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LUBRICANT

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This invention relates to lubricating oil compositions and more particularly to lubricating oil compositions consisting principally of a petroleum lubricating oil fraction and having improved characteristics, especially with respect to oxidation and corrosion, by reason of the incorporation therewith of a minor proportion of the reaction product of a stearonitrile and a phosphorus sulfide.

Phosphorus sulfides, suitable for the preparation of the addends of my present invention, include the pentasulfide (P_2S_5), heptasulfide (P_4S_7) and the tri- or sesquisulfide (P_2S_3).

It has previously been suggested that the extreme pressure characteristics of a lubricant may be improved by the addition thereto of relatively large proportions of polymerized aliphatic nitriles prepared by heating an aliphatic nitrile in the presence of a polymerizing agent such as metal chlorides, chlorides of phosphorus and sulfur, phosphorus pentasulfide, elemental phosphorus or sulfur. It has been suggested that such polymerized aliphatic nitriles may be used alone as extreme pressure lubricants or that they may be added to ordinary mineral oil lubricants and greases to impart extreme pressure lubricating characteristics to such mineral lubricants.

The lubricating oil composition of my present invention is not to be confused with such extreme pressure lubricants consisting of polymerized aliphatic nitriles or mixtures thereof with other lubricants.

I am at present unable definitely to identify, by chemical formula, my improved lubricating oil addends. However, they definitely appear to consist primarily of chemically combined stearonitrile, phosphorus, and sulfur, as distinguished from a polymer of stearonitrile containing little or no phosphorus or sulfur. This fact is apparent from the following observation:

a. A maximum of 2 moles of the stearonitrile reacts with each mole of phosphorus sulfide, for instance P_2S_5. This has been shown by the removal of excess nitrile by low pressure distillation after a reasonable reaction period.

b. Excess nitrile is not substantially polymerized under the reaction conditions described herein, since excess nitrile may be recovered from the reaction mixture by distillation in the original boiling range of the stearonitrile.

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These stearonitrile-phosphorus sulfide reaction products may be prepared by heating a mixture of the stearonitrile and phosphorus sulfide, advantageously to a temperature of about 150–300° F., until a homogeneous mixture is obtained. The time required for the completion of the reaction is largely dependent upon the reaction temperature employed. For instance, using a reaction temperature of 150° F., completion of the reaction may require say 22 hours, while using a reaction temperature of 300° F., the reaction may be completed in say 1 to 6 hours.

The proportion of stearonitrile and phosphorus sulfide used may be varied somewhat; however, a molecular proportion of the nitrile and phosphorus sulfide of about 1:½ has been used with advantage. It is desirable that substantially all of the stearonitrile be reacted with the phosphorus sulfide and as previously noted a maximum of 2 moles of the stearonitrile will react with 1 mole of the phosphorus sulfide. Any substantial excess of the stearonitrile is not desirable.

The reaction product of stearonitrile with any one of the phosphorus sulfides previously noted have been found to be oil soluble and, when compounded with lubricating oil fractions, substantially to inhibit corrosion of the bearing metal in contact with the oil and materially to stabilize the oil composition against deterioration. Further these stearonitrile-phosphorus sulfide reaction products have been found to be particularly effective deactivators of various metals, alloys, and metal compounds known to accelerate the deterioration of the oil. For instance, it has previously been recognized that oxidation of many lubricating oil compositions is materially accelerated by contact with certain bearing metals or alloys, notably copper-lead alloys. It is also recognized that the presence of various metallo-organic substances, included in the oil composition for improving the characteristics of the lubricant in various respects, may ultimately detrimentally affect the oxidation and corrosion characteristics of the lubricant. Copper-lead alloy, for example, is known materially to catalyze oxidation of the oil. Also, various metal compounds, notably calcium organic compounds, for instance the calcium salt of octyl-salicylates, used in lubricating oil compositions as detergents and oxidation inhibitors, have been found actually to effect

an increase over the normal rate of corrosion of copper-lead bearing alloys by the lubricant and the normal rate of oxidation of the lubricating oil composition at the termination of the induction period.

I have discovered that the corrosion and oxidation characteristics of petroleum lubricating oil fractions either alone or compounded with various other addends, and even in the presence of prooxidant metals, may be substantially improved by incorporating therewith a minor proportion of one of these stearonitrile-phosphorus sulfide reaction products.

These stearonitrile-phosphorus sulfide reaction products have been found to be compatible with other desirable lubricating oil addends and the inclusion of such other addends, especially addends of the type used as detergent, is within the contemplation of my present invention and constitutes an important aspect thereof. The inclusion of said so-called detergents, for instance in internal combustion engine lubricants, has been found highly advantageous. An especially effective lubricating oil composition contemplated by my present invention is one comprising, in addition to the lubricating oil constituent and my stearonitrile-phosphorus sulfide reaction product, a minor proportion of the calcium salt of an octyl salicylate, particularly iso-octyl salicylate or capryl salicylate. These calcium salts have been found particularly effective as detergents in lubricating oil compositions, as more fully described in U. S. Patents Nos. 2,339,692 and 2,347,547, issued respectively on January 18, 1944, and April 25, 1944, each on an application of Willard L. Finley.

The invention also contemplates lubricating oil compositions containing my stearonitrile-phosphorus sulfide reaction products and other known detergents, for example such as calcium cetyl phenolate, phenolates of tertiary amyl phenol sulfide, barium phenolate of diamyl phenol sulfide, metal sulfonates, soaps, especially basic soaps, highly basic, calcium detergents and various other known detergents of these general types.

When used in conjunction with these detergents, particularly the calcium compounds such as previously mentioned, these stearonitrile-phosphorus sulfide reaction products and the detergents have been found to complement each other so that the effectiveness of each is promoted. The tendency of the detergent to promote oxidation of the oil and corrosion of bearing metal at the termination of the oxidation induction period is minimized by the presence of said reaction products without destroying the effectiveness of either the detergent or my new inhibitors.

My new type of inhibitor may be prepared as previously noted by reacting stearonitrile with either phosphorus pentasulfide, phosphorus heptasulfide, or phosphorus trisulfide. The reaction products of lauronitrile with these phosphorus sulfides have been found to have low oil solubility. However the reaction products of stearonitrile with these phosphorus sulfides have been found to be sufficiently soluble in petroleum lubricating oil fractions to permit their use for the purpose of the present invention, and to be readily soluble in such oils at room temperature over a range at least as high as 1%, based on the weight of the oil. Stearonitriles prepared from double pressed stearic acid, containing about 50% stearic acid and 50% palmitic acid, have been found satisfactory for use in the preparation of my improved addends.

The stearonitrile-phosphorus sulfide reaction products used as an addition agent in the compounding of my improved lubricating oil composition may be prepared as presently described. For convenient subsequent reference, the reaction products and the method used in preparing the same will be designated A, B, C, and D respectively.

Inhibitor A

This reaction product was prepared by reacting phosphorus pentasulfide (P_2S_5) with a stearonitrile, prepared from double pressed stearic acid containing approximately equal proportions of stearonitrile and palmitonitrile, having an average molecular weight of 251. One mole of the nitrile and 100 grams of P_2S_5 (0.475 mole) were charged to a reactor equipped with a stirrer, thermometer and heater. The stirrer was started, the mixture slowly heated to 300° F. and held at that temperature for 1 hour. During this heating the mixture slowly turned to deep red color and became homogeneous at 300° F. Upon cooling to room temperature, this red liquid thickened to the consistency of a thick syrup. Naphtha was then added to reduce the viscosity of the mixture and the solution was filtered through a filter aid to remove any unreacted P_2S_5. The filtrate was then topped to remove the added naphtha. By this operation a yield of 216 grams of the reaction product was obtained having an acid number of 170.8 and containing 7.76% phosphorus and 20% sulfur.

Inhibitor B

This product was prepared by the method of the preceding example except that 251 grams (1 mole) of the stearonitrile was heated with 0.58 mole of P_2S_5 and the temperature was held at 300° F. for 6 hours. The resulting product was found to have an acid number of 283.5 and to contain 8.18% phosphorus, 20.95% sulfur, and 2.95% nitrogen.

Inhibitor C

The reactor used in the preceding examples was charged with 125.5 grams of the stearonitrile and 104 grams (0.3 mole) of P_4S_7. The mixture was stirred and heated to a temperature of 300° F. for 14 hours. The mixture was then cooled to 200° F. and filtered while hot through a bed of filter aid to remove any excess or unreacted phosphorus sulfide. The filtrate was a thick dark red liquid having an acid number of 131.4, a saponification number of 256.2 and containing 8.34% phosphorus, 15.6% sulfur, and 3.47% nitrogen.

Inhibitor D

In the preparation of this inhibitor, the reactor previously used was charged with 251 grams (1 mole) of the stearonitrile and 65 grams (0.412 mole) of P_2S_3 was added. The stirrer was started and the mixture heated for 1 hour at a temperature of 300° F. The mixture was then cooled to 200° F. and filtered through a filter aid. The product was a clear, dark red, viscous liquid having an acid number of 17.2, a saponification number of 157.8 and containing 4.88% phosphorus and 10.5% sulfur.

The reaction products of stearonitrile with these phosphorus sulfides are very active chemically. They react readily with water, amines, alcohols, metallic oxides, and the like. The materials themselves appear to be stable at 400° F.

That they contain more than one type of reaction product is indicated by the fact that about 80% of the phosphorus present may be readily removed by boiling with caustic, while the remainder of the phosphorus withstands long periods of digestion. Purification of the product is difficult because of its viscosity and its chemically very active characteristics.

The characteristics of the lubricating oil constituent determined by conventional laboratory tests are very little affected by these inhibitors. This is illustrated by the following Table I in which there are set forth, in the first column, the characteristics of a solvent treated SAE 10 Mid-Continent base oil. In the second column there appear the characteristics of this base oil having incorporated therewith 0.1% of the reaction product previously designated "Inhibitor A." In the third column there are set forth the characteristics of this base oil having incorporated therewith 1% of the previously referred to calcium salt of isooctyl salicylate, but containing none of my present addends. In the fourth column, there are set forth the characteristics of the base oil having incorporated therewith 0.75% of the calcium iso-octyl salicylate and 0.25% of the reaction product previously designated "Inhibitor B." In each instance the percentages given are based on the weight of the oil constituent.

Table I

Gravity, ° API	29.5	29.7	29.3	29.4
Flash, ° F	405	420	415	420
Fire, ° F	480	475	480	480
Viscosity, 100° F., S. U. S	249.6	251.8	258.5	252.8
Viscosity, 210° F., S. U. S	49.0	49.2	49.5	49.5
Viscosity index	92.7	94	93.3	97.8
Pour, °F	5	5	5	5
Carbon residue	.039	.04	.331	.25
Carbon residue (ash free)	.039	.04	.163	.08
Ash	0.0	.0	.168	.17
Acid No	.025	.075	2.3	0.4
Sap No	.16	.28	-----	-----
Color, NPA	2—	3+	2½	3+
Stability, 45' at 350° F	4+	4+	3½+	3½—
Sulfur, per cent	.20	-----	.20	-----
Calcium, per cent	-----	-----	.084	.048
Phosphorus, per cent	-----	.013	-----	.024

In the third and fourth columns of the foregoing tabulation, opposite acid No., the values are basic, due to the presence of the calcium salt.

As the lubricating oil constituent of my improved lubricating oil composition, various lubricating oil fractions may be used. For instance, solvent treated Mid-Continent neutral such as described in the foregoing tabulation or a blend of such neutrals with bright stock or a solvent refined lubricating oil fraction from a Pennsylvania crude or various blends of such lubricating oil fractions may be employed.

The proportion of the stearonitrile-phosphorus sulfide reaction products used in the compounding of my improved lubricating oil composition may be varied somewhat, but in any case only a minor proportion is used. Concentrations as low as 0.05%, by weight, may frequently be used with advantage, particularly where no metal salt detergent is present. Concentrations of about 0.5% have been found frequently to be desirable. The optimum concentration depends to a considerable extent upon the nature of the mineral oil constituent and the nature and amount of the detergent or other addends present. It is generally recognized that phosphorus acidity has a tendency to promote sludge formation. By the proper proportioning of my addend and a calcium salt detergent in the lubricating oil composition of my present invention, the phosphorus

acidity, due to the presence of the inhibitor, is neutralized thereby avoiding the sludge-forming tendency of the phosphorus. Where too little inhibitor is used, corrosion may occur. Where too much inhibitor is used, objectionable phosphorus acidity may result in the absence of a neutralizing detergent or may not be completely neutralized if the proportion of the detergent used is insufficient. Where the calcium salt of iso-octyl salicylate, for instance, is used as a detergent, satisfactory results have been obtained where the calcium salt detergent and the inhibitor were used in proportions ranging from 2 to 10 parts of the calcium salt to 1 part of the inhibitor. Optimum ratios where other detergents are used may be readily determined experimentally. In the absence of a detergent, it is usually preferred to use not in excess of about 0.2% of the phosphorus-containing addend where sludging is particularly objectionable.

