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LUBRICANT COMPOSITION

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The present invention comprises improvements in or relating to lubricating compositions and relates more particularly, though not exclusively, to lubricating compositions for use in internal combustion engines which may be either petrol- or oil-operated. In the latter case the invention is applied to the so-called "heavy duty" lubricating oils employed in diesel and other types of oil engines.

It is one object of the invention to provide a lubricating composition in which the tendencies of the lubricant to form products corrosive to metals (e. g. metal bearing surfaces) and to form deleterious oxidation products in the lubricant are inhibited, and another object is to provide a composition which possesses also detergent properties. The latter properties tend to secure a clean running engine during use of the lubricant by preventing the deposition of gum or lacquer on the lubricated parts and by maintaining solid particles and sludge (formed in any part of the engine or in the lubricant) in suspension therein. Such properties are of particular importance in oil engines such as diesel engines.

The present invention contemplates the use in a lubricating composition of a metallic derivative of an organic substituted dithiophosphate, some examples of which latter type of compound have already been proposed for incorporation in lubricating oils.

According to this invention a lubricating composition comprises a lubricating oil base and a minor proportion of (*a*) the tin-salt of an oil-soluble petroleum sulphonic acid and (*b*) a polyvalent metal salt (which is soluble in the oil base) of an organic dithiophosphoric acid.

It has already been proposed to add a variety of metal salts of organic dithiophosphoric acids to oils.

These additives are known in general to impart to the oil good resistance to oxidation and to inhibit to a greater or less extent the formation of products corrosive to composite metal bearings.

Some of them also possess "detergent" or sludge dispersive properties, especially effective in this connection being the alkaline earth metal salts of the straight chain dithiophosphoric acids having ten or more carbon atoms.

It has been found, however, that these dithiophosphates of relatively high molecular weight are much less effective as inhibitors of oxidation and bearing corrosion than those of low molecular weight which latter, however, are relatively ineffective as detergents and sludge dispersing agents.

An advantage of the present invention lies in

the fact that by the use of the combination of additives herein disclosed lubricating compositions can be provided possessing all these properties to a high degree.

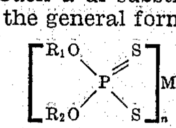
A further advantage of the compositions of the present invention is that they provide superior protection to ferrous metal surfaces against rusting (and consequent wear) due to the presence of condensed water, carbon dioxide, hydrobromic acid etc. normally present in small amounts in the combustion space.

The additives of the present invention also confer upon the base oil an improved film rupture strength.

The combination of desirable features provided by the lubricating compositions of this invention cannot be obtained by the random selection of any compound possessing detergent properties with any oxidation or corrosion inhibitor, as very often the presence of the detergent militates against the normal action of the inhibitor, rendering it relatively ineffective, probably by preventing it from forming a film on the surfaces of metal catalysts that may be prevent. Furthermore many of the detergent compounds formerly proposed as lubricant additives are themselves corrosive to composite metal e. g. copper-lead bearings.

A feature of the present invention is that not only do the two additives not interfere with one another's normal actions, but also in many instances they co-operate to give improved results over and above those obtained with either additive used alone.

According to one form of the present invention a lubricating composition comprises a lubricating oil base and a minor proportion each of the tin salt of an oil soluble petroleum sulphonic acid and a metal salt (which is soluble in the oil base) of an organic di-substituted dithiophosphoric acid derived at least in part from an alkylated phenol. Such a di-substituted salt can be represented by the general formula



where n represents the valency of a metal M, R_1 is any suitable organic radicle and R_2 is an alkylated aromatic radicle.

The radicle R_2 in the general formula quoted above is conveniently such as to have not less than five carbon atoms in the alkyl group and may be derived, for example, from p-tertiary amyl phenol, p-octyl phenol or octyl cresol. The radicle R_1 is such as to provide an oil soluble product and may be derived, for example, from an aliphatic alcohol (e. g. butyl amyl or lauryl alcohol), a cyclic alcohol (e. g. cyclohexanol or methyl cyclohexanol), a phenol (e. g. cresol or octyl cresol) or an aromatic alcohol such as benzyl alcohol.

It will be understood that appropriate radicles for R_1 and R_2 in the general formula quoted above will always be such that the di-substituted metal salt is soluble in the lubricating oil base.

