United States Patent Office

2,833,713

Patented May 6, 1958

2,833,713

CORROSION INHIBITED MOTOR OILS

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No Drawing. Application April 18, 1955
Serial No. 502,222

3 Claims. (Cl. 252—32.7)

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 lifter rise 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, higher 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 crank-case 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. Camshaft and valve-lifter combinations of different metals create different requirements on the lubricant in that certain types of anti-wear additives may be effective with some cam-lifter metal combinations but ineffective with other metal combinations. 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.

It is an object of this invention to provide a lubricant composition which will not cause sticking of hydraulic valve-lifters and which will inhibit cam follower wear and/or pitting. Another object of the invention is to provide a crank-case lubricant which will be substantially

free of any tendency to cause valve-lifter sticking and which will have cam follower anti-pitting and anti-wear properties. Another object of the invention is to provide an improved lubricant for internal combustion engines. Still another object of the invention is to provide a method of preventing the sticking of hydraulic valve-lifters and the pitting and/or wear of cam followers in internal combustion engines. Other objects and advantages of the invention 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., from about 0.05% to about 3% of a mixture of high molecular weight unsaturated fatty acids obtained as a by-product still-residue in the manufacture of sebacic acid by the distillation of castor oil in the presence of sodium hydroxide. A method of obtaining such by-product still-residues in the preparation 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 by the W. C. Hardesty Company under the trade name "D–50 acids," and as "VR–1 acids" by Rohm and Haas Company. Lubricant compositions containing small amount of "D–50 acids" have exhibited excellent anti-wear and/or pitting properties as well as anti-rust properties.

Since as stated above, camshafts and valve-lifters are frequently fabricated of combinations of different metals which may not be equally responsive to any one inhibitor, a series of tests are required to determine the suitability of any one compound for the inhibition of rusting and/or wear of valve-lifters and camshaft followers. The following tests have been used to evaluate the wear and/or rusting inhibiting properties of the above described lubricant additive.

I. CADILLAC TEST

This test is carried out in a Cadillac engine equipped of carburized steel valve-lifters and hardened alloy armed cams, and using two sets of conditions designated Cadillac "hot" test and Cadillac "cold" test. In the Cadillac "hot" test, the engine is operated for 50 hours using a cycle of two hours' running and two hours' off at a speed of 2,000 R. P. M. with a water outlet temperature of

165° F. and a load of 0 grade horsepower. In the Cadillac "cold" test, the test period is 50 hours with a cycle of two hours' running and two hours' off. The engine is operated at 1,000 R. P. M. with a water outlet temperature of 100° F. and a load of 0 brake horsepower. An unleaded fuel composed of 90% straight run naphtha and 10% alkylate is used. At the end of the test period, the cam-lifter surfaces are examined and wear measurements made.

II. 180° F. CHEVROLET TEST

This test is made in a six-cylinder Chevrolet engine equipped with cast-iron lifters and forged steel cams operating at 2500 R. P. M. with a load of 45 brake horsepower and oil sump temperature of 180° F. and a water outlet temperature of 180° 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 60 hours with inspection for valve pitting made at the end of 20, 40 and 60-hour periods.

III. CHRYSLER TEST

This test is carried out in a Chrysler V–8 engine equipped with chilled cast iron cam followers and an alloy cast iron camshift and—lifters. The engine is operated for 120 hours with a two hours' on and a one hour off cycle at 1200 R. P. M. with a water outlet temperature of 165° F. and a load of 0 brake horsepower. At the end of the test period, the cam lifters are examined for pitting and measured for wear.

IV. BUICK "HOT" TEST

This test is the same as the Cadillac "hot" test except that a Buick engine is used.

V. MODIFIED INDIANA HYDRAULIC VALVE-LIFTER RUST TEST

This test is carried out in a Chevrolet Powerglide engine operating at 2500 R. P. M. and a load of 45 B. H. P. with an oil temperature of 120° F. and a water temperature of 85–95° F. The test engine is operated at these conditions for 20 hours with a 4 hour running and 4 hour off cycle. At the end of 20 hours the dipstick, rocker arm shaft and valve lifters are inspected for rust. Valve lifters free of rust are rated 10 and badly rusted lifters are rated 1.

The effectiveness of the herein described mixture of high molecular weight unsaturated fatty acids in inhibiting corrosion and/or rusting is demonstrated by the data in Table I. These data were obtained by subjecting (1) a solvent extracted SAE 10 motor oil base and (2) the oil of (1) containing 0.16% of the fatty acid mixture designated "D–50 Acids" to the above described tests.

Table I

Sample No.	Cadillac Test, inches		180° F. Chevrolet Test	Chrysler Test, inches	Buick Test, inches	Hydraulic Valve Lifter Rust Test		
	Cold	Hot				DS [1]	RAS [2]	VL [3]
1	0.001	0.002	10 Hvy pitted.	0.006	0.002	Mod.	Mod.	[4] 5.5
2	0.0003	0.0003	Perfect.	0.003	0.0003	Clean.	Sl.	9.5

[1] DS=dipstick.
[2] RAS=rocker armshaft.
[3] VL=valve lifters.
[4] 10=perfect.

