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LUBRICATING OIL

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This invention relates to a lubricating oil composition having improved characteristics especially with respect to oxidation and corrosion. My improved lubricating oil composition may be used with particular advantage as a heavy duty oil lubricant for gasoline and Diesel engines, and is also particularly desirable as a turbine oil, as an hydraulic fluid or for like purposes.

In my Patent 2,379,312, I have described and claimed a novel class of compounds resulting from the reaction of an alkylated phenol with the condensation product of a terpene, such as present in turpentine, and phosphorus pentasulfide, P_2S_5. The turpentine-P_2S_5 condensation product is the subject of my co-pending application Serial No. 494,688, filed July 14, 1943.

I have now discovered that the compounds to which my Patent 2,379,312 is directed are especially effective in repressing or inhibiting the deterioration of lubricating oil compositions and the corrosion of metal parts in contact therewith.

I am at present unable to definitely define by chemical formula either the condensation products of turpentine and P_2S_5, or the products resulting from the reaction of said condensation products with the alkylated phenols. For brevity, I shall herein refer to the former as the turpentine-P_2S_5 condensation product and to the compounds resulting from the reaction of said condensation products with the alkylated phenols as my inhibitor.

The characteristics of the inhibitor used in the compounding of the lubricating oil composition of my present invention vary somewhat depending upon the characteristics of the turpentine-P_2S_5 condensation product and the nature and proportions of alkylated phenol used in its preperation. Generally, these compounds are relatively acidic and are highly soluble in mineral oils.

The lubricating oil composition of my present invention may consist solely of the lubricating oil constituent and my inhibitor. However, the inhibitors of my present invention have been found to be compatible with other desirable lubricating oil addends and the inclusion of such other addends, especially addends of the type known as detergents, is within the contemplation of my present invention and constitutes an important aspect thereof.

The inclusion of certain so-called detergents, for instance, in internal combustion engine lubricants, has been found highly advantageous. An especially effective lubricating oil composition for the lubrication of internal combustion engines, and the like, contemplated by the present invention, is one comprising, in addition to the lubricating oil fraction and my inhibitor, a minor proportion of a calcium-containing detergent, for instance, a calcium salt of iso-octyl salicylate, or a calcium salt of capryl salicylate. These and

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various other organic calcium salts have been found particularly effective as detergents in lubricating oil compositions used in internal combustion engines, the two particularly named calcium compounds being more fully described in Letters Patent 2,347,547 and 2,339,692, issued on applications of Willard L. Finley.

A further highly effective lubricating oil composition contemplated by my present invention is one comprising, in addition to the lubricating oil constituents and my inhibitor, a calcium petroleum sulfonate, as a detergent. Other detergents which may be used with advantage include the barium phenolate of sulfurized diamyl phenol, such as currently marketed under the trade name "Aerolube B," metallic phenolates of sulfurized tertiary amyl phenol, such as currently marketed under the trade names "Calcium Paranox" and "Barium Paranox," and various other metallic soaps, either basic or neutral, metallic sulfonates, alcoholates and alkoxides and metallic derivatives of alkylated salicylic acid.

When used in conjunction with these detergents, particularly the calcium salts, including the calcium petroleum sulfonates previously mentioned, these detergents and my inhibitors have been found to complement each other, so that the effectiveness of each is promoted. For example, the phosphorus acidity of the inhibitor appears to be neutralized by the calcium of the detergent, thus minimizing any tendency of the former to promote sludge formation. Further the tendency of the detergent to promote oxidation of the oil at the termination of its oxidation induction period is also minimized by the presence of my inhibitor. Each of these desirable ends is accomplished without destroying the effectiveness of either the detergent or the inhibitor.

The proportions of the inhibitor used in the compounding of my improved lubricating oil compositions may be varied somewhat but, in any case, only a minor proportion is used. The optimum proportion to be used will depend upon whether or not a detergent, such as previously mentioned, is present and the particular use to which the lubricating oil composition is to be put. The optimum proportion will also vary, depending upon the particular member of my new class of inhibitors used.