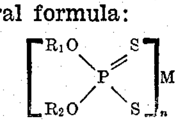
While, as already indicated, it is preferred to employ compounds wherein R_2 contains at least five carbon atoms in the alkyl group, it is within the scope of the invention to employ compounds in which the alkyl group of R_2 is short, or even absent, provided that R is of such a nature as to confer upon the metal salt adequate oil solubility.

Preferred specific examples of di-substituted dithiophosphoric acids a metal salt of which is employed in accordance with the invention are:

Di(octyl-cresyl) dithiophosphoric acid
Octyl-cresyl cresyl dithiophosphoric acid
Octyl cresyl 2-ethyl hexyl dithiophosphoric acid
Di(p-octyl phenyl) dithiophosphoric acid
Di(t-butyl cresyl) dithiophosphoric acid
Octyl cresyl n-butyl dithiophosphoric acid
Octyl cresyl cyclohexyl dithiophosphoric acid

Preparation of such metal salts is conveniently effected by first reacting the alkylated phenol with phosphorus pentasulphide with or without the presence of an appropriate hydroxylic organic compound for simultaneous reaction to produce a mixed di-substituted dithiophosphate. The acid is conveniently neutralized with caustic soda and a desired metal salt produced by the addition of a suitable salt of the said metal.

According to another form of the present invention the lubricating composition last referred to is modified by the incorporation in the lubricating oil base (either in place of or in addition to the organic di-substituted dithiophosphate derived from an alkylated phenol) of a minor proportion of an oil soluble metal salt of an organic di-alkyl or di-cycloalkyl dithiophosphoric acid. The last-mentioned salt is represented by the following general formula:



where R_1 and R_2 are alkyl or cyclo-alkyl groups having at least five and preferably not more than ten carbon atoms either in a straight or branched chain or ring, and where n represents the valency of the metal M.

Radicles R_1 and R_2 of the formula quoted above are preferably, but not necessarily, similar and may, for example, be derived from amyl alcohol, the hexyl alcohols such as n-hexyl alcohol, methyl isobutyl carbinol and 2-ethyl butanol, 2 ethyl hexanol, nonyl alcohol, cyclohexanol and methyl cyclohexanol.

Preferred specific examples of di-alkyl or dicycloalkyl dithiophosphoric acids, a metal salt of which is employed in accordance with the present invention, are:

Di(n-hexyl) dithiophosphoric acid
Di(2-ethyl hexyl) dithiophosphoric acid
Di(methyl cyclohexyl) dithiophosphoric acid
Diamyl dithiophosphoric acid, and
Di(α-methyl isoamyl) dithiophosphoric acid.

It will be appreciated however that mixed dithiophosphoric acids may be employed in the production of the oil soluble salts.

Preparation of the di-alkyl or di-cycloalkyl dithiophosphates may be effected by first reacting an appropriate alcohol or mixture of alcohols with phosphorous pentasulphide to produce the thiophosphoric acid from which the desired metal salt may be prepared for example by first neutralising the acid with caustic soda and then adding a suitable salt of the metal the dithiophosphate of which is desired. It is possible, however, to prepare certain salts, e. g. those of zinc by direct reaction of a metal oxide with the dithiophosphoric acid.

According to one form of the invention a chromium salt of the organic di-substituted dithiophosphate is employed, the desirability of employing organic compounds of both tin and chromium in a lubricating composition having been already proved. Other dithiophosphate salts may, however, be employed such as those of barium, calcium, strontium, magnesium, zinc, aluminium, nickel, cobalt, tin, cadmium and manganese.

According to the invention also the lubricating compositions of the kind above referred to may also include in its composition (1) a hydroxy-substituted aromatic thioether and/or di- or polysulphide, and/or (2) an aromatic phosphite or thiophosphite ester derived from such an aromatic thioether and/or di- or polysulphide. As an alternative to ingredients (1) and (2) or in addition thereto a yet further ingredient viz. (3) a tri-aryl phosphite may be included in the lubricating composition.

As examples of the third addition agent may be quoted:

(1) Di(3-carbomethoxy-4-hydroxyphenyl) thioether, disulphide or polysulphides.
(2) Di(3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite.
(3) Triphenyl phosphite, tri(p.t-amyl phenyl) phosphite.

