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SALTS OF 2,4-DINAPHTHENYL-3-THIAGLUTARIC ACIDS AND 1,3-DIAMINOPROPANES

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6 Claims. (Cl. 260—501)

This invention relates to addition agents for liquid petroleum distillate fuels and stable liquid petroleum distillate fuels containing the same. More particularly, the invention is concerned with the stabilization of liquid petroleum distillate fuels tending toward instability during storage by incorporation therein of new salt compositions.

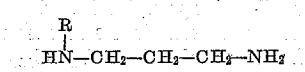
Liquid petroleum distillate fuels often exhibit a tendency toward instability during storage at ordinary atmospheric temperatures. For example, straight run distillate fuel oils can form sludge during storage despite their high content of normally stable paraffinic hydrocarbons. Where sludge deposition occurs in such oils, it is usually attributed to the presence in the oils of materials that are not normally present, e.g., impurities picked up during refining, or perhaps remaining in the oil due to incomplete refining, rather than to the inherent instability of the oil itself. Sludge formation in straight run fuel oils is considered to be chiefly a problem of oxidation and the formation of insoluble oxygenated products.

Unlike straight run distillate fuel oils, catalytically cracked fuel oil distillates are rich in olefinic, aromatic and mixed olefinic-aromatic components. Sludging in the latter oils is considered to involve primarily condensation and/or polymerization type reactions which result in the formation of insoluble reaction products of relatively high molecular weight.

Distillate fuel oil compositions containing mixed straight run and catalytically cracked fuel oil distillates have proved especially troublesome with regard to sludge deposition during storage at normal atmospheric temperatures. It has been found that the sludging characteristcs of such mixed, or blended, fuel oil distillates are strikingly poor, much poorer than can be accounted for from the known sludging characteristics of the individual component fuel oil distillates alone. While the sludge formed in mixed distillate fuel oils no doubt contains some sludge of the type formed in each component oil, the sludge formed in the blended fuel oils is consistently greatly in excess of the amount that can be accounted for from the known sludging tendencies of the individual component oils, thus indicating the existence of a special problem.

Gasolines tend to form gum during storage. In contrast to fuel oil sludge, which is recognized as an insoluble precipitate in the fuel oil, the gums formed in gasoline are soluble therein and do not appear as such except upon evaporation of the gasoline. The problem of gum formation is considered to involve primarily the oxidation of reactive olefinic linkages.

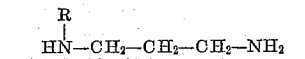
We have found that the storage stability of liquid petroleum distillate fuels can be substantially improved by incorporation therein of small amounts of the multifunctional, novel salt compositions of this invention. The compounds included by this invention are the salts of 2,4-dinaphthenyl-3-thiaglutaric acids and 1,3-diaminopropanes having the general formula:



where R is an aliphatic radical containing from 8 to 30 carbon atoms. The invention not only includes the novel 2,4-dinaphthenyl-3-thiaglutarates themselves, but also stable liquid petroleum distillate fuel compositions containing these salts.

The salts of this invention are prepared by neutralization of 2,4-dinaphthenyl-3-thiaglutaric acid with a 1,3-diaminopropane that contains a long-chain, aliphatic radical-substituted, secondary amino grouping. The aforesaid neutralization reaction normally takes place spontaneously at room temperature with evolution of heat, but in some cases moderate heating may be desirable in order to accelerate the reaction. In no case should the reaction be carried out at temperatures in excess of about 195° F., since decomposition of the resulting ammonium salt may occur with prolonged exposure to temperatures substantially in excess of this limit. Depending upon whether the desired salt is a substantially neutral diammonium salt, or a diaminodiammonium salt, the mol ratio of the acid to diamine may vary between about 1:1 and about 1:2.

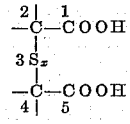
The diaminopropanes that form salts included by this invention may be illustrated by the generic formula:



