atoms; *a* is an integer of from 0 to 5; *b* is an integer of from 0 to 1; *a*+2*b* is an integer of from 1 to 5, neutralized to from 0.75 to 1 times the amount of titratable amine nitrogen with oxalic or tartaric acid.

11. A fuel concentrate composition having a suitable solvent for admixture with a liquid hydrocarbon fuel boiling in the range of 150° to 400° F. and from 10 to 70 weight percent of a salt according to claim 6.

12. A fuel concentrate composition having a suitable solvent for admixture with a liquid hydrocarbon fuel boiling in the range of 150° to 400° F. and from 10 to 70 weight percent of a salt according to claim 9.

13. A fuel concentrate composition having a suitable solvent for admixture with a liquid hydrocarbon fuel boiling in the range of 150° to 400° F. and from 10 to 70 weight percent of a salt according to claim 10.

References Cited

UNITED STATES PATENTS

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3,438,757	4/1969	Honnen et al.	44—63X
3,468,639	9/1969	Lindstrom et al.	44—71X

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W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

44—71; 260—268, 501.2, 501.17

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,565,592 Dated February 23, 1971

Inventor(s) ENVER MEHMEDBASICH

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

Col. 2, line 57, " $(x^1/n^1)Y \cdot \{(-\overset{1}{N}(-U^1-\overset{1}{N}-)_{a^1})R^1_{c^1}H^3_{+a^1-c^1}\}$ "
should read $--(x^1/n^1)Y \cdot \{(-\overset{1}{N}(-U^1-\overset{1}{N}-)_{a^1})R^1_{c^1}H^3_{+a^1-c^1}\}$.
line 60, "hydrocarobn" should read --hydrocarbon--.

Col. 3, line 47, " $X(-UNH-)_{1}UX$ " should read $--X(-UNH-)_{2}UX--$;
line 50, " $R^2-\begin{array}{c} CH-CO \\ | \quad \diagup \\ CH_2-C \quad N- \end{array}$ " should read $--R^2-\begin{array}{c} CH-CO \\ | \quad \diagup \\ CH_2-CO \quad N- \end{array}$

Col. 5, lines 14-16, delete the sentence starting with "The and ending with "3,438,757." Insert in lieu thereof --In copending application Serial No. 647,611, file June 21, 1967, and now U.S. 3,438,757, the method of preparation is considered superfluous.--

Col. 7, line 70, " $((R^3CO-)_{c^1}H_{+a-c})$ " should read
 $--(R^3CO-)_{c^1}H_{+a-c}--$.

Col. 8, line 26, " $x^1/n^1)Y \cdot \{(-\overset{1}{N}(-U^1-\overset{1}{N}-)_{a^1})R^1_{c^1}H^3_{+a^1-c^2}\}$ "
should read $--x^1/n^1)Y \cdot \{(-\overset{1}{N}(-U^1-\overset{1}{N}-)_{a^1})R^1_{c^1}H^3_{+a^1-c^1}--$

Signed and sealed this 14th day of September 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents