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ADDITIVE FOR LEADED GASOLINE

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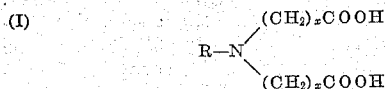
This invention relates to gasoline containing tetraethyllead. More particularly the invention relates to leaded gasoline containing additives which increase the stability of the TEL and reduce deposits.

Gasolines containing tetraethyllead and scavengers associated with TEL have a tendency to deposit insoluble lead decomposition products while in storage. This instability of the so-called leaded gasolines not only decreases the octane number of the deteriorated gasoline, but also may result in difficulties in the engine from the soluble portions of the decomposition products. This problem is particularly serious in the case of leaded gasolines to be used for automotive engines wherein a limit has been imposed of 3.0 cc. of lead fluid per gallon of gasoline. Thus the octane loss due to lead fluid decomposition cannot be compensated for by adding an excess of lead fluid. Although in the case of aviation gasoline as much as 6 cc. of lead fluid has been used, lead decomposition is very undesirable because of the difficulty of meeting the tremendously high octane demand of present performance airplane motors.

An object of the invention is a leaded gasoline composition of improved resistance to deterioration in storage. Another object of the invention is a leaded gasoline composition of improved stability of the TEL in storage. Other objects will become apparent in the course of the detailed description of the invention.

The objects of the invention are attained by a composition comprising essentially a tetraethyllead-containing gasoline as the major component and an effective amount of an additive derived by the reaction of a hereinafter defined amine and a hereinafter defined amino-carboxylic acid.

The amino-carboxylic acids which are suitable for the purposes of the invention are represented by the configuration:

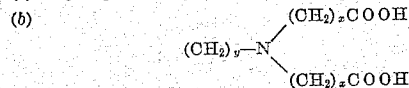


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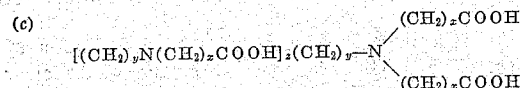


wherein "x" is an integer from 1 to 3 and preferably "x" is 1; "R" is a member selected from the class consisting of

(a) Hydrogen



and



wherein "y" is an integer from 2 to 3 and preferably 2; and "z" is an integer from 1 to 3.

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Iminodiacetic acid is an example wherein R is hydrogen and x is 1. Ethylenediaminetetraacetic acid is an example wherein R is member (b) and y is 2 and x is 1. Tetraethylenepentamineheptaacetic acid is an example of an acid where R is member (c), x is 1, y is 2 and z is 3.

The amino acids of the invention may also be described as amino aliphatic carboxylic acids wherein at least one amino nitrogen holds 2 carboxylalkyl groups.

The amines suitable for the purposes of the invention are: (1) aliphatic amines, either primary, secondary, or tertiary wherein at least one aliphatic group contains at least 8 carbon atoms, and (2) heterocyclic amines which contain at least one aliphatic substituent having at least 8 carbon atoms therein and at least one ring nitrogen has a valence which is not part of the ring structure, excluding the pyrrole types. Illustrative examples of these amines are octylamine, decylamine, tetradecylamine, octadecylamine, dioctylamine, dioctadecylamine, stearylimidazoline, and oleylimidazoline.

The preferred amines are the fatty acid amines. Those mixtures of amines which are obtained from natural vegetable oils, such as palm oil, coconut oil, soya bean oil, tall oil, and cottonseed oil are suitable. Particularly suitable is the mixture of amines derived from tallow. Of even greater interest are the high molecular weight amines which are obtained as a bottoms fraction in the distillative purification of the mixture of amines prepared from tallow. These amines are commercially available under the designation corresponding to the amine product from the particular oil or fat, e.g., tallowamine bottoms. The bottoms product amines have one disability in that the quality of the material is variable and therefore the amine salt of the amino-carboxylic acid produced therefrom will vary in quality from batch to batch of the amine bottoms material.

