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STABILIZATION OF PETROLEUM HYDROCARBONS

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27 Claims. (Cl. 252—47)

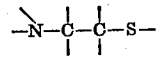
This invention relates to the improvement of petroleum hydrocarbons and particularly to the stabilization of such petroleum hydrocarbons against the deleterious catalytic action of metals, and still more particularly to the treatment of petroleum lubricating oils to render them non-corrosive to metals.

It is known that various metals, and particularly copper, in contact with petroleum hydrocarbons or dissolved therein, tend to catalyze the deterioration of such petroleum hydrocarbons, accelerating the formation of gum, sludge, and corrosive products. It has been proposed to stabilize petroleum hydrocarbons against oxidation by the addition of various anti-oxidants. However, most antioxidants are relatively ineffective in the presence of catalytic metals, such as copper, since such catalytic metals also accelerate the oxidation and destruction of the antioxidant. The viscous petroleum hydrocarbon oils, in particular, deteriorate to form acidic products which are frequently highly corrosive to metals and alloys with which they come into contact, and particularly the newer bearing alloys. The production of corrosive products is particularly noticeable in the highly refined lubricating oils which possess very desirable characteristics in other respects.

It is an object of the present invention to provide compounds for addition to petroleum hydrocarbons to inhibit the deterioration of such hydrocarbons in the presence of catalytically active metals. Another object is to provide a method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils. A further object is to provide a method of inhibiting the corrosion of alloy bearing metals of the character of cadmium-silver and copper-lead bearing alloys by petroleum lubricating oils in contact therewith. 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 petroleum hydrocarbons a small amount, sufficient to retard deterioration thereof, of an organic compound having an amino nitrogen atom and a divalent sulfur atom, each singly bonded to adjacent aliphatic carbon atoms, the second valence of the sulfur atom being satisfied by hydrogen or an aliphatic radicle. I have found that, when such compounds are added to the petroleum hydrocarbons, they will prevent the deterioration caused by the catalytic action of metals normally active to catalyze deterioration thereof. In particular, I have found that the addition of such compounds to viscous petroleum hydrocarbon oils, that is, those having a viscosity of at least 35 seconds Saybolt Universal at 100° F., will inhibit the deterioration and formation of corrosive products in such oil, which corrosive products would tend to corrode metals, and particularly bearing alloys of the character of cadmium-silver and copper-lead bearing alloys.

The compounds of my invention are characterized by the presence of the structural unit



in which the carbon atoms are aliphatic carbon atoms. I believe that this is the effective part of the molecule which renders the compounds effective for my purpose. The free valence of the sulfur may be satisfied by hydrogen or an aliphatic radicle and the free valences of the nitrogen may be satisfied by hydrogen, aliphatic or aromatic radicles. The compounds may contain, as substituents, sulfur, hydroxy, amino, alkoxy or aryloxy radicles, but should preferably be free from aromatic rings. Amongst the compounds which I have found to be particularly effective for my purpose are:

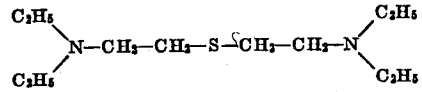
Bis(beta-aminoethyl) sulfide

$H_2N—CH_2—CH_2—S—CH_2—CH_2—NH_2$

1,6-hexamethylene di(beta-aminoethyl) sulfide

$H_2N—CH_2—CH_2—S—CH_2—(CH_2)_4—CH_2—S—CH_2—CH_2—NH_2$

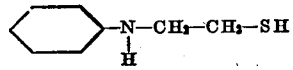
Bis(beta-diethylaminoethyl) sulfide



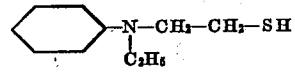
n-Propyl beta-aminoethyl sulfide

$H_2N—CH_2—CH_2—S—CH_2—CH_2—CH_3$

Beta-phenylaminoethanethiol



Beta-(N-phenyl-N-ethyl)-aminoethanethiol



While my compounds may be employed to advantage in the various petroleum hydrocarbons, that is, the hydrocarbons of petroleum origin, such as gasoline, kerosene, gas oil, Diesel-engine

