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COLOR STABILIZER FOR OILS

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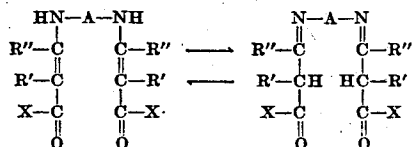
12 Claims. (Cl. 252—47)

This invention relates to the stabilization of mineral oils against deterioration in color, and particularly to the color stabilization of viscous petroleum oils.

It is well known that mineral oils tend to deteriorate in color and general appearance on exposure to the action of heat and light. It is highly desirable to provide products which will retain their color and satisfactory appearance over substantial periods of time. Numerous materials have been proposed for stabilizing mineral oils against deterioration in color. I have found new materials which are particularly effective for preventing deterioration in color of mineral oils.

It is an object of the present invention to provide new viscous mineral oil products which are more stable with respect to deterioration in color and appearance than those known heretofore. Another object is to provide a method for inhibiting deterioration in color of viscous mineral oils. A further object is to provide a class of compounds to be added to viscous petroleum oils and which, when so added, will inhibit the deterioration in color of such oils. Still further objects are to provide new compositions of matter and to advance the art. Other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which comprises incorporating in viscous petroleum oils small proportions of oil soluble compounds of the group of esters and amides of organic acids having two beta-amino-crotonic acid residues linked through the beta-amino nitrogen atoms to separate carbon atoms of a single divalent aliphatic radical which are free of acidic substituents, that is, having no acidic groups other than that of the crotonic acid. Such compounds may be represented by the formula



wherein A represents a divalent aliphatic radical with each nitrogen attached to a different carbon of the aliphatic group, R' represents hydrogen or a hydrocarbon radical, R'' represents a hydrocarbon radical and X an organic group containing a single oxygen or nitrogen directly bonded

to the carbon of the C=O group and otherwise consists of carbon and hydrogen. As shown by the above formula, it is believed that my compounds probably exist in equilibrium in two forms in a manner similar to the keto-enol forms of acetoacetic ester and the formulae, as given, represent such equilibrium. Since the crotonic structure is usually assigned to this type of compound in the literature, I have employed the corresponding nomenclature herein. I have found that, when such compounds are incorporated in viscous petroleum oils, they are very effective in inhibiting deterioration in color of such oils.

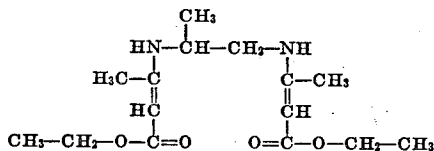
By the term "viscous petroleum oils," I mean oils of petroleum origin, including cracked, reformed and polymerized products, as well as the straight run distillates, which oils boil above the kerosene range and preferably have a viscosity of at least 35 seconds Saybolt Universal at 100° F. Amongst such oils, I intend to include Diesel oils, gas oils, furnace oils, white oils and greases, as well as the usual lubricating oils, but to exclude the substantially non-viscous products such as gasoline, kerosene and the like.

By the term "alkylene" as used hereinafter, I mean divalent aliphatic hydrocarbon radicals in which each valence is on a different carbon atom. By the terms "beta-amino-crotonic acids" and "a beta-amino-crotonic acid," I intend to include beta-amino-crotonic acid itself and its homologs in which the amino and carboxyl groups are on adjacent aliphatic carbon atoms and which are obtained by condensing a beta-ketonic acid with an amine, so that the oxygen of the keto group is split off and replaced with an amino nitrogen. By "an N,N'-alkylene-di(beta-amino-crotonic) acid," I mean such compounds in which the amine is an alkylene diamine which has been condensed with two mols of the beta-keto acid so that one, and only one, beta-keto acid group is condensed with each nitrogen of the alkylene diamine. By the term "unsubstituted N,N'-alkylene-di(beta-amino-crotonic) acid," I mean to include only those compounds in which the beta-amino-crotonic acid group is that of beta-amino-crotonic acid itself and not of its homologs and in which the alkylene radical is a hydrocarbon radical; that is, to include only those compounds in which R' represents hydrogen, R'' represents a methyl radical and A consists of carbon and hydrogen.