My inhibitors have been found to increase the oxidation induction period of calcium iso-octyl salicylate, for instance, and to maintain a low rate of oxygen absorption both with and without the presence of copper-lead bearing metal. In some instances, the inhibitor has been found completely to eliminate the induction period, i. e., completely to deactivate the calcium of the detergent, and to maintain a low rate of oxygen absorption throughout the conventional oxygen absorption tests, thus avoiding the high rate of oxidation which normally occurs following the induction period.

The results of oxygen absorption tests carried out at 360° F. show that my new class of inhibitors are strong metal deactivators and efficient anti-oxidants. For example, by the addition of 0.15% of my inhibitor previously identified as A, the oxygen absorption rate of the previously identified solvent treated Mid-Continent SAE base 10 oil was reduced from 2.8 cc. per minute per 100 grams of oil to 2.2 cc. per minute. The addition of 0.5% of inhibitor D to the same base oil reduced the oxygen absorption rate to 1.25 cc. per minute. In the presence of copper-lead bearing metal, and also in the presence of 0.01% of Fe_2O_3, in the form of an oil soluble iron-naphthenate, recognized to be strong pro-oxidants, these pro-oxidant metals were found to be deactivated by small proportions of my inhibitors.

The results of oxygen absorption and corrosion tests, carried out at 360° F., of the previously described solvent treated Mid-Continent base oil and of blends of the base oil with the indicated proportions of my inhibitors previously identified, in the presence of recognized pro-oxidants, are set forth in the following Table II.

Table II

Inhibitor	Oxygen absorption rate in presence of iron-naphthenate	In presence of Cu-Pb bearing	
		O_2 absorp. rate	Bearing corrosion loss
	Cc./min.	*Cc./min.*	*Mgs.*
None	45.5	25.6	5.8
0.15% of A	4.6	4.2	0.3
0.5% of A	3.1	3.6	
0.5% of C	2.8	2.8	None
0.5% of D	2.8	3.6	None

In each instance the oxygen absorption rate is expressed in cubic centimeters of oxygen, at normal temperature and pressure, absorbed per minute per 100 grams of the lubricant.

A blend of the previously identified base oil with 1% of the calcium iso-octyl salicylate had, in the absence of copper-lead bearing metal, an induction period of 170 minutes and during said induction period the oxygen absorption rate of the blend was 1.5 cc. per minute. By the addition of 0.15% of my inhibitor A to this blend, the oxidation induction period was increased to 360 minutes, during which period the oxygen absorption rate was 1.07 cc. per minute. By the addition of 0.5% of my inhibitor A to the blend, the oxidation induction period was entirely eliminated, and, though the average oxygen absorption rate throughout the test was slightly in excess of the rate preceding the termination of the induction period of the blend alone, the marked increase of the oxygen absorption rate following the termination of the induction period was avoided by the presence of my inhibitor. Where 0.5% of my inhibitor C was added to this blend, the oxidation induction period was eliminated and the average oxygen absorption rate throughout the test was only 0.9 cc. per minute. Where 0.5% of my inhibitor D was added to the blend, the induction period was extended to 388 minutes, during which period the oxygen absorption rate was 0.9 cc. per minute.

In the presence of copper-lead bearing metal, a blend of the previously identified base oils and 1% of the calcium iso-octyl salicylate had an oxidation induction period of 107 minutes, during which period the oxygen absorption rate was 2.1 cc. per minute. The copper-lead bearing corrosion loss during the test was 11 mgs. By the addition of 0.5% of my inhibitor A to this blend, the induction period was eliminated and, though the average oxygen absorption rate throughout the test was slightly in excess of that of the uninhibited blend prior to the termination of the induction period, the marked increase in the oxygen absorption rate at the termination of the induction period, due to the activity of the detergent, was avoided.

By the addition of 0.5% of my inhibitor C to the blend of the base oil and the detergent, the induction period even in the presence of copper-lead bearing metal was eliminated. The average oxygen absorption rate throughout the test was only 1.1 cc. per minute and no bearing corrosion loss was experienced. By the addition of 0.5% of my inhibitor D to this blend, the oxidation induction period was increased to 205 minutes and throughout this period the mean oxygen absorption rate was 1.4 cc. per minute, bearing corrosion loss being completely avoided.

