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LUBRICATING OIL

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This invention relates to lubricating oils; more particularly to lubricating oils having anticorrosion and detergent properties.

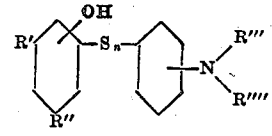
It is now generally known in the lubricating oil art that ordinary lubricating oils, either conventionally refined or solvent refined and of either naphthenic or paraffin base stocks, tend to decompose at high operating temperatures to form corrosive decomposition products which attack certain types of alloy bearings. Many different types and kinds of film-forming and anticorrosion agents have been added to lubricating oils to prevent the formation of these corrosive decomposition products or to inhibit their attack on the metal surfaces with which they come in contact.

It is also generally known that lubricating oils intended for heavy duty service in modern types of internal combustion engines require more than improved corrosion resistance. Under severe service conditions the decomposition products which form in ordinary lubricating oils tend to polymerize to yield resin-like bodies which form sludge and build up lacquer-like deposits on the cylinder walls and pistons of the engine, thus decreasing its efficiency or even stopping its operation altogether. Various types and kinds of compounds having detergent properties have been added to lubricating oils to disperse the sludge and prevent its deposition on parts of the engine.

The addition of both a corrosion inhibitor and a detergent to the lubricating oil is not always successful because the two agents are sometimes incompatible and work against each other. Compounds have also been added to lubricating oils which possess both anticorrosion and detergent properties. However, such compounds are not always available and may be either too weak in their anticorrosion or detergent properties to make the oil satisfactory for heavy duty service.

We have discovered that the compounds to be described hereinafter possess excellent corrosion inhibiting properties and at the same time possess mild detergent properties when dissolved in lubricating oils. These compounds are particularly advantageous for use in lubricating oils because of their compatibility with other types of compounds that have good detergent properties but are somewhat lacking in corrosion inhibiting properties, particularly when leaded fuels are used. Apparently combustion of leaded fuels which contain ethylene dichloride and ethyl bromide along with the lead tetraethyl produce hydrochloric and hydrobromic acids on combustion and our amine type products neutralize these halogen acids and thereby reduce corrosion. Accordingly, unlike many other corrosion inhibitors, these compounds may be either used alone, in cases where a strong corrosion inhibitor is needed and where the problem of detergency is of secondary importance, or they may be used with compounds having strongly detergent properties when it is necessary that the oil have both strong anticorrosion and detergent properties. The compounds to be described herein are highly oil soluble and may also be employed to dissolve more difficultly oil soluble compounds in lubricating oils.

The compounds which we add to our lubricating oil are new compounds. Their general formula is as follows:



in which one or both of R' and R'' are alkyl radicals of from about 1 to 20 carbon atoms, R''' and R'''' are short chain alkyl groups and n is the integer 1 or 2.

In these compounds the total number of carbon atoms in R' and R'' does not ordinarily exceed about twenty since the presence of extremely long chain alkyl groups tends to decrease the oil solubility of the compound. Accordingly, if R' or R'' is hydrogen, the alkyl group may be anywhere from 1 to 20 carbon atoms in length, preferably 8 to 14. If both R' and R'' are alkyl groups then the total number of carbon atoms in the two is preferably within the range of about 8 to 14, not usually over about 20. As indicated by the formula above, the —OH group and —NR'''R'''' group may have any unoccupied position on the benzene ring.

The above compounds may be prepared by reacting an alkyl phenol with a di-N-substituted aniline and sulfur chloride or sulfur dichloride. Suitable alkyl phenols include; 2,4-diamylphenol, p-tertiary-octylphenol, p-tertiary-butyl-o-cresol, 2,4-ditertiary-octylphenol, p-dodecylphenol, and others having one or two alkyl groups of from 1 to 20 carbon atoms. Suitable di-N-substituted anilines include; dimethylaniline, methylethylaniline, diethylaniline, dipropylaniline, methylbutylaniline, and others having alkyl groups up to about 5 carbon atoms in length.

The alkyl phenol and di-N-substituted aniline are joined by a sulfur group as shown in the general formula. To join the two benzene rings

with a single sulfur atom, sulfur dichloride is employed. When sulfur chloride is used the benzene rings are linked by two sulfur atoms.