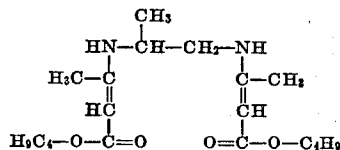
While the broad class of compounds will be effective for my purpose, I have found that some of the most desirable compounds are the esters

and amides of the unsubstituted N,N'-alkylene-di(beta-amino-crotonic) acids and particularly those in which the alkylene radical contains from two to ten carbon atoms, and preferably those in which the alkylene radical contains from two to six carbon atoms. Compounds which I have found to be particularly effective for my purpose are:

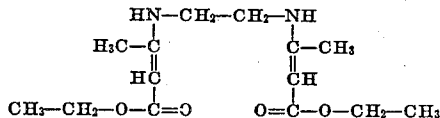
N,N' - propylene - di(ethyl - beta - amino-crotonate)



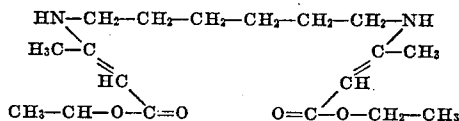
N,N' - propylene - di(butyl - beta - amino-crotonate)



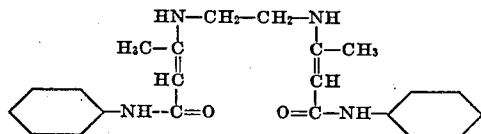
N,N' - ethylene - di(ethyl - beta - amino-crotonate)



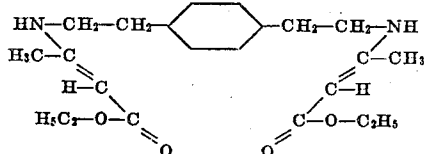
N,N' - hexamethylene - di(ethyl - beta-amino-crotonate)



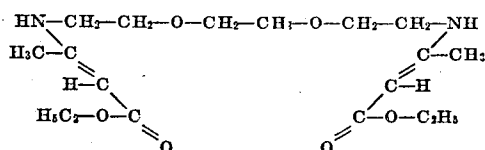
N,N' - ethylene - di(beta - amino - crotonanilide)



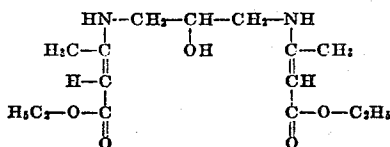
N,N' - (beta,beta' - 1,4 - diethylphenylene) - di-(ethyl-beta-amino-crotonate)



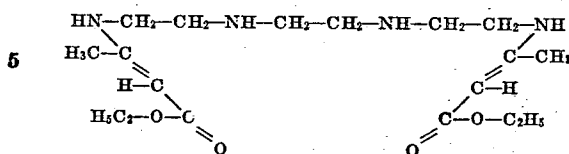
N,N' - (3,6 - dioxaoctamethylene) - di - (ethyl-beta-amino-crotonate)



N,N' - (2 - hydroxy - trimethylene) - di - (ethyl-beta-amino-crotonate)



N,N' - (3,6 - diaza - octamethylene) - di-ethyl-beta-amino-crotonate)



10 The compounds of my invention may be employed in oils in concentrations ranging from about 0.02% to about 2% by weight. Preferably, only from about 0.02% to about 0.5% will be employed, since this is usually sufficient to

15 impart satisfactory color stability. I preferably employ the pure compounds, but mixtures may also be used, or the reactants may be added to the oil and the stabilizers produced in situ. They may be employed in the presence of other addition agents which are added to improve service performance, such as pour-point depressants, metal deactivators, corrosion inhibitors, gum solvents, viscosity index improving agents and materials to increase lubricity.