The amine salts of amino-carboxylic acids utilizable as hydrocarbon oil additives are readily prepared by heating the desired amine and the desired amino-carboxylic acid at a temperature below the decomposition temperature of the individual components for a suitable period of time. The temperature and the time are dependent upon the particular reactants used. In general, the temperature at which the reaction is carried out is between about 30° C. and about 200° C.; the time needed for the reaction to be completed will be between about 15 minutes and about 3 hours. It is preferred to utilize a temperature between about 140° C. and about 180° C.; the corresponding time will be dependent on the type of reactants charged.

The relative amounts of amine and amino-carboxylic acid utilized is dependent upon the number of carboxylic acid groups in the acid and also upon the degree to which the carboxylic acid groups are to be reacted. When it is desired to react all the carboxylic acid groups, it is better to operate with an excess of amine over the stoichiometric requirement. In general, the molar ratio of amine to acid is between about 0.5 and 1.5 of the stoichiometric requirement for reactions with all the carboxylic groups in the acid. It is preferred to operate with a molar ratio of amine and amino-carboxylic acid such that all the carboxylic groups will be reacted, i.e., at least the stoichiometric requirement.

The amine salt of amino-carboxylic acid is readily prepared by admixture of the desired amounts of the reactants and heating the mixture to the desired temperature and maintaining said mixture at that temperature for the necessary time. The appearance of the reactants changes when the reaction begins and completion of the reaction is observed visually by disappearance of the individual reactants. The reaction product mixture is cooled to room temperature and may be utilized as an additive without further treatment. However, when an

excess of one reactant has been used, it may be desirable to purify the reaction product mixture. This purification is readily carried out by treating the mixture with a solvent, such as benzene or hexane, filtering to remove the insoluble material and recovering the purified reaction product, i.e., the amine salt of amino-carboxylic acid, by evaporating away the solvent.

The leaded gasoline which forms the major component of the composition of the invention may be any mixture of hydrocarbons which meets the requirement with respect to boiling range, freezing point, and sulfur content of commercial gasolines for the particular purpose. For example, the commonly called motor gasoline boils over the range from about 100° F. to 400° F. The exact distribution of components in this boiling range varies with the season of the year in order to provide better starting characteristics in winter and lower vapor losses in summer. Aviation gasolines generally boil over the range of about 100° F. and 375° F. In some instances, the so-called aviation safety fuels boil from about 175° F. to about 375° F. The composition of the gasoline itself may vary in accordance with commercial practice. For example, a third-grade fuel may contain only virgin materials which have been brought to the required octane number by the addition of TEL. In general, the so-called regular grade gasolines and premium grade gasolines contain cracked components, either thermally cracked, and/or catalytically cracked, and may contain gasoline boiling range polymers from the polymerization of propylene and butylene and/or may contain alkylate from the alkylation of isobutane, propylene and butylene. Aviation gasoline, on the other hand, may consist almost entirely of materials derived by various conversion processes from petroleum components. For example, aviation gasoline may contain essentially only alkylate, polymer, and catalytically reformed naphtha. Benzene and toluene may also be added to some aviation gasolines.

In addition to the hydrocarbon components, gasolines contain various anti-oxidants, such as N,N'-di-*t*-butyl-*para*-phenylenediamine and metal deactivators. Also, they may contain compounds designed to decrease the effect of TEL decomposition in the combustion chamber, such as tricresylphosphate. Furthermore, in addition to the hydrocarbon components, the gasoline may contain minor amounts of materials which assist in good engine performance under specific conditions of operation. For example, alcohols and ethers may be present to avoid carburetor icing. Or alcohols may be present to prevent formation of ice crystals in storage or in transfer lines. Still further, most commercial gasolines contain dyes of one type or another. Also, they may contain minor amounts of detergent compositions which solubilize water and prevent formation of a haze.

It is to be understood that the term "leaded gasoline" used in this specification and in the claims is intended to include hydrocarbon mixtures which are usable in engines of the automotive and airplane type using spark ignition, which gasolines contain appreciable amounts of tetraethyllead or the so-called ethyl fluid which consists of tetraethyllead and lead scavengers, as well as the usual additives added to gasoline, examples of which have been cited above. In general, the amount of tetraethyllead in the formation of TEL fluid which is present in leaded gasoline is between about 0.5 and 6 cc. per gallon of gasoline.

