

UNITED STATES PATENT OFFICE

2,336,074

LUBRICATING OIL

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No Drawing. Application May 16, 1942,
Serial No. 443,307

7 Claims. (Cl. 252-48)

This invention relates to improved oils, particularly lubricating oils of the crankcase type. Although lubricating oils of the present invention are highly desirable for use in crankcases of passenger automobiles they are especially valuable for heavy duty use in truck, bus, aeroplane, marine and Diesel engines which operate for long periods of time at high temperatures.

The principal objects of the invention are to provide a lubricating oil of the heavy duty type which is resistant to oxidation and sludge formation, being non-corrosive to alloy bearings and other metal parts and free from varnish formation and ring sticking tendencies under the severe conditions of heavy duty service. These objects, and others which will appear hereinafter, are accomplished by us by providing a hydrocarbon oil containing bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides and salts thereof. These compounds and their preparation will be described in greater detail hereinafter.

When conventional lubricating oils are subjected to high operating temperatures for long periods of time, as in heavy duty service, they tend to decompose with the formation of complex and objectionable oxidation and decomposition products. Under the high temperature conditions prevailing in the engine these decomposition products polymerize to form lacquer-like deposits on or between the moving parts causing these parts to stick. Even larger quantities of polymerization products remain dispersed in the partly oxidized crankcase oil, and are readily precipitated to form a sludge when the engine cools or when fresh oil is added to the engine. These precipitated sludges become caked on heated metal surfaces and cut down the effective life of the engine.

A number of oil soluble detergents of the type of metal soaps, phenolates and alcoholates have been proposed and used in crankcase oils to dissolve or disperse the sludge and prevent lacquer deposits and stuck piston rings. Unfortunately, however, the great majority of these substances increase the rate of oxidation and their presence results in an increased concentration of acidic oxidation products in the oil. Increased quantities of these acidic oxidation products in the oil create in turn an even more serious difficulty for they attack and corrode alloy bearings commonly employed in internal combustion engines. Alloys composed of copper-lead, silver-cadmium, nickel-cadmium, etc. are widely used and are subject to attack by the acidic oxidation products formed in the oil.

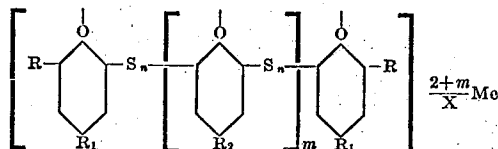
Certain anti-corrosion agents which have no detergent properties, have been added to lubricating oils in order to counteract the corrosive effect of the oxidation products of the oil. Although many of the detergents and anti-corrosion agents which have been previously mentioned perform their individual functions in lubricating oils the two separate additives do not cooperate to produce a satisfactory anti-corrosion and detergent action when used together. The function of a corrosion inhibitor is to cover the bearing surfaces and other corrodable parts of the engine with a passivating film that prevents corrosion of the metal by the organic acids and other corrosive products of the oil. A detergent, as its name implies, operates to remove adhering solids in the metal parts of the engine and thus produce a clean metal surface. Consequently mixtures of detergent with a corrosion inhibitor have proven to be ineffective over any extensive period of time since the detergent action of the sludge inhibitor tends to remove the corrosion inhibitor from the metal surface thus rendering it ineffective for the purpose intended.

The bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides and salts thereof avoid the above-described difficulties by possessing not only excellent corrosion inhibiting properties but also detergent characteristics, thus enabling us to provide a lubricating oil having a single additive effective to inhibit corrosion, sludge and varnish formation, ring sticking and other difficulties experienced with lubricating oils serving in a heavy duty capacity. These compounds are also extremely heat stable and are not easily decomposed in the oil at the high operating temperatures often encountered. They are also practically water insoluble and are not extracted from the oil by contact with water nor do they tend to promote the formation of emulsions with water in the oil.

Another advantage to be obtained by our use of bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides or their salts lies in their solubilizing action on certain materials which are known to be good detergents, anti-oxidants, etc. or have good corrosion inhibiting properties but which cannot ordinarily be used because of their oil insolubility. Certain dithiophosphates, such as di-(p-tertiary amyl phenol) dithiophosphate; calcium, barium, aluminum, zinc and magnesium stearates, palmittates, naphthenates, etc. are difficultly soluble in lubricating oils but because of their solubility in the compounds described herein it is possible to

add them to oils in this way in amounts sufficiently large to be effective.

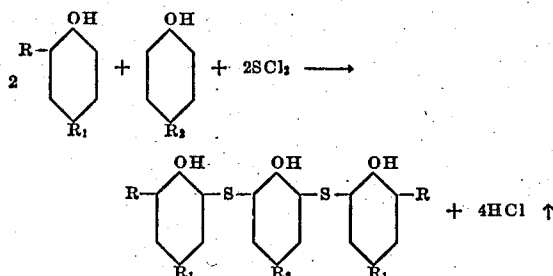
The bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides and salts thereof employed by us in preparing our improved lubricating oils are new chemical compounds and may be represented by the general formula:



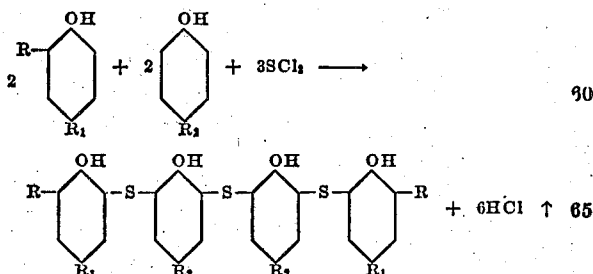
in which R, R₁ and R₂ are alkyl radicals, *n* is the small whole number 1 or 2 and *m* is the small whole number 1 or 2, Me is hydrogen or a salt-forming radical and X is the valence of Me. These compounds are described and claimed in our copending application, Serial No. 443,306, filed May 16, 1942.

The bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides and salts thereof illustrated by the general formula above may be prepared by reacting mixtures of 2,4-dialkyl phenols and 4-alkyl phenols with sulfur dichloride (SCl₂) or sulfur monochloride (S₂Cl₂) depending upon the type of sulfide desired as the reaction product. The salts of these compounds may be prepared from the resulting reaction product as will be described hereinafter.

When reacting two molecular proportions of 2,4-dialkyl phenol with one mole of 4-alkyl phenol and sulfur dichloride, for example, bis-(2,4-dialkyl phenol)-4-alkyl phenol dithio ether is formed as follows:



When using 2 moles of 2,4-dialkyl phenol mixed with 2 moles of 4-alkyl phenol with sulfur dichloride the reaction proceeds in the same way but with the formation of bis-(2,4-dialkyl phenol)-di-4-alkyl phenol trithio ether, a compound having four aryl groups, as follows:



If an excess of 4-alkyl phenol is employed the resulting product may have 5 or more aryl groups connected with sulfur linkages. Because of their high molecular weight these latter compounds tend to be resinous in character and we therefore prefer those of lower molecular weight as lubricating oil additives.

When sulfur monochloride is substituted in place of the sulfur dichloride the aryl groups are bound together with two sulfur atoms, —S—S—, and *n* in the general formula above becomes 2. These compounds possess similar properties to those in which a single sulfur atom links the different aryl groups and are also valuable in our improved lubricating oils.

In preparing these new compounds it is convenient to dissolve the various reactants in an inert solvent such as carbon disulfide, carbon tetrachloride, petroleum naphtha, ethylene dichloride, chlorobenzene, chloroform or the like. Merely mixing together the various reactants in the desired molecular proportions will cause the reaction to be brought about. No catalyst is ordinarily necessary. The reaction vessel should be fitted with agitating means and means for removing the HCl liberated. Towards the end of the reaction when the evolution of HCl has slowed considerably the preparation may be completed by heating the reaction mass to 50–60° C. for a few minutes to expel most of the remaining HCl. The product may then be washed with a dilute alkaline solution to remove traces of the acid. In the event that the material tends to emulsify during the washing step the addition of a small amount of butanol will help prevent emulsification. After washing the excess solvent may be removed from the product by evaporation under reduced pressure.

Salts of these compounds may be prepared by simple neutralization of the product with appropriate amounts of a desired salt-forming base such as NaOH, KOH, Ba(OH)₂, Ca(OH)₂, BaS, etc. or by double decomposition of the sodium salt with a desired metal salt such as, for example ZnCl₂, SnCl₂, AlCl₃, etc. Metal salts of these compounds may also be prepared by reacting the compounds just described with appropriate molecular amounts of finely powdered metallic aluminum, metallic magnesium turnings calcium metal, etc. A small amount of mercury chloride may be added to start the reaction. The reaction mixture may be gently heated on a steam bath at first but may require cooling later because of the exothermic character of the reaction. Metal salts may also be prepared by heating the compounds described with an alcoholate of a lower boiling alcohol, sodium methylete or aluminum butylate, for example, under conditions such that the lower alcohol is driven off.

