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METAL DEACTIVATORS FOR ORGANIC MATERIALS

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This invention relates to fuel compositions containing imide-amide reaction products of ethylenediamine tetraacetic acid. More particularly, it relates to hydrocarbon oil compositions such as gasolines containing as an additive such a reaction product that inhibits the harmful catalytic effect of metals on the oxidation stability of the oil.

Hydrocarbon oils such as gasoline, kerosene, diesel oil, fuel oils, etc., in contact with air frequently undergo oxidative deterioration which has an adverse effect upon the marketability of the oil. The problem is most often encountered with olefinic gasoline such as cracked, thermally reformed, and polymer gasolines, but is also serious with other hydrocarbon oils.

It has been the practice to incorporate oxidation inhibiting additives in gasolines and other hydrocarbon oils. However, the oils are often contaminated with metals or metal compounds that catalyze the oxidation reactions. The conventional antioxidant additives in general are either not effective in suppressing catalyzed oxidation or must be used in such large concentrations as to be uneconomical.

Contamination of hydrocarbon oils with metals that catalyze oxidation can occur in a number of ways. For example, it is frequently necessary to subject sulfur-containing gasolines, particularly cracked gasolines, to a sweetening treatment for converting odoriferous mercaptans to less objectionable sulfur compounds. The gasoline is sweetened by contact with a copper-containing reagent such as cupric chloride. The treated gasoline usually contains small amounts of copper or copper compounds which catalyze oxidation. Even hydrocarbon oils that have not undergone copper sweetening may contain copper or other oxidation catalyzing metals as the result of contact with such metals during refining, storage, or transportation. Although copper is one of the most troublesome metals in catalyzing oxidation a number of others present a similar problem, including iron, cobalt, nickel, titanium, chromium, lead, zinc, vanadium, manganese, and compounds thereof.

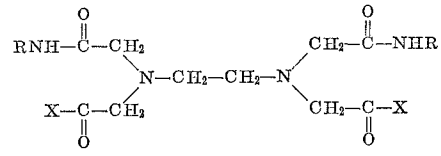
The present invention is based on our discovery that the harmful catalytic effect of copper and other metals and compounds thereof on the oxidation stability of hydrocarbon oils can be suppressed effectively by the addition to the oil of a minor amount of certain imide-amide reaction products of ethylenediamine tetraacetic acid, the latter compound being abbreviated hereinafter as "EDTA."

The imide-amide reaction products employed in the compositions of our invention are obtained by reacting EDTA with a C_4–C_{24} primary aliphatic amine under conditions adapted to yield a product that consists essentially of partial imide and amide compounds, more than 25% but less than 75% of the carboxyl groups of said EDTA being converted to imide or amide forms. The products having the greatest advantages and that are therefore employed in the preferred compositions of the invention are those in which an average of two of the carboxyl groups of EDTA are converted to imide or amide groups.

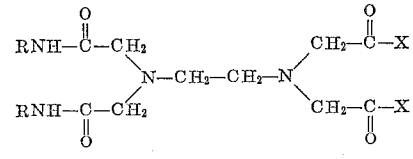
The compositions of the invention in general comprise hydrocarbon oils normally susceptible to metal catalyzed oxidation containing an amount sufficient to suppress the catalyzed oxidation of a partial imide-amide reaction product of the type described. Such compositions for which the greatest benefits of the invention are realized are olefinic gasolines containing a minor amount of the described EDTA reaction product which has an average composition corresponding to the monoimide or diamide form.

The reaction products that we employ to suppress catalysis of oxidation are obtained by reacting EDTA with an aliphatic primary amine having from 4 to 24 carbon atoms per molecule under selected reaction conditions. The most important reaction conditions are temperature, reaction time, and mol ratio of amine to EDTA. These conditions are so selected that a reaction product is formed containing compounds of the following general formulae:

(I)

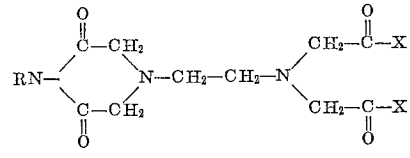


(II)



and

(III)



wherein R is an aliphatic group of 4 to 24 carbon atoms, such as alkyl, alkenyl, cycloalkyl, alkylaminoalkyl, or dialkylaminoalkyl; and X is —OH or —OH.RNH_2.

The above compounds present in the reaction product can be in the diamide form such as compounds I and II, or in the monoimide form such as compound III. We use the terms "imide" and "amide" and the term "imide-amide" to mean any of these possible compounds or mixtures of the same, the common feature of the three types of compounds being that each contains a total of two amine salt groups or carboxyl groups. Such compounds are the characterizing and predominant components of the reaction product, although other possible products of amidization of EDTA may be present in minor amounts. The essential feature is that an average of more than 25% but less than 75% of the carboxyl groups of the EDTA are converted to the imide or amide forms. The rest remain as carboxyl groups or are converted to amine salt groups. The preferred reaction products have an average composition corresponding to the diamide or monoimide forms.

