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2,883,339

LUBRICANT COMPOSITIONS

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This invention pertains to improved lubricant compositions and more particularly pertains to internal combustion engine lubricant compositions which inhibit cam follower pitting and/or wear and which inhibit the sticking of hydraulic valve-lifters.

Many modern automobile engines are designed with hydraulic valve-lifters for smoother and more efficient engine operation. In the operation of hydraulic valve-lifters, the lifters ride on the cam shaft converting the rotary motion of the cam into a reciprocating motion, which in turn opens and closes the valves. The bottom of the valve-lifter is known as the cam follower. The hydraulic part of the valve-lifter functions by means of a plunger on the inside of the valve lifter barrel, together with a ball-check and a spring. To obtain higher efficiency and greater horsepower, larger valves, high valve spring pressures and camshafts which produce more rapid valve opening and closing are employed. In the operation of such engines, greatly increased pressures are encountered where the camshaft lobes come into contact with the faces of the valve-lifters resulting in excessive and severe cam and lifter wear as well as pitting of the cam followers. This wear and/or pitting cannot be adequately inhibited by most present-day internal combustion engine crankcase lubricants. Surprisingly, the type of anti-wear properties which will inhibit piston ring and/or cylinder wear are not necessarily the same as the anti-wear properties necessary to prevent cam and lifter wear and/or pitting; hence many lubricants which are effective in inhibiting ring and cylinder wear are ineffective in preventing cam and lifter wear. A further complicating factor in this problem is caused by the materials used in making the camshaft and valve-lifters since different metals and metal combinations are used for this purpose in the various engines. Furthermore, because of the small clearances between the plunger and the barrel of hydraulic valve-lifters, extremely small amounts of deposits such as varnish and/or rusting may cause sticking of the valve-lifter. Hence, it is essential for good engine operation to provide a lubricant which will, in addition to inhibit wear and/or pitting, also inhibit the formation of varnish and/or rusting in the valve-lifter.

As the compression ratio of automobile engines has been increased, the problem of deposit formation on the backs of intake valves has increased. Larger amounts of sticky deposits form and cause valve sticking and power loss. In extreme cases valve burning is caused. The problem of reducing or eliminating these deposits has been particularly vexatious.

It is an object of this invention to provide a lubricant composition which will be substantially free of any tendency to cause valve lifter sticking and/or rusting and which will have improved cam follower anti-pitting and anti-wear properties. Another object is to provide a lu-

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bricant for internal combustion engines which is improved with respect to oxidation stability, detergency, and dispersant powers. An additional object is to provide a lubricant composition which has a substantially lessened tendency to form intake valve deposits. A further object of this invention is to provide a method of reducing or eliminating the sticking and/or rusting of hydraulic valve lifters, the pitting and/or wear of cam followers, the corrosion of bearings, and the formation of intake valve deposits in internal combustion engines. Other objects and advantages will become apparent from the following description thereof.

In accordance with the herein described invention, the above objects can be attained by incorporating in a viscous oil, i.e. an oil having a Saybolt Universal viscosity above about 80 seconds at 100° F. and containing between about 0.002 and 10% of a neutralized phosphorus- and sulfur-containing detergent-type lubricating oil additive, between about 0.001 and 5% of the polymerization products of unsaturated fatty acids, and between about 0.001 and 5% of an oil-soluble phenol. The detergent additive may be one such as an alkaline earth metal, e.g. barium, neutralized reaction product of a phosphorus sulfide and a hydrocarbon such as butylene polymers. The polymerization products of the unsaturated fatty acids, for example linoleic acid, have a molecular weight between about 400 and 2000. The oil-soluble phenol may contain one or more aromatic nuclei and they may contain one or more hydroxyl groups. The preferred phenols are alkylated monohydric phenols. A viscosity index improver such as a polybutylene VI improver, is preferably contained in the lubricating oil composition in an amount between about 1 and 20%. Detergent-type additives have been employed in lubricating oils in order to inhibit formation of sludge and/or varnish-like products which are deposited in the engine and/or about the valves and rings of the engine. When lubricating oil compositions having a neutralized phosphorus- and sulfur-containing detergent-type additive are used for lubricating internal combustion engines having hydraulic valve lifters, there results excessive pitting and/or wear of the cam followers and sticking and/or rusting of the valve lifters. This is even more pronounced when the detergent additive is one which has excess basicity. In addition the oxidation stability of the lubricating oil is diminished and a greater degree of bearing corrosion occurs. Whereas, oil soluble phenolic compounds have no beneficial effect in reducing pitting and/or wear of the cam followers and the polymerization products of the unsaturated fatty acids improve but do not eliminate this problem, it has been discovered to my surprise that the use of both additives together in the oil prevents pitting and/or rusting of the cam followers. At the same time the formation of intake valve deposits (which are believed caused in part by the large amount of viscosity index improver required in multi-branded oils) is reduced at least to a harmless level.