The improved characteristics of the lubricating oil compositions of my present invention are further illustrated by results of tests, conventionally known as the Bus Engine sludging test, in which oil at a temperature of 250° F. is subjected to accelerated oxidizing conditions while being continuously splashed against alloy bearings and against a steel roof member, the temperature of the latter being maintained at 500° F. In these tests the oil and test equipment were inspected at 45 hour intervals to ascertain the rate of oil deterioration, bearing corrosion and carbon and lacquer deposits in the test apparatus. In the present instance, these tests were carried out on the previously identified solvent treated Mid-Continent SAE 10 base oil alone, on said base oil having incorporated therein varying proportions of my inhibitor A, on a blend of said base oil having incorporated therein 1% of the calcium salt of iso-octyl salicylate (CIOS) and on blends

of the base oil containing various proportions of the detergent and of my inhibitor B. The results of these tests, including characteristics of the lubricant before and after the test, duration of test and the amount of sludge deposit and bearing corrosion loss, together with the identity of the lubricant tested, are set forth in the following table.

Table III

Inhibitor type	None	A	A	None	B	B
Inhibitor, per cent	None	.05	0.10	None	0.15	0.25
CIOS, per cent	None	None	None	1.0	0.75	0.75
Tests on fresh lubricant:						
Vis. at 210° F.—S. U. S.	49.0	49.2	49.2	49.5	49.3	49.5
Neutralization No.	0.025	0.05	0.075	2.3	0.9	0.4
Results at termination of test:						
Duration of test, hrs.	180	180	180	135	135	135
Vis. at 210° F.—S. U. S.	113.0	59.0	54.3	80.2	51.0	52.4
Neutralization No.	9.2	4.0	1.4	11.5	0.8	0.6
Sludge on roof, gms.	17.7	5.2	2.4	11.1	0.9	10.3
Cu-Pb bearing loss, mgs.	300	14	8	906	None	None

In the foregoing tabulation the neutralization number is expressed as milligrams of potassium hydroxide per gram of oil required to neutralize the oil, excepting the neutralization number of the fresh samples containing the detergent, which were basic. The tests of the sample of the third column was continued to 225 hours with little change in the results. Similarly the test of the sample of the fifth column was continued to 270 hours with little change in results. In each instance, the area of copper-lead bearing metal exposed to the oil was 26.81 sq. cm.

The results of these tests show that the members of my new class of inhibitors are very active stabilizers against deterioration, as appears from the neutralization numbers, viscosity changes, sludge deposits and bearing corrosion losses under the accelerated oxidizing conditions of the test.

Since my new class of inhibitors are readily oil-soluble, they may be incorporated in the oil constituent, or blend thereof, in any convenient manner, for instance by simply adding the inhibitor with agitation.

I claim:

1. A lubricating oil composition consisting principally of a petroleum lubricating oil fraction and containing in solution in said oil from about 0.05 to about 1%, by weight, of the reaction product of stearonitrile and a phosphorus sulfide of the group consisting of P_2S_5, P_2S_3, and P_4S_7.

2. A lubricating oil composition consisting principally of a petroleum lubricating oil fraction and containing about 1% of the calcium salt of an octyl salicylate and about 0.05 to about 0.5% of the reaction product of stearonitrile and a phosphorus sulfide of the group consisting of P_2S_5, P_2S_3 and P_4S_7.

3. A lubricating oil composition consisting principally of a petroleum lubricating oil fraction, and containing in solution the reaction product of stearonitrile and a phosphorus sulfide of the group consisting of P_2S_5, P_2S_3 and P_4S_7, said reaction product being present in an amount approximating 0.05 to 0.2% by weight on the weight of the oil.

4. A lubricating oil composition consisting principally of a petroleum lubricating oil fraction and containing in solution in said oil from about 0.05 to about 1% by weight of the reaction product of stearonitrile and a phosphorus sulfide of the group consisting of P_2S_5, P_2S_3 and P_4S_7 and an amount of the calcium salt of an octyl salicylate equal to about 2 to about 10 times the weight of said reaction product present.

5. A lubricating oil composition consisting principally of a petroleum lubricating oil fraction and containing in solution in said oil from about 0.05 to about 1%, by weight, of the reaction product of stearonitrile and P_2S_5.

6. A lubricating oil composition consisting principally of a petroleum lubricating oil fraction and containing in solution in said oil from about 0.05 to about 1% by weight, of the reaction product of stearonitrile and P_2S_3.

FRANKLIN M. WATKINS.

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