where R is an aliphatic radical containing from 8 to 30 carbon atoms. Thus, the present invention includes, for example, the use of 2,4-dinaphthenyl-3-thiaglutarates of long-chain alkyl-, alkenyl-, and alkadienylaminopropylamines. Specific examples of such diamino compounds are 3-octylaminopropylamine, 3-decylaminopropylamine, 3-tetradecylaminopropylamine, 3-tetradecenylaminopropylamine, 3-eicosylaminopropylamine, 3-eicosenylaminopropylamine, 3-docosylaminopropylamine, 3-docosenylaminopropylamine, 3-docosodienylaminopropylamine, and 3-triacontanylaminopropylamine. Within the general class of 1,3-diaminopropanes capable of forming the salts of this invention, the diamines in which the long-chain, aliphatic N-substituent of the secondary amino grouping is an alkyl or alkenyl group containing at least 12 and preferably from 12 to 18 carbon atoms are considered to form especially effective addition agents. Examples of 1,3-diaminopropanes which are considered to form especially effective 2,4-dinaphthenyl-3-thiaglutarates for the purposes of this invention are the 3-dodecyl-, 3-hexadecylaminopropylamines, and especially the 18 carbon alkyl-, alkenyl-, and alkadienyl-substituted 1,3-diaminopropanes, such as the 3-octadecyl-, 3-octadecenyl, and 3-octadecadienylaminopropylamines. Although aliphatic hydrocarbon N-substituted 1,3-diaminopropanes are preferred, the invention also includes salts derived from diamines in which the N-substituent of the secondary amino grouping is itself substituted with one or more groups that contain elements such as oxygen, sulfur, nitrogen or halogens and that do not interfere with the oil-solubility of the salt. Representative examples of 1,3-diaminopropanes containing such substituents are 3-ricinoleylaminopropylamine and 3-(chlorostearyl)aminopropylamine. Mixtures of 1,3-diaminopropanes such as are formed when the long-chain, aliphatic N-substituent in the secondary amino grouping is derived from mixed fatty acids obtained from naturally occurring fats and oils form highly effective 2,4-dinaphthenyl-3-thiaglutarates within the scope of this invention. In such instances the aliphatic N-substituent in the secondary amino grouping will be a straight-chain monovalent hy-

drocarbon radical containing from 8 to 20 carbon atoms. Examples of such mixtures of 1,3-diaminopropanes are 3-"tallow"-aminopropylamine, 3 - "soya" - aminopropylamine, and 3-"coco"-aminopropylamine where the respective N-substituents are mixed alkyl and unsaturated alkyl groups derived from animal tallow (C_{14}–C_{18}) fatty acids, soybean (C_{16}–C_{20}) fatty acid, and coconut (C_8–C_{18}) fatty acids.

The 2,4-dinaphthenyl-3-thiaglutaric acids from which are formed the addition salts of this invention are acids containing an alicyclic hydrocarbon grouping attached to a 3-thiaglutaric acid residue:

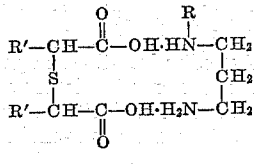


where x is a number from 1 to 2, whether the alicyclic grouping is attached to the 2 and 4 carbon atoms, or whether the 2 and 4 carbon atoms themselves are part of the structure forming an alicyclic link. Since alicyclic or cycloaliphatic hydrocarbons are conventionally called "naphthenes," the term "naphthenyl" is used herein and in the appended claims to denote the alicyclic substituents of the 3-thiaglutaric acids.

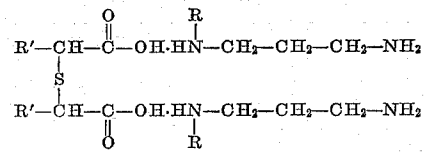
The method of making the 2,4-dinaphthenyl-3-thiaglutaric acids is disclosed in detail in copending application Serial No. 387,308, filed October 20, 1953, and now abandoned, in the names of Pellegrini and Stevens. Although for this reason it is considered unnecessary to describe the preparation of these acids in detail, in the interest of clarity it may be briefly mentioned that such acids can be made by halogenating a naphthenic acid containing a secondary or tertiary carbon atom in the alpha position to the carboxylic acid group and reacting the alpha-halonaphthenic acid thus obtained with an alkali metal mono-sulfide, di-sulfide or mixtures thereof to form a 2,4-dinaphthenyl-3-thiaglutaric acid.

