

## UNITED STATES PATENT OFFICE

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## COMPOUNDED HYDROCARBON PRODUCTS

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This invention relates to a new antioxidant additive for aliphatic hydrocarbon products and especially to a class of additives which are especially useful as detergent and anticorrosion agents for mineral lubricating oils.

The new class of additives comprises the alkyl esters of p-hydroxy dithiobenzoic acid and analogous compounds having other aryl nuclei and salts of all such compounds. These compounds are very effective antioxidants for a wide variety of aliphatic hydrocarbon products, such, for example, as mineral lubricating oils, paraffin waxes, hydrocarbon polymers, natural rubber, synthetic rubber and the like. The metallic salts of these compounds have the further advantage of acting as detergents and sludge dispersers when incorporated in crankcase lubricating oils. They are especially valuable for this purpose, since they do not have the disadvantage, common to many metal derivatives of organic compounds known to the art, of corroding alloy bearings, such as the cadmium-silver and copper-lead bearings now widely used in automotive engines.

These salts have the further advantage of being substantially non-water-sensitive, that is, they do not tend to be removed from oil solution when lubricating oils containing them come into contact with water. Many metal-containing organic compounds, otherwise satisfactory as detergent additives for use in internal combustion engine lubricants, do have this undesirable property of water sensitivity. Absence of this characteristic is of particular importance in marine service where contact with sea water very often occurs.

It is therefore one of the principal objects of the invention to provide a new class of addition agents for oils which are to be used as crankcase lubricants for internal combustion engines which exhibit the desirable properties of promoting general engine cleanliness, reducing ring sticking, piston skirt varnish formation and the like, and which not only do not exhibit the corrosion promoting tendencies characteristic of many of the metal compounds known to the art, but also inhibit the corrosiveness of oils to which they are added.

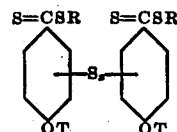
The new class of additives which are employed in accordance with the present invention may be defined as those compounds which have the structure



where Ar is an aromatic nucleus, which for illustration may be a benzene nucleus, a diphenyl

nucleus, or a condensed ring nucleus, such as naphthalene, where T is hydrogen, a metal equivalent of hydrogen selected from groups I, II, III, IV and VIII of the periodic table or a salt forming nonmetallic group, X is sulfur, selenium or tellurium, and R is an aliphatic radical, and where the TO— and —CXR groups are in the 1, 4 positions relative to each other on a six-membered carbon ring structure. In this class of compounds the metals selected for the preparation of the salts are from groups I, II, III, IV and VIII of the periodic table and are preferably cobalt, nickel, tin, zinc, aluminum, copper, sodium, potassium, calcium, magnesium, or barium. For many applications the alkaline earth metal salts are particularly preferred. Useful salts may also be formed from the nonmetallic basic groups, such as the onium groups. Thus T in the above formula may also represent ammonium, quaternary ammonium, phosphonium, sulfonium or pyridonium groups and the like. R in the formula may represent any saturated aliphatic group containing up to 20 carbon atoms and may be either straight or branched. If the additive is to be dissolved in a mineral oil, the group R should contain at least two carbon atoms. In these compounds alkyl side chains may be attached to the nucleus, but such side chains are not ordinarily required for oil solubility when the R group of the compound contains at least two carbon atoms.

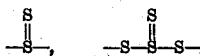
It is intended that the above definition include also the sulfides of the various compounds, which may be formed by treating the compounds with sulfurizing agents such as sulfur monochloride or dichloride or other sulfur halide. Generally, reaction with sulfur dichloride under proper conditions will give a monosulfide derivative, and reaction with sulfur monochloride will give a disulfide derivative. However, depending upon ratios of reactants used, conditions of reaction and purity of the sulfur halides, a product whose sulfur content lies somewhere between a monosulfide and a disulfide may be obtained. Also, by suitable means it is possible to prepare polysulfides having up to four atoms of sulfur. Thus it is intended that the invention include compounds having the following general structure:



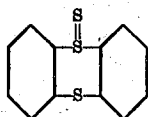
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55 where R is an alkyl radical, T is hydrogen or a

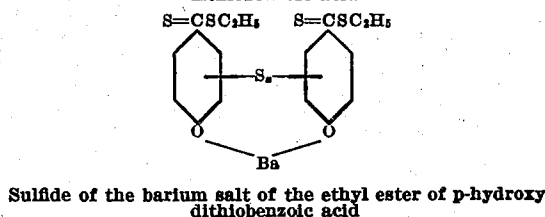
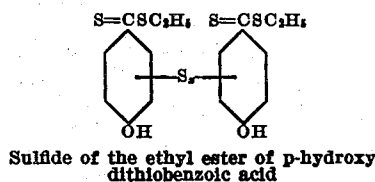
metal equivalent of hydrogen, the metal being selected from groups I, II, III, IV and VIII of the periodic table, or a salt forming non-metallic group, and  $x$  is in an integer, from 1 to 4. It should be understood that the group  $S_x$  in the above formula is not necessarily intended to represent merely straight chain sulfur linkages between the aryl groups, e. g.  $-S-$ ,  $-S-S-$ ,  $-S-S-S-$ , etc., but also other types such as



and the like, as well as more than one linkage of sulfur, as for example:



It should also be understood that the sulfurized compounds of the present invention may include sulfide polymers having three or more aromatic nuclei linked by sulfur atoms, as well as mixtures of monosulfides, disulfides, trisulfides, sulfide polymers and the like. The sulfide compounds may be illustrated by the following examples:



As specific examples of the compounds most preferred for use in accordance with the present invention may be mentioned the ethyl ester of p-hydroxy dithiobenzoic acid, the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid, the sulfide of the ethyl ester of p-hydroxy dithiobenzoic acid, the sulfide of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid, the octyl ester of p-hydroxy dithiobenzoic acid, the barium salt of the octyl ester of p-hydroxy dithiobenzoic acid, the sulfide of the octyl ester of p-hydroxy dithiobenzoic acid, the sulfide of the barium salt of the octyl ester of p-hydroxy dithiobenzoic acid, the cetyl ester of p-hydroxy dithiobenzoic acid, the zinc salt of the isododecyl ester of p-hydroxy dithiobenzoic acid, the disulfide of the calcium salt of the amyl ester of p-hydroxy dithiobenzoic acid, the sulfide of the tin salt of the octadecyl ester of p-hydroxy dithiobenzoic acid, and the wax alcohol ester of p-hydroxy dithiobenzoic acid.

The hydroxy compounds used as such in accordance with the present invention or for preparing salts to be so used may be conveniently prepared by reaction of an alkyl aryl ether with carbon disulfide in the presence of a Friedel-Crafts catalyst, whereby rearrangement occurs to form a hydroxy group in place of the aroxy group, and a  $-CSSR$  group is formed in the para position to the hydroxy group. For ex-

ample, the ethyl ester of p-hydroxy dithiobenzoic acid may be formed by reaction of phenetol with carbon disulfide in the presence of aluminum chloride in accordance with the method described by Jörg (Ber., vol. 60: 1466 (1927)). The metallic salts of these compounds are conveniently formed by reaction with a metallic base, such as barium hydroxide. To obtain the best yields, the water produced during the reaction should be removed as formed. The sulfides of either the hydroxy compound or its salt may be formed by reaction with a sulfurizing agent, such as sulfur monochloride or dichloride.

Generally, when the additives of the present invention are incorporated in lubricating oils containing oil base stocks the concentration is between the approximate limits of 0.02% and 5.0% and preferably from 0.1% to 2.0%, although larger amounts may be used for some purposes. When the additives are incorporated in high molecular weight hydrocarbon polymers, the amounts are generally between about 0.1% and 5.0%, preferably between 0.2% and 2.0%. Similar proportions are usually preferred for use with other products.

The following examples illustrate the preparation of a few of the preferred examples of the new additives.

#### EXAMPLE 1

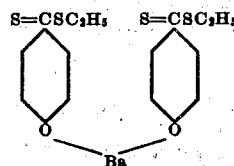
##### Ethyl ester of p-hydroxy dithiobenzoic acid

A three-way flask equipped with a stirrer, a thermometer and a return condenser fitted with a water trap was charged with 50 grams of phenetol, 80 grams of dry carbon disulfide and approximately 75 grams of dry aluminum chloride. All air vent lines were closed with calcium chloride drying tubes. The reaction started at about 25° C., and the mixture was gradually heated to a final temperature of 70° to 85° C. during a total heating period of five hours. No hydrogen chloride gas was evolved after four hours. The crude product was removed from the flask and given a quick wash with cold water to remove water soluble organic and inorganic materials. The water insoluble product, after drying, weighed 28.0 grams. The melting point was approximately 50° to 57° C.