EXAMPLE 1

Preparation of chromium di(octyl-cresyl) dithiophosphate

88 grams of octyl cresol (a mixture of diisobutyl cresols commercially available) were placed in a 250 c. c. round-bottomed flask, heated to 130° C., and treated with 24.3 grams of powdered phosphorus pentasulphide, added in small portions over a period of 30 minutes with mechanical stirring, the temperature being maintained at 130–140° C. until evolution of hydrogen sulphide was almost complete and most of the phosphorus pentasulphide had disappeared.

The reaction was then completed by heating slowly to 150° C. and maintaining this temperature with stirring for five minutes.

After cooling, the product was dissolved in petroleum ether and filtered from a little sulphur and unreacted phosphorus pentasulphide, the solvent being then distilled off under reduced pressure, yielding an amber viscous liquid.

The acidity of the product, determined by titrating an alcoholic solution with standard caustic soda solution in the presence of a phenolphthalein indicator, corresponded to an apparent molecular weight of 529 as compared with a theoretical molecular weight of 533 for di(octyl-cresyl) dithiophosphoric acid.

This product was mixed with nine times its weight of water in a beaker, heated to 40–50° C. and neutralised by adding caustic soda solution gradually with stirring until alkaline to phenolphthalein indicator.

This sodium salt solution was then heated to 90° C. and a further small amount of caustic soda added, a clear solution just alkaline to phenolphthalein thereby being obtained.

To this solution was added rapidly with stirring a 10% aqueous solution of chrome alum (at 90° C.) containing 15% excess of the theoretical chromium, when the violet chromium dithiophosphate was precipitated as a viscous liquid.

After cooling, the aqueous solution was decanted from this liquid which was then dissolved in petroleum ether, dried over anhydrous sodium sulphate, filtered, and freed from solvent by distillation. An 82% theoretical yield of the product was obtained.

Of a number of products prepared by this method, one typical one prepared on a larger scale had the following approximate analysis:

Chromium, 1.20%; sulphur, 8.4%; phosphorus, 4.3%
Chromium salt of di(octyl-cresyl) dithiophosphoric acid, 43%
Sodium salt of di(octyl-cresyl) dithiophosphoric acid, 5%
Free di(octyl-cresyl) dithiophosphoric acid, 29%
Octyl cresol and other neutral products, 23%

(The molecular weight of the free acid in this case was 600.)

The mixed product obtained by this method is referred to subsequently as "chromium di-(octyl-cresyl) dithiophosphate A."

EXAMPLE 2

Using the method of Example 1, with the exception that the temperature of precipitation of the cromium salt was 50–60° C. instead of 90° C. and that the concentration of the sodium salt solution was 5 per cent instead of 10 per cent, products were obtained having a higher concentration of chromium salt.

One such product, prepared from a free acid of molecular weight about 675 had the following analysis:

Chromium, 1.86%; phosphorus, 4.34%
Chromium salt of di(octyl-cresyl) dithiophosphoric acid, 72%
Sodium salt of di(octyl-cresyl) dithiophosphoric acid, 13%
Free di(octyl-cresyl) dithiophosphoric acid, 15%

This product is referred to subsequently as "chromium di(octyl-cresyl) dithiophosphate B."

It will be understood that in employing the compounds of this invention either pure metal salts may be used, or mixtures such as products of Examples 1 and 2. While minor amounts of the free dithiophosphoric acids and their sodium salts in the products are not objectionable it is preferred to utilise materials containing not more than about 20% of the free acid (and preferably less) and not less than about 65% of the polyvalent metal salt.

If desired, the residual free acid may be substantially neutralised by heating the product (preferably in oil solution) with a metal oxide or hydroxide (such as zinc oxide or calcium or barium hydroxide) to produce, for example, a mixture of chromium and zinc salts associated with a minor amount of sodium salt.

EXAMPLE 3

Using the method of Example 1, 1170 grams of 2-ethyl hexanol were reacted with 500 grams of phosphorus pentasulphide, a reaction temperature of 100 to 110° C. proving adequate and the reaction being concluded by heating to 130° C. A dark liquid was obtained having a molecular weight of 380 as compared with a theoretical molecular weight of 354 for di(2-ethyl hexyl) dithiophosphoric acid.

The zinc salt of the latter acid was prepared in the present example by heating a mixture of 101 grams of the acid and 11.1 grams of zinc oxide for half an hour at 120° C. to 130° C. The reaction product was dissolved in petroleum ether, filtered from excess of zinc oxide and the solvent removed by distillation to yield a yellow viscous liquid having 8.30% by weight of zinc as compared with a theoretical amount of 8.22% for zinc dioctyl dithiophosphate.