fuels, furnace oils and lubricating oils, they are of particular advantage in the viscous petroleum oils, and particularly the petroleum lubricating oils. They may be employed in concentrations of from about 0.005% to about 10%. In the petroleum hydrocarbons of relatively low viscosity, they will preferably be employed in concentrations of from about 0.005 to 0.02%. In the more viscous hydrocarbons, they will generally be employed in the concentration of from about 0.02 to 10%, but preferably from about 0.10% to 2%. They may be employed in the presence or absence of other addition agents, such as anti-oxidants, pour-point depressants, oiliness agents, film strength improving agents, and viscosity index improving agents and, in gasoline, in the presence of antiknock agents such as tetraethyl lead. They may be employed in the pure state or in the form of mixtures or solutions. They may be employed in greases, cutting oils and insulating oils.

While it is preferred to incorporate the compounds directly in the petroleum hydrocarbons, effective results may also be secured by adding the components of the compounds to the hydrocarbons and then causing them to react therein to produce the compounds in situ.

In order to illustrate more clearly the preferred embodiments of my invention and the preferred modes of carrying the same into effect, the following examples are given:

Example 1

Into a solution of 0.4 mole (17.2 g.) of ethylenimine in 100 cc. of water was passed a slow stream of hydrogen sulfide, the reaction vessel being cooled in ice water. The product was a clear solution with a small amount of oily material on top. The water was removed under reduced pressure, leaving 18.3 g. of a colorless, almost odorless oil which boiled at 124–126° C. at 17 mm. This product was bis(beta-aminoethyl) sulfide, $S(CH_2CH_2NH_2)_2$, as shown by its boiling point and neutralization equivalent (calculated 120, found 123). The yield was 76% of the theory.

Example 2

A sealed Carius tube containing 13.9 g. (0.15 mol) of aniline and 4.5 g. (0.075 mol) of ethylene sulfide was heated for 4 hours at 130–135° C. and then for 10 hours at 160–170° C. At the end of this time the tube was cooled in a dry ice-acetone mixture, opened, and the contents distilled under reduced pressure. The yield of beta-phenylaminoethanethiol, boiling at 140–143° C./12 mm., was 65% of the theoretical amount. Analysis, sulfur (found) 20.40%; (calculated) 20.91%.

Example 3

A mixture of 17.2 parts of ethylenimine and 30.4 parts of n-propanethiol, without solvent or catalyst, is heated in a closed vessel at 100° C. for 20 hours. The reaction product is then subjected to distillation, whereupon a small amount of unchanged starting materials is first removed, then 37 parts of a homogeneous liquid boiling at 84–87° C. at 23 mm. pressure is obtained. This product, a colorless oil, boils on redistillation at 85–86° C. at 25 mm. pressure. Other physical constants are:

$$d_4^{25}: 0.9295;\ N_D^{25}: 1.4831$$

Analyses indicate that it is the expected propyl-beta-aminoethyl sulfide,

$$CH_3CH_2CH_2SCH_2CH_2NH_2$$

obtained in 78 per cent yield.

Calculated for $C_5H_{13}NS$: S, 26.89. Found: 26.82, 26.87. Neutralization equivalent: Calculated: 119; Found: 119.5.

Example 4

A mixture of 11 parts of ethylenimine and 18 parts of hexane-1,6-dithiol is heated in a closed vessel at 100° C. for 23 hours. There is obtained, on distillation of the reaction product, 25 parts of an oil boiling around 200° C. at 6 mm. pressure. The product, on redistillation in an atmosphere of nitrogen, boils at 196–200° C. at 2 mm. pressure. It is a pale yellow oil which crystallizes on standing to a solid melting at 38–40° C. Analyses indicate that this product is the expected 1,6-hexamethylene di-(beta-aminoethyl) sulfide, $NH_2CH_2CH_2S(CH_2)_6SCH_2CH_2NH_2$, obtained in 89 per cent yield.