The detergent-type lubricating oil additive used is a neutralized phosphorus- and sulfur-containing additive. These additives are usually used in amounts of from about 0.002 to about 10%, and preferably from about 0.01% to about 5%. Among the phosphorus- and sulfur-containing addition agents are the neutralized reaction products of a phosphorus sulfide and a hydrocarbon, an alcohol, a ketone, an amine or an ester. Of the phosphorus sulfide reaction product additives, the neutralized reaction products of a phosphorus sulfide such as a phosphorus pentasulfide, and a hydrocarbon (note U.S. 2,316,082) are preferred.

The preferred hydrocarbon used for reaction with the phosphorus sulfide is a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefin hydrocarbons, such as propylene, butylenes, amylenes or copolymers thereof. Such polymers may be obtained by the polymerization of mono-olefins of less than 6 carbon atoms in the presence of a catalyst, such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and iso-mono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably from about 500 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid phase of a hydrocarbon mixture containing mono- and isomono-olefins, such as butylene and isobutylene at a temperature of from about -80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts type, such as for example, boron fluoride, aluminum chloride, and the like. In the preparation of these polymers, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline can be used.

Paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, waxes, and the like can be reacted with phosphorus sulfide. Olefins having 16 to 30 carbon atoms or higher may be reacted with the phosphorus sulfide. Other hydrocarbons that can be reacted with a phosphorus sulfide are aromatic hydrocarbons such as benzene, naphthalene, diphenyl, alkylated aromatic hydrocarbons such as benzene having alkyl substituents containing preferably at least 8 carbon atoms and the like.

The phosphorus sulfide-hydrocarbon reaction product can be readily obtained by reacting a phosphorus sulfide, for example P_2S_5 with the hydrocarbon at a temperature of from about 200° F. to about 500° F., and preferably from about 200° F. to about 400° F., using from about 1% to about 50%, and preferably from about 5% to about 25% of the phosphorus sulfide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere, such as for example, an atmosphere of nitrogen above the reaction mixture. Usually, it is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a hydrocarbon solvent, such as hexane, filtering and subsequently removing the solvent by suitable means, such as by distillation. If desired, the reaction product can be further treated with steam at an elevated temperature of from about 100° F. to about 600° F.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The term "neutralized reaction product" of a phosphorus sulfide and a hydrocarbon" as used herein means a phosphorus sulfide-hydrocarbon reaction product having at least 1% of its titratable acidity neutralized by the reaction with a basic reagent. The phosphorus sulfide-hydrocarbon reaction product when neutralized with a basic reagent containing a metal constituent is characterized by the presence or retention of the metal constituent of the basic reagent. The term also includes those products which contain the metal constituent in excess of the amount stoichiometrically necessary to replace the acidic hydrogen atoms contained in the phosphorus sulfide-hydrocarbon reaction product. Such compounds are known in the art as having "excess basicity" or as having "an alkaline reserve." Prior to neutralization the reaction product can

be hydrolyzed and clayed to remove inorganic acids of phosphorus as described in U.S. 2,688,612 issued to R. W. Watson, September 7, 1954.