In the preparation of my improved lubricating oil composition, I have found it advantageous to prepare the inhibitor in solution in about an equal weight of a petroleum lubricating oil fraction, as hereinafter more fully described. As a motor oil which does not contain detergents, 0.2 to 0.5% of the 50% concentrate of my inhibitor may, with advantage, be admixed with the lubricating oil constituent. When used as an anti-oxidant in turbine oils or hydraulic oils, the 50% concentrate may be added to the lubricating con-

stituent in proportions advantageously ranging from about 0.1 to about 0.3% by weight. In heavy duty oils containing detergents, such as previously mentioned, for use in gasoline or Diesel engines, the 50% concentrate of my inhibitor may, with advantage, be added in proportions ranging from about 1% to about 5% by weight, depending upon the nature and concentration of the detergent, the severity of the service for which the lubricating oil composition is to be used and the particular inhibitor employed.

However, these inhibitors are acidic phosphorus derivatives and phosphorus acidity has been found to have a general tendency to promote polymerization and sludge formation in mineral lubricating oils. In internal combustion engine lubricants, where sludge formation must be minimized, the use of the inhibitor in proportions exceeding about 1% by weight, in the absence of detergents such as previously noted, is not generally advisable. However, proportions within the indicated range will be found not to cause noticeable or objectionable sludging under such conditions. In gear lubricants, for example, where polymerization and sludging is less critical, larger proportions of the inhibitor may be employed.

For optimum results, when used in conjunction with one of the previously-noted calcium detergents, the proportion of the inhibitor should generally not exceed that which will be neutralized by the calcium salt detergent, for, with an excess of the inhibitor, residual phosphorus acidity will remain with its characteristic tendency to promote sludge formation. The optimum ratio of the inhibitor to the detergent will depend upon the basicity of the detergent and upon the amount of P_2S_5 equivalent used in the preparation of the inhibitor, and may be determined for any particular set of conditions by simple test.

Various petroleum lubricating oil fractions may be used, for instance, solvent-treated Mid-Continent neutrals or a blend of such Mid-Continent neutrals with bright stock or a solvent-refined lubricating oil fraction from a Pennsylvania crude. Characteristics of two lubricating oil constituents which have been used with advantage, and which were used in the compounding of the lubricants hereinafter set forth as illustrative of my invention, appear in the following Table I, in which base oil A is a solvent-treated Mid-Continent, S. A. E. 10 oil and base oil B is a sulfonated Mid-Continent S. A. E. 30 oil prepared by treating a raw Mid-Continent stock with 40 pounds of 99.3% sulfuric acid per barrel, separating the sludge formed, neutralizing the acid oil with lime, heating the mixture to drive off all water present and filtering the dehydrated oil.

Table I

	Base oil	
	A	B
Gravity, ° A. P. I.	29.5	25.5
Flash, ° F.	405	435
Fire, ° F.	480	500
Viscosity at 100° F. SUS	249.6	512.1
Viscosity at 210° F. SUS	49.0	60.2
Viscosity index	92.8	77.0
Pour, °F.	5	5
Percent sulfur	0.20	0.35
Percent calcium		0.061

The invention will hereinafter be illustrated by specific examples of my improved lubricating oil composition. Since the characteristics of the inhibitor are somewhat affected by the characteristics of the turpentine-P_2S_5 condensation product used in its preparation and the nature and proportions of the alkylated phenol reacted therewith, the illustrations of my lubricating oil compositions will include a description of the preparation of the particular inhibitor used.

In the preparation of the intermediate turpentine-P_2S_5 condensation product to be used in preparing my inhibitor, the molar ratio of turpentine to P_2S_5 used is with advantage approximately 3:1, though this ratio may be varied somewhat as subsequently described.

The reaction of turpentine with P_2S_5 is highly exothermic and proceeds spontaneously after being initiated by slight heating. A desirable method of effecting the reaction is to heat the turpentine in a vessel to about 200° F. or slightly higher and then, without further heating, slowly stirring in the phosphorus pentasulfide in the powdered form. The heat of reaction is great and, consequently, the addition should be made slowly, so as to avoid the possibility of the reaction's becoming uncontrollable. The characteristics of the inhibitor are favorably affected by using in its preparation a turpentine-P_2S_5 condensation product in the preparation of which the temperature during the mixing was not permitted to exceed about 250° F., although higher temperatures are permissible.