Calculated for $C_{10}H_{24}N_2S_2$: C, 50.85; H, 10.17; S, 27.12. Found: C, 51.02; H, 10.04; S, 26.74. Neutralization equivalent: Calculated, 236; Found, 241.

The effectiveness of the compounds of the type given was determined by a procedure similar to that described in the Analytical Edition of Industrial and Engineering Chemistry, volume 6, page 419 (1934), modified by suspending in the oil strips which had been cut from cadmium-silver bearings and placed in such a fashion that the strips were completely immersed while the air which was bubbled through the oil washed over the metal surfaces. In this test, a volume of 300 cc. of oil was used through which washed air was bubbling at a rate of 10 liters per hour, the oil temperature being maintained at 171° to 172° C. The cadmium-silver strip was removed at various intervals and weighed. From the curve showing loss in weight against time there was determined the time required for a loss of ten milligrams per square inch of exposed surface to occur. Viscosity determinations were made on the oil after oxidation to determine the degree of thickening caused by dissolved decomposition products.

Example 5

Using a solvent-extracted Mid-Continent oil, having a Saybolt Universal viscosity of 63 seconds at 210° F. (an SAE–30 oil), the effectiveness of typical compounds included in this invention are given in the following Table I. In all of the tests, the compounds were incorporated in the oil by simple stirring and heating.

Table I

Compound	Concentration, percent by weight	Hours to 10 mg./sq. in. corrosion of cadmium-silver	Saybolt Universal viscosity at 210° F. after 100 hours
None—control		17	116
Bis(beta-aminoethyl) sulfide	0.25	222	77
Hexamethylene di(beta-aminoethyl) sulfide	0.25	282	74
	0.05	122	78
Beta(phenylamino) ethanethiol	0.25	93	82
Beta (N-phenyl-N-ethyl-amino) ethanethiol	0.25	66	

In the following tests, the method of evaluation was somewhat different but serves to show the corrosion inhibiting power of this type of compound. The method is as follows:

Fifty grams of a commercial paraffin base oil of an SAE–20 grade, to which had been added 0.5% of the compound under test, were placed in a 125 cc. Erlenmeyer flask. The flask was

fitted with a cork stopper containing a 1 mm. capillary tube which extended within ¼ inch of the bottom of the flask. Weighed strips, approximately 1⅜ inches by ½ inch, cut from cadmium-silver and copper-lead bearings of the type used in present day internal combustion engines, together with similar strips cut from sheets of autobody steel, were suspended in the flask in such a fashion as to be immersed to approximately half their lengths in oil. The unit was placed in an oil bath maintained at substantially 175° C., and air which had been passed through two washing bottles of distilled water, was bubbled through the capillary tube at a rate of 2.5 to 3.0 liters per hour. The strips of cadmium-silver and copper-lead bearing metals were removed at intervals and weighed after washing with chloroform and acetone. From the curve of loss in weight against time of exposure, it was possible to determine the time at which a 10 mg. loss per 10 gms. of bearing metal occurred.

Example 6

Compound	Hours to 10 mg./10 gm. loss	
	Cadmium-silver	Copper-lead
None—control	21	Below 20
Bis (beta-diethylaminoethyl) sulfide	30	42

Example 7

Compound	Hours to 10 mg./10 gm. loss	
	Cadmium-silver	Copper-lead
None—control	Below 20	Below 20
n-Propyl-(beta-aminoethyl) sulfide	25	40

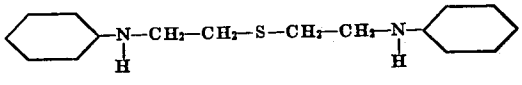
Example 8

Stabilizing action on gasoline was measured by determining the effect of an aminoethylsulfide on the induction period (Voorhees and Eisenger, S. A. E. Journal, volume 24, 584 (1929)) of a gasoline with and without the addition of copper in the form of copper oleate and in the presence of a gum inhibitor, p-benzylaminophenol.

