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LUBRICATING COMPOSITIONS HAVING OIL-SOLUBLE PHOSPHORUS-CONTAINING CONDENSATION PRODUCTS

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The present invention relates to oleaginous base lubricants having increased load carrying capacity and improved resistance to oxidation. More particularly, it relates to lubricants containing a novel condensation product as an extreme pressure agent and anti-oxidant.

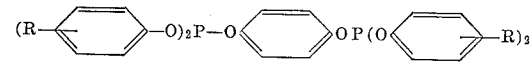
Mineral oil and synthetic lubricants, in the form of greases or free-flowing liquids, are called upon to ease friction and prevent damage to machinery operated at temperatures to as high as about 450° F. At elevated temperatures an internal combustion engine using these lubricants is an ideal oxidizing machine since the lubricant is violently agitated in the presence of air for long periods of time. In addition the stability of the lubricants is further drastically reduced due to contact with metallic surfaces which give up metallic particles to the lubricant that act as powerful oxidation catalysts. Furthermore, water also causes corrosion of metallic surfaces and accentuates oxidation of the lubricant. Aside from being stable under conditions of use the lubricant must exhibit anti-wear and load carrying or extreme pressure characteristics.

It has now been discovered that an oil-soluble condensation product of an alkylated phenol, phosphorous trichloride and hydroquinone is an excellent extreme pressure agent and when added in small effective amounts to oleaginous base lubricating oils provides a lubricant composition improved in oxidation resistance and anti-wear and extreme pressure characteristics. The alkyl-substituted phenols, including thiophenols, which are employed in the preparation of the condensation product are the monohydric phenols having at least one alkyl group, for instance, in an ortho- or para-position, i.e. nonmeta position. Representative alkyl phenols are those in which the alkyl group contains 1 to 18 carbon atoms, preferably 4 to 12 carbon atoms, for example, amyl phenol, octyl phenol, monyl phenol, p-tert-butyl phenol, p-tert-octyl phenol, the corresponding thiophenols, a mixture of phenols and the like. The alkylated phenol is one that gives an oil-soluble product in the condensation reaction.

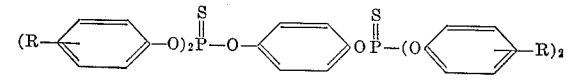
In the preparation of the condensation product of the present invention, the alkyl-substituted phenol, phosphorous trichloride and hydroquinone are reacted to provide an oil-soluble product. In the reaction the alkylated phenol to phosphorous trichloride to hydroquinone molar ratio is about 4:2:1, although slightly less or greater amounts of a given component may be used. Any method may be employed to produce the condensation product, but the preferred method comprises the following: a two-step procedure wherein (1) a stoichiometric amount of the alkyl-substituted phenol dissolved in a suitable solvent is slowly added to the phosphorous trichloride in the presence of a hydrogen chloride acceptor such as pyridine. In this first step $(RO)_2PCl$ is formed, wherein R represents the alkyl-substituted phenyl radical of the phenol. (2) In the second step the proper amount of hydroquinone dissolved in a suitable solvent is then slowly added and allowed to react with the remaining chlorine atom to couple the two $(RO)_2PCl$ molecules and from the condensation product of the present invention.

It has also been found that sulfurizing the condensation product or treating the condensation product with a phosphorous sulfide also gives products having the desired properties. Sulfurizing of the condensation product can be accomplished in accordance with methods well-known in the art, as for instance, heating one mole of condensation product with about 1 to 3 moles of sulfur. The phosphorous sulfide-treated derivative can be obtained by heating the condensation product with about 0.01 to 5.0 weight percent of phosphorous sulfide, for example, phosphorous pentasulfide, preferably about 0.05 to 0.5%. These reactions are usually conducted at temperatures of about 100 to 200° C., for say from about 2 to 50 or more hours.

The condensation product of an alkylated phenol, phosphorous trichloride and hydroquinone may be represented structurally as follows:



The sulfurized derivative of the above product can be represented structurally as follows:



R in the above structural formulae is an alkyl group of 1 to 18 carbon atoms, preferably 4 to 12 carbon atoms. The formula of the phosphosulfurized (i.e. phosphorous sulfide-treated) derivative is conjectural. At the low temperatures employed and since hydrogen sulfide is evolved during the reaction, one would expect the phosphorous sulfide to add on the aliphatic chain via the sulfur atom.

The lubricating oil base stock used in the present invention is of lubricating viscosity and can be for instance a solvent extracted or solvent refined oil obtained in accordance with conventional methods of solvent refining lubricating oils. Generally, lubricating oils have viscosities from about 20 to 250 SUS at 210° F. The base oil may be derived from paraffinic, naphthenic, asphaltic or mixed base crudes, and if desired, a blend of solvent-treated Mid-Continent neutrals and Mid-Continent bright stocks may be employed. A particularly suitable base oil used in the preparation of the composition may be described as a liquid mineral oil fraction having a viscosity index of about 100.