Although the high molecular weight unsaturated fatty acid mixture, described herein, can be suitably used alone in a base oil to overcome corrosion and/or rusting, they are usually used in combination with detergent-type additives, particularly those which contain sulfur and/or phosphorus and sulfur, which function to inhibit the formation of sludge and/or varnish like products deposits in the engine and/or used about the valves and rings of the engine. Additives of this type 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 of the type described in U. S. 2,316,082, issued to C. M. Loane et al. April 6, 1943, are preferred.

As taught in the U. S. 2,316,082 patent, the preferred hydrocarbon constituent of the reaction is a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefin hydrocarbons, such as propylene, butenes, 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.

Another suitable polymer is that obtained by polymerizing in the liquid phase, a hydrocarbon mixture comprising substantially C_3 hydrocarbons in the presence of an aluminum chloride-complex catalyst. The catalyst is preferably prepared by heating aluminum chloride with iso-octane. The hydrocarbon mixture is introduced into the bottom of the reactor and passed upward through the catalyst layer, while a temperature of from about 50° F. to about 110° F. is maintained in the reactor. The propane and other saturated gases pass through the catalyst while the propylene is polymerized under these conditions. The propylene polymer can be fractionated to any desired molecular weight, preferably from about 500 to about 1000, or higher.

Essentially paraffinic hydrocarbons, such as bright stock residuums, lubricating oil distillates, petrolatums, or paraffin waxes, can be reacted with the phosphorus sulfide, as well as high molecular weight olefinic hydrocarbons such as cetene (C_{16}), cerotene (C_{26}), melene (C_{30}), and mixed high molecular weight alkenes obtained by cracking petroleum oils.

Other preferred olefins suitable for the preparation of the phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms,

and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained by the dehydrogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

As a starting material there can be used the polymer or synthetic lubricating oil obtained by polymerizing unsaturated hydrocarbons resulting from the vapor phase cracking of paraffin waxes in the presence of aluminum chloride which is fully described in U. S. Patents 1,955,260, 1,970,402 and 2,091,398.

Other hydrocarbons that can be reacted with a phosphorus sulfide are aromatic hydrocarbons, such as for example, benzene, naphthalene, toluene, xylene, diphenyl and the like, or an alkylated aromatic hydrocarbon, such as for example, benzene having an alkyl substituent having at least 4 carbon atoms, and preferably at least 8 carbon atoms, such as a long chain paraffin wax.

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 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. 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 alkaline earth metal or an alkali metal, such as for example, potassium hydroxide, sodium hydroxide, sodium sulfide, calcium oxide, lime, barium hydroxide, barium oxide, etc. Other basic reagents can be used, such as for example, ammonia or an alkyl or aryl-substituted ammonia, such as amines. 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, K_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.

Other phosphorus sulfide reaction products which can be used are the reaction products of a phosphorus sulfide and a fatty acid ester of the type described in U. S. 2,399,243; the phosphorus sulfide-degras reaction products of U. S. 2,413,332; the reaction product of an alkylated phenol with the condensation product of P_2S_5 and turpentine of U. S. 2,409,877 and U. S. 2,409,878; the reaction product of a phosphorus sulfide and stearonitrile of U. S. 2,416,807, etc.

The high molecular weight unsaturated fatty acid mixture and the sulfur and/or phosphorus and sulfur-containing detergent-type additive can be added individually to the base motor oil or they can be pre-mixed in the desired proportions preferably in the proportion of from about 1% to about 30% of the fatty acid material and from about 99% to about 70% of the defined detergent-type additive, at a temperature of about 70° F. to about 150° F. and the resultant mixed product added to the base oil. Because of the complexities of the compounds concerned it has not been possible to determine definitely what takes place when the fatty acid mixture and the defined detergent-type additive are heated together. There is some indication that there is some interaction between the two, with the probable formation of a complex, since the viscosity of heated blends of the components is higher than either of the components. It has been observed that with heated blends of the fatty acid mixture and a barium neutralized reaction product of P_2S_5 and a polybutene of about 1000 molecular weight a maximum viscosity increase is obtained with a blend of 20% of the former and 80% of the latter. This viscosity increase is illustrated by the data in Table II.

Table II

VISCOSITIES OF BLENDS

[Viscosity, SUS at 210° F.]

Blend No.	Composition, Wt. Percent		Blending Temp., °F.	Theoretical, From Viscosity Blending Chart	8 Hrs. After Blending, Room Temp. Storage
	A	B			
1	100	0		349	349
2	99	1	150	350	372
3	98	2	150	351	376
4	97	3	150	352	397
5	96	4	150	353	412
6	95	5	150	354	464
7	94	6	150	355	499
8	93	7	150	356	582
9	92	8	150	357	630
10	91	9	150	358	718
11	90	10	150	359	757
12	80	20	150	364	844
13	70	30	150	375	692
14	60	40	150	383	627
15	50	50	150	398	563
16	40	60	150	405	522
17	30	70	150	418	506
18	20	80	150	426	475
19	10	90	150	439	456
20	0	100		452	452
21	80	20	70	364	[1] 840

[1] Viscosity determined immediately after blending.