#### EXAMPLE 2

##### Barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid

5 grams of the product prepared as in Example 1 were added slowly to 250 ml. of warm chloroform in a reaction vessel provided with a reflux condenser. The ester went into solution slowly. To the warm chloroform solution 4 grams of  $Ba(OH) \cdot 8H_2O$  were slowly added. Water was liberated from the reaction during this process, and was removed as formed by means of a water trap attached to the condenser. After all of the  $Ba(OH) \cdot 8H_2O$  had reacted, i. e., after about one hour, the chloroform and all other volatile materials were removed from the barium salt by evaporation. This salt was believed to have the following structure:



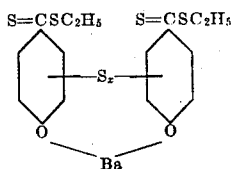
## Analysis of the salt

|               | Theory   | Found    |
|---------------|----------|----------|
|               | Per cent | Per cent |
| Barium.....   | 25.9     | 24.7     |
| Sulfur.....   | 23.0     | 21.9     |
| Carbon.....   | 40.6     | 42.8     |
| Hydrogen..... | 3.39     | 4.47     |

## EXAMPLE 3

*Sulfide of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid*

To 5 grams of the barium salt prepared as in Example 2 and dissolved in 200 ml. of dry chloroform were added 3 grams of  $S_2Cl_2$  at 25° C. After standing for about one hour at 25° C. the solution was evaporated to remove the solvent. This product is believed to have the structure:



the value of  $x$  being substantially 2.

In the following examples various tests were applied to determine the value of the additives in compounded lubricating oils.

## EXAMPLE 4

*Corrosion test*

In order to determine the effect of the barium salt prepared as in Example 2 in preventing the corrosion of a copper-lead alloy when in contact with a blended oil containing the same, 0.75% of the salt was dissolved in a refined mineral lubricating oil of 63 seconds viscosity Saybolt at 210° F. and a viscosity index of 40, and this blend was compared with an unblended sample of the same base stock in a corrosion test conducted as follows:

500 cc. of the oil to be tested were placed in a glass oxidation tube (13" long and 2 1/8" diameter) fitted at the bottom with a 1/4" bore air inlet tube perforated to facilitate air distribution. The oxidation tube was immersed in a heated bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. To increase the severity of the test, the bearings were washed and weighed at the end of each four hour period and then polished and reweighed before continuing for another four-hour period. When submitted to this test the blend prepared as described above was found to cause a bearing weight loss of 21 mg. in 16 hours, while the unblended base stock caused a loss of 62 mg. in only 4 hours.

## EXAMPLE 5

*Corrosion test*

A blend consisting of 0.75% of the sulfurized barium salt prepared as described in Example 3

dissolved in a base oil of 52 seconds Saybolt viscosity at 210° F. and viscosity index of 104 was submitted to the test described in Example 4, and was found to cause a loss of weight of copper-lead bearings amounting to 28 mg. in 16 hours, while a sample of the blank base oil caused a loss of 80 mg. in 4 hours.

## EXAMPLE 6

*Copper strip test*

To determine the staining tendency of lubricating oil blends containing new additives a test was applied which consisted of a modification of the conventional A. S. T. M. corrosion test (Test-D 130-30) known as the copper strip test, with modifications embodying the employment of 3 hour test periods at a temperature of 210° F. If the strip is not stained or if only a light brassy stain is shown, the oil is considered satisfactory. Oils which produce a definitely brassy red, red-brown, blue or black stain are generally considered not satisfactory. This test was applied to the blends of lubricating oil and additive prepared in Examples 4 and 5 containing 0.75% of the barium salt and the sulfurized barium salt. In each case the copper strip showed only a slight red stain after a 3 hour test, and the oil blends were considered satisfactory.

## EXAMPLE 7

*Carbon black dispersion test*

A carbon black dispersion test was carried out to measure the comparative effectiveness of the barium salt described in Example 2 as an agent for dispersing sludge in lubricating oil. In this test 6% by weight of activated carbon was added to the oil blend containing the additive and thoroughly dispersed in the oil by stirring with an "egg beater" type mixer for 15 minutes while the temperature of the oil was maintained at 250° F. 250 cc. of the blend was then placed in a 250 cc. graduated cylinder and allowed to settle for 24 hours while the temperature was maintained at 200° F. If an additive is not a dispersing agent, the carbon black settles rapidly at this point leaving clear oil at the top in an hour or two. A very effective disperser will maintain the carbon black in suspension so that no change in the opaque slurry is apparent even after a 24-hour period. With all but the most potent dispersers stratification occurs with a black layer at the bottom (high concentration of carbon black) and a blue opaque layer at the top (reduced carbon black concentration). Cases of this type, known as "blue line" separations, are only detectable in reflected light. The base oil used for the test was a solvent extracted Mid-Continent oil of 52 seconds Saybolt viscosity at 210° F. The results of the test when applied to a blend containing 0.75% of the barium salt in the base oil showed no settling of the carbon black during the 24-hour period. A similar test of the base oil alone showed a volume of 140 cc. of supernatant oil at the end of the test period.

