Patented Nov. 14, 1944 2,362,624

UNITED STATES PATENT OFFICE

2,362,624

LUBRICANT

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No Drawing. Application January 21, 1943, Serial No. 473,120

17 Claims. (Cl. 252—48)

This invention relates to improved oil compositions and particularly to improvements in lubricating oil compositions intended for use in internal combustion engines, such as spark ignition engines and compression ignition engines under severe conditions wherein corrosion, piston ring sticking, cylinder wear, carbon, and varnish formation may be encountered.

Straight petroleum lubricants are effective within certain defined limits of engine operating conditions, but when these limits are exceeded such lubricants frequently fail to give the desired performance demanded of them. In modern engines, designed to give increased performance, these limits are frequently exceeded and the use of straight mineral oils as lubricants promotes excessive varnish and carbon formation and corrosion to hard metal alloyed bearings.

It is an object of the present invention to provide a lubricant for internal combustion engines which will be effective in providing adequate lubrication for such engines. It is another object of the present invention to provide lubricants which are resistant to oxidation. It is a further object of the invention to provide a lubricant which will not be conducive to the formation of varnish and/or carbon, which will reduce engine wear, and which will be non-corrosive. Other objects and advantages of the invention will become apparent as the description thereof proceeds.

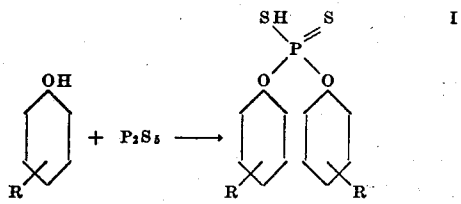
We have discovered that an improved lubricant having the above desired characteristics can be obtained by blending a lubricating oil, preferably a viscous petroleum oil, with from about 0.001% to about 10%, and preferably from about 0.01% to about 3% of the hereinafter described additive. This additive is a product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide and subsequently reacting the resultant reaction product with a sulfur chloride. The final product so obtained can be employed as such or as the neutralized product thereof, obtained in the manner hereinafter described. The alkylated hydroxyaromatic compound employed in the reaction can be an alkylated hydroxy benzene compound or an alkylated hydroxy polycyclic aromatic compound, such as, for example, an alkylated naphthol. The hydroxyaromatic compound employed may be phenol, a cresol, a xylenol, crude cresylic acids, naphthol, etc. Suitable alkylated hydroxyaromatic compounds are alkylated phenols obtained by mixing a phenol with sulfuric acid and passing an olefin or a mixture of olefins, preferably in the gaseous phase, through the liquid mixture, and subsequently washing the resultant product with water and a dilute caustic soda solution. Examples of suitable olefins which can be employed are butylene, isobutylene, amylene, and other olefins or mixtures of olefins. For example, refinery gases normally containing gaseous olefins, as well as cracked distillates or other high boiling hydrocarbon mixtures normally containing liquid olefins, can be used.

The alkylated hydroxyaromatic compound, such as the alkylated phenol or the alkylated naphthol, is reacted with a phosphorus sulfide such as P_2S_3, P_2S_5, P_4S_7 and preferably with P_2S_5, and the resultant product is then reacted with a sulfur chloride, such as S_2Cl_2 or SCl_2. The reaction of the alkylated hydroxyaromatic compound with the phosphorus sulfide can be carried out at room temperature or higher, the reaction being slower at the lower temperatures. We have found that the reaction is best conducted at a temperature of from about 200° F. to about 500° F. and preferably from about 300° F. to about 350° F. The reaction with sulfur chloride is best carried out at refluxing temperatures of about 200° F. to about 250° F.

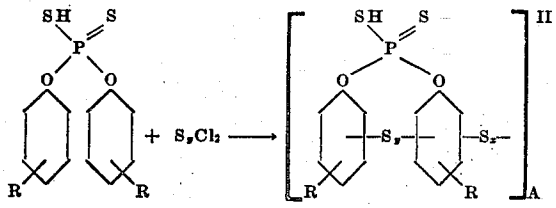
As aforesaid, the product resulting from the reaction of the sulfur chloride with the alkylated hydroxyaromatic compound-phosphorus sulfide reaction product can be employed as such, or the metal salts of the final reaction product can be employed. The metal salts can be obtained by neutralizing the final reaction products with an alkali hydroxide such as sodium hydroxide and potassium hydroxide, or with an alkali sulfide such as sodium sulfide or potassium sulfide, or by neutralization with a carbonate, hydroxide, or an oxide of an alkaline earth metal such as, for example, calcium and barium oxides and hydroxides. Heavy metal salts of the reaction product can be obtained by treating the neutralized product with a salt of the desired heavy metal, for example, tin, titanium, aluminum, chromium, cobalt, etc. The neutralization can be carried out in aqueous solution or by adding to the neutralized product the dry neutralizing agent, such as dry KOH, NaOH, Na_2S, Na_2CO_3, $KHCO_3$, CaO, etc. Ammonia or alkyl or aryl substituted ammonia compounds, such as amines can also be used as the neutralizing agent.