Amines suitable for reaction with EDTA to form the desired products are primary aliphatic amines having from 4 to 24 carbon atoms per molecule. An especially preferred amine is the product known as Primene 81–R. This is a mixture of branched chain, primary, alkyl amines in which the amine group is attached to a tertiary carbon atom and which have 12 to 15 carbon atoms per molecule and an average molecular weight of about 213. When this type of amine is employed, products according to the structural Formulae I, II or III above are formed in which R is a branched chain alkyl group of 12 to 15 carbon atoms.

Another commercial mixture of amines suitable for the reaction is the product known as Primene JM–T.

This is essentially a mixture of branched chain, primary alkyl amines of structure similar to the amines of Primene 81–R, but containing 18 to 24 carbon atoms per molecule. Typical examples of other suitable amines are 2-ethylhexylamine, octylamine and dodecylamine.

In the products made from amines of the types described above, R is an aliphatic hydrocarbon group of 4 to 24 carbon atoms. Other amines can also be used which form products in which R is an aliphatic group of 4 to 24 carbon atoms but not necessarily an aliphatic hydrocarbon group. Thus a suitable class of amine includes the Duomeen products. One of such products, known as Duomeen 12, is a propylenediamine derivative having the structure

$$H_2N—CH_2—CH_2—CH_2—NH—C_{12}H_{25}$$

This type of amine fits the definition of primary amines used for making the desired products, the prmiary amino group being the reactive group of the molecule. In compounds of the Formulae I, II, or III prepared from this type of amine the substituent R has the structure,

$$—(CH_2)_n—NH—R'$$

wherein n is 2 or 3 and R′ is an aliphatic hydrocarbon group of 8 to 18 carbon atoms.

Of the selected reaction conditions used in forming the imide-amide products, reaction temperature is particularly important. The temperature must be above about 200° C. and preferably is in the range of about 200 to 220° C.

Reaction time must be sufficient to yield the desired partial imide or amide products. The proper reaction time can be determined by measuring the acid number of the reaction product and continuing the reaction until the acid number of the desired product is obtained. The acid number of a particular imide-amide product will depend on the degree of amidation (more than 25% but less than 75%) as well as on the EDTA-amine mol ratio and the molecular weight of the amine. In general, products, suitable for the compositions of the invention are obtained by continuing the reaction until the acid number is in the range of 70 to 300. This range includes the products we have described in which more than 25% but less than 75% of the carboxyl groups of EDTA are amidized. The preferred imide-amide product for the compositions of the invention is the diamide-diacid obtained by reacting 1 mol of EDTA with two mols of Primene 81–R. The theoretical acid number of this product, assuming that Primene 81–R is $C_{14}H_{29}NH_2$, is 165. Therefore, in preparing this preferred product the reaction is continued until the reaction product has an acid number of about 165.

Mol ratio of amine to EDTA is also important. The amount of the amine must be sufficient to convert each molecule of EDTA to a partial imide or amide. Therefore, the minimum mol ratio of amine to EDTA is 1:1. This minimum mol ratio can convert more than 25% of the carboxyl groups of EDTA to imide or amide groups if at least a portion of the product is in the monoimide form. The preferred range of mol ratio of amine to EDTA is from about 2:1 to 3:1. Concentrations of amine can be employed which under some conditions are capable of forming reaction products of excessive amide content, i.e. 75% or more of the carboxyl groups converted to amide or imide forms. The desired products of lower degree of amidization are obtained with such high mol ratios by terminating the reaction when the proper acid number of the reaction product is reached, as discussed above.

Preparation of a specific additive for use in the compositions of the invention is described in the following example.

Example 1.—In a flask fitted with a mechanical stirrer and a water trap were placed 1 gram-mol of ethylenediamine tetraacetic acid, 2 gram-mols of Primene 81–R and 250 ml. of water. This mixture was refluxed until the acid number was about 158, which required about 1 hour. During this period the temperature of the reactants was in the range of 200 to 205° C. Excess amine was stripped under vacuum. The product obtained was a viscous brown liquid. Analysis of the product indicated an average composition corresponding to that of the diamide. The acid number of the product was determined according to ASTM D974, which measures the mg. of KOH required to titrate the acidity of 1 g. of sample. The acid number was 158, indicating an average composition close to that of the diamide-diacid product.

The product of Example 1 was tested as a metal deactivating additive for an unstable olefinic gasoline containing copper. The gasoline was a Pennsylvania thermally reformed gasoline of high olefin content. The test employed was the oxygen bomb test used for determining the oxidation induction periods of gasoline samples as described in Ind. Eng. Chem. (Ind. Ed.), vol. 24, p. 1375 (1932). In this test the gasoline in a glass bottle is exposed at 211.6° F. to oxygen at 100 lbs. per square inch in a steel bomb. The induction period is the time in minutes before rapid oxidation begins.

