United States Patent Office

2,725,357

Patented Nov. 29, 1955

2,725,357

LUBRICATING OILS CONTAINING HYDROXY AND ALKOXY-METAL OXYARYLALKYL AMINES

Herman D. Kluge and Fred W. Moore, Wappingers Falls, N. Y., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application May 10, 1952, Serial No. 287,266

4 Claims. (Cl. 252—42.7)

The present invention relates to improved lubricating compositions, and more particularly to mineral lubricating oils containing minor amounts of metal-containing derivatives of hydroxyarylalkyl amines.

Mineral lubricating oils, such as crankcase oils, which are subjected to elevated temperatures in service, tend to undergo oxidative and other deterioration with the formation of gums and sludges, which form varnish-like deposits on the surfaces of valves, rings, pistons, and other engine parts. Such deposits decrease the efficiency of operation of the engine, and result in piston sticking and scoring of the cylinder walls.

It is common practice to add to mineral lubricating oils small amounts of so-called "detergent" compounds of various types, which have the property either of reducing the formation of gums and sludges, or of dispersing and altering the character thereof so as to reduce the formation of varnish-like deposits upon the engine parts. Among the effective compounds which have been suggested for this purpose are the hydroxyarylalkyl amines, and particularly the metal salts of such compounds wherein the hydroxyl hydrogen is replaced by metal. Lubricant additives of this type are obtained according to U. S. 2,403,453, for example, by interreacting a hydroxy-aromatic compound with an aldehyde above formaldehyde and with ammonia. Other compounds of this class, which have been suggested as detergents in lubricating oils, include the condensation products of a hydroxyaromatic compound with formaldehyde and a secondary amine, and the metal salts of such condensation products, as described in U. S. 2,363,134, and the metal salts of condensation products of a hydroxy-aromatic compound with an aldehyde and an aliphatic polyamine wherein each amino group has at least one hydrogen atom, as described in U. S. 2,353,491.

We have now found that metal derivatives of hydroxyarylalkyl amines wherein the metal is linked both to an oxyarylalkyl amine group and to a hydroxy or alkoxy group are unexpectedly superior in their detergent properties to the corresponding metal derivatives of hydroxyarylalkyl amines of the prior art, wherein the metal is linked only to one or more oxyarylalkyl amine groups. In accordance with our invention, superior lubricating oil additives are prepared by replacing the hydroxyl hydrogen of a hydroxyarylalkyl amine with an —MOR group, wherein M is a divalent metal and R is hydrogen or a lower aliphatic hydrocarbon group, suitably containing from one to about five carbon atoms. Preferably, R is an aliphatic hydrocarbon group containing from one to three carbon atoms, and M is a metal chosen from the group consisting of alkaline earth metals and zinc. With particular advantage, where the compounds are to be employed as additives in airplane engine oils or the like, where the character of the combustion chamber deposits is an important consideration, M may be a metal chosen from the group consisting of magnesium and zinc. For regular heavy duty motor oils, however, the heavier metals such as calcium and barium may be suitably employed in forming the derivatives of this invention.

The above compounds may be produced from the corresponding hydroxyarylalkyl amines. The alkoxy metal derivatives are readily obtained by reacting a hydroxyarylalkyl amine with a divalent metal alcoholate, such as calcium methylate, zinc butylate, etc., employing at least one mol proportion of metal alcoholate for each mol proportion of hydroxy group present in the hydroxyarylalkyl amine compound. Hydroxy metal derivatives may conveniently be obtained by hydrolysis of the corresponding alkoxy metal derivative.

Hydroxyarylalkyl amines employed in forming these derivatives are compounds wherein both a hydroxy group and an aliphatic hydrocarbon group containing an amine group are directly attached to an aryl group, which may be a phenyl group or a polynuclear aryl group such as naphthyl, anthracyl, diphenyl, etc. The aryl group may contain other substituents also, such as hydrocarbon groups, halogens, sulfur-containing groups, nitro groups, etc. in so far as these do not impair the properties of the compound as a lubricating oil additive. Preferably, the compound contains at least one aliphatic hydrocarbon group of sufficient chain length to impart oil-solubility to the molecule. Typical compounds of this class which may be mentioned include aminobutyl phenol, aminoethyl undecyl phenol, aminomethyl octyl naphthol, dimethylaminomethyl diamyl phenol, N,N'-bis (2-hydroxy-5-octylbenzyl)-1,2-diaminoethane, and the like, as well as various polymers of such compounds.

The hydroxyarylalkyl amines may be obtained by various methods, such as by reacting a hydroxyaromatic aldehyde, or a hydroxyaromatic compound containing a halogen-substituted aliphatic hydrocarbon group attached to the aromatic nucleus, with ammonia or with a primary or secondary amine. According to a preferred embodiment of our invention, a lubricating oil additive is prepared by first condensing a hydroxyaromatic compound having at least one unsubstituted position on the aromatic nucleus with an aldehyde and with ammonia or a primary or secondary amine; and the condensation product obtained, comprising the normal monomeric condensation product and various polymers thereof, is then treated with a metal alcoholate as described above. The condensation may be carried out by heating the reactants together at a moderately elevated temperature, such as a temperature in the range of about 100–200° F., in the presence or absence of a solvent. The reactants are preferably employed in approximately equivalent reacting proportions, i. e., about equimolecular proportions of hydroxyaromatic compound and of aldehyde and equimolecular proportions or less of amine depending upon the number of reactive amine groups which it contains.

Typical hydroxyaromatic compounds which may be employed in the above condensation reaction include phenol, diamyl phenol, pentacosyl phenol, alpha- and beta-naphthol, octadecyl alpha- and beta-naphthol, catechol, benzylphenol, chlorophenol, hydroquinone, hydroxydiphenyl, phenol resins, and the like. The preferred compounds of this class are alkyl hydroxyaromatic compounds containing at least one aliphatic hydrocarbon

substituent group of from about 5 to about 30 carbon atoms. The terms "alkyl hydroxyaromatic," "alkyl phenol," etc., are used for convenience in the specification and claims to mean compounds containing one or more aliphatic hydrocarbon groups, which may be either saturated or unsaturated in character.

Aldehydes employed in the condensation reaction are preferably aliphatic aldehydes such as formaldehyde, acetaldehyde, butyraldehyde, furfuraldehyde, etc., although aromatic aldehydes such as benzaldehyde, toluic aldehyde, etc., may also be employed if desired. The aldehydes may contain substituent groups such as hydrocarbon groups, alkoxy groups, nitro groups, halogens, etc., in so far as these do not interfere in the condensation reaction.

Amines which may be employed in the condensation are compounds containing at least one primary or secondary amine group. They are preferably aliphatic hydrocarbons containing one or more amino groups, such as for example methylamine, ethylamine, hexylamine, ethylene diamine, etc., although aromatic amines such as aniline may also be employed if desired. The amines may also contain substituent groups, as discussed above in connection with the aldehyde reactants.

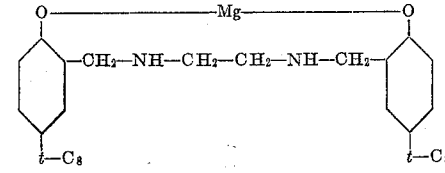
The hydroxyarylalkyl amine derivatives of this invention may be employed in lubricating oils in various amounts, ranging from very small amounts up to amounts representing the limits of their solubilities. For ordinary purposes, they are suitably employed in amounts within the range of from about 0.1 to about 5.0 per cent by weight, and preferably within the range of from about 0.25 to about 2.0 per cent by weight of the lubricating composition. In addition to these compounds, other lubricating oil additives may also be employed if desired, such as extreme pressure agents, pour depressants, corrosion inhibitors, and so forth.