Ordinarily, the reaction is carried out with the alkyl phenol and di-N-substituted aniline dissolved in a chlorinated solvent such as ethylene dichloride trichloroethylene, carbon tetrachloride, chloroform, etc. or other suitable solvent such as carbon disulfide. The reaction is brought about by merely adding the sulfur chloride or sulfur dichloride to the solution at temperatures preferably below room temperature. The reaction is exothermic and it is generally advisable to surround the reaction vessel with a coolant such as ice water. After the sulfur chloride or sulfur dichloride has been added the reaction mixture is allowed to stand for a few hours until the reaction is complete. During the reaction, hydrogen chloride is formed and part is retained as the amine hydrochloride, the rest being evolved. The reaction is substantially complete when hydrogen chloride is no longer evolved.

To recover the reaction product, the reaction mixture may be treated with a dilute solution of a mild alkali to neutralize the hydrochloric acid in the reaction mixture and free the amine compound from its salt. After washing, the aqueous fraction is discarded and the solvent fraction evaporated to obtain the product. When the compounds are to be blended directly in lubricating oils, a part of the lubricating oil may be added to the solvent fraction and the excess solvent evaporated away. Other lubricating oil additives may be added to the mixture at this time if desired.

Although the compounds may be used directly as prepared by the method just described, they may also be used in the form of their metal salts. Some of the metal salts of these compounds, particularly the alkaline earth metal salts, have improved detergent properties. These metal salts may be made by merely adding a metal hydroxide, such as barium hydroxide, calcium hydroxide, sodium hydroxide, etc. to the reaction mixture after the compound has been formed and heating it to remove the water of reaction. Other metal salts may be prepared by treating the free amino compound with powdered aluminum metal, magnesium turnings, calcium metal, etc. or by heating with an alcoholate of a low boiling alcohol such as methanol. The metal salts may also be prepared by methods of double decomposition as by heating the sodium salt with a salt such as zinc chloride, aluminum sulfate, copper nitrate, etc.

Since the compounds described herein are new the preparation of a number of representative compounds of the group, and metal salts thereof, is given in the following examples. It should be understood, however, that these examples are given primarily by way of illustration and are not intended to limit our invention to the use of the particular compounds described.

Example 1

2-hydroxy-3,5-di-tert-amyl-4'-diethylaminodiphenyl disulfide

A solution of 75 parts by weight of diethylaniline and 120 parts by weight of 2,4-diamylphenol in 240 parts by weight of ethylene dichloride was stirred in a flask cooled to 10° C. by an ice-water bath. To this liquid was added slowly 74 parts by weight of sulfur monochloride, the temperature in the flask being kept below 15° C. When all the sulfur monochloride was added, the product was let stand 12 hours at room temperature and then treated with sodium carbonate solution. The aqueous fraction was discarded and the ethylene dichloride layer washed a second time with sodium carbonate solution. Addition of n-butyl alcohol assisted in giving a good separation into two layers. The product was added to 225 parts of S. A. E. #10 oil, vacuum-dried with a final temperature of 120° C., and filtered, giving a clear, oil-soluble, 50% oil solution of 2-hydroxy-3,5-di-tert-amylphenyl-4' - diethylaminodiphenyl-disulfide.

Example 2

2-hydroxy-3,5-di-tert-amyl-4'-dimethylaminodiphenyl disulfide

Into 61 parts by weight of dimethylaniline and 120 parts by weight of 2,4-diamylphenol in 240 parts by weight of ethylenedichloride was dropped with stirring 74 parts by weight of sulfur monochloride, external cooling being employed to prevent the temperature from rising above 20° C. When the addition was complete, the product was stirred two hours at room temperature and then washed twice with sodium carbonate solution. A little n-butyl alcohol was added to prevent emulsion formation. The ethylene dichloride solution was dissolved in 200 parts by weight of S. A. E. #10 oil and vacuum-dried with a final temperature of 120° C. The product was filtered to remove a small amount of inorganic material, giving a clear, oil-soluble, 50% oil solution of 2-hydroxy - 3,5 - tert-amyl - 4' - dimethylaminodiphenyl disulfide.

Example 3

2-hydroxy-5-tert-octyl-4'-dimethylaminophenyl disulfide

To 53 parts by weight of p-tert-octylphenol and 31.2 parts by weight of dimethylaniline in 120 parts by weight of ethylene dichloride was added slowly, with stirring, 38 parts by weight of sulfur monochloride. The flask was immersed in an ice-water bath to prevent the reaction temperature from rising above 20° C. The addition required about one hour and at its conclusion the mixture was stirred two hours longer with no external cooling. After the ethylene chloride solution was twice washed with sodium carbonate solution it was added to 100 parts by weight of S. A. E. #10 oil and the solvents removed by vacuum distillation. The product was filtered to remove a slight inorganic precipitate, giving a 50% oil solution of the 2-hydroxy-5-tert-octyl-4'-dimethylaminodiphenyl disulfide.