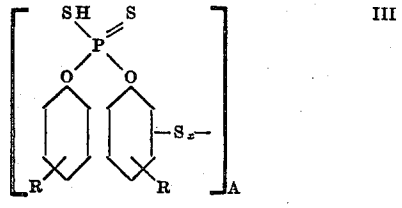
While the exact chemical and structural nature of the additive resulting from the above described sequence of reactions has not been definitely established and is largely obscure, it is believed that the reactions which probably take place and the products which probably are obtained can be illustrated by the following formu-

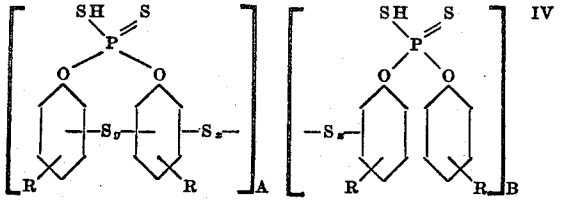
lae and equations. It is to be understood, however, that we do not wish to be held and limited by these formulae and equations. In the first step of preparing the improved additive wherein the alkylated arylol is reacted with a phosphorus sulfide, for example phosphorus pentasulfide, the following is believed to occur:



We do not definitely know the exact structure of the reaction product obtained when the product I is reacted with a sulfur chloride, but believe one or more of the compounds illustrated by the following empirical formulae are obtained:







wherein R is an aliphatic substituent, preferably an alkyl radical of sufficient molecular weight to render the products oil-soluble, y is 1 or 2, A and B are 1, 2, 3, 4 or 5, and wherein in formulae II and III x is 0 when A is 1, and ½ or 1 when A is greater than 1, and in formula IV x is ½ or 1.

The metal salts, prepared in the manner above described, may be represented by the above empirical formulae by substituting M (representing the metal equivalent of the hydrogen substituent) for the H of the mercapto (—SH) group.

The preparation of the herein described additive is exemplified by the following examples which are intended to be illustrative and not limitative of the invention.

Example 1.—Four mols of diamyl phenol were reacted with one mol of phosphorus pentasulfide within a temperature range of 300 to 350° F.; the reaction being completed in two hours. Two mols of the resultant reaction product, dissolved in three volumes of ethylene dichloride, were reacted with one mol of S_2Cl_2 at a temperature of 210° F., and refluxed for sixteen hours to eliminate hydrogen chloride. At the end of this period the reaction product was stripped of the ethylene dichloride by distillation. The final product contained 4.72% phosphorus, 15.6% sulfur and showed an acidity of 80 milligrams KOH per gram of product.

Example 2.—The sodium soap of the product obtained in Example 1 was prepared by treating the same with sodium sulfide at a temperature of 350° F. for two hours. The resultant product analyzed 3.92% phosphorus, 10.7% sulfur, and had an acidity of 3.6 milligrams KOH per gram of product. The product showed a strong positive test for sodium.

The effectiveness of these reaction products in improving the stability of lubricating oils is demonstrated by the following test: 250 cc. of the oil to be tested are heated at 332° F. in a 500 cc. glass beaker in the presence of 5 sq. in. of copper and 10 sq. in of iron. Four glass rods of about 6 millimeter diameter are suspended in the oil which is agitated with a glass stirrer having a 40° blade pitch and rotated at 1300 R. P. M. At stated intervals samples are taken and sludge, acidity, and viscosity values determined. The glass rods are also inspected for evidence of varnish formation. Varnish values are based on a visual rating in which a glass rod free of any varnish is given a rating of 10, while a badly varnished rod is given a rating of 1. Rods having appearances between these extremes are given intermediate values.

The following oils were subjected to the above described tests and the results obtained tabulated in Table I below.

1. The control oil (an SAE 20 high grade motor oil).

2. The control+1.5% of the additive of Example 1.

3. Control+1.5% of the neutralized additive of Example 2.

Table I

Oil	Vis. at 100° F. increase (48 hrs.)	Mg. sludge/10 g. oil			Acidity mg. KOH/g. oil			Varnish rating		
		24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.	24 hrs.	48 hrs.	72 hrs.
1	1,158	350	975	-----	9.9	16.6	-----	4.5	1	-----
2	----------	98	268	488	1.9	3.8	5.6	1	1	-----
3	96	23	33	138	1.7	2.9	3.9	10	10	10

It will be noted that oil No. 2 inhibited sludge and acidity formation, and oil No. 3 was very effective in materially inhibiting sludge and acidity formation and prevented varnish formation.