Table I below gives the results of the oxygen bomb stability tests of samples of the gasoline with and without different additives. The tests covered by Table I include (*a*) the olefinic gasoline containing no additives, (*b*) the gasoline containing a conventional antioxidant, p-n-butylaminophenol, (*c*) the gasoline containing the conventional antioxidant and a catalytic metal compound, cupric oleate, (*d*) the gasoline containing p-n-butylaminophenol, cupric oleate and the EDTA-amine reaction product of Example 1. The table indicates the concentrations of the various additives in the gasoline samples and gives the oxidation induction period in minutes.

TABLE I

Additives in olefinic gasoline sample

Antioxidant, p-n-Butylaminophenol, Wt. Percent	Copper, Mg./Liter	EDTA Amide and Concn., Wt. Percent	Oxidation Induction Period by O_2 Bomb Test, Min.
None	None	None	30
0.02	None	None	615
0.02	1	None	135
0.02	1	0.006% Diamide from reaction of 1 mol EDTA + 2 mols Primene 81–R.	620

The above table demonstrates that by adding 0.006 weight percent of the diamide of EDTA with Primene 81–R to the inhibited, copper-containing gasoline, the induction period was raised from 135 to 620 minutes. In contrast, products of high degree of amidization do not show such superiority in suppressing the catalytic effect of metals on oxidation. We have made a test of a sample of the same olefinic gasoline as described above containing 0.006 weight percent of the tetraamide of EDTA and dodecylamine (acid number 0.32). The sample also contained the conventional oxidation inhibitor (0.02 weight percent) and cupric oleate (1 mg./l.). The addition of the tetraamide to the inhibited copper-containing gasoline increased the induction period. However, the increase was only from 135 to 255 minutes, which is a substantially smaller improvement than obtained with the additives used in the composition of our invention.

The partial amide reaction products used in our compositions are also effective for improving oxidation stability in unsaturated hydrocarbon oils that contain catalytic metals but no oxidation inhibitor. We have made oxygen bomb tests of an olefinic gasoline sample that was a mixture of catalytically cracked and thermally cracked naphtha. The test was applied to (*a*) the gasoline containing no additives, (*b*) the gasoline containing copper but no other additive, and (*c*) the gasoline containing

of an olefinic gasoline normally subject to oxidation containing an oxidation catalyzing metal and a minor amount, sufficient to suppress the oxidation catalyzing effect of said metal, of an imide-amide reaction product of one mol of ethylenediamine tetraacetic acid with two mols of a mixture of branched chain, alkyl, primary amines of which the amine group is attached to a tertiary carbon atom, said amines having 12 to 15 carbon atoms per molecule, and said imide-amide reaction product having an average composition corresponding to that of the diamide and having an acid number of about 158.

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DANIEL E. WYMAN, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

copper and the diamide employed in the compositions of our invention as prepared in Example 1. Table II below gives the results:

TABLE II

Copper, mg./l.	EDTA Amide and Concn., Wt., percent	Induction Period by O_2 Bomb Test, Minutes
None	None	145
1.0	None	70
1.0	0.006% Diamide from reaction of 1 mol EDTA+2 mols Primene 81-R.	152

Although reaction products of EDTA with amines in which 25% or less of the carboxyl groups are converted to the imide-amide form are effective in suppressing the harmful catalytic effect of metals, such products have a serious drawback. They are easily extractable from hydrocarbon oils by water and by dilute acid and alkaline solutions. The partial amides employed in our compositions are markedly superior in this respect. We have subjected different reaction products of EDTA and Primene 81-R to a test that demonstrates this point. In this test 0.2 g. of the additive was added to a 100 ml. sample of isooctane. Then the sample was shaken vigorously with 100 ml. of tap water or with an aqueous alkaline or acid solution. The water and oil layers were allowed to separate and 50 ml. of the supernatant isooctane layer was pipetted into a tared beaker. The isooctane was then evaporated from the beaker at 230° F. in a current of heated air for 20 minutes. The beaker was weighed to determine the weight of the residue, and the percent extraction of the additive from the original isooctane solution was calculated from the weight of the residue. The table below gives the results obtained with two different EDTA-Primene 81-R reaction products, one being essentially a tetra salt, i.e., all of the carboxyl groups of EDTA converted to the amine salt form and the other being essentially the disalt-diamide, the latter being the type of additive used in the compositions of our invention.