EXAMPLE 4

Tin salt of octyl cresyl 2-ethyl hexyl dithiophosphoric acid

Using the method of Example 1, there were obtained from a mixture of 330 grams of octyl cresol and 195 grams of 2-ethyl hexanol by the action of 166.5 grams of phosphorus pentasulphide, 647 grams of a viscous amber liquid, representing a 97% yield.

This had a molecular weight of 540, as compared with a theoretical value of 444.

Using the method of Example 2, there were obtained from 42 grams of this material, and 12.4 grams of stannous chloride in cold concentrated aqueous solution, 34.6 grams (72%) of an extremely viscous brown liquid containing 12.5% of tin.

EXAMPLE 5

Mixed chromium-zinc salt of di(2-ethyl hexyl) dithiophosphoric acid

19 grams of di(2-ethyl hexyl) dithiophosphoric acid (of M. W. 380) prepared as described in Example 3 were stirred for 20 minutes at 70–80° C. with moist chromic hydroxide freshly precipitated from a 10% aqueous solution containing 4.2 grams of chrome alum by the addition of ammonia. 1.5 grams of zinc oxide were then added and the heating continued for a further 15 minutes, after which the temperature was slowly raised to 130° C. to complete the reaction and eliminate the water formed.

The product, after dissolving in petroleum ether, filtering and removal of solvent, contained 1.30% of chromium, and 5.10% of zinc, the composition being approximately as follows:

Chromium salt of di(2-ethyl hexyl) dithiophosphoric acid, 29%
Zinc salt of di(2-ethyl hexyl) dithiophosphoric acid, 67%
Free di(2-ethyl hexyl) dithiophophoric acid, 3%

Other known methods for the preparation of the metal dithiophosphates of this invention may also be employed e. g. direct reaction between the free acid and a metal oxide in alcohol-benzene solution at 40–50° C. (applicable especially to the alkaline earth metal and magnesium salts), or direct reaction between a metal hydroxide, such as barium hydroxide and the free acid by heating together in mineral oil solution in presence of a current of air to remove liberated water.

Alternatively metathesis may be carried out in alcoholic solution between an alkali metal salt of a dithiophosphoric acid and an alcohol soluble metal salt.

Many of the salts can be prepared in good yield by the method of Example 2, the conversion to the metal salt being in many cases (e. g. tin, cadmium, nickel, cobalt) more satisfactory than that obtained in the case of chromium. Better conversion is also obained in the case of the dialkyl dithiophosphates than with the alkylated aryl dithiophosphates.

EXAMPLE 6

Tin petroleum sulphonate for use in conjunction with the product of Examples 1 to 5 was prepared as follows:

4 lbs. of an oil-concentrate containing 45% of sodium petroleum sulphonate (derived from the so-called "mahogany acids" of molecular weight about 400 to 420) was mixed with 3½ gallons of water and heated to 90° C., a milky solution being obtained. To this solution was added while being stirred, a cold solution of ½ lb. of stannous chloride ($SnCl_2 2H_2O$) in 500 ccs. of water. Tin petroleum sulphonate in oil solution was precipitated.

After cooling, the aqueous solution was decanted and the product washed by boiling with 1 gallon of water. The boiled mixture was further mixed with 4 lbs. of mineral oil and the resulting composition passed through a De Laval centrifuge. The oil concentrate mainly free from water was heated at 250° F. in a stream of air to remove further moisture.

By this procedure there was obtained 7 lbs. 6½ ozs. (representing a 96% yield) of an oil solution of tin petroleum sulphonate which was shown by analysis to contain 21% of tin petroleum sulphonate and 2.74% of tin by weight. The product was free from sodium, and is capable of use as an oil solution in appropriate quantity with a lubricating oil base for introducing into the latter a desired proportion of tin petroleum sulphonate.

PROPORTIONS

While the terms "minor proportion" would cover the use of the additives of this invention in a general way, the following proportions give an indication of the amounts contemplated:

The metal dithiophophate, 0.1–2% (preferably 0.2–1%)

The tin petroleum sulphonate, 0.05–2% (preferably 0.1–1%)

The third additive, 0.01–1% (preferably 0.05–0.5%).

TEST RESULTS

Numerous examples of the invention are given below in conjunction with the results of tests which serve to illustrate in various respects the desirability of the lubricating compositions provided by the present invention.