The neutralized phosphorus-sulfide-hydrocarbon reaction product can be obtained by treating the acidic reaction product with a suitable basic compound, such as hydroxide, carbonate, oxide, or sulfide of an alkali or alkaline earth metal, such as for example, potassium hydroxide, sodium hydroxide, sodium sulfide, calcium oxide, lime, barium hydroxide, barium oxide, etc. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the acidic reaction product either as such or dissolved in a suitable solvent, such as naphtha with a solution of the basic agent. As an alternative method the reaction product can be treated with solid alkaline compounds such as KOH, NaOH, Na_2CO_3 , CaO, BaO, $Ba(OH)_2$, Na_2S , and the like, at an elevated temperature of from about 100° F. to about 600° F. Neutralized reaction products containing a heavy metal constituent, such as for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron, and the like, can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocarbon reaction product which has been treated with a basic reagent such as above-described.

The unsaturated fatty acids which may be polymerized are those natural or synthetic mono-carboxylic acids which generally will have two or more unsaturated linkages. If natural fatty acids are employed they will usually have 16 to 26 carbon atoms, most frequently 18 carbon atoms, but if synthetic unsaturated fatty acids are used they may have a lesser or greater number of carbon atoms. Examples of the natural fatty acids are those such as linoleic, linolenic, ricinoleic (which upon heating forms linoleic acid), linoleaidic, elaidolinolenic, eleostearic, arachidonic, eicosatrienaic, cetoleic, docosatrienoic and the like. The free fatty acids can be polymerized either thermally or with the assistance of catalysts. A method of thermally polymerizing free fatty acids (see U.S. 2,482,761) consists of hydrolyzing a fat or an oil, adding a small portion of water, and heating in a pressure vessel until substantially all of the di- and tri-unsaturated fatty acids present polymerize. The resultant product is then heated at a reduced pressure to distill off vaporizable constituents, leaving behind the polymerized unsaturated fatty acids. The polymerization reaction is carried out at a temperature of about 300° to 360° C. for about three to eight hours at a pressure varying between 75 and 500 p.s.i.g. The polymerization product may consist of monomers, dimers, trimers, and higher polymers of the unsaturated fatty acids. The various fats or oils which may be hydrolyzed to produce the free fatty acids used in the above thermal polymerization are those such as sardine oil, linseed oil, soybean oil, castor oil, peanut oil, palm oil, olive oil, cottonseed oil, sunflower seed oil, and the like.

Another method of preparing the polymerized fatty acids consists of subjecting fats and oils such as have been listed supra (without previous hydrolysis) to a thermal or catalytic polymerization to cause polymerization of the esters of the unsaturated carboxylic acids to the dimers, trimers, and higher polymerization products thereof, followed by hydrolysis to yield the corresponding polymers of the acids. A large source of the polymerized unsaturated fatty acids are those residual acids obtained by methanolysis (see U.S. 2,450,940) of the semi-drying or drying type oils such as castor oil, soybean oil, and others listed supra, polymerizing the methyl esters, removing unpolymerized compounds, saponifying the residual esters and freeing polymerized acids therefrom. The products of catalytic polymerization of semi-drying oils such as the BF_3 polymerization products of soybean oil, cottonseed oil, or the like also produce polymers suitable for use in the invention.