When the additives of the present invention are to be used in lubricating oil compositions the base stocks employed may be straight mineral lubricating oils, or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been

carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloro ethyl ether, propane, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed, either alone or in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additives present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel service, particularly with high speed Diesel engines, and in gasoline engine service, oils of higher viscosity index are often required, for example up to 75 or 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention the lubricating oils may also contain other agents, such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like, may also be employed.

Assisting agents which are particularly desirable are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol,  $C_8H_{17}OH$ , lauryl alcohol,  $C_{12}H_{25}OH$ , cetyl alcohol,  $C_{16}H_{33}OH$ , stearyl alcohol, sometimes referred to as octadecyl alcohol,  $C_{18}H_{37}OH$ , and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols, such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or

octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

The additives of the present invention will in some instances be used advantageously in lubricating oils in conjunction with other detergent additives such as metal soaps of fatty acids, metal naphthenates, metal phenates, metal mahogany sulfonates, metal phenol sulfonates, metal phenol sulfide salts and the like.

In addition to being employed in crankcase lubricants the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, process oils, general machinery oils, greases and rust preventive compositions. They may also be used in motor fuels, kerosene, paraffin waxes (particularly high melting point waxes), and in high molecular weight polymerized hydrocarbon products.

Among the various high molecular weight polymerized hydrocarbon products in which the additives of the present invention may find use are natural rubber and various synthetic rubbers such as those prepared from butadiene, isoprene, isobutylene and copolymers of these with each other and/or with other olefinic materials. The function of the additives in these compositions is that of inhibiting breakdown or depolymerization of the polymers caused by the action of heat and/or oxidation either during use or in storage. Also in some instances they serve to inhibit breakdown caused merely by mechanical working. The additives may be used alone as the sole inhibitor in these rubber-like compositions or they may be employed in conjunction with other antioxidants, vulcanization accelerators, and the like.

The new additives have been found to be particularly useful for preventing the breakdown of the molecular weight of polymerized isobutylene. A test showing the value of the additive in preventing such deterioration is described in the following example.

#### EXAMPLE 8

A polymerized isobutylene product suitable for use as an insulating material and as a plasticizer for natural or synthetic rubber and having a molecular weight of about 88,000, as determined by the Staudinger viscosity method, was blended with 0.25% of the ethyl ester of p-hydroxy dithiobenzoic acid by mixing with the polymer on a laboratory rubber mill at 87° F. for 15 minutes, the roll clearance being 0.017". A blank sample (polymer without the inhibitor) was also milled for 15 minutes at 87° F. (room temperature). The exact temperature of the polymer after milling was found to be 160° F. The products were then placed in an oven at 300° F. for 24 hours. An opening in one end of the oven allowed free access of the sample to air during the heating period. After the samples had been heated their

molecular weights were again determined. The results are as follows:

| Sample                       | Initial molecular weight | Approx. molecular wt. after 15 min. milling at room temperature | Approx. molecular wt. after 24 hrs. at 300° F. |
|------------------------------|--------------------------|-----------------------------------------------------------------|------------------------------------------------|
| Blank                        | 88,000                   | 67,000                                                          | 20,000                                         |
| Polybutene + 0.25% inhibitor | 88,000                   | 74,000                                                          | 58,000                                         |

It will be seen from these results that the additive inhibited to a slight extent the depolymerization resulting from the milling operation and to a considerable extent the loss in molecular weight brought about by heating in the presence of air.

#### EXAMPLE 9

A test similar to that described in Example 8 was applied to samples of a synthetic rubber consisting of a copolymer of isoprene and isobutylene (1.45% isoprene + 98.55% isobutylene) both with and without an inhibitor consisting of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid, prepared as described in Example 2. The blended product contained 2% of the barium salt. The results of the test are as follows:

| Sample                   | Initial molecular weight | Approx. molecular wt. after 15 min. milling at room temperature | Approx. molecular wt. after 24 hrs. at 300° F. |
|--------------------------|--------------------------|-----------------------------------------------------------------|------------------------------------------------|
| Blank                    | 57,000                   | 52,000                                                          | 22,000                                         |
| Copolymer + 2% inhibitor | 57,000                   | 51,000                                                          | 33,000                                         |

These results clearly show that the barium salt was effective in inhibiting depolymerization brought about by heating in the presence of air.