The preparation of the bis-(2,4-diamyl phenol)-4-amyl phenol dithio ether will now be described. In this preparation 2,4-diamyl phenol is reacted with 4-amyl phenol and sulfur dichloride. As will be apparent we may use other 2,4-dialkyl phenols with other 4-alkyl phenols in the preparation of these new compounds. The various alkyl groups R, R₁ and R₂ in the general formula above may be all the same or may be all different. In this way it is possible to control the viscosity and oil solubility of the resulting compound. For good oil solubility compounds employed should have at least one, preferably more, alkyl groups of from 4 to 14 carbon atoms.

Of the various 2,4-dialkyl phenols which may be employed by us may be mentioned 2,4-diamyl phenol, 4-tertiary butyl orthocresol, 2-dodecyl-4-tertiary amyl phenol, 2,4-di-tertiary butyl phenol, 2-butyl-4-isopropyl phenol, 2-butyl-4-amyl phenol, 2-isopropyl-4-octyl phenol, etc. As 4-alkyl phenols we may use those such as p-cresol, 4-isobutyl phenol, 4-tertiary amyl phenol, 4-ethyl hexyl phenol, 4-octyl phenol, and the like. As

will appear from what has been said before the relative amounts of the 2,4-dialkyl phenol and 4-alkyl phenol can vary considerably depending upon the type of product desired. Ordinarily two molecular proportions of the 2,4-dialkyl phenol with one or two moles of the 4-alkyl phenol is preferred.

Example

164 parts by weight of p-tertiary amyl phenol and 468 parts by weight of 2,4-di-p-tertiary amyl phenol were dissolved in 260 parts by weight of benzol. 206 parts by weight of sulfur dichloride was then added to the solution with stirring, the temperature being maintained below 40° C. As soon as all the sulfur dichloride had been added the mixture was warmed to 50–60° C. for 10 minutes to complete the reaction and expel most of the HCl. The reaction mixture was then washed with warm dilute sodium carbonate solution to remove dissolved hydrogen chloride. The washed reaction product was then heated under reduced pressure to remove the benzol. Bis-(2,4-diamyl phenol)-4-amyl phenol dithio ether was obtained as a brown viscous product.

The barium salt of this product was obtained by dissolving 60 parts by weight thereof in 80 parts by weight of aromatic petroleum naphtha and 40 parts by weight of 95% alcohol. 41 parts by weight of finely ground $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was added and the mixture heated and solvents and water boiled off. More naphtha was added from time to time to replace that lost by evaporation. When the temperature has reached 125–135° C. the neutralization was substantially complete and all of the water had been expelled. The solution was then diluted with naphtha and after cooling filtered from traces of inorganic barium salts. The solvent was then removed by evaporation under reduced pressure. The product was a stiff viscous dark-colored liquid, easily soluble in light paraffin base lubricating oil.

If desired lubricating oil may be added to the product before all of the solvent has been removed by evaporation. This step facilitates blending of the oil with the additive and enables us to obtain a product containing 50–60% or more, of the additive suitable for sale and distribution to the trade for blending purposes.

Of the various bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides which may be employed by us we prefer to use the alkaline earth metal salts and particularly those salts in which the alkyl groups are of from 4 to 14 carbon atoms in length. These compounds are so very effective that it is possible to improve lubricating oils to a great extent by the use of very small amounts of the compound. In lubricating oils intended for ordinary purposes where high temperatures occur only occasionally, from 0.1–0.8% of the bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfide is sufficient. In an oil intended for heavy duty service it is generally advisable to use a little more, as for example 0.5–3% in the oil.

The effectiveness of the bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides in lubricating oils as corrosion inhibitors, detergents and anti-oxidants is demonstrated by the following results obtained by subjecting a S. A. E. # 10 solvent refined Pennsylvania oil containing 0.5% by weight of the barium salt of bis-(2,4-diamyl phenol)-4-amyl phenol dithio ether to the standard Underwood oxidation test. A sample of oil containing 0.5% of the barium salt of bis-(2,4-diamyl phenol)-di-4-amyl phenol trithio ether and a control

at the same time. The test consisted in heating 1500 cc. of the oil at 325° C. and continuously spraying a portion of the hot oil against a 3" x 10' freshly sanded copper baffle and two freshly sanded bearings to be tested for corrosion for 5 hours while permitting free circulation of air during the heating period. Samples of the oxidized oil were then examined for A. P. I. gravity, neutralization number and the bearings were examined for weight loss due to the effects of corrosion. The neutralization number indicates the formation of acids resulting from oxidation of the oil. The A. P. I. gravity also indicates the decomposition in the oil during the test, the lower values indicating a greater degree of decomposition. Results were as follows:

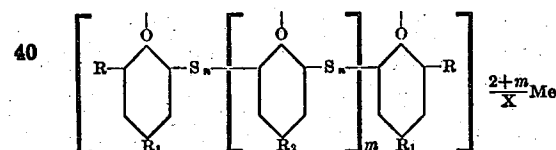
Underwood oxidation test

Composition	A. P. I. grav. used oil	Bearing loss, mg.		Neut. No.
		Cu-Pb	Ag-Cd	
Oil-control	25.4	96	1029	7.1
Oil+0.5% barium salt of bis-(2,4-diamyl phenol)-4-amyl phenol dithio ether	29.4	23	52	0.6
Oil+0.5% barium salt of bis-(2,4-diamyl phenol)-di-4-amyl phenol trithio ether	29.9	24	0	0.4

The results of these tests clearly show the anti-oxidant and anti-corrosion properties of oils treated with our new bis-(2,4-dialkyl phenol)-4-alkyl phenol sulfides.

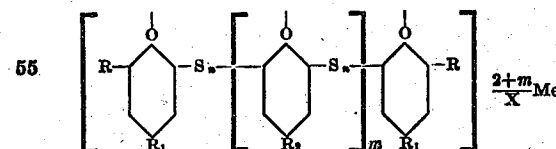
What we claim is:

1. A lubricating oil composition containing lubricating oil and small amounts of a compound having the general formula



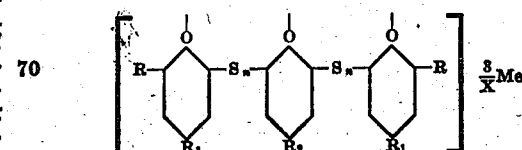
in which R, R₁ and R₂ are alkyl radicals, n is a small whole number less than 3, m is a small whole number less than 3, Me is a metal, and X is the valence of Me.

2. A lubricating oil composition containing lubricating oil and 0.1–3.0% of a compound having the general formula



in which R, R₁ and R₂ are alkyl radicals, at least one of which has from 4 to 14 carbon atoms, n is a small whole number less than 3, m is a small whole number less than 3, Me is a metal, and X is the valence of Me.

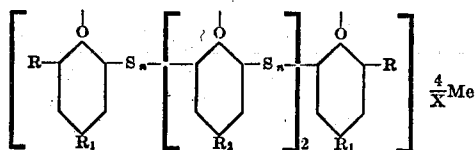
3. A lubricating oil composition containing lubricating oil and small amounts of a compound having the general formula



in which R, R₁ and R₂ are alkyl radicals, n is a

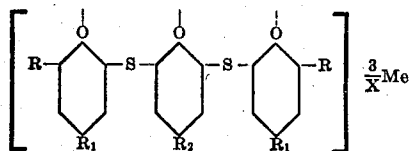
small whole number less than 3, Me is a metal, and X is the valence of Me.

4. A lubricating oil composition containing lubricating oil and small amounts of a compound having the general formula



in which R, R₁ and R₂ are alkyl radicals, n is a small whole number less than 3, Me is a metal, and X is the valence of Me.

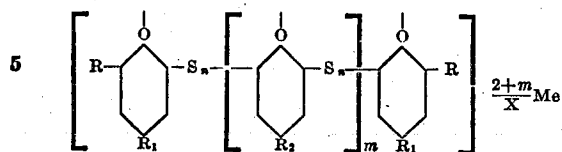
5. A lubricating oil composition containing lubricating oil and small amounts of a compound having the general formula



in which R, R₁ and R₂ are alkyl radicals, Me is a metal, and X is the valence of Me.

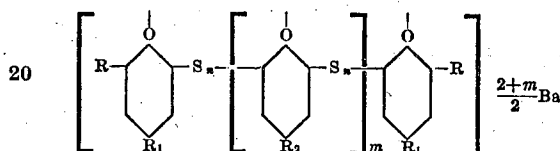
6. A lubricating oil composition containing lu-

bricating oil and 0.1-3.0% of a compound having the general formula



10 in which R, R₁ and R₂ are alkyl radicals, at least one of which has from 4 to 14 carbon atoms, n is a small whole number less than 3, m is a small whole number less than 3, Me is an alkaline earth metal, and X is the valence of Me.

15 7. A lubricating oil composition containing lubricating oil and 0.1-3.0% of a compound having the general formula



20 in which R, R₁ and R₂ are alkyl radicals, at least one of which has from 4 to 14 carbon atoms, n is a small whole number less than 3, and m is a small whole number less than 3.

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WILLIAM D. THOMAS, JR.