The preparation of typical compounds of our invention is described in Examples 2, 3, 5 and 6 below. The superior detergency characteristics of these compounds in lubricating oils is shown in comparison to those of the corresponding metal salts of hydroxyarylalkyl amines of the prior art, the preparation of which is described in Examples 1 and 4.

EXAMPLE I

A condensation product of p-tert-octaylphenol with formaldehyde and with ethylene diamine was prepared in the following manner: 1020 grams (5 moles) of p-tert-octylphenol and 220 grams (2.5 moles) of ethylene diamine in the form of a 68.5 per cent water solution were dissolved in 1.5 liters of ethanol, and 450 grams (5.5 moles) of formaldehyde in the form of a 36.5 per cent water solution added dropwise at such a rate that the temperature of the reaction mixture remained below 95° F. Then the reaction mixture was heated to reflux for 6 hours and allowed to stand overnight. The reaction mixture was taken up in ether and washed with saturated sodium chloride solution, and finally with water until neutral to Brilliant Yellow. The ether was then evaporated off, benzene added and the latter finally stripped off under reduced pressure. The product obtained was a clear, amber-colored solid.

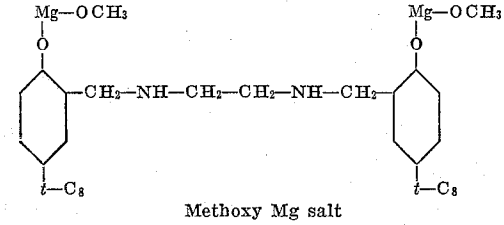
The normal magnesium salt of the above condensation product was prepared by reacting 248 grams (0.5 mole) of the condensation product, in the form of a solution in 650 grams of 300 SAE grade lubricating oil (diluted with toluene), with 510 milliliters (0.5 mole) of magnesium methylate in methanol solution. After the reaction was completed the solvent was stripped off under reduced pressure, and 894 grams of an oil solution containing 244 grams of reaction product were recovered. Additional lubricating oil was added to form a 25 per cent concentrate of the reaction product. This solution analyzed 2.11 per cent of ash (MgO) and 1.25 per cent nitrogen, as compared with the theoretical values of 1.93 and 1.35, respectively, for the compound



Mg salt of N,N'-bis(2-hydroxy-5-t-octyl benzyl)-1,2-diamino ethane

EXAMPLE II

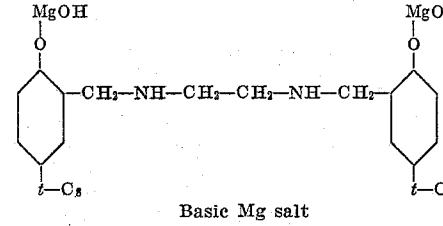
The condensation product of p-tert-octylphenol with formaldehyde and ethylene diamine was prepared as described in Example 1. This condensation product was converted to the dimethoxymagnesium derivative by treating it with magnesium methylate in the following manner: 595 grams (1.2 moles) of the condensation product were dissolved in toluene and added dropwise to 2425 milliliters of a 0.95 molar methanol solution of magnesium methylate (2.4 moles). 500 grams of 300 SAE grade lubricating oil were added and the mixture refluxed until the reflux temperature of toluene was reached. An additional 500 grams of lubricating oil were then added, the solution filtered and the toluene finally stripped off. 1600 grams of solution were obtained, containing 600 grams of reaction product. A 25 per cent concentrate of this product was prepared by adding an additional 800 grams of 300 SAE grade lubricating oil. This solution analyzed 3.25 per cent ash (MgO), 1.93 per cent magnesium and 1.24 per cent nitrogen, as compared with the theoretical values of 3.47 per cent, 2.08 per cent and 1.21 per cent, respectively, for the compound