A—Barium-containing neutralized, hydrolyzed and clayed reaction product of P_2S_5 and a polybutene of about 1000 molecular weight.

B—"D-50 acid."

While such detergent-type additives effectively inhibit the formation of sludge and/or varnish-like products in the engine they do not possess corrosion and/or rusting inhibiting properties or anti-wear properties. However, when used in combination with the herein described mixture of high molecular weight unsaturated fatty acids complete engine protection is obtained. This is demonstrated by the data in Table III in which performance tests are tabulated together with the so-called conventional L-4 test. This test is made on a standard Chevrolet six-cylinder engine, equipped with three pairs of copper-lead bearings, operating for 36 hours at 3150 R. P. M. and a load of 30 B. H. P. with an oil sump temperature of 280° F. and a water outlet temperature of 200° F. The copper-lead alloy bearings are weighed before and after the test period and loss in weight noted; a bearing weight loss in

excess of 0.2 gram is failing. The following compositions were subjected to the tests in Table III:

Sample A.—Solvent extracted SAE 10 Oil.

Sample B.—Sample A+4.3% of a barium-containing neutralized reaction product of P_2S_5 and a polybutene of about 1000 molecular weight +.75% of a sulfurized dipentene (35% sulfur)+10 p. p. m. silicone polymer antifoam agent.

Sample C.—Sample B+0.16% "D–50 Acid."

Table III

Sample No.	Cadillac Test, inches		180° F. Chevrolet Test	Chrysler Test, inches	Buick Test, inches	L–4 Test	Hydraulic Valve Lifter Rust Test		
	Cold	Hot					DS [1]	RAS [2]	VL [3]
A	0.001	0.002	10 heavy pitted.	0.006	0.002	Fail	Mod	Mod	[4] 5.5
B	0.001	0.002	do	0.006	0.002	Pass	Severe	Severe	5.5
C	0.0003	0.0003	perfect	0.003	0.0003	do	Clean	Slight	9.5

[1, 2, 3, 4] Supra (Table I).

It will be noted from the above data that the oil containing the detergent additive passed the L–4 test but was no better than the base oil alone in the other tests, and even somewhat less effective than the base oil in the valve-lifter rust test. However, the oil containing the detergent additive in combination with the mixture of high molecular weight unsaturated fatty acids was effective in all the tests and had no deleterious effect on the copper-lead bearings in the L–4 test.

Concentrates of a suitable lubricating oil base containing 10% to about 50% or more of the herein described mixture of high molecular weight unsaturated fatty acids, alone, or in combination with more than 10% of other additives, such as detergent-type additives, can be used for blending with other hydrocarbon lubricating oils or other lubricating oil bases in the proportions desired for the particular conditions of use to give a finished product containing from about 0.05% to about 3% of the mixture of high molecular weight unsaturated fatty acids.

While the present invention has been described by the use of the mixture of fatty acids in petroleum lubricating oils, other lubricating oil bases can be employed such as hydrocarbon oils, natural or synthetic such as those obtained by the polymerization of olefines, as well as synthetic lubricating oils of the alkylene oxide type, for example "Ucon oils" marketed by Carbide and Carbon Corporation, and the polycarboxylic acid ester type oils such as the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, etc.

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 within the spirit of the appended claims.

We claim:

1. A lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil and from about 0.05% to about 3% of a mixture comprising essentially polymeric long chain unsaturated polybasic carboxylic acids, said acid mixture comprising monomers, dimers, trimers and higher fatty acid polymers in the ratio of from about 45% to about 55% of a monomer and dimer fraction having a molecular weight in the range of from about 300 to about 600 and from about 45% to about 55% of a trimer and higher polymer fraction having a molecular weight in excess of 600 and from about 0.002% to about 10% of an alkaline earth-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer.

2. A composition as described in claim 1 in which the neutralized reaction product is a barium-containing neutralized reaction product of a phosphorus sulfide and a butylene polymer.

3. A lubricating oil concentrate comprising essentially a viscous hydrocarbon oil and more than 10% of a mixture comprising essentially polymeric long chain unsaturated polybasic carboxylic acids, said acid mixture comprising monomers, dimers, trimers and higher fatty acid polymers in the ratio of from about 45% to about 55% of a monomer and dimer fraction having a molecular weight in the range of from about 300 to about 600 and from about 45% to about 55% of a trimer and higher polymer fraction having a molecular weight in excess of about 600, and more than 10% of an alkaline earth-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer said concentrate being capable of dilution with a hydrocarbon oil to form a homogeneous mixture containing from 0.05% to 3% of said fatty acid mixture, and from about 0.002% to about 10% of said neutralized phosphorus sulfide-olefin polymer reaction product.

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