It should be understood that while various polymerized unsaturated fatty acids may be used, they do not all provide the same effect, and indeed there may be pronounced differences when used in the composition of this invention. A highly preferred source of the polymerized unsaturated fatty acids is obtained as a by-product still residue in the manufacture of sebacic acid by the dry distillation of castor oil in the presence of sodium hydroxide. A method of obtaining such by-product still residues in the manufacture of sebacic acid is described in U.S. 2,470,849, issued to W. E. Hanson May 24, 1949. The mixture of high molecular weight unsaturated fatty acids comprises monomers, dimers, trimers, and higher polymers in the ratio of from about 45% to about 55% of a monomers and dimers fraction having a molecular weight in the range of from about 300 to 600, and from about 45% to about 55% of a trimers and higher polymer fraction having a molecular weight in excess of 600. The fatty acid polymers result in part from a thermal polymerization of fatty acid type constituents of the castor oil, and in part from other reactions, such as the inter-molecular esterification, of such acid to form high molecular weight products. The acid mixture, which is mainly a mixture of polymeric long chain polybasic carboxylic acids, is further characterized by the following specifications:

- Acid No.—150 to 164.
- Saponification No.—175 to 186.
- Free Fatty Acids—75 to 82%.
- Iodine Value—44 to 55.
- Non-saponifiables—2.5% to 5%.

A fatty acid mixture such as above described is marketed under the trade name "D-50 Acids," and also as "VR-1 Acids."

The polymerization products of the unsaturated fatty acids may have a molecular weight between about 400 and 2000. Those polymers having a molecular weight higher than about 500, and especially those having molecular weights averaging about 800 or higher are particularly preferred for use in this invention. The polymerization products may consist primarily of dimers and trimers of linoleic acid, for example Emery 955 Dimer Acid which contains 85% of the dimer, 12% of the trimer, and 3% of the monomer of linoleic acid may be used. Especially preferred polymerized unsaturated acids are the polymerization products of acids such as linoleic acid having a molecular weight between about 400 and 2000, wherein the polymerization products consist of more than about 40% of the trimer and higher molecular weight polymers of linoleic acid with the remainder consisting primarily of monomers and dimers of linoleic acid.

The polymerization products of the unsaturated fatty acids should be used in an amount between about 0.001 and 5.0% in the oil, preferably between about 0.05 and 2.0%, for example about 0.2%. The amount of polymerized fatty acids, as well as the amount of phenolic compound used, may be varied depending upon the oil in which it is employed, the materials used in making the camshaft and valve-lifters, the valve spring pressures and other factors which affect the degree of pitting and wear.

The oil-soluble phenol is employed in an amount between about 0.001 and 5%, preferably between about 0.05 to 2%. The phenol may have one or more hydroxyl groups attached to an aromatic nucleus. The automatic nucleus may consist of one, two or three rings. The preferred phenols are alkylated monohydric phenols such as cresols, xylenols, mesitols, 2,6-di-tert-butyl p-cresol, 2,4,6-tri-tert-butyl phenol, 2,4-dimethyl-6-tert octyl phenol, amyl phenols, thymol, cyclohexyl phenol, nonyl phenol, phenols alkylated with olefin polymers such as polypropylene, polybutylene, etc., which have from 6 to 24 carbon atoms in the polymer, wax-substituted phenols and the like. Also included in this definition of alkylated monohydric phenols are the alkylene bis phenols

such as methylene diphenol, methylene bis p-octyl phenol and similar compounds. Phenol itself, as well as the various naphthols, and anthranols may be used if desired. Dihydric and trihydric phenols such as catechol, tert-butyl catechol, pyrogallol, phloroglucinol, are quite effective.

Phenols which contain sulfur in the molecule should not be used. It has been found that such compounds do not provide the beneficial effect of the phenols which are free of sulfur in the molecule. Certain of the sulfur-containing phenols such as thiocresols have an aggravating effect on the problem of pitting and/or wear of the cam followers.

Any of a number of different viscosity index improvers may be used in the lubricating oil composition. For example, polymers of butylenes, e.g. polyisobutylene which is sold commercially as "Paratone," may be used. Acrylic acid esters such as the commercially available "Acryloids" may be employed. Polymers of isobutylene such as, Paratone, are preferred and are very effective for reducing the change in viscosity of the oil with change in temperature. The amount of viscosity index improver, of course, depends upon the improvement in viscosity index which is desired and the effectiveness of the particular viscosity index improver. Generally between about 1 and 20% of the viscosity index improver is employed in the lubricating oil composition.