This invention is not to be considered as limited by any of the examples described herein which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

#### I claim:

1. A material consisting essentially of non-gaseous aliphatic hydrocarbons containing about 0.02% to about 5% of a compound having the structure



where Ar is an aromatic nucleus, T is a salt forming entity selected from the group consisting of hydrogen, a metal valence equivalent of hydrogen, the metal being selected from groups I, II, III, IV and VIII of the periodic table, and a non-metallic basic group, X is a non-metal of group VI of the periodic table, and R is an aliphatic radical, and where the TO— and —CXXR groups are in the 1,4 positions relative to each other on a six membered carbon ring structure.

2. A mineral oil containing about 0.02% to about 5% of a compound having the structure



where Ar is an aromatic nucleus, T is a salt forming entity selected from the group consisting of hydrogen, a metal valence equivalent of hydrogen, the metal being selected from groups I, II, III, IV and VIII of the periodic table, and a non-metallic basic group, X is a non-metal of group VI of the periodic table, and R is an aliphatic

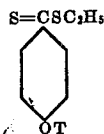
radical, and where the TO— and —CXXR groups are in the 1,4 positions relative to each other on a six membered carbon ring structure.

3. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of a compound of the formula



where R is an aliphatic radical and T is a salt forming entity selected from the group consisting of hydrogen, a metal valence equivalent of hydrogen, the metal being selected from groups I, II, III, IV and VIII of the periodic table, and a non-metallic basic group.

4. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of a compound of the formula



where T is a member of the group consisting of hydrogen and an alkaline earth metal valence equivalent of hydrogen.

5. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of the ethyl ester of p-hydroxy dithiobenzoic acid.

6. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of the barium salt of an alkyl ester of p-hydroxy dithiobenzoic acid.

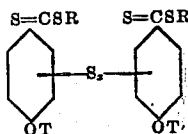
7. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid.

8. A material consisting essentially of non-gaseous aliphatic hydrocarbons containing about 0.02% to about 5% of a member of the group consisting of reaction products of a sulfur halide with a compound of the formula



where R is an aliphatic radical, and salts of such reaction products selected from the group consisting of metal salts derived from metals of groups I, II, III, IV and VIII of the periodic table and salts formed from non-metallic basic radicals.

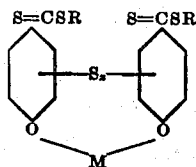
9. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of a compound having the structure



where R is an alkyl radical, T is a salt forming entity selected from the group consisting of hydrogen, a metal valence equivalent of hydrogen, the metal being selected from groups I, II,

III, IV and VIII of the periodic table, and a non-metallic basic group, and  $x$  is an integer, from 1 to 4.

10. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of a compound having the structure



where  $M$  is an alkaline earth metal.

11. A lubricant comprising a major proportion of a mineral oil of the lubricating oil range and about 0.02% to about 5% of the sulfide of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid.

12. A normally solid high molecular weight aliphatic hydrocarbon polymeric material containing about 0.1% to about 5% of a compound having the structure



where  $\text{Ar}$  is an aromatic nucleus,  $\text{T}$  is a member of the group consisting of hydrogen, a metal valence equivalent of hydrogen, the metal being selected from groups I, II, III, IV and VIII of the

periodic table, and a non-metallic basic group,  $\text{X}$  is a non-metal of group VI of the periodic table, and  $\text{R}$  is an aliphatic radical, and where the  $\text{TO}-$  and  $-\text{CXRR}$  group groups are in the 1, 4 positions relative to each other on a six membered carbon ring structure.

13. A normally solid high molecular weight aliphatic hydrocarbon polymeric material containing about 0.1% to about 5% of a compound of the structure



where  $\text{R}$  is an aliphatic radical and  $\text{T}$  is a salt forming entity selected from the group consisting of hydrogen, a metal valence equivalent of hydrogen, the metal being selected from groups I, II, III, IV and VIII of the periodic table, and a non-metallic basic group.

14. A high molecular weight polybutene containing about 0.1% to about 5% of the ethyl ester of p-hydroxy dithiobenzoic acid.

15. A high molecular weight rubber-like copolymer of isobutylene and isoprene containing about 0.1 to about 5% of the barium salt of the ethyl ester of p-hydroxy dithiobenzoic acid.

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