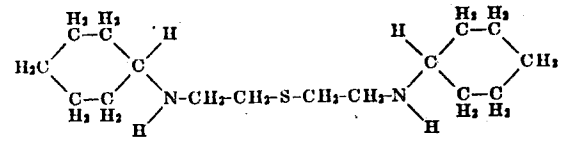
Stabilizer	Concentration, percent by weight		Percent by weight of copper (as oleate)	Induction period
	Stabilizer	p-Benzyl-amino-phenol		
				Minutes
None	None	None	None	210
None	None	0.0012	None	360
None	None	0.0012	0.0001	60
Di (beta-aminoethyl) sulfide	0.005	0.0012	0.0001	230

It will be understood that the above examples are illustrative only and are not intended to be limiting. Still other compounds of my invention which may be employed are:

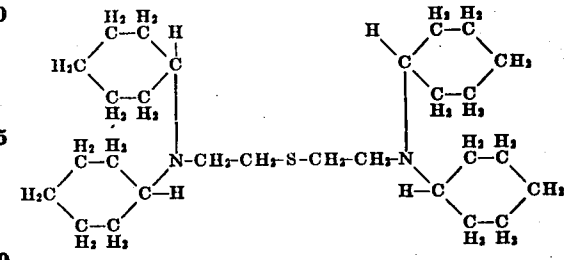
Bis(beta-phenylaminoethyl) sulfide



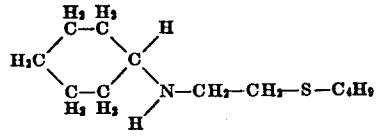
Bis(beta-cyclohexylaminoethyl) sulfide



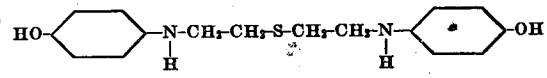
Bis(beta-dicyclohexylaminoethyl) sulfide



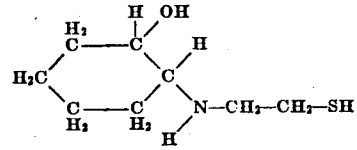
Beta-cyclohexylaminoethyl butyl sulfide



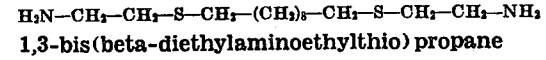
Bis[beta(p-hydroxyphenylamino)ethyl] sulfide



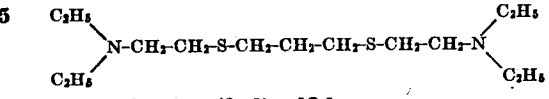
Beta(o-hydroxycyclohexylamino)ethanethiol



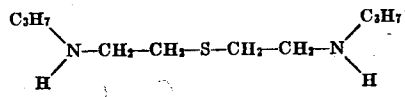
Decamethylene-di(beta-aminoethyl) sulfide



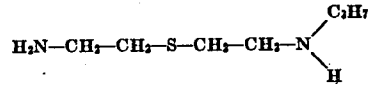
1,3-bis(beta-diethylaminoethylthio) propane



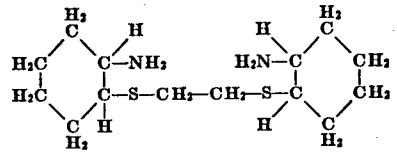
Bis(propylaminoethyl) sulfide



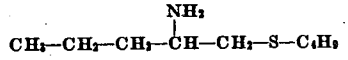
Beta-amino-beta'-propylamino-diethyl sulfide