The gasoline is the major component of the composition of the invention. The defined amine salts of amino-carboxylic acid are present in an amount sufficient to improve the stability of the tetraethyllead against deterioration in storage. Generally only a very small amount of amine salt of amino-carboxylic acid is utilized. The particular amount used is dependent on the particular use of the composition, but in general will be between about 0.0005 and about 0.5% by weight of

the composition. More usually the usage will be between about 0.002% and 0.02% by weight.

Examples of the defined amine salts of amino-carboxylic acids are set out below. Illustrations of the compositions containing various amounts of illustrative examples and the beneficial results derived from the presence of the defined salt in leaded gasoline are set out as determined by various tests. It is to be understood that the examples of the defined amine salts of amino-carboxylic acids and the illustrative leaded gasoline compositions containing these salts are illustrative only and do not limit the scope of the invention.

SALT I

The amine used in this example is sold by Armour & Co. under the name, "Tallowamine Bottoms." This material is obtained as a bottoms product from the distillation of the spectrum of amines produced from tallow. The tallowamine bottoms utilized in this example contained 3.55% nitrogen and had a molecular weight of 421. This material is predominantly the secondary amine with the remaining portion primary amine. Ethylenediaminetetraacetic acid—25 g. (0.086 mole) and 150 g. (0.356 mole) of tallowamine bottoms were stirred for 15 minutes at 150° C. The reaction product was a clear brown liquid which analyzed 4.40% nitrogen. This liquid product was completely soluble in an SAE 30 lubricating oil.

SALT II

The amine in this example is sold by Armour & Co. under the designation Duomeen S. This amine has the structure $\text{RNH}(\text{CH}_2)_3\text{NH}_2$, where R is an aliphatic group containing 18 carbon atoms. 0.86 mole of Duomeen S. and 0.46 mole of ethylenediaminetetraacetic acid were stirred at 155° C. for 20 minutes. The product was an orange-yellow in color and contained 7.91% nitrogen and was soluble in gasoline.

SALT III

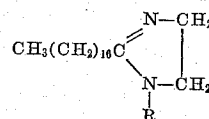
In this example, the amine used is sold by Armour & Co. under the name, "Cocoamine Bottoms." This material is the bottoms product from the distillation of the spectrum of amines made from coconut oil. 150 g. of the cocoamine bottoms and 25 g. of ethylenediaminetetraacetic acid were stirred at 148° C. for 15 minutes. The product was diluted with 300 ml. of hexane and filtered. The hexane was removed by evaporation. The brown waxy solid product was completely soluble in gasoline and lube oil. A yield of 173 g. of product containing 2.99% nitrogen was obtained.

SALT IV

In this example, the amine utilized was principally *t*-octadecylamine sold under the name of Primene JM-R. 100 g. of this amine and 20 g. of ethylenediaminetetraacetic acid were stirred at 165° C. for 10 minutes. The product was clear orange colored viscous liquid containing 5.47% nitrogen and was soluble in gasoline.

SALT V

In this example, the amine was purchased as "Alroamine S." This material is an imidazoline derived from stearic acid having the following structure:



and a molecular weight of 360. 43.2 g. (0.12 mole) of this imidazoline and 8.76 g. (0.03 mole) of ethylenediaminetetraacetic acid were stirred at 150° C. for 15 minutes. The product weighed 51 g. and was a clear brown liquid containing 8.28% nitrogen. The product was soluble in lube oil.

5 SALT VI

Iminodiacetic acid (0.1 mole) and 0.2 mole of tallowamine bottoms were stirred at about 170° C. The reaction product was a light brown waxy solid which was completely soluble in gasoline. The product of this reaction contained 5.06% nitrogen.