The effectiveness of the herein described additive in inhibiting corrosion to lead-containing bearings is demonstrated by the data presented in Table II. These data were obtained by immersing a 3 x .5 centimeter lead strip in 25 grams of oil maintained at a temperature of about 320° F. At intervals the lead strip was removed, rinsed with naphtha and weighed.

Table II

Oil	Mg. Pb corrosion at hours				
	24	48	72	96	120
Oil A—Control high grade 20 SAE motor oil	0	1.3	6.1	21.2	41.2
Oil B—Control + 1.5% of the product obtained as in Example 2 above	0.0	0.0	3.5	------	19.0

The above data show the marked corrosion in-

hibition obtained by the addition of small amounts of the herein described additive to lubricating oils.

Although we have described our invention as applied to mineral lubricating oils our invention contemplates the use of neutralized reaction products of a phosphorus sulfide and an alkylated hydroxyaromatic compound in products other than the mineral lubricating oils such as, for example, fuel oils, insulating oils, non-drying vegetable and animal oils, synthetic oils, greases and the like.

While we have described our invention by reference to various representative constituents and have illustrated the same by reference to specific examples thereof, our invention is not to be limited to the various representative compounds named or to the specific examples given but includes within its scope such modifications as come within the spirit of the appended claims.

We claim:

1. A composition comprising an oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide and reacting the resultant reaction product with a sulfur chloride.

2. A composition comprising an oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated phenol with a phosphorus sulfide and reacting the resultant reaction product with a sulfur chloride.

3. A composition as described in claim 2 in which the phosphorus sulfide is phosphorus penta-sulfide and the sulfur chloride is S_2Cl_2.

4. A composition as described in claim 2 in which the phosphorus sulfide is P_2S_5 and the sulfur chloride is SCl_2.

5. A composition comprising an oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated hydroxy polycyclic aromatic compound with a phosphorus sulfide and reacting the resultant reaction product with a sulfur chloride.

6. A composition as described in claim 5 in which the alkylated hydroxy polycyclic aromatic compound is an alkylated naphthol.

7. A lubricant comprising a viscous mineral oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide and then reacting the resultant reaction product with a sulfur chloride.

8. A lubricant as described in claim 7 in which the alkylated hydroxyaromatic compound is an alkylated phenol and the phosphorus sulfide is phosphorus pentasulfide.

9. The composition comprising an oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide, reacting the resultant reaction product with a sulfur chloride and subsequently neutralizing the product.

10. The composition comprising an oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide, reacting the resultant reaction product with a sulfur chloride and subsequently neutralizing the product with an alkaline neutralizing reagent containing a metal constituent.

11. A composition comprising an oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide, reacting the resultant reaction product with a sulfur chloride and subsequently neutralizing the last mentioned reaction product with sodium sulfide.

12. A lubricant comprising a mineral oil and from about 0.001% to about 10% of the product obtained by reacting an alkylated phenol with a phosphorus sulfide, reacting the resultant reaction product with a sulfur chloride and neutralizing the product so obtained with a basic reagent having a metal constituent.

13. A lubricant composition as described in claim 12 in which the basic reagent contains sodium.

14. A lubricant composition as described in claim 12 in which the basic reagent contains potassium.

15. A lubricant composition as described in claim 12 in which the basic reagent contains calcium.

16. An improvement agent for hydrocarbon lubricating oils comprising the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide and reacting the resultant reaction product with a sulfur chloride.

17. An improvement agent for hydrocarbon lubricating oils comprising the product obtained by reacting an alkylated hydroxyaromatic compound with a phosphorus sulfide, reacting the resultant reaction product with a sulfur chloride and then neutralizing the product so obtained.

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DISCLAIMER

2,362,624.—*James W. Gaynor*, Chicago, Ill., and *Clarence M. Loane*, Hammond, Ind. LUBRICANT. Patent dated Nov. 14, 1944. Disclaimer filed Feb. 20, 1946, by the assignee, *Standard Oil Company*.

Hereby enters this disclaimer to claims 12, 13, 14, 15, and 17 of said specification and also to the subject matter of claims 9 and 10 except as they apply to compositions in which the oil is other than a hydrocarbon lubricating oil or a mineral lubricating oil.

(*Official Gazette April 9, 1946.*)