25 A naphthenic base oil of SAE 70 grade was used in evaluating the color stabilizing action of the various esters. Fifty grams of oil was placed in 250 cc. beakers and heated at 300° F. for 6 hours in air in a well agitated oil bath. Color changes were measured on the A. S. T. M.-Union colorimeter. In this instrument, low readings indicate light-colored oils while high readings show dark-colored oils. Plus or minus signs indicate that the color reading is slightly greater or slightly

35 less than the value given. The compounds used in these evaluation tests were N,N'-ethylene-di(ethyl-beta-amino-crotonate), N,N'-hexamethylene-di(ethyl-beta - amino-crotonate) and N,N'-propylene-di(ethyl - beta-amino-crotonate). These compounds were prepared by known methods of reaction between ethylacetoacetate and ethylenediamine, hexamethylenediamine and propylenediamine, respectively. Brief descriptions of the preparation of representative compounds are given in the following examples to illustrate their preparation.

EXAMPLE 1

50 Twenty-six grams of ethyl acetoacetate, dissolved in 75 cc. of absolute alcohol, was mixed with a solution of 11.6 grams hexamethylenediamine in 25 cc. alcohol. The mixture became warm and was allowed to stand for a few hours. 55 It was then carefully evaporated on a steam bath, a pale yellow liquid remaining which weighed 33 grams. This was crystallized from petroleum ether, the crystalline product boiled with toluene, containing a crystal of iodine, and the resulting product crystallized from benzene. The final material was a white solid, melting at 69-70° C., and having a nitrogen content of 8.06% compared to a calculated value of 8.23%. This compound was N,N'-hexamethylene-di(ethyl - beta-amino-crotonate).

65 The corresponding ethylenediamine derivative was made in the same manner and melted at 125° C.

EXAMPLE 2

70 PREPARATION OF N,N'-PROPYLENE-DI(ETHYL-BETA-AMINOCROTONATE)

Sixty-five parts by weight of ethyl acetoacetate, dissolved in 100 cc. absolute alcohol, were mixed 75 with 22 parts of 35.8% propylenediamine dis-

solved in 50 cc. absolute alcohol. The mixture became warm and, after standing one hour, was evaporated on a steam bath. It was then taken up in benzene, dried over anhydrous sodium sulfate, and the solvent removed by evaporation. The residue was a viscous red liquid, weighing 70 grams, and having a nitrogen content of 10.15%.

The product was also prepared by direct mixing of the two components, using no solvent, in the following manner. Twenty-six parts by weight of ethyl acetoacetate and 8.6 parts of 85.8% propylenediamine were mixed by dropping the diamine into the ester. The mixture became warm but, on cooling in an ice bath, became cloudy and separated into two layers. After standing overnight, the lower layer (water) was removed and the upper layer dried with anhydrous magnesium sulfate. A yield of 27 grams of a yellow oil was obtained, having a nitrogen content of 9.61%. This product was lighter colored than the preceding material, the difference being due to the length of time the material was exposed to heating during its isolation.

EXAMPLE 3

PREPARATION OF N,N'-PROPYLENE-DI(BUTYL-BETA-AMINOCROTONATE)

Fifteen and eight-tenths parts by weight of butyl acetoacetate were mixed with 4.4 parts of 85.8% propylenediamine. The mixture became warm and, after about five minutes, separated into two layers. The upper layer was taken up in benzene, dried over anhydrous sodium sulfate, and the solvent removed by evaporation. A clear yellow liquid was obtained weighing 17 grams.

The results, obtained with these compounds in the above color stabilization tests, are given in the following Tables I, II and III:

TABLE I

Color stabilizing effect of N,N'-ethylene-di-(ethyl-beta-amino-crotonate)

(Naphthenic base S. A. E. 30 oil used, original color 2½)

Concentration of stabilizer—Percent by weight	Color reading after heating test	Color increase
None—control	5+	2½+
0.02	3½+	1
0.05	3+	½+
0.10	3+	½+

TABLE II

Color stabilizing effect of N,N'-hexamethylene-di (ethyl-beta-amino-crotonate)

(Naphthenic base S. A. E. 30 oil used, original color 2½)

Concentration of stabilizer—Percent by weight	Color reading after heating test	Color increase
None—control	7+	4½+
0.1	3½	1

TABLE III

Color stabilizing effect of N,N'-propylene-di-(ethyl-beta-amino-crotonate)

(Naphthenic base S. A. E. 20 oil used, original color 4½ (53 true color units))

Concentration of stabilizer—Percent by weight	A. S. T. M. color after test	True color after test	Percent inhibition
0.00	5 Dil. ²	1010	
0.03	4 Dil. ²	554	58
0.05	7½	251	79
0.10	7+	207	84

¹ True color in the above table is measured in arbitrary units which have no scientific significance but which are useful for comparative purposes.