Example 4

2-hydroxy - 3 - methyl-5-tert-butyl-4'-dimethylaminodiphenyl disulfide

To 82 parts by weight of p-tert-butyl-o-cresol and 61 parts by weight of dimethylaniline, stirred in 240 parts by weight of ethylene dichloride below 20° C. was added slowly 74 parts by weight of sulfur monochloride. The reaction mixture remained at room temperature for 16 hours and was then washed twice with sodium carbonate solution. A small amount of n-butyl alcohol aided in breaking the emulsion formed during the washing. The ethylene dichloride solution was mixed with 170 parts by weight of S. A. E. #10 oil and vacuum-dried at 120° C. to remove the solvents. The material was filtered, removing small amounts of sodium carbonate and sodium chloride, giving a clear 50% solution

of 2-hydroxy-3-methyl-5-tert-butyl-4'-dimethylaminodiphenyl disulfide in oil.

EXAMPLE 5

Barium salt of 2-hydroxy-3,5-di-tert-amyl-4'-diethyldiphenyl disulfide

To 100 parts by weight of 50% oil solution of 2 - hydroxy-3,5-di-tert-amyl-4'-diethylaminodiphenyl disulfide was added 100 parts by weight of n-butyl alcohol and 35 parts by weight of barium hydroxide octahydrate. The mixture was stirred in an oil bath at 130–140° C. and Solvesso #1 (toluol petroleum fraction) was added. The Solvesso was replaced as it boiled off until finally all butyl alcohol and water had been evaporated. The mixture was filtered and the Solvesso #1 removed in vacuo to give a clear, brown, approximately 50% oil solution of the barium salt of 2-hydroxy - 3,5 - di - tert-amyl-4'-diethylaminodiphenyl disulfide.

EXAMPLE 6

Barium salt of 2-hydroxy-3,5-di-tert-amyl-4'-dimethylaminodiphenyl disulfide

To 78 parts by weight of a 50% oil solution of 2-hydroxy-3,5-di-tert-amyl-4'-dimethylaminodiphenyl disulfide was added an equal volume of n-butyl alcohol and 12 parts by weight of barium hydroxide. This mixture was stirred at 140° C. and Solvesso #1 was added to replace the alcohol as it evaporated. When all water and butyl alcohol had evolved, the mixture was filtered through Hyflo and vacuum-dried to remove the Solvesso, giving an oil solution of the barium salt of 2-hydroxy-3,5-di-tert-amyl-4'-dimethylaminodiphenyl disulfide.

EXAMPLE 7

2 - hydroxy-3,5-di-tert-octyl-4'-diethylaminodiphenyl disulfide

In 275 parts by weight of ethylene dichloride were mixed 159 parts by weight of 2,4-di-tert-octylphenol and 75 parts by weight of diethylaniline. This solution was cooled in an ice-water bath and stirred during the dropwise addition of 70 parts by weight of sulfur monochloride, the reaction temperature being kept below 20° C. After the mixture had stood several hours it was treated with sodium carbonate solution, separated and washed again. The ethylene dichloride layer was added to 275 parts by weight of S. A. E. #10 oil and all solvents removed by drying in vacuo at 120° C. The residue was filtered to give a clear 50% oil solution of 2-hydroxy-3,5-di-tert-octyl-4'-diethylaminodiphenyl disulfide.

EXAMPLE 8

2 - hydroxy - 5 - dodecyl-4'-diethylaminodiphenyl disulfide

To 131 parts by weight of p-dodecylphenol and 75 parts by weight of diethylaniline in 250 parts by weight of ethylene dichloride was added slowly 70 parts by weight of sulfur monochloride. External cooling was necessary to keep the reaction temperature below 20° C. The mixture stood overnight before being twice washed by a solution of sodium carbonate. Addition of n-butyl alcohol during the washing facilitated separation into two layers. The ethylene dichloride solution was combined with 240 parts by weight, of S. A. E. #10 oil, vacuum-dried at 120° C. and filtered, giving a clear 50% oil solution of 2-hydroxy-5-dodecyl-4'-diethylaminodiphenyl disulfide.