Examples

The storage stability tests were carried out using 250 ml. of leaded gasoline in a pint bottle provided with a vented stopper. The bottle was maintained in a constant temperature room at 90° F. for the time of the test which may be either 2 or 4 months. At the completion of the storage time, the contents of the bottle are passed through a filter and the total gasoline insoluble deposits are recovered. These are dried and weighed to determine the "total deposit" as mg./250 ml. of gasoline. The total deposits are then washed with a triple solvent which consists of equal volumes of acetone, methyl alcohol and chloroform. The material which is insoluble in the triple solvent is dried and weighed to obtain "insoluble deposit" as mg./250 ml. of gasoline.

In the first series of tests, a regular grade motor gasoline containing 3.0 cc. TEL fluid was used. The storage period was 4 months. The results of the test on this 3 cc. containing gasoline are set out in Table I. (0.0018% is 5 lbs./1000 bbls. (42 gal.) of gasoline.)

TABLE I

Test No.	Additive	Percent Present	Total Deposit	Insoluble Deposit
1.	None	None	8.2	5.0
2.	Salt I	0.0018	4.6	1.8
3.	Salt II	0.0018	5.3	2.9
4.	Salt IV	0.0018	8.5	3.9
5.	Salt III	0.0018	8.1	4.3

Salts I and II not only reduce the insoluble deposits, but also the total deposit. This is a valuable feature in that it definitely improves the appearance of the gasoline. While Salts III and IV do not improve the total amount of deposit formed, they did significantly decrease the amount of insoluble deposits.

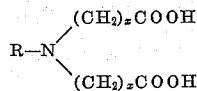
Tests Nos. 6 and 7.—In these tests, the gasoline was an aviation gasoline containing 4.5 cc. of TEL fluid per gallon of gasoline. The total time of storage was 2 months. The sample containing no additive developed 3.3 mg. of insoluble deposits (Test No. 6). The sample containing 0.0018 weight percent of Salt I developed no measurable amount of insoluble deposit (Test No. 7). These tests show that the salt obtained by reacting tallowamine bottoms and ethylenediaminetetraacetic acid is extremely effective in inhibiting the decomposition of tetraethyllead present in leaded gasoline.

Thus having described the invention, what is claimed is:

1. A composition consisting essentially of a gasoline containing between about 0.5 and 6 cc. per gallon of tetraethyllead and between about 0.0005 and 0.5 weight percent of an amine salt of an amino-carboxylic acid obtained by reacting, at a temperature between about 30° C. and 200° C., a molar ratio of amine to acid between

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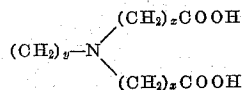
about 0.5 and 1.5 of the stoichiometric requirement to react all the carboxylic groups in the acid, an amine selected from the class consisting of (1) aliphatic amines wherein an aliphatic group contains at least 8 carbon atoms and (2) imidazoline containing an aliphatic substituent having at least 8 carbon atoms is present, with (B) an amino-carboxylic acid having the configuration



wherein R is selected from the class consisting of

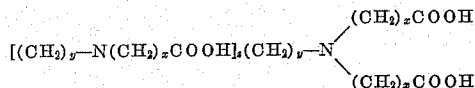
(a) Hydrogen

(b)



and

(c)



wherein x is an integer from 1 to 3, y is an integer from 2 to 3, and z is an integer from 1 to 3.

2. The composition of claim 1 wherein said salt is obtained by reacting tallowamine bottoms and ethylenediaminetetraacetic acid at a temperature between about 140° C. and 180° C.

3. The composition of claim 1 wherein said salt is obtained by reacting an amine having the structure $\text{RNH(CH}_2\text{)}_3\text{NH}_2$ wherein R is an aliphatic group containing about 18 carbon atoms and ethylenediaminetetraacetic acid at a temperature between about 140° C. and 180° C.

4. The composition of claim 1 wherein said salt is obtained by reacting tallowamine bottoms and iminodiacetic acid at a temperature between about 140° C. and 180° C.

5. The composition of claim 1 wherein said amine is stearylimidazoline.

6. The composition of claim 1 wherein said acid is tetraethylenepentamineheptaacetic.

7. The composition of claim 1 wherein said salt is present in an amount between about 0.002 and about 0.02 weight percent.

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