² In these cases the color was so dark that it was necessary to dilute the test samples in order to obtain accurate readings.

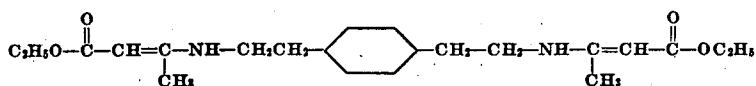
The above tests illustrate the stabilizing action of alkylenediamine-acetoacetic ester products. The related alkylenediamine-acetoacetamide derivatives will also exert a stabilizing action. This may be demonstrated through use of N,N'-ethylene-di(beta-amino-crotonanilide).

The N,N'-ethylene-di(beta-amino-crotonanilide) was prepared as follows: 8.6 grams of 69.8% ethylenediamine and 35.4 grams of acetoacetanilide were dissolved in 150 cc. of absolute alcohol. After about 10 minutes, the solution became warm spontaneously and a white crystalline precipitate formed. After standing several hours, the precipitate was separated by filtration and crystallized from acetone. Forty-one grams of product were obtained, melting at 200 to 201° C.

Two-tenths per cent of this last compound was dissolved in 20 grams of a naphthenic base SAE 30 oil and heated, together with a control sample in 50 cc. beakers to 160 to 165° C. for six hours. The colors of the heated oil samples were then compared with the original oil in a Duboscq colorimeter. The results of the tests are as follows:

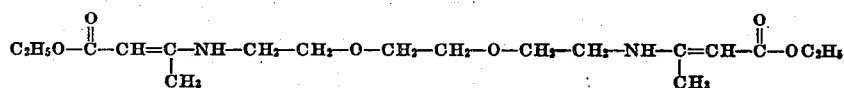
	Per cent color increase
Untreated oil—control	520
Treated oil	203

9.80 grams of 1,4-bis(beta-aminoethyl)benzene and 15.6 grams of ethyl acetoacetate were mixed by dropping the melted amine onto the ester. The mixture became warm and cloudy. After standing a short time, benzene was added and the solution allowed to stand over night. This was then washed with water, dried over sodium sulfate, and the solvent removed over a steam bath. Seventeen grams of a cream colored solid were obtained, which, upon crystallization from ethyl alcohol, melted at 94–95° C. The product has the structure



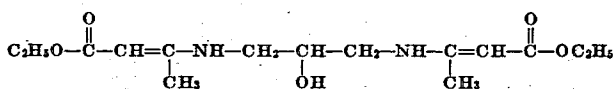
N,N'-(beta,beta'-1,4-diethylphenylene)-di-(ethyl-beta-amino-crotonate)

14.8 grams of triglycoldiamine and 26 grams of ethylacetoacetate were mixed as in the preceding example and worked up in the same fashion. A deep red liquid weighing 33 grams was obtained which has the following structure:



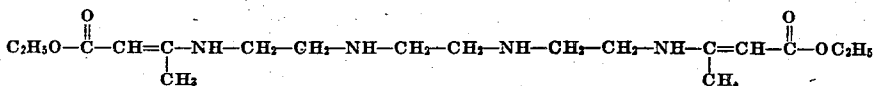
N,N'-(3,6-dioxa-octamethylene)-di-(ethyl-beta-amino-crotonate)

9.1 grams of 1,3-diaminopropanol-2 and 26 grams of ethyl acetoacetate were mixed as in the preceding example and worked up in the same fashion, yielding 26 grams of a material which was liquid at steam bath temperature but which crystallized slowly on standing. This compound has the following structure:



N,N'-(2-hydroxy-trimethylene)-di-(ethyl-beta-amino-crotonate)

14.6 grams of triethylene tetramine were mixed with 26 grams of ethyl acetoacetate and treated as in the preceding example leaving 33 grams of a red liquid which contained 14.4% nitrogen. The compound has the structure:



N,N'-(3,6-diaza-octamethylene)-di-(ethyl-beta-amino-crotonate)

The effectiveness of the above compounds as color stabilizers was determined by dissolving 0.2% of each in 20 grams of a naphthene base SAE 30 oil contained in 50 cc. beakers. A small piece of autobody steel (1/2" x 1/2") was added to each beaker and the whole immersed in an oil bath for 6 hours at 150° C. Color changes were measured on a Duboscq colorimeter and the per cent color increase calculated for each oil. The results are as follows:

Compound added to oil:	Percent color increase
None—control	376
N,N'-(beta,beta'-1,4-diethylphenylene)-di-(ethyl-beta-amino-crotonate)	47
N,N'-(3,6-dioxa-octamethylene)-di-(ethyl-beta-amino-crotonate)	84
N,N'-(2-hydroxy-trimethylene)-di-(ethyl-beta-amino-crotonate)	42
N,N'-(3,6-diaza-octamethylene)-di-(ethyl-beta-amino-crotonate)	108

In order to show the superiority of my compounds over compounds of somewhat similar type disclosed in the prior art, comparative tests were performed. In these tests, the color reading on the heated oils was converted to true color units and the per cent inhibition in color formation in the oil brought about through the use of these compounds was calculated on this basis. Employing such procedure a comparison of the effectiveness of the compounds of my invention with other known derivatives of diamines is given in Table IV. All compounds were employed in 0.1% concentration in a naphthene base SAE 30 oil.

TABLE IV

Compound:	Per cent color inhibition
N,N'-ethylene-di(ethyl-beta-amino-crotonate)	92

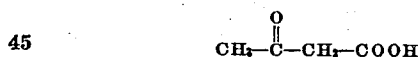
N,N'-hexamethylene-di(ethyl-beta-amino-crotonate)	91
Tetrabutyl ethylenediamine	74
Tetramethyl hexamethylenediamine	0

It will be understood that the above tests are given for illustrative purposes only and that my

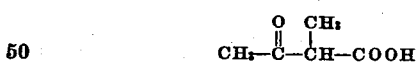
invention is not to be limited thereto. Various other esters and amides of other N,N'-alkylene-di(beta-amino-crotonic) acids coming within my invention may be employed. For example, other suitable beta-ketonic acids, whose esters

and amides can be used in the preparation of compounds of my invention, are:

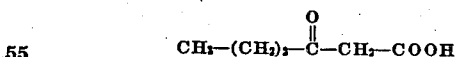
acetoacetic acid



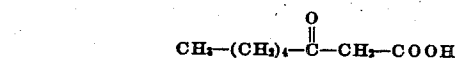
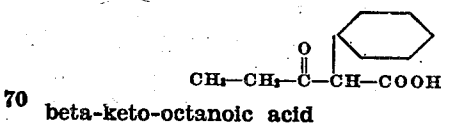
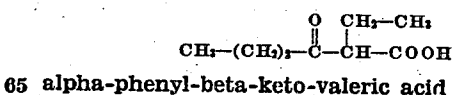
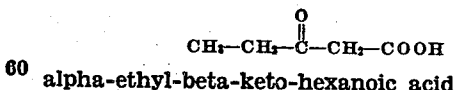
alpha-methyl-beta-keto-butyric acid



beta-keto-caproic acid



beta-keto-valeric acid



The ester and amide groups may have any

hydrocarbon radical bonded to the oxygen or nitrogen thereof. Preferably, the hydrocarbon radical, bonded to the oxygen of the ester group, contains only 2 to 5 carbon atoms, that is, X in the formula represents the radical of an alcohol of 2 to 5 carbon atoms. Suitable hydrocarbon radicals are:

Ethyl	Methyl-n-propyl methyl
Propyl	Methyl isopropyl methyl
Isopropyl	Dimethyl ethyl methyl
Butyl	Amyl
Isobutyl	Isoamyl
Sec. butyl	Allyl
Tert. butyl	Benzyl
3-methyl butyl	Phenyl
2-methyl butyl	Diphenyl
Diethyl methyl	2-ethyl-hexyl
Tert. butyl methyl	2-methyl-pentyl

and the like.