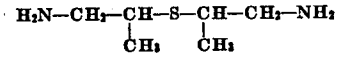
Bis(o-aminocyclohexylthio) ethane



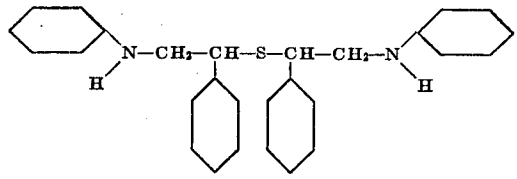
2-aminopentyl butyl sulfide



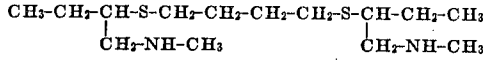
Bis(beta-aminoisopropyl) sulfide



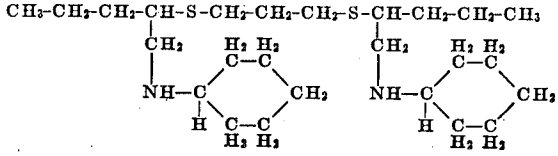
Bis[(beta-phenylamino-alpha-phenyl) ethyl] sulfide



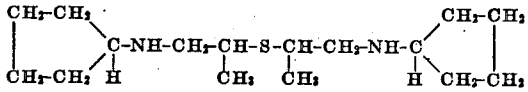
1,4-bis[(1-ethyl-2-methylamino) ethylthio] butane



1,3-bis[(1-propyl-2-cyclohexylamino) ethylthio] propane



Bis[(1-methyl-2-cyclopentylamino) ethyl] sulfide



Many other compounds will be apparent to those skilled in the art. Some of these compounds are known and the methods of preparing them are described in the literature. Others are new, for example, the compounds of Examples 3 and 4. Examples 1, 2, 3 and 4 give illustrative methods of preparing the compounds.

It will be apparent that, by my invention, I have been able to effectively stabilize petroleum hydrocarbons generally against the deleterious catalytic action of metals such as copper, cadmium, silver and the like. My compounds are particularly effective in petroleum lubricating oils for retarding the formation of products corrosive to metals, and particularly to cadmium, silver, copper, lead, and like bearing alloys under service conditions.

By the term "petroleum hydrocarbons" as used herein and in the claims, I means to include the various hydrocarbons of petroleum origin such as natural oils, cracked products, polymerized products, reformed products, alkylated products, hydrogenated products and products which have been refined in any of the usual ways as by treatment with sulfuric acid or with extraction solvents or by removal of wax, etc.

I claim:

1. The method of inhibiting the deterioration of petroleum hydrocarbons in the presence of metals normally active to catalyze deterioration thereof, which comprises incorporating in the petroleum hydrocarbons a small amount, sufficient to retard deterioration thereof, of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by a member of the group consisting of hydrogen and aliphatic radicals.

2. The method of inhibiting the deterioration of petroleum hydrocarbons in the presence of metals normally active to catalyze deterioration thereof, which comprises incorporating in the petroleum hydrocarbons a small amount, sufficient to retard deterioration thereof, of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by an aliphatic radical.

3. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to retard such corrosion and formation of corrosive products, of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by a member of the group consisting of hydrogen and aliphatic radicals.

4. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to retard such corrosion and formation of corrosive products, of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by an aliphatic radical.

5. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to retard such corrosion and formation of corrosive products, of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by an aliphatic radical, said organic compounds being free of aromatic rings.

6. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to retard such corrosion and formation of corrosive products, of a beta-aminoethyl sulfide in which the amino nitrogen and the sulfur are in the same open chain and the second valence of the sulfur is satisfied by an aliphatic radical.

7. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to retard such corrosion and formation of corrosive products, of a beta-aminoethyl sulfide in which the amino nitrogen and the sulfur are in the same open chain and the second valence of the sulfur is satisfied by an aliphatic radical, and the other two valences of the amino nitrogen are satisfied by members of the group consisting of hydrogen and aliphatic radicals.

8. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to retard such corrosion and formation of corrosive products, of an open chain beta-aminoethyl sulfide in which the second valence of the sulfur is satisfied by an aliphatic radical and which sulfide is free of aromatic rings.