For purposes of comparison, test results include those for unmodified lubricating oil bases employed in producing the examples of compositions proposed by the present invention, and also, in certain instances, for compositions including only one of the additives. The constituents of said compositions are given in percentage proportions by weight in all tests.

Test 1.—Oxidation resistance

As a means of examining the oxidation resistance of the compositions proposed by the present invention, a modification of the well-known British Air Ministry oxidation test was employed. In this test 40 ccs. of the oil were oxidised by heating at 160° C. for two periods of 6 hours in glass tubes in the presence of a stream of air blown through at a rate of 15 litres per hour. Lubricating compositions were oxidised under the standard conditions of the British Air Ministry oxidation test except that a temperature of 160° C. was employed and that a copper catalyst, consisting of a rolled polished piece of copper foil 2¼" x 1", was present. The catalyst was replaced by a fresh one at the end of the first period of 6 hours' oxidation.

The test results obtained were:

Test No.	Lubricating Composition	Viscosity Increase (per cent)	Acidity (mgs. of KOH per gram)	Per cent insoluble in petroleum ether (B. P. below 40° C.)
1	Oil "B"	33.6	1.00	0.45.
2	Oil "B"+0.5% Zinc di(α-methyl isoamyl)dithiophosphate +0.2% Tin Petroleum Sulphonate	25.0	0.45	0.34.
3	Oil "B"+0.6% Chromium di(octyl cresyl)dithiophosphate "B" +0.2% Tin Petroleum Sulphonate	21.5	0.56	Trace.
4	Oil "B"+0.6% Zinc di(octyl cresyl)dithiophosphate +0.2% Tin petroleum Sulphonate	22.7	0.56	Very slight trace.
5	Oil "B"+0.6% Chromium di(2-ethyl hexyl)dithiophosphate +0.2% Tin petroleum Sulphonate	19.3	0.56	Slight trace.
6	Oil "B"+0.5% Zinc di-n-hexyl dithiophosphate +0.5% Chromium octyl cresyl cresyl di-thiophosphate +0.2% Tin Petroleum Sulphonate	17.5	0.45	Do.
7	Oil "B"+1.0% Cobalt Octyl cresyl n-butyl dithiophosphate +0.5% Tin Petroleum sulphonate	19.3	0.56	Trace.

Oil "B" as employed in these and in ensuing tests consisted of a blend of 94% of a solvent refined paraffinic type mineral oil of viscosity about 150 seconds Redwood at 140° F. and 6% of a blend of viscosity about 330 seconds Redwood at 140° F. containing a brightstock.

It would seem that whereas all the compositions tested have greatly improved oxidation resistance as compared with the base oil, those comprising metal salts of alkylated aromatic dithiophosphates are especially effective, particularly as regards the inhibition of sludge formation.

Test 2.—Bearing corrosion

The following test was employed for obtaining information as to the tendency for corrosion of composite metal bearings, particularly copper-lead bearings, to occur in use of lubricating compositions provided by the invention.

400 ml. of lubricant was weighed into 1500 ml. tall lipless glass beakers, eight of which were heated in a circular electrically heated oil bath thermostatically controlled to maintain the lubricant temperature at 140° C. The beakers were equipped with closely fitting aluminum covers having central slides which were normally closed but capable of being opened for the insertion of a test specimen. The slides when closed allowed sufficient clearance for centrally

placed steel stirring rods to revolve freely. The latter were electrically driven from a common driving shaft at 400±40 R. P. M. and carried at their lower end slotted holders to which lead test-pieces were attached by means of screws. For the test-pieces rectangular plates of pure lead 1¾'' by 1'' were mounted vertically just below the surface of the lubricant with the longer axis horizontal. Copper strips, as catalysts, ½'' wide and bent into a semicircle 3¾'' in diameter were placed wholly below the surface of the lubricant and attached by means of vertical copper wires to corks fitted in the beaker covers. Each beaker was also fitted with a thermometer.

Tests were conducted for a maximum total time of 30 hours in periods of six hours, the copper and lead specimens being removed every two hours and replaced by fresh clean ones. Copper catalysts were cleaned with carborundum powder and washed in petroleum ether. Lead specimens were flattened, scraped with a special Skartsen scraper and finally polished, by brushing in one direction with a type of stiff wire brush known as "file carding" before washing in benzene and weighing. After a 2-hour period a further washing in benzene, brushing with a camel hair brush and re-weighing was effected. The cumulative corrosion at any given time was calculated by adding together the weight losses of the lead specimens after each 2-hour period. These cumulative losses were plotted against time, and from the curves obtained, the times required for certain fixed corrosion losses to be reached, were read off.