Amongst the other aliphatic diamines which may be reacted with such esters and amides, I have found the following to provide particularly suitable compounds:

Butylenediamine
Decamethylenediamine
3-ethyl-pentamethylenediamine
2-ethyl-hexamethylenediamine
3,4-diaminohexane
1,3-diaminobutane
2-methyl-propylenediamine
Beta,beta'-diaminodiethyl sulfide
Beta,beta'-diaminodiethyl ether
1,4-di(aminoethyl) benzene
1,2-di(aminoethyl) benzene
1-aminoethyl-4-aminomethyl benzene
Beta-aminoethyl-gamma-aminopropyl ether
1,8-di(aminoethyl) naphthalene
1,8-di(aminomethyl) naphthalene
1,2-di(aminomethyl) benzene
Diethylenetriamine

While, in the above tests, my compounds have been added to refined oils, they can be added to unrefined oils or to the oils at any suitable stage in the refining process wherein they may serve to stabilize the oils and be carried through the refining operations with the oils. They may be added in very small quantities during each of the various stages of the refining processes. They may be included with the refining agent as in solvent extraction processes, and through such medium be transferred into the oil. They may also be added to oils of synthetic origin which are substantially of the hydrocarbon type such as are derived from polymerized olefines, hydrogenation of carbon oxides, reaction products of chlorinated waxes and aromatic hydrocarbons, or polymerized cracked waxes.

From the above disclosure, it will be apparent that, by my invention, it has been made possible to produce viscous mineral oils of high color stability, particularly under conditions of exposure to heat and light.

This is a continuation-in-part of my copending application Serial No. 299,259 filed October 13, 1939.

I claim:

1. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of a di-ester of an N,N'-ethylene-di(beta-amino-crotonic) acid which, except for the N of the amino groups and the O of the ester groups, consists of carbon and hydrogen.

2. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of a di-ester of N,N'-ethylene-di(beta-amino-crotonic) acid which, except for the N of the amino groups and the O of the ester groups, consists of carbon and hydrogen.

3. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of N,N'-ethylene-di(ethyl-beta-amino-crotonate).

4. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of N,N'-hexamethylene-di(ethyl-beta-amino-crotonate).

5. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of an N,N'-alkylene-di(alkyl-beta-amino crotonate) which, except for the N of the amino groups and the O of the ester groups, consists of carbon and hydrogen and in which the alkyl group contains from 2 to 5 carbon atoms.

6. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of an N,N'-propylene-di(alkyl-beta-amino crotonate) which, except for the N of the amino groups and the O of the ester groups, consists of carbon and hydrogen and in which the alkyl group contains from 2 to 5 carbon atoms.

7. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of an unsubstituted N,N'-propylene-di(alkyl-beta-amino crotonate) in which the alkyl group contains from 2 to 5 carbon atoms.

8. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of N,N'-propylene-di(ethyl-beta-amino crotonate).

9. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of a compound of the group consisting of di-esters and amides of organic acids having two beta-amino-crotonic acid residues linked through the beta-amino nitrogen atoms to separate carbon atoms of a single divalent aliphatic radical containing from 2 to 10 carbon atoms, which compound is free of acidic groups other than the crotonic acid carboxyl group.

10. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of a di-ester of an organic acid having two beta-amino-crotonic acid residues linked through the beta-amino nitrogen atoms to separate carbon atoms of a single divalent aliphatic radical containing from 2 to 10 carbon atoms, which compound is free of acidic groups other than the crotonic acid carboxyl group.

11. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially inhibit such deterioration, of a di-ester of an un-

substituted N,N'-alkylene-di(beta-amino-crotonic) acid which is free of acidic groups other than the crotonic acid carboxyl group and in which the alkylene group contains from 2 to 10 carbon atoms.

12. A viscous petroleum oil normally tending to deteriorate in color having incorporated therein a small proportion, sufficient to materially

inhibit such deterioration, of an N,N'-alkylene-di(ethyl-beta-amino crotonate) which, except for the N of the amino groups and the O of the ester groups, consists of carbon and hydrogen and in which the alkylene group contains from 2 to 10 carbon atoms.

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