TABLE III

Additive	Acid No.	Percent Loss of Additive From Isooctane After Shaking 5-Minutes With Equal Volume of—		
		Tap Water	1% HCl in Water	1% NaOH in Water
Essentially tetra salt	180	99	97	99
Essentially disalt-diamide	84	32	21	89

We have made additional oxygen bomb tests in the manner previously described, on compositions of our invention containing metals other than copper. In these particular tests the hydrocarbon oil was an olefinic gasoline blend of catalytically cracked and thermally cracked gasolines. In these tests we used three different EDTA/amine products, which we call products "X", "Y", and "Z."

Product "X" was a diamide reaction product of 1 mol of EDTA and two mols of Primene 81–R. Its acid number was 158.

Product "Y" was a diamide-disalt reaction product of one mol of EDTA and four mols of Primene 81–R. Its acid number was 105.

Product "Z" was a partial amide reaction product of one mol of EDTA and four mols of 2-ethylhexylamine. Its acid number was 100 and its composition was about 65% amide and 35% amine-salt.

The results of the oxygen bomb tests on the uncontaminated gasoline and on samples containing copper, manganese or cobalt are given in Table IV. The table indicates the amount of metal, the amount of the particular EDTA/amine reaction product and the oxidation induction period observed. The results show that all three metals greatly reduced the induction period of the gasoline and that addition of the specified EDTA/amine reaction products largely restored the lost induction period.

TABLE IV

Metal, 1 mg./liter (in Gasoline +0.005 Wt. Percent p-Butylaminophenol)	EDTA/Amine Product, Wt. Percent	Induction Period by O_2 Bomb Tests, Minutes
None	None	835
Cu	None	60
Cu	0.01% EDTA/Primene 81R Product "X".	755
Cu	0.01% EDTA/Primene 81R Product "Y".	710
Cu	0.01% EDTA/2-ethylhexylamine Product "Z".	350
Mn	None	305
Mn	0.01% EDTA/Primene 81R Product "X".	670
Mn	0.01% EDTA/Primene 81R Product "Y".	685
Mn	0.01% EDTA/2-ethylhexylamine Product "Z".	685
Co	None	190
Co	0.01% EDTA/Primene 81R Product "X".	630
Co	0.01% EDTA/Primene 81R Product "Y".	480
Co	0.01% EDTA/2-ethylhexylamine Product "Z".	700

The concentration of metal deactivating imide-amide additive in the compositions of the invention will depend on the particular oil with which the additive is incorporated, including the concentration of catalytic metal in the oil, the oxidation instability of the oil and the manner in which the oil is to be used. Normally, an additive concentration of 0.001 to 0.1 weight percent will suffice, although more or less can be used. The metal deactivator additives can be used alone but preferably are used in admixture with an antioxidant additive, such as p-n-butylaminophenol, and can be used with other additives such as dyes, dispersants, anticorrosion agents, and antiknock agents. They can be added to oils in the pure form or as concentrates in solvents such as alcohols, Stoddard solvent, kerosene, etc. The concentrates can also contain other additives such as those mentioned.

The invention has been described in considerable detail with particular reference to certain perferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

We claim:

1. The liquid fuel composition consisting essentially of a major amount of hydrocarbon oil and a minor amount, sufficient to suppress the catalytic effect of metals on oxidation of said oil, of an imide-amide reaction product of ethylenediamine tetraacetic acid with a primary, alkyl amine having 4 to 24 carbon atoms per molecule, said product being formed by converting an average of more than 25% but less than 75% of the carboxyl groups of said ethylenediamine tetraacetic acid to the imide-amide forms.

2. The liquid fuel composition of claim 1 in which said reaction product has an acid number in the range of 70 to 300.

3. The liquid fuel composition of claim 1 in which said hydrocarbon oil is an olefinic gasoline and said reaction product has an acid number in the range of 70 to 300.

4. The liquid fuel composition consisting essentially

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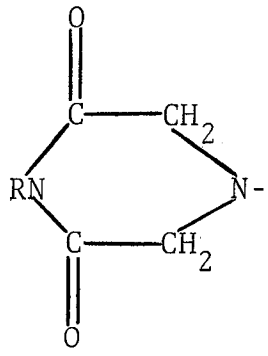
CERTIFICATE OF CORRECTION

Patent No. 3,173,770 March 16, 1965

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 30 to 35, formula (III), the left-hand portion of the formula should appear as shown below instead of as in the patent:



column 6, TABLE IV, third column, under the heading "Induction Period by O_2 Bomb Test, Minutes", lines 4 and 5 should appear as shown below instead of as in the patent:

350
710

Signed and sealed this 28th day of September 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

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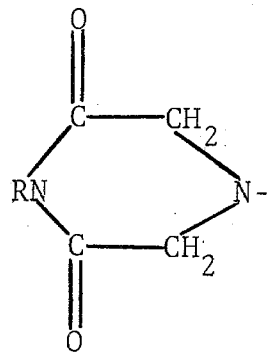
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