The 2,4-dinaphthenyl-3-thiaglutaric acids capable of forming the salts of this invention include those derived from the well-known petroleum naphthenic acids. As is well-known in the art, the petroleum naphthenic acids are obtained by caustic soda extraction of naphtha, kerosene, gas oil and lubricating distillates. Conventional petroleum naphthenic acids contain from about 7 to 30 carbon atoms and possess an average molecular weight ranging from about 200 to about 450. Although 2,4-dinaphthenyl-3-thiaglutaric acids that have been derived from petroleum naphthenic acids are preferred because of their relatively low cost, our invention is not limited thereto. The invention also includes salts of 2,4-dinaphthenyl-3-thiaglutaric acids derived from synthetic naphthenic acids such as cyclopentylacetic acid, 2,2,3-trimethylcyclopentylacetic acid, hexahydrobenzoic acid (cyclohexane carboxylic acid), cyclohexylacetic acid, 3-methylcyclohexylacetic acid, cyclohexylpropionic acid, cyclohexylstearic acid and corresponding alkyl cyclohexyl or dicyclohexyl fatty acids.

As indicated, the reaction products of the above-described neutralization of the 2,4-dinaphthenyl-3-thiaglutaric acid with the long-chain, aliphatic N-substituted 1,3-diaminopropanes vary from the substantially neutral diammonium salts to salts of the diamino-diammonium type, depending upon whether the acid:diamine ratio in the neutralization reaction is 1:1 or 1:2. In the former instance the substantially neutral diammonium salts are considered to have the following probable generic formula:



where R′ is a naphthenyl or alicyclic hydrocarbon substituent and R is as defined above. In the latter instance the diamino-diammonium salts are considered to have the following probable generic formula:



where R and R′ are as defined above. The term "substantially neutral" is employed to describe salts in which substantially no unneutralized carboxyl or amino groups are present.

The preparation of the 2,4-dinaphthenyl-3-thiaglutarates included by this invention, previously described in general, is illustrated by the following specific examples.

EXAMPLE I

A substantially neutral diammonium salt of a 2,4-di-petroleum naphthenyl-3-thiaglutaric acid was prepared by stirring 596 grams (1 mol) of a 2,4-di-petroleum naphthenyl-3-thiaglutaric acid with 400 grams (1 combining gram molecular weight) of 3-"tallow"-aminopropylamine at room temperature. The 2,4-di-petroleum naphthenyl-3-thiaglutaric acid employed had the following analysis:

Neutral equivalent	298
Percent S	3.24
Molecular wt. (based on neutral equivalent)	596

The 3-"tallow"-aminopropylamine referred to was a mixture of 3-fatty alkyl- and alkenylaminopropylamines containing approximately 80 percent active ingredient and had a theoretical molecular weight of 320, a combining weight of approximately 400 and a melting range of approximately 44° to 48° C. The fatty alkyl- and alkenyl-substituents of the diamine were derived from animal tallow fatty acids. Accordingly, the 3-"tallow"-aminopropylamine contained predominantly 3-oleylaminopropylamine together with substantial but lesser proportions of 3-octadecyl- and 3-hexadecylaminopropylamines, and small amounts of 3-myristyl- and 3-linoleylaminopropylamines.

The crude product of the foregoing reaction contained the mixed substantially neutral diammonium salts of 2,4-di-petroleum naphthenyl-3-thiaglutaric acid and 3-C_{14-18} alkyl-, alkenyl-, and alkadienylaminopropylamines, the predominant component of which mixture was the substantially neutral diammonium salt of 2,4-di-petroleum naphthenyl-3-thiaglutaric acid and 3-oleylaminopropylamine. This product was a brown, viscous liquid having the following analysis:

Nitrogen, percent	2.83
Sulfur, percent	1.84

EXAMPLE II

A diamino-diammonium salt of 2,4-di-petroleum naphthenyl-3-thiaglutaric acid was prepared by stirring 596 grams (1 mol) of the 2,4-di-petroleum naphthenyl-3-thiaglutaric acid of Example I with 800 grams (2 combining gram molecular weights) of the 3-"tallow"-aminopropylamine of Example I, at room temperature.

The crude product of the foregoing neutralization reaction contained the mixed diamino-diammonium addition salts of 2,4-di-petroleum naphthenyl-3-thiaglutaric acid and mixed 3-C_{14-18} alkyl-, alkenyl-, and alkadienylaminopropylamines, the predominant component of which was the diamino-diammonium addition salt of 2,4-di-petroleum naphthenyl-3-thiaglutaric acid and 3-oleylamino-

propylamine. The crude reaction product prepared as indicated was a brown, viscous liquid having the following analysis:

Nitrogen, percent	4.28
Sulfur, percent	1.42

The foregoing examples indicate the manner and ease of preparation of the addition salts of this invention, and the salts prepared therein are representative specific embodiments of the disclosed class. Other specific salts included by the invention can be prepared by reaction in the indicated molar proportions of other herein disclosed 1,3-diaminopropanes with the 2,4-di-petroleum naphthenyl-3-thiaglutaric acid referred to in the examples, or with other members of the herein disclosed class of 2,4-dinaphthenyl-3-thiaglutaric acids.