EXAMPLE 9

2-hydroxy-3,5-di-tert-amyl-4'-dimethylaminodiphenyl sulfide

In 225 parts by weight of ethylene dichloride were mixed 120 parts by weight of 2,4-diamylphenol and 6. parts by weight of dimethylaniline. While this solution was stirred at 10–20° C., 53 parts by weight of sulfur chloride was slowly dropped in. The mixture was stirred three hours more at 25–30° C. and was then washed well with aqueous sodium carbonate. The ethylene chloride layer was combined with 185 parts by weight of S. A. E. #10 oil, vacuum-dried at 120° C. and filtered to give a 50% solution of 2-hydroxy-3,5-di-tert-amyl-4'-dimethylaminodiphenyl sulfide.

In most of the above examples the compound was prepared in a 50% oil solution. This method of preparation is advantageous in that the product is easily handled and can be stored, sold and shipped in this form. Blending with lubricating oils is also greatly facilitated.

The amount of additive employed in our improved lubricating oils may vary from about 0.1 to 5% by weight based on the weight of the compounds in the lubricating oil.

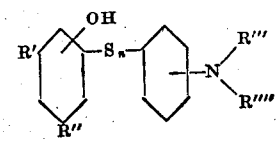
To illustrate the effectiveness of these new compounds in preventing corrosion of alloy bearings by lubricating oils, a copper-lead alloy bearing was attached to a copper strip and a Mid-Continent, solvent refined S. A. E. #30 grade oil heated to 325° F. was sprayed against the copper strip and the bearing for ten hours. At the end of the test, it was found that the copper-lead bearing was corroded and that the neutralization number of the oil was greatly increased. Other tests using the same oil with small amounts of the new compounds added thereto were also made. The results of these tests are summarized in the following table.

Additive	Concentration	Corrosion, mg.		Neut. No.	
		5 hr.	10 hr.	Before	After
	Per cent				
None		81	99	0.06	11.60
Product Ex. 1	0.5	0	0	0.06	1.59
Product Ex. 5	0.5	0	2	−0.13	2.56
Product Ex. 2	0.5	0	3	0.08	3.64
Product Ex. 6	0.75	0	0	−0.18	1.60

Other tests, including operating tests on the oil in different types of internal combustion engines, have also been made and have shown that the compounds described in the preceding examples are effective in preventing corrosion of alloy bearings by the oil. These tests have also shown that the above compounds have detergent properties when dissolved in lubricating oils.

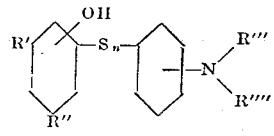
We claim:

1. A lubricating oil composition comprising a predominating amount of mineral lubricating oil and an effective amount of a compound of the group consisting of those having the general formula:



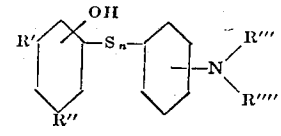
in which R′ and R″ are radicals of the group consisting of hydrogen and alkyl radicals at least one being an alkyl radical, R‴ and R⁗ are alkyl radicals of from 1 to 5 carbon atoms inclusive, and n is a small whole number not greater than 2, and the metal salts of such compounds.

2. A lubricating oil composition comprising a predominating amount of lubricating oil and 0.1 to 5% by weight, based on the amount of lubricating oil present therein of a compound of the group consisting of those having the general formula:



in which R′ and R″ are members of the group consisting of hydrogen and alkyl radicals at least one being an alkyl radical of not more than 20 carbon atoms, R‴ and R⁗ are alkyl radicals of from 1 to 5 carbon atoms inclusive, and n is a small whole number not greater than 2, and the metal salts of such compounds.

3. A lubricating oil composition comprising a predominating amount of a lubricating oil and 0.1 to 5% by weight, based on the amount of lubricating oil present therein, of a compound of the group consisting of those having the general formula:



in which R′ and R″ are alkyl radicals having a total of not more than about 20 carbon atoms, R‴ and R⁗ are alkyl radicals of from 1 to 5 carbon atoms inclusive, and n is a small whole number not greater than 2, and the metal salts of such compounds.

4. A lubricating oil composition containing a predominating amount of a lubricating oil and 0.1 to 5% by weight, based on the amount of lubricating oil present therein, of 2-hydroxy-3,5-di-tertiaryamyl-4′-diethyldiphenyl sulfide.

5. A lubricating oil composition containing a predominating amount of a lubricating oil and 0.1 to 5% by weight, based on the amount of lubricating oil present therein, of the barium salt of 2-hydroxy-3,5-di-tertiaryamyl-4′-diethyldiphenyl sulfide.

6. A lubricating oil composition containing a predominating amount of a lubricating oil and 0.1 to 5% by weight, based on the amount of lubricating oil present therein, of 2-hydroxy-3,5-di-tertiaryamyl-4′-dimethyldiphenyl sulfide.

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