After the addition is completed, it is usually necessary to apply heat externally to complete the reaction. The temperature during this last stage is preferably maintained at about 300° F., though temperatures of about 200° F. to 400° F. may be employed. This second stage of the operation should be continued until all of the P_2S_5 is dissolved. The material thus prepared is a viscous liquid at elevated temperatures which solidifies on cooling to room temperature.

The turpentine-P_2S_5 concentration products, thus prepared, are, in the absence of excess turpentine, brittle, resinous solids which dissolve readily in lubricating oils or in excess turpentine to form liquids. Such solutions of high concentration are relatively viscous. However, the viscosity of the solution decreases rapidly as the proportion of the solvent is increased from 25% to 75%.

In general, my inhibitor may be prepared by adding the alkylated phenol gradually to the turpentine-P_2S_5 condensation product prepared as previously described. Such addition is advantageous at a temperature of about 230° F. However, this temperature may be varied, temperatures as high as 300° F. being used without damage to the product.

In reacting the alkylated phenol with the turpentine-P_2S_5 condensation product, very little heat is evolved. After the alkylated phenol has been added, the mixture is maintained at an elevated temperature, advantageously about 200° F. for about an hour with stirring.

The proportions of the alkylated phenol may be varied over a considerable range without loss of the effectiveness of the resulting inhibitor. The optimum proportion of alkylated phenol used is, to a considerable extent, dependent upon the ratio of turpentine to P_2S_5 used in the preparation of the intermediate condensation product. Particularly desirable results have been obtained using proportions of reactants equivalent to about 2 moles of P_2S_5, 6 moles of turpentine and 3 moles of alkylated phenol, assuming the molecular weight of turpentine to be 136. However, the proportions of these constituents

may be varied somewhat. Satisfactory results may be obtained where for each two moles of P_2S_5, 5 to 7 moles of turpentine and 1 to 5 moles of the alkylated phenols are used. However, I have found it desirable that the total number of moles of turpentine and alkylated phenol used for each two moles of P_2S_5 fall within a range of about 8 to 10. Also, in the preparation of the turpentine P_2S_5 condensation product used in preparing the inhibitor, I have found it desirable that no unreacted P_2S_5 remain in the product.

In the preparation of my new class of inhibitors, considerable latitude is permissible in the selection of the alkylated phenol used. In general, the alkyl radical of the alkylated phenol should be a saturated aliphatic group. Each molecule of the alkylated phenol may contain one or more such groups. The number of carbon atoms in each aliphatic group is not critical. Desirable products may be obtained where each such group contains from 1 up to 12 to 16, or even up to 25 to 35 carbon atoms. Alkylated phenols containing 5 or more carbon atoms in each alkyl group have been found especially desirable in the preparation of my new inhibitors, because of the great oil solubility of the resultant products. The alkyl group or groups may be either normal or branched chain.

Alkylated phenols, herein designated codimer alkylated phenols, such as prepared by the reaction, in the presence of sulfuric acid, of phenols with the olefines in commercial codimer, resulting from the phosphoric acid polymerization of mixed olefines of 4 carbon atoms or less per molecule and comprising propylene, butene-1, butene-2 and iso-butylene, the codimer consisting of a major portion of C_8 olefines, together with some C_6, C_7, C_9, C_{10}, C_{11}, C_{12} and higher olefines, have been used with advantage. These codimer alkylated phenols are comprised primarily of mono- and poly-alkylated phenols having alkyl groups, as noted above, but with C_8 alkyl groups predominating.

I have further used with advantage in the preparation of my improved inhibitors, alkylated phenols, herein designated codimer bottoms alkylated phenols, herein designated codimer bottoms alkylated phenols, prepared by the method just described for the preparation of codimer alkylated phenols except that the phenol was reacted with codimer bottoms, the codimer bottoms used being the bottoms obtained by a redistillation of the previously described codimer to a 350 to 360° F. end point overhead. This bottoms was comprised primarily of C_{12} olefines, but contains some somewhat lower and some somewhat higher molecular weight olefines.

In the preparation of the turpentine-P_2S_5 condensation product, either steam-distilled wood turpentine or gum spirits may be used. Such turpentine consists mainly of alpha pinene, a bicylic terpene having the empirical formula $C_{10}H_{16}$. Pure alpha pinene and other more costly terpenes will react similarly with P_2S_5, but, for reasons including economic considerations, I prefer to use the more readily available turpentines. The turpentine used in the specific examples herein was a technical grade steam-distilled wood turpentine comprising about 90% alpha pinene.

The following specific examples of inhibitors used in the compounding of my improved lubricating oil compositions and the procedure by which such inhibitors may be prepared are given as illustrative of my invention. It will be understood, however, that my invention is not limited to lubricating oil compositions containing the particular inhibitors illustrated.

Example I

2040 grams of turpentine was placed in a flask equipped with stirrers, a thermometer and a funnel and heated to a temperature of 240% F. There was then slowly added with stirring 1110 grams of powdered phosphorous pentasulfide at a rate such that the temperature of the mixture did not rise above 275° F. After all of the phosphorus pentasulfide had been added, the temperature of the mixture was raised to 300° F. and maintained at this temperature for 2 hours, at the end of which period all of the P_2S_5 had dissolved and the product was a viscous amber-colored liquid. This turpentine-P_2S_5 condensation product was then cooled to 230° F. and 1230 grams of p-tert-amylphenol was added and the mixture heated for 1 hour at a temperature of 200° F. with stirring. The resulting product was found by analysis to have an acid number of 46.5 and a saponification number of 132.1, and to contain 6.82% phosphorus and 17.4% sulfur 4380 grams of this product was admixed with 4380 grams of a light petroleum lubricating oil fraction having the characteristics set forth in the following Table II. The 50% concentrate thus prepared was found by analysis to have an acid number of 30, a saponification number of 65.5 and an A. P. I. gravity of 11.4 and to contain 3.42% phosphorus and 9.55% sulfur.

Example II

To a turpentine-P_2S_5 condensation product, prepared as described in the foregoing example from 1632 grams of turpentine and 888 grams of P_2S_5, at a temperature of 300° F. there was added 1404 grams of diamylphenol, and the mixture heated at 250° F. for 1 hour with stirring. To the resulting product there was added 3,924 grams of the base oil used in Example I to produce a 50% concentrate which was found by analysis to have an acid number of 27.5, a saponification number of 60.7 and an A. P. I. gravity of 13.4, and to contain 3.04% phosphorus and 8.30% of sulfur.

Example III

To a turpentine-P_2S_5 condensation product, prepared as in Example I from 2040 grams of turpentine and 1110 grams of P_2S_5, at a temperature of 230° F. there was added 1425 grams of a butene alkylated phenol having a phenol number of 294.3 and an apparent molecular weight of 190. The mixture was heated at a temperature of 200° F. for 1 hour with stirring. The resultant product was found by analysis to have an acid number of 57.5, a saponification number of 136.0 and to contain 7.13% of phosphorous and 17.82% sulfur, 4575 grams of the product prepared as described was thoroughly blended with an equal weight of the light petroleum lubricating oil fraction used in Example I to produce a 50% concentrate of the inhibitor. This concentrate was found by analysis to have an acid number of 30.3, saponification number of 65.6 and an A. P. I. gravity of 12.2 and to contain 3.75% phosphorus and 9.31% sulfur.

Example IV

To a turpentine-P_2S_5 condensation product prepared as in Example I, from 2040 grams of turpentine and 1110 grams of P_2S_5, there was added 1700 grams of a codimer alkylated phenol having a phenol number of 247.4 and an apparent

molecular weight of 227. The mixture was reacted by heating at a temperature of 250° F. for 1 hour with stirring. 4850 grams of the product thus prepared was then intimately blended with an equal weight of the petroleum lubricating oil fraction of the type used in Example I to produce a 50% concentrate of the inhibitor. This concentrate was found by analysis to have an acid number of 25.8, a saponification number of 61.6 and an A. P. I. gravity of 12.6 and to contain 3.22% phosphorus and 8.63% sulfur.

EXAMPLE V

To a turpentine-P_2S_5 condensation product prepared as in Example I from 816 grams of turpentine and 444 grams of P_2S_5, there was added 1293 grams of a codimer bottoms alkylated phenol having a phenol number of 129.6 and an apparent molecular weight of 432. This mixture was caused to react by heating at a temperature of 200° F. for one hour with stirring. The product was then diluted and intimately blended with an equal weight of the petroleum lubricating oil fraction used in Example I to produce a 50% concentrate of the inhibitor. This concentrate was found by analysis to have an acid number of 17.5, a saponification number of 43.0 and an A. P. I. gravity of 16.3, and to contain 2.78% phosphorus and 6.87% sulfur.

EXAMPLE VI

To a turpentine-P_2S_5 condensation product, prepared as in Example I from 2040 grams of turpentine and 1110 grams of P_2S_5, cooled to a temperature of 230° F., there was added 1755 grams of diamyl phenol and the mixture heated with stirring for about 1 hour at a temperature of 190 to 200° F. The product was found by analysis to have an acid number of 51.2, a saponification number of 120.4 and to contain 6.26% phosphorus and 16.3% sulfur.

EXAMPLE VII

A turpentine-P_2S_5 condensation product, prepared as in Example I from 2040 grams of turpentine and 1110 grams of P_2S_5, was admixed with 2050 grams of codimer alkylated phenol having a phenol number of 203.7 and an apparent molecular weight of 275 and the mixture heated at 200° F. for 1 hour with stirring. The product was found by analysis to have an acid number of 51.3 and a saponification number of 117.6 and to contain 3.98% phosphorus and 15.82% sulfur.

EXAMPLE VIII

A turpentine-P_2S_5 condensation product, prepared as in Example I from 1632 grams of turpentine and 888 grams of P_2S_5, was reacted as previously described with 2149 grams of a codimer bottoms alkylated phenol having a phenol number of 151.2 and an apparent molecular weight of 371. The product was found by analysis to have an acid number of 45.5, a saponification number of 104.5 and to contain 5.15% phosphorus and 13.93% sulfur.

EXAMPLE IX

A turpentine-P_2S_5 condensation product, prepared as in Example I from 2040 grams of turpentine and 1110 grams of P_2S_5, was admixed with 2670 grams of codimer bottoms alkylated phenol consisting of equal proportions of a codimer bottoms alkylated phenol having a phenol number of 125.9 and an apparent molecular weight of 445 and a codimer bottoms alkylated phenol having a phenol number of 124.7 and an apparent molecular weight of 448. The mixture was heated for 1 hour at 200° F. with stirring. The product was found by analysis to have an acid number of 45.8 and a saponification number of 98.0 and to contain 4.82% phosphorus and 12.68% sulfur.

EXAMPLE X

A turpentine-P_2S_5 condensation product, prepared as in Example I, from 1632 grams of turpentine and 888 grams of P_2S_5, was reacted as previously described with 2570 grams of codimer bottoms alkylated phenol consisting of equal proportions of a codimer bottoms alkylated phenol having a phenol number of 134.9 and an apparent molecular weight of 415 and a codimer bottoms alkylated phenol having a phenol number of 127.5 and an apparent molecular weight of 441. The product was found by analysis to have an acid number of 40 and a saponification number of 97.1 and to contain 4.72% phosphorus and 12.12% sulfur.

The light petroleum lubricating oil fraction used as the diluent in various of the foregoing specific examples was a Mid-Continent neutral having the characteristics set forth in the following table:

Table II

Gravity, °A. P. I.	27.9
Flash, °F	365
Fire, °F	405
Viscosity at 100° F., SUS	107.8
Viscosity at 210° F., SUS	39.5
Pour, °F	20
Color	2—

The codimer alkylated phenol and the codimer bottoms alkylated phenol were those previously described herein.

For the purpose of further illustrating my invention and the advantage derived therefrom, I have herein set forth the results of oxygen absorption and bearing corrosion tests of various of my improved lubricating oil compositions. The advantages of my present invention with respect to oxidation and corrosion characteristics of my improved lubricating oil compositions are illustrated by their mean oxygen absorption rates, as compared with the oxygen absorption rates of the base oil, and the corrosion losses of bearing metal in contact with the respective lubricants.

These tests were carried out in a closed system in which pure oxygen was circulated through 156 grams of the lubricant being tested. The pressure of the system was maintained constant by introducing oxygen from a burette, and the sample was maintained at 360° F. and in contact with two pieces of copper-lead bearings having an approximate combined area of one square inch of copper-lead alloy surface and one square inch of steel surface. The rate of oxygen absorption is calculated as milliliters of oxygen absorbed per minute per 100 grams of oil, measuring the oxygen under standard condition of temperature and pressure. The bearing corrosion loss is reported as milligrams, the plus sign indicating gain in weight.

When subjected to the foregoing test, the mean oxygen absorption rate of base oil A, previously identified, was 25.6 milliliters, and the bearing corrosion loss was 5.8 milligrams. By incorporating in this base oil 0.1% of my inhibitor prepared as described in Example II, the mean oxygen absorption rate was reduced to 9.5 milliliters and the bearing corrosion loss reduced to 5.2 milligrams. By compounding with this same base oil

0.25% of said inhibitor, the mean oxygen absorption rate was reduced to 2.0 milliliters and the bearing corrosion loss completely eliminated, there being an increase in the bearing weight of 1.2 milligrams.

The proportions of inhibitor indicated as used in each of the tests herein are based on the weight of the undiluted inhibitor, as distinguished from the 50% concentrate previously described.

Further illustrations of my improved lubricating oil compositions and the characteristics thereof with respect to oxygen absorption rates and bearing corrosion losses are set forth in the following Table III. In each instance, the inhibitor was compounded with previously identified base oil B, the characteristics of base oil B without the inhibitor being included for comparison.

Table III

Inhibitor		Mean rate of O_2 absorption ml. per min. per 100 gms.	Bearing metal corrosion loss, mgs.
Identity	Proportion, per cent		
None		21.6	9.8
Example I	0.1	4.08	+1.5
Example VI	0.1	3.80	+0.6
Example III	0.1	4.28	+0.2
Example VII	0.1	3.74	+2.0
Example VIII	0.1	4.15	+1.5
Example IX	0.1	3.19	+1.2
Example X	0.1	4.07	+1.7

From the results of these tests, it appears that though the base oil had high corrosion rates and high oxygen absorption rates, the lubricating oil compositions prepared therefrom, in accordance with my invention, showed in each instance substantially reduced oxygen absorption rates and bearing corrosion losses. These results are obtained where the composition consists solely of the lubricating oil constituent and my inhibitor or also contains a detergent, such as previously noted, for instance, calcium petroleum sulfonates. However, the latter compositions are particularly advantageous, as previously noted herein.

I claim:

1. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil and a minor proportion, effective to retard oxidation of the oil, of an inhibitor resulting from the reaction of an alkylated phenol with the condensation product of turpentine and phosphorus pentasulfide, the alkyl group of the alkylated phenol being a saturated aliphatic radical.

2. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil and about 0.1 to 2.5%, based on the weight of the oil constituent, of an inhibitor resulting from the reaction of an alkylated phenol with the condensation product of turpentine and phosphorus pentasulfide, the alkyl group of the alkylated phenol being a saturated aliphatic radical.

3. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil and a minor proportion, effective to retard oxidation of the oil, of an inhibitor resulting from the reaction of diamyl phenol with the condensation product of turpentine and phosphorus pentasulfide.

4. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil and a minor proportion, effective to retard oxidation of the oil, of an inhibitor resulting from the reaction of an alkylated phenol with the condensation product of turpentine and phosphorus pentasulfide, the alkyl group of the alkylated phenol being a saturated aliphatic radical containing at least 5 carbon atoms.

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