As indicated, the salt compositions of this invention have been found effective in small concentrations to alleviate problems of storage instability of liquid petroleum distillate fuels. For example, the salts of this invention effect a marked improvement in the storage stability of petroleum distillate fuels boiling in the gasoline range, especially cracked gasolines, which are particularly troublesome with regard to gum formation. The salts of this invention are also useful as sludge inhibitors in distillate fuel oils such as are used for domestic heating and for heating purposes in some industrial processes, typical of which are the so-called No. 2 fuel oils, i.e., distillate oils boiling within the approximate range of 350° to 750° F. and having a minimum API gravity of about 26. The salts of this invention are especially valuable for inhibiting sludge deposition in mixtures of straight run and catalytically cracked distillate fuel oils, which oils, as indicated above, are especially troublesome. The problem of sludging in mixed distillate fuel oils is serious when the volume ratio of the catalytically cracked and straight run oil is between about 9:1 and 1:9. The problem is particularly troublesome when the ratio is within the range of about 4:1 and 1:4.

The salts of this invention are highly suited for use in fuels in view of their ashless characteristics.

Naturally, the various salts of the herein disclosed class do not possess exactly identical effectiveness, and the most advantageous concentration of each such salt will depend to some extent upon the particular compound used. Also, the minimum effective inhibitor concentration may vary somewhat according to the specific nature of the distillate fuel to be inhibited. In general, however, the herein disclosed salts are useful in concentrations of as little as about 0.005 percent to about 1.0 percent by weight of the composition. Major improvement of the storage stability characteristics of gasolines and distillate fuel oils is usually obtainable by incorporation therein respectively of from about 0.01 to about 0.5 weight percent, and from about 0.01 to about 0.05 percent by weight of the herein disclosed class of salts. In some cases involving fuel oils it will be advantageous to add as much as about 0.1 percent by weight of the inhibitor, and in unusual instances involving either distillate fuel it may be found desirable to add as much as about 1.0 percent by weight of the inhibitor.

The 2,4-dinaphthenyl-3-thiaglutarates included by this invention may be incorporated in the liquid distillate fuels in any suitable manner. Thus, the salts may be formed in situ in the fuel, they may be added, per se, directly to the fuel, or they may be added in the form of concentrates, either immediately after distillation and/or blending of the distillate fuels, or, as in the case of fuel oils, after the fuel has been stored for a substantial period of time. In the case of blended fuels, such as mixed catalytically cracked and straight run distillate fuel oils, the salts of this invention may be formed in situ in, or added per se or in the form of concentrated solutions or dispersions to either the straight run or the catalytically cracked fuel oil distillate prior to the blending of these components to form a mixed fuel oil. Regardless of the nature of the fuel to be inhibited, it is generally preferred to employ preformed salts, usually in the form of concentrates, in the blending procedure. Suitable concentrates containing the addition agents of this invention comprise, for example, mineral oil solutions or dispersions containing from about 10 to 75 weight percent, and preferably from about 25 to 50 weight percent active ingredient. Where the concentrates are in the form of dispersions it may be desired to heat the concentrates and/or the fuel, e.g., in the case of a fuel oil to about 100° to 140° F., in order to facilitate blending. An alternate blending procedure involves the incorporation in the fuel at storage temperature of concentrated solutions of the inhibitors in solvents, other than mineral oils, that have a high degree of solubility for the inhibitors and that do not adversely affect the stability or other characteristics of the fuel. Examples of such concentrates are 10 to 75 weight percent, e.g., 50 weight percent, solutions of the substantially neutral salts and the diamino-diammonium salts of 3-"tallow"-aminopropylamine and 2,4-dinaphthenyl-3-thiaglutaric acid in solvents such as benzene, toluene, hexane, methyl isobutyl ketone and methyl ethyl ketone.

The utility of the herein disclosed class of 2,4-dinaphthenyl-3-thiaglutarates has been demonstrated by subjecting liquid petroleum distillate fuels containing small concentrations of the same to standard stability tests. For example, mixtures of catalytically cracked and straight run fuel oil distillates containing minute amounts of representative salts of the class included by the invention have been subjected to a standard accelerated stability test. These test samples were made up by adding the desired concentration of each additive to be tested to separate samples of a fuel oil mixture containing 50 percent by volume of a straight run No. 2 fuel oil distillate and 50 percent by volume of a catalytically cracked fuel oil distillate.