The following results were obtained:

It will be seen from the foregoing test results, and particularly from tests 8–13, that a higher degree of protection against corrosion is obtained by the use of the combination of additives of this invention than would be obtained by the use of either additive separately in comparable proportions, and that furthermore the use of tin petroleum sulphonate gave results superior to those obtained by the use of other metal petroleum sulphonates such as those of calcium and sodium, especially as regards the retardation of the rate of increase of corrosion in the later stages of the test. The remaining test results are quoted to illustrate the wide range of compounds and proportions which may be employed in order to obtain lubricating compositions possessing a high degree of resistance against the formation of products corrosive to composite metal bearings.

Test 3.—Protection against rusting

A simple test was devised to demonstrate the effectiveness of the lubricating compositions of this invention in affording protection against the rusting of ferrous metal surfaces in presence of moisture and carbon dioxide.

Rectangular plates of mild steel 3'' x 1'', polished with emery cloth and washed with petroleum ether, were weighed and completely immersed in the oil under test for five seconds at room temperature, allowed to drain in a vertical position for 15 minutes, and placed horizontally across two short pieces of glass rod at the bottom of a 4'' diameter glass dish.

Test No.	Lubricating composition	Lead specimen weight loss (mgs.) after—		Hours run to weight loss of—		
		12 hrs.	18 hrs.	20 mgs.	50 mgs.	100 mgs.
8 [1]	Oil "B"	283	-------	4	6	8
9	Oil "B" + 0.5% Tin Petroleum Sulphonate	113	-------	4	6	10
10 [1]	Oil "B" + 0.3% Chromium di(octyl cresyl) dithiophosphate "B"	20	281	12	14	15
11 [1]	As test No. 10 + 0.2% Tin Petroleum Sulphonate	24	63	10	17	20
12 [1]	As test No. 10 + 0.2% Calcium Petroleum Sulphonate	15	143	13	15	17
13	As test No. 10 + 0.2% sodium petroleum sulphonate	19	83	12	16	18
14	Oil "B" + 0.5% Zinc di(α-methyl isoamyl)dithiophosphate + 0.2% Tin petroleum sulphonate	19	25	16	26	30
15	Oil "B" + 0.4% Chromium di(p-octyl phenyl)dithio- + 0.1% Tin petroleum sulphonate	20	142	12	15	17
16	Oil "B" + 0.4% Magnesium di(2-ethyl hexyl)dithiophosphate + 0.4% Tin petroleum sulphonate	37	-------	11	12	14
17	Oil "B" + 0.3% Cadmium octyl cresyl cyclohexyl dithiophosphate + 0.1% Tin petroleum sulphonate	16	203	13	14	16
18	Oil "B" + 0.5% Nickel di(methyl cyclohexyl)dithiophosphate + 0.2% Tin petroleum sulphonate	14	18.5	22	over 30	---------
19	Oil "B" + 0.6% Manganese di(tertiary butyl cresyl) dithiophosphate + 0.4% Tin petroleum sulphonate	35	103	9	16	28
20	Oil "B" + 0.8% Tin octyl cresyl 2-ethyl hexyl dithiophosphate + 25% Tin petroleum sulphonate	17	24	15	over 30	---------
21	Oil "B" + 2.0% Zinc di(2-ethyl hexyl)dithiophosphate + 0.2% Tin Petroleum Sulphonate + 0.2% tri(p-tertiary amyl phenyl) phosphite	10	13	29	over 30	---------
22	Oil "B" + 0.5% Zinc di(methyl cyclohexyl) dithiophosphate + 2.0% Tin petroleum sulphonate + 0.5% Octyl cresol thioether	47.5	-------	8	12	16

[1] Figures quoted against tests marked thus were the mean of 2 or 3 tests.

The compound described as octyl cresol thioether in test No. 22 was prepared by the action of sulphur dichloride on octyl cresol in carbon tetrachloride solution.

It would seem that to obtain the most effective inhibition of corrosion, the amount of tin petroleum sulphonate employed should not exceed the amount of metal dithiophosphate.

The dish was then filled with distilled