9. The method of inhibiting the deterioration and formation of corrosive products in viscous petroleum hydrocarbon oils which comprises incorporating therein a small amount, sufficient to

retard such corrosion and formation of corrosive products, of an open chain primary beta-aminoethyl sulfide in which the second valence of the sulfur is satisfied by an aliphatic radical and which sulfide is free of aromatic rings.

10. A composition of matter comprising hydrocarbons of petroleum origin having incorporated therein a small proportion of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by a member of the group consisting of hydrogen and aliphatic radicals.

11. A composition of matter comprising hydrocarbons of petroleum origin having incorporated therein a small proportion of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by an aliphatic radical.

12. A petroleum lubricating oil having incorporated therein a small proportion of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by a member of the group consisting of hydrogen and aliphatic radicals.

13. A petroleum lubricating oil having incorporated therein a small proportion of an organic compound having an amino nitrogen atom and a divalent sulfur atom each singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by an aliphatic radical.

14. A petroleum lubricating oil having incorporated therein a small proportion of an organic compound having an amino nitrogen atom and a divalent sulfur atom singly bonded to adjacent aliphatic carbon atoms in open chain configuration, the second valence of the sulfur atom being satisfied by an aliphatic radical, said organic compounds being free of aromatic rings.

15. A petroleum lubricating oil having incorporated therein a small proportion of a beta-aminoethyl sulfide in which the amino nitrogen and the sulfur are in the same open chain and the second valence of the sulfur is satisfied by an aliphatic radical.

16. A petroleum lubricating oil having incorporated therein a small proportion of a beta-aminoethyl sulfide in which the amino nitrogen and the sulfur are in the same open chain and the second valence of the sulfur is satisfied by an aliphatic radical, and the other two valences of the amino nitrogen are satisfied by members of the group consisting of hydrogen and aliphatic radicals.

17. A petroleum lubricating oil having incorporated therein a small proportion of an open chain beta-aminoethyl sulfide in which the second valence of the sulfur is satisfied by an aliphatic radical and which sulfide is free of aromatic rings.

18. A petroleum lubricating oil having incorporated therein a small proportion of an open chain primary beta-aminoethyl sulfide in which the second valence of the sulfur is satisfied by an aliphatic radical and which sulfide is free of aromatic rings.

19. A composition of matter comprising hydrocarbons of petroleum origin having incorporated therein a small proportion of 1,6-hexamethylene di-(beta-aminoethyl) sulfide.

20. A composition of matter comprising hydrocarbons of petroleum origin having incorporated therein a small proportion of bis-(beta-phenylaminoethyl) sulfide.

21. A composition of matter comprising hydrocarbons of petroleum origin having incorporated therein a small proportion of bis-(beta-dicyclohexylaminoethyl) sulfide.

22. A petroleum lubricating oil having incorporated therein a small proportion of 1,6-hexamethylene di-(beta-aminoethyl) sulfide.

23. A petroleum lubricating oil having incorporated therein a small proportion of bis-(beta-phenylaminoethyl) sulfide.

24. A petroleum lubricating oil having incorporated therein a small proportion of bis-(beta-dicyclohexylaminoethyl) sulfide.

25. The method of inhibiting the deterioration of petroleum hydrocarbons in the presence of metals normally active to catalyze deterioration thereof, which comprises incorporating in the petroleum hydrocarbons a small amount, sufficient to retard deterioration thereof, of 1,6-hexamethylene di-(beta-aminoethyl) sulfide.

26. The method of inhibiting the deterioration of petroleum hydrocarbons in the presence of metals normally active to catalyze deterioration thereof, which comprises incorporating in the petroleum hydrocarbons a small amount, sufficient to retard deterioration thereof, of bis-(beta-phenylaminoethyl) sulfide.

27. The method of inhibiting the deterioration of petroleum hydrocarbons in the presence of metals normally active to catalyze deterioration thereof, which comprises incorporating in the petroleum hydrocarbons a small amount, sufficient to retard deterioration thereof, of bis-(beta-dicyclohexylaminoethyl) sulfide.

MELVIN A. DIETRICH.