The stability test referred to above was carried out on the mixed fuel oil compositions by heating 600 gram samples of the fuel oil compositions for a period of 16 hours at 210° F. in loosely stoppered, one-quart clear glass bottles. Following the heating period each test sample was cooled to room temperature and filtered by suction through a tared, medium porosity fritted glass Gooch-type crucible. The sludge in each crucible was washed with heptane. Complete removal of the sludge adhering to the inside of the botles was obtained by means of a rubber policeman and heptane. The respective crucibles were dried in an oven maintained at 210° F. for 1 hour, cooled in a desiccator and reweighed. The increase in weight was recorded as milligrams of sludge per 600 grams of oil.

The fuel oil mixtures referred to as Blends A and B in the following table were 1:1 by volume mixtures of eastern Venezuela straight run and fluid catalytically cracked No. 2 fuel oil distillates. Blend A had the following properties:

Gravity, ° API	28.7
Specific gravity (60°/60° F.)	0.8833
Viscosity, SUS @ 100° F.	35.6
Color, NPA	2—
Pour point, ° F.	0
Flash point, OC, ° F.	180
Neutralization value, acid No.	0.05
Distillation:	
Initial boiling point, ° F.	385
End boiling point, ° F.	642
Bromine No.	16.5
Olefins, wt. percent	22.3
Aromatics, vol. percent	26.2
Aniline point, ° F.	116
Ash, oxide, weight percent	<0.01

The foregoing values are similar to, and are considered typical of, those for the corresponding properties of Blend B, also referred to in the table.

Table A

Fuel Oil Composition	Sludge, Mg./600 G. Oil, After 16 Hrs.
1. Blend A—50/50 Mixture of E.V.S.R. and F.C.C. No. 2 Fuel Oil Distillate	18.2
2. Blend A plus 0.05 Wt. percent 3-"Tallow"-ammoniumpropylammonium - 2,4 - Dinaphthenyl - 3 - Thiaglutarate of Example I	5.1
3. Blend A plus 0.05 Wt. percent of Di-(3-Aminopropyl-"Tallow" - ammonium) - 2, 4 - Dinaphthenyl - 3 - Thiaglutarate of Example II	3.1
4. Blend B—50/50 Mixture of E.V.S.R. and F.C.C. No. 2 Fuel Oil Distillate	31.8
5. Blend B plus 0.02 Wt. percent of Ethylene Diamine Mono-Petroleum Naphthenate	315.0
6. Blend B plus 0.02 Wt. percent of Ethylene Diamine Di-Petroleum Naphthenate	34.8

Compositions 2 and 3 in the foregoing table are specific embodiments of the invention. The results shown in the table for these compositions are considered typical of those obtainable with the 2,4-dinaphthenyl-3-thiaglutarate addition salts of this invention. Comparison of the results obtained for Compositions 2 and 3 with those obtained for blank Composition 1 clearly indicates the marked improvement in sluding ceharacteristics of mixed distillate fuel oils that is obtainable with the salts included by this invention. Comparison of the results obtained for Compositions 5 and 6 with those obtained for Composition 4 in the foregoing table indicates that the results obtained by the salts of this invention are not typical of those obtained by diamine salts of carboxylic acids in general.

The utility of the herein disclosed salts has been further demonstrated by subjecting other liquid distillate petroleum fuels to stability tests. For example, compositions comprising thermally cracked gasoline distillate and salts of this invention have been subjected to the standard oxidation stability test ASTM D525–49. According to this test, the gasoline sample is introduced into an oxidation bomb and oxygen is added to a pressure of about 100 p.s.i. The charged bomb is placed in a boiling water bath and the gas pressure in the bomb is recorded. The end of the induction period, i.e., the point at which rapid absorption of the oxygen by the gasoline takes place, is the time when a sharp drop in pressure (at least 2 p.s.i. in 15 minutes) occurs.