Methoxy Mg salt

EXAMPLE III

The dihydroxymagnesium derivative of tert-octylphenolformaldehyde-ethylene diamine condensation product was prepared by hydrolysis of the corresponding dimethoxymagnesium derivative in the following manner: 1600 grams of the oil concentrate obtained in Example 2, containing 0.6 mole of the dimethoxymagnesium derivative, were diluted with toluene, 22 milliliters (1.2 mole) of water added and the solution heated under reflux. The water was finally distilled off, the solution filtered and the toluene stripped off. The product analyzed 3.20 per cent ash (MgO), as compared to the theoretical value of 3.48 per cent for the compound



Basic Mg salt

EXAMPLE IV

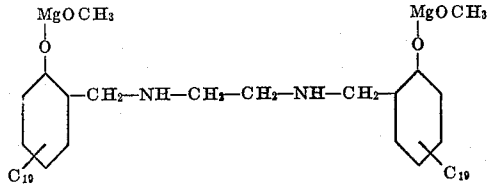
A condensation product of alkyl (C_{22}) phenol with formaldehyde and ethylene diamine was prepared as described in Example 1, employing 1.95 moles of the alkyl phenol, 0.975 mole of ethylene diamine and 3 moles of formaldehyde in the reaction. The alkyl (C_{22}) phenol was obtained by alkylating phenol with a propylene

polymer fraction containing about 22 carbon atoms per molecule. The alkylation was carried out by heating phenol and the propylene polymer together at a temperature of 80° C. for 6 hours in the presence of $AlCl_2.HSO_4$ as the catalyst, employing a mol ratio of phenol to propylene polymer of about 3:1. The product was dissolved in hexane, filtered, and stripped free of solvent. The unreacted phenol was then distilled off. The residue was dissolved in alcoholic caustic and refluxed 7 hours to destroy any sulfonates present. The caustic solution was neutralized with concentrated HCl, extracted with ether, and the ether solution washed neutral with water. The ether was evaporated and the residue fractionated under diminished pressure. The alkyl phenol fraction distilling from 170° C. at 250 microns to 250° C. at 100 microns of mercury was employed in the condensation reaction with formaldehyde and ethylene diamine as described above. This alkyl phenol had a hydroxyl number of 141 and a molecular weight of 375, indicating that it contained an average of 21.8 alkyl carbon atoms per molecule.

The normal magnesium salt of the above condensation product was prepared as described in Example 1 by reacting it with magnesium methylate solution in equimolar proportions in the presence of benzene as a solvent.

EXAMPLE V

A condensation product of alkyl (C_{19}) phenol with formaldehyde and ethylene diamine was prepared as described in Example 4. The alkyl (C_{19}) phenol was obtained as described in Example 4 except that a propylene polymer fraction having about 19 carbon atoms and boiling at 100–120° C. under a pressure of 1–2 millimeters of mercury was used. The condensation product was converted into the dimethoxymagnesium derivative by treating it with magnesium methylate in a mol ratio of 1:2, as described in Example 2. The reaction product obtained was diluted with 300 SAE grade lubricating oil to form a 25 per cent concentrate. This solution analyzed 2.27 per cent ash (MgO), as compared with the theoretical value of 2.19 per cent for the compound



EXAMPLE VI

The dihydroxymagnesium derivative of alkyl (C_{19}) phenol - formaldehyde - ethylene diamine condensation product was prepared by hydrolysis of the dimethoxymagnesium derivative of Example 5 according to the method described in Example 3, except that the condensation product and water were reacted in approximately equimolar proportions. The product obtained analyzed 2.06 per cent MgO, as compared with the theoretical value of 2.26.