Grease compositions may be prepared by the incorporation or formation in the oleaginous base of grease-thickening fatty acid soaps of metals such as the alkaline metals of groups I and II of the periodic table. The soap content of the grease is generally about 2–25%. Although the use of high viscosity oils (above 100 SUS at 100° F.) gives harder greases, the use of a low viscosity non-naphthenic 100% solvent refined neutral Mid-Continent base lubricating oil provides a grease having better low temperature pumpability. The soaps are usually the alkali metal or alkaline earth metal, e.g. lithium, barium, calcium, etc.; salts of natural or synthetic long-chain carboxylic acids, such as stearic, hydroxy stearic or lauric acids, say of 12 to 20 carbon atoms.

The base oil of the fluid lubricant or grease may be a synthetic oil of lubricating viscosity. One type of synthetic oleaginous base used is an ester synthetic oil of lubricating viscosity which consists essentially of carbon, hydrogen and oxygen, e.g. di-2-ethylhexyl sebacate. Various of these lubricating materials have been described in the literature and generally their viscosity ranges from the light to heavy oils, e.g. about 50 SUS at 100° F. to 250 SUS at 210° F. and preferably 30 to 150 SUS at 210° F. These esters are of improved thermal stability, low acid number, and high flash and fire points. The complex esters, diesters, monoesters and polyesters may be used

alone or to achieve the most desirable viscosity characteristics, complex esters, diesters and polyesters may be blended with each other or with naturally-occurring esters like castor oil to produce lubricating compositions of wide viscosity ranges which can be "tailor-made" to meet various specifications. This blending is performed, for example, by stirring together a quantity of diester and complex ester at an elevated temperature, altering the proportions of each component until the desired viscosity is reached.

These esters are prepared fundamentally by the action of acids on alcohols. The mere mixture of an alcohol and acid at the proper temperature will react to produce an equilibrium mixture which includes the monoester. The same is true for the reactions of organic dibasic acids and glycols to produce synthetic lubricant polyester bright stock. The diesters are frequently of the type alcohol-dicarboxylic acid-alcohol, while complex esters are generally of the type X–Y–Z–Y–X in which X represents a monoalcohol residue, Y represents a dicarboxylic acid residue and Z represents a glycol residue and the linkages are ester linkages. These esters have been found to be especially adaptable to the conditions to which turbine engines are exposed, since they can be formulated to give a desirable combination of high flash point, low pour point, and high viscosity at elevated temperature, and need contain no additives which might leave a residue upon volatilization. In addition, many complex esters have shown good stability to shear. Greases which use these esters as the oleaginous base also have most of these characteristics.

Suitable mono- and dicarboxylic acids used to make synthetic ester lubricant bases can be branched or straight chain and saturated or unsaturated and they frequently contain from about 2 to 12 carbon atoms. The alcohols usually contain from about 4 to 12 carbon atoms. In general, the useful glycols include the aliphatic monoglycols of 4 to 20 or 30 carbon atoms, preferably 4 to 12.

The compositions of this invention incorporate a small amount of the condensation products sufficient to inhibit oxidation in the base oil of lubricating viscosity which is the major portion of the composition. This amount is generally about 0.1 to 10% or more. The preferred concentration should be the minimum amount to give adequate protection for the particular application desired and usually will be about 0.25 to 5%. In some cases where oil solubility might limit the amount of additive employed, dispersants may be used to increase the concentration. In these cases, it has been found that increased solubility is best obtained in highly refined oils by dissolving the dispersant in the oil before dissolving the additive.

Materials normally incorporated in lubricating oils and greases to impart special characteristics can be added to the composition of this invention. These include corrosion inhibitors, additional extreme pressure agents, anti-wear agents, etc. The amount of additives included in the composition usually ranges from about 0.01 weight percent up to about 20 or more weight percent, and in general they can be employed in any amounts desired as long as the composition is not unduly deleteriously affected.

The following examples are included to further illustrate the present invention but are not to be considered limiting.

EXAMPLE I

Condensation product of paratertiary octyl phenol, PCl_3 and hydroquinone

A 5 liter, fluted, 4-necked flask, equipped with a powerstat controlled heating mantle, thermometer, motor driven paddle stirrer and nitrogen inlet tube was used. The flask was flushed with nitrogen and a blanket of nitrogen continued during the addition of octyl phenol. The flask was then charged with 514 g. (6.5 moles) pyridine followed by 274 g. (2 moles) of PCl_3 in 500 g. toluene. The PCl_3 was weighed directly into the toluene to minimize contact with air and hydrolysis with the moisture in the air. After mixing the flask's contents thoroughly, 824 g. (4 moles) paratertiary octyl phenol dissolved in 1000 g. toluene were added dropwise over 2.5 hours. During this addition 400 g. toluene were added to reduce the viscosity of the agitating mass, and the temperature rose from room temperature to 53° C. Some cooling was employed by blowing a stream of air on the outside of the flask. After the addition of the phenol a Dean-Stark trap, and water cooled reflux condenser capped with a drying tube were attached to the flask. The nitrogen blanket was discontinued and entrance neck of the flask plugged. Agitation was continued and heat was applied to the mantle. The flask contents had a white precipitate, but the mixture was fluid enough for good mixing. After 1.3 hours and at a temperature of 102° C. the contents of the flask had turned to a tan color. One and a quarter hours later at 116° C. the toluene was refluxing and some of it was removed periodically through the trap. Some pyridine was lost in this process. After about 3.5 hours and the temperature still at 116° C. the run was shut down for overnight. The reaction mass now had an orange color. The next morning, 80 g. (1 mole) pyridine was added to insure the presence of enough pyridine to take up the hydrogen chloride formed in the next step. Then 110 g. (1 mole) of hydroquinone dissolved in 800 g. of ether was added while stirring the mass. The heat was turned on and after 15 minutes and at 55° C. ether was removed periodically to raise the temperature of the refluxing mixture. After 3.25 hours the removal of ether was discontinued since the pot temperature was 113° C. The removed ether contained no HCl when tested with a few drops of NaOH and phenophthalein indicator. The reaction was allowed to continue for 4.25 hours at 112–113 C.

The mass was then transferred to a breaker and allowed to stand overnight. The next day it was filtered through a Büchner funnel and the filter cake washed with ether and toluene and discarded. The filtrate weighed 2837 g. and 1987 g. of this were washed with a dilute solution of $NaHCO_3$ using ether and methanol to break the emulsion formed. This was followed by 3 washes with 1:2 parts of water and methanol. The crude undried product was then topped to 185° C. at 10 mm. The product weighed 632 g. representing a 91.5% yield. It was a cloudy off white viscous liquid and analyzed 5.79% P, 0.0% Cl and acid number 0.5.

EXAMPLE II

Sulfurization of condensation product Example I

To a one liter, fluted, 4-necked flask equipped with a reflux condenser motor driven stirrer, thermometer, and powerstat controlled heating mantle were charged 297 g. (0.3 mole) of the product described in Example I, 19.2 g. (0.6 mole) flowers of sulfur and 100 g. toluene. After heating and stirring the mixture for one hour the temperature was 135° C. and the toluene was not refluxing. One hundred grams of toluene were then added to obtain refluxing at lower temperature. This occurred at 123° C. The mixture was then refluxed and stirred for 27 hours and a clear yellow solution resulted. It was then topped to 195° C. at 12 mm. The clear yellow product weighed 314 g. It analyzed 5.52% P, 5.25% S and 0.0% Cl.

EXAMPLE III

Phosphorus pentasulfide treat of the condensation product of octylphenol, phosphorus trichloride and hydroquinone

A similar condensation product prepared as in Example I having 6.16% P, 0.0% Cl was treated with 0.28% P_2S_5 with agitation at about 150° C. for 5.5 hours in an open flask. The odor of H_2S was evident during the first 2 hours. The product analyzed, 6.20% P and had an acid number of 1.4.

EXAMPLE IV

Condensation product of para tertiary butyl phenol, phosphorus trichloride, and hydroquinone

This product was prepared in the same manner as Example I. After addition of the butyl phenol the reaction mass was maintained at toluene reflux temperature for 6.5 hours. After the addition of the hydroquinone-ether solution and removal of the ether the mass was refluxed at 114° C. for 3.25 hours. Part of the product was washed the same as Example I and then dried. It was topped to 175° C. at 13 mm. The yield was 80% of the theoretical. The viscous, cloudy off white product analyzed 7.22% P and 0.0% Cl.

EXAMPLE V

Sulfurization of the condensation product of p.-tert.-butyl phenol, phosphorus trichloride and hydroquinone

A product similar to that prepared in Example IV was sulfurized for 24 hours at 118° C. in Example II procedure. It was topped to 186° C. at 12 mm. The product was a soft solid and analyzed 6.98% P, 7.21% S and had an acid number of 14.9.

EXAMPLE VI

Various amounts of the compounds of Example I through IV were incorporated in an oil blend (identified in Table I below) and the lubricant compositions were subjected to a modified railroad oxidation test. For purposes of comparison a run without the additive of the present invention was included. In this test, 350 cc. of the oil are charged to a large tube and maintained at 285° F. in an oil bath for 144 hours while introducing 5 liters of oxygen per hour at the bottom of the tube in the presence of a copper on lead coupon measuring 1 x 3 inches.

TABLE I.—MODIFIED RAILROAD OXIDATION TEST
Oil Blend B*

	Example				
	None	I	II	III	IV
Additive:					
Concentration, percent		0.5	1.0	1.0	1.0
Sample No. 803		6,065	6,089	6,088	6,079
Oil Blend:					
Sample No. 750	6,041	6,032	6,054	6,053	6,050
KV/100° F	27.63	27.38	28.44	28.46	28.06
RR Oxidation Test:					
KV/100° F	34.6	27.45	28.80	28.2	28.0
Viscosity Rise, percent	25	0.26	0.13	−0.9	0.0
Catalyst Wt. Chge. mg.	−5.7	+1.0	+0.5	+0.7	−5.1
Acid Number	1.30	0.90	0.72	1.93	1.69
Pentane Insol. percent	0.033	0.013	0.006	0.011	0.005
Initial pH	2.7	1.8	2.3	1.9	1.6

*Oil Blend B consisted of a 30/70 blend of Solvent Refined Mid-Continent Neutrals, having viscosity indices of 95 and viscosities of about 80 and 160 SUS at 100° F., respectively, plus 1% of a methacrylate ester polymer which is a commercial ashless detergent.

The data of Table I demonstrate that the addition of small amounts of the additives of the present invention improves the oxidative stability of the oil remarkably with reference to percent viscosity change, metal corrosiveness and pentane insolubles formation.

EXAMPLE VII

One weight percent of the compounds of Examples II and III and a mixture of .5 weight percent of the compound of Example I and .5 weight percent of the compound of Example II were each incorporated into a base oil B (identified in Table I) and the lubricant compositions were subjected to Shell 4-ball extreme pressure and wear tests. For purposes of comparison base oil A (identified in Table II) and base oil B without the additives of the present invention were also tested. The results of the tests are shown in Table II.

The data of Table II demonstrate that the additives of the present invention in addition to being excellent antioxidants also possess extreme pressure and antiwear properties.

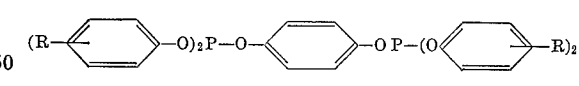
TABLE II.—SHELL FOUR BALL TESTS

	Sample Number	Wear	Extreme Pressure	
		2 Hrs. 7 Kg. 110° C. 640 r.p.m. Average Wear Scar mm.	Weld, Kg.	Mean Hertz Load
Oil:				
Base Oil (A) [1]	750-6, 076	0.54	141	11.4
Base Oil (B) [2]	750-6, 075	0.51	141	16.6
Oil (B) Containing:				
1.0% Example II	750-6, 054	0.22	141	26.1
1.0% Example III	750-6, 053	0.23	141	25.9
0.5% Example I plus 0.5% Example II	750-6, 058	0.23	158	26.7

[1] Base Oil (A) is a 30/70 blend of Solvent Refining Mid-Continent Neutrals, having V.I.'s of about 95 and viscosities of about 80 and 160 SUS at 100° F., respectively.
[2] Base Oil (B) is Base Oil (A) plus 1% ashless detergent as in tests of Table I.

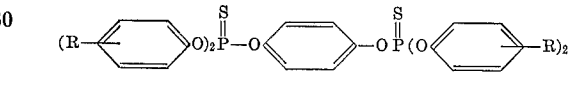
We claim:

1. An oleaginous lubricant composition consisting essentially of a mineral base oil of lubricating viscosity and an amount sufficient to give improved antioxidant and extreme pressure properties to the composition of an oil-soluble condensation product having the structural formula:



wherein R is an alkyl group of 1 to 18 carbon atoms.

2. An oleaginous lubricant composition consisting essentially of a mineral base oil of lubricating viscosity and an amount sufficient to give improved antioxidant and extreme pressure properties to the composition of an oil-soluble condensation product having the structural formula:



wherein R is an alkyl radical of 1 to 18 carbon atoms.

3. The composition of claim 2 wherein R is an alkyl group of 4 to 12 carbon atoms.

4. The composition of claim 1 wherein the condensation product is phosphosulfurized.

5. The composition of claim 1 wherein the condensation product is present in the range of about 0.25 to 5% by weight of the lubricant composition.

6. An oleaginous lubricant composition consisting essentially of a mineral base oil of lubricating viscosity and an amount sufficient to give improved antioxidant and extreme pressure properties to the composition of

an oil-soluble condensation product having the structural formula:



wherein R is an alkyl group of 4 to 12 carbon atoms.

7. The composition of claim 2 wherein R in the structural formula is a para-tertiary alkyl radical.

8. The composition of claim 7 wherein the condensation product is phosphorsulfurized.

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