The results obtained by the foregoing tests are presented in Table B below:

Table B

	Additive Concentration		Induction Period, Minutes
	G./100 Ml.	Mols/100 Ml.	
1. Blank Gasoline—Thermally Cracked Distillate			94
2. Blank Gasoline plus 2,4,6-Tri-t-butylphenol (Standard)	0.0525	0.0002	240
3. Blank Gasoline plus 3-"Tallow"-ammoniumpropyl-ammonium-2,4-Dinaphthenyl-3-Thiaglutarate of Example I	0.1992	0.0002	316
4. Blank Gasoline plus Di-(3-Aminopropyl - "Tallow" - ammonium) - 2,4 - Dinaphthenyl - 3 - Thiaglutarate of Example II	0.2792	0.0002	522

Compositions 3 and 4 in Table B are specific embodiments of the invention. Comparison of the induction periods for these compositions with those for gasoline Composition 2 (inhibited with a standard commercial inhibitor) and for uninhibited gasoline Composition 1 indicates the improvement obtainable by the salts of this invention.

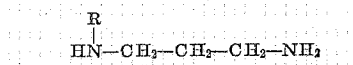
It will be understood that the foregoing embodiments of the invention are merely illustrative and that other members of the class of sludge inhibiting salts included by the invention can be substituted therein in the same or equivalent concentrations within the herein disclosed ranges to prepare distillate fuel compositions having similarly improved stability characteristics. Specific examples of other salts that are suitable for the purposes of this invention and which can be used in lieu of those in the above-indicated embodiments are the substantially neutral diammonium salts and the diamino-diammonium salts of 3-lauryl-, 3-octadecyl-, 3-octadecenyl-, and 3-octadecadienylamino - propylamines and 2,4 - di - petroleum naphthenyl-3-thiaglutaric acid, 2,4-di-cyclopentyl-3-thiaglutaric acid, 2,4-di-cyclohexyl-3-thiaglutaric acid and 2,4-di-cyclohexylhexa-decyl-3-thiaglutaric acid.

If desired, the stable distillate fuel compositions of this invention may contain, in addition to the additives disclosed herein, other improvement agents. For example, fuel oil compositions may contain additionally oxidation inhibitors, flash point control agents, corrosion inhibitors, anti-foam agents, ignition quality improvers, combustion improvers and other additives adapted to improve the oils in one or more respects. Gasoline compositions may contain additionally anti-knock agents, corrosion inhibitors, dyes, color inhibitors, ignition control additives, and other conventional additives.

It will be apparent to those skilled in the art that many variations of the invention may be resorted to without departing from the spirit thereof. Accordingly, only such limitations should be imposed as are indicated in the claims appended hereto.

We claim:

1. A salt of a 2,4-dinaphthenyl-3-thiaglutaric acid and a 1,3-diaminopropane having the general formula:



where R is an aliphatic radical containing from 8 to 30 carbon atoms, the molecular ratio of said acid and said 1,3-diaminopropane in said salt being in the range of about 1:1 to 1:2.

2. A salt of (*a*) a 2,4-dinaphthenyl-3-thiaglutaric acid whose naphthenyl substituents are derived from petroleum naphthenic acids, and (*b*) a 1,3-diaminopropane selected from the group consisting of 3-alkyl- and 3-alkenylaminopropylamines wherein the alkyl and alkenyl substituents contain from 12 to 18 carbon atoms, the molecular ratio of said acid and said 1,3-diaminopropane in said salt being in the range of about 1:1 to 1:2.

3. A substantially neutral diammonium salt of (*a*) a 2,4-dinaphthenyl-3-thiaglutaric acid whose naphthenyl substituents are derived from petroleum naphthenic acids, and (*b*) mixed 3-alkyl- and 3-alkenylaminopropylamines wherein said alkyl and alkenyl substituents contain from 14 to 18 carbon atoms.

4. A substantially neutral diammonium salt of (*a*) a 2,4-dinaphthenyl-3-thiaglutaric acid whose naphthenyl substituents are derived from petroleum naphthenic acids, and (*b*) 3-oleylaminopropylamine.

5. A diamino-diammonium salt of (*a*) a 2,4-di-naphthenyl-3-thiaglutaric acid whose naphthenyl substituents are derived from petroleum naphthenic acids, and (*b*) mixed 3-alkyl- and 3-alkenylaminopropylamines wherein said alkyl and alkenyl substituents contain from 14 to 18 carbon atoms.

6. A diamino-diammonium salt of (*a*) a 2,4-di-naphthenyl-3-thiaglutaric acid whose naphthenyl substituents are derived from petroleum naphthenic acids, and (*b*) 3-oleylaminopropylamine.

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