The phosphorus- and sulfur-containing detergent-type additive, the polymerization products of unsaturated fatty acids and the oil-soluble phenol can be added individually to the lubricating oil base or they can be pre-mixed (preferably together with the viscosity index improver) in the desired proportions and the resultant mixture then added to the lubricating oil base. Concentrations of a suitable oil base containing more than 10%, for example up to 50%, of the detergent-type additive, with more than about 5%, for example up to 25%, of the polymerization products of the unsaturated fatty acids, and more than about 5%, for example up to 25%, of the phenol can be used for blending with the hydrocarbon oils in the proportions desired for the particular conditions of use to provide a finished product containing the desired amounts of these additives, e.g., 0.002 to 10% of the detergent additive, 0.001 to 5% of the polymerized acids and 0.001 to 5% of the phenol. The lubricating oil base may also contain other additives such as VI improvers, bearing corrosion inhibitors and the like.

A number of performance tests for evaluating the ability of the lubricating oil to inhibit pitting and/or wear as well as its ability to prevent rusting of the hydraulic valve-lifters were made. The tests made to determine the anti-pitting and anti-wear properties of the oil is known as the L-S-5 test established by the General Motors Research Division. The test is made on a 1953 Chevrolet Power Glide engine equipped with chilled iron lifters, forged steel cams, steel rocker arm shafts, malleable iron rocker arms and operating at 3150 r.p.m. with a load of 30 brake horsepower, an oil sump temperature of 255° F. and a water outlet temperature of 200° F. Dual valve springs are installed to give an assembled static valve spring load of 240 pounds at 0.330 inch valve opening. The test is continued for 24 hours at the end of which the cam followers are inspected for pitting and over-all wear.

The effectiveness of the additives for preventing pitting of the cam followers is shown in the table which follows. In obtaining the data presented in this table various additives for preventing pitting and/or wear of the cam followers were added to the oil composition of Sample 1. Sample 1 was composed of the following:

Composition Sample 1.—SAE 10W-30 oil + 3.3% of a barium-containing neutralized reaction product of P_2S_5 and a polybutene of about 1000 molecular weight + 0.75% of a sulfurized dipentene (35% sulfur) + 11% of Paratone + 31 p.p.m. anti-foam agent.

Sample No.	Amount and Type of Anti-Pitting and Anti-Wear Additive	Liters Pitted
1	None	10
2	0.36% Nonyl Phenol	10
3	0.16% D-50 Acid	3
4	Sample No. 3 plus 0.20% Nonyl Phenol	None
5	Sample No. 3 plus 0.20% p-cresol	None
6	Sample No. 3 plus 0.20% 2,6 di-t-butyl p-cresol	None
7	Sample No. 3 plus 0.20% amyl phenol	1
8	Sample No. 3 plus 0.32% polypropylene phenol ¹	None
9	Sample No. 3 plus 0.20% t-butyl catechol	1
10	Sample No. 3 plus 0.50% methylene bis p-octyl phenol	None
11	Sample No. 3 plus 0.30% nonyl phenol sulfide	3
12	Sample No. 3 plus 0.20% thiocresols	7

¹ Molecular weight of 425.

Sample 1 shows that unless an anti-pitting and anti-wear additive is present in the oil almost all of the cam follower surfaces will be pitted. Sample 2 shows that the oil-soluble phenol does not impart any improved anti-pitting and anti-wear properties to the oil. Sample 3 shows that the polymerization products of the unsaturated fatty acids improve the oil only slightly in the latter respect. However, Samples 4 through 10 show that when the oil-soluble phenol and the polymerization products of the unsaturated fatty acids are used together in the oil the problem of pitting and/or wear of the cam followers is eliminated. Samples 11 and 12 indicate that the phenol must not contain sulfur in the molecule, Sample 12 pointing out in particular that thiocresols increase the problem of pitting and/or wear.