Table I below shows the detergency characteristics of the products of the above examples as measured by the High Temperature Deposits Test. This is a bench test designed to show the varnishing characteristics of an oil under service conditions. The test is carried out by repeatedly dipping an aluminum cylinder one inch in diameter and three inches long into a beaker containing a sample of the test oil maintained at 525° F. for a period of 20 hours. The test specimen is then washed with pentane and dried, and the weight of deposits found by the increase in weight. The test specimen is then brushed to remove loose deposits and the weight of the deposits remaining determined; this affords an indication of the character of the deposits. This test correlates well with the lacquer forming and oil ring sticking characteristics of a cylinder oil in actual service. The lubricating oil compositions of the table were made up by adding sufficient of the oil concentrates obtained in the examples to a refined paraffin distillate lubricating oil to form a 1 per cent solution of the reaction product.

Table I

HIGH TEMPERATURE DEPOSITS TEST

Additive	Deposits, mg.	
	Total deposits	After brushing
None (base oil)	452	326
1% Reaction product of Example I	120, 71	54, 38
1% Reaction product of Example II	3, 2	3, 2
1% Reaction product of Example III	5, 3	5, 3
1% Reaction product of Example IV	152, 78	19, 11
1% Reaction product of Example V	45, 35	2, 4
1% Reaction product of Example VI	70, 81	9, 13

As shown by the above table, all of the compounds of this invention were strikingly superior in their detergency characteristics to the normal metal derivatives of hydroxyarylalkyl amines of the prior art. Thus a lubricating oil containing 1 per cent of an alkoxy- or hydroxy metal derivatives, obtained as described in Examples 2 and 3 respectively, gave only about one thirtieth the amount of total deposits and only about one tenth the amount of adherent or varnish-like deposits (after brushing) found with the same lubricating oil containing an equal amount of the corresponding prior art metal derivative, obtained as described in Example 1. The test results obtained with the reaction products of Examples 4, 5 and 6, which were derived from condensation products of higher molecular weight alkyl pheonls, also show the outstanding superiority of the alkoxy- and hydroxy-metal derivative, although a larger amount of deposits was obtained with these compounds than with the corresponding compounds of Examples 2 and 3, and the alkoxy-metal derivatives was considerably superior to the hydroxy-metal derivative.

The above compounds of this invention were also found to possess excellent corrosion resistance properties as measured by the familiar MacCoull corrosion test, and other favorable characteristics as lubricant additives at least equivalent to those of the corresponding prior art compounds.

While the above examples relate to derivatives obtained from condensation products of alkyl phenols with formaldehyde and with ethylene diamine, the invention is not to be constructed as limited to these particular hydroxyarylalkyl amines, since the compounds of this general class are of closely similar chemical properties and of similar activity in lubricating oil compositions, as discussed above. Also, other divalent metals may be employed in place of magnesium, particularly other alkaline earth metals and zinc, and other lower alkoxy groups may be employed in place of the methoxy groups of the compounds described in the examples.

The hydroxy-metal oxyarylalkyl amines disclosed hereinabove are claimed as components of lubricating oil compositions in our copending application Serial No. 358,534, filed May 29, 1933.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating composition comprising a mineral lubricating oil containing about 0.1 to about 0.5 per cent by weight of N,N'-bis(2-alkoxymetaloxy-5-alkylbenzyl)-1,2-diaminoethane, wherein the metal is selected from the group consisting of alkaline earth metals and zinc, the alkoxy group is a C_1 to C_5 alkoxy group and the alkyl group is a C_5 to C_{30} alkyl group.

2. Claim 1 wherein the metal is magnesium.
3. Claim 1 wherein the alkoxy group is methoxy.
4. Claim 3 wherein the metal is magnesium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,353,491	Oberright	July 11, 1944
2,406,564	Rogers	Aug. 27, 1946
2,424,204	Zimmer	July 15, 1947
2,431,011	Zimmer	Nov. 18, 1947
2,451,346	McNab et al.	Oct. 12, 1948
2,459,114	Oberright	Jan. 11, 1949
2,518,379	Rogers	Aug. 8, 1950
2,610,982	Hutcheson	Sept. 16, 1952