An additional series of experiments (Automotive Diesel L-5 engine tests and L-4 engine tests) showed that the presence of the oil-soluble phenol in the lubricating oil composition containing the detergent additive and the polymerization products of the unsaturated fatty acids, improved the oxidation stability of the oil and reduced the bearing corrosion weight loss.

Performance tests which evaluated the ability of the lubricating oil to inhibit the formation of intake valve deposits were made. The tests made were known as the Cadillac Cold Test. The test is made on a 1954 Cadillac engine operating at 2000 r.p.m. for 100 hours of continuous running under conditions of no load and a water temperature of 165° F. Sample 3 of the preceding table as well as Samples 13 and 14 which contained added phenols were evaluated in the tests. The results show:

Engine intake valve deposits

Sample No.	Amount and Type of Anti-Pitting and Anti-Wear Additive	Amount of Deposits
3	None	Moderate to Heavy.
13	Sample No. 3 plus 0.35% nonyl phenol	Slight.
14	Sample No. 3 plus 0.50% 2,6 di-t-butyl p-cresol	Slight.

The above tests show that the presence of the phenol in the lubricating oil composition inhibits greatly the amount of intake valve deposits which are formed. In addition the deposits are not of such a hard nature.

While the present invention has been described by the use of our additives in petroleum lubricating oils other lubricating oil bases can be employed. For example oils obtained by the polymerization of olefins, synthetic lubricating oils of the alkylene oxide type, for example, "Ucon Oils," and the polycarboxylic acid ester type oils such as the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, etc., may be used.

Unless otherwise stated, the percentages stated herein and in the claims are weight percentages.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as come with the spirit of the appended claims.

I claim:

1. A lubricating oil composition comprising a major proportion of a mineral lubricating oil base, between about 0.002 and 10% of an alkaline earth-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer, between about 0.001 and 5% of the polymerization products of unsaturated fatty acids having from 16 to 26 carbon atoms, said polymerization products having a molecular weight between about 400 and 2000, and between about 0.001 and 5% of an oil soluble phenol selected from the group consisting of alkylated monohydric phenols and alkylated dihydric phenols.

2. The composition of claim 1 wherein the polymerization products of the unsaturated fatty acids consist of more than about 40% of the trimer and higher molecular weight polymers, the remainder being essentially monomers and dimers of the unsaturated fatty acids.

3. The composition of claim 1 wherein said unsaturated acid is linoleic acid.

4. The composition of claim 1 which also contains between about 1 and 20% of a viscosity index improver.

5. A lubricating oil composition comprising a major proportion of a mineral lubricating oil base, between about 0.002 and 10% of a phosphorus sulfide-olefin polymer reaction product which has been neutralized with a basic barium compound, between about 0.05 and 2% of the polymerization products of linoleic acid, said polymerization products having a molecular weight between about 400 and 2000 and consisting of more than about 40% of the trimer and higher molecular weight polymers of linoleic acid and the remainder being essentially monomers and dimers of linoleic acid, and between about 0.05 and 2% of an oil-soluble alkylated monohydric phenol.

6. The composition of claim 5 which also contains between about 1 and 20% of a viscosity index improver.

7. An addition agent for a lubricating oil composition comprising a concentrated solution of a mineral lubricating oil base containing more than about 10% of an alkaline earth-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer, more than about 5% of the polymerization products of unsaturated fatty acids having from 16 to 26 carbon atoms, said polymerization products having a molecular weight between about 400 and 2000, and more than about 5% of an oil-soluble phenol selected from the group consisting of alkylated monohydric phenols and alkylated dihydric phenols, said concentrated solution being capable of dilution with a mineral lubricating oil base to form a homogeneous mixture containing between about 0.002 and 10% of the neutralized phosphorus sulfide-olefin polymer reaction product, between about 0.001 and 5% of the polymerization products of the unsaturated fatty acids, and between about 0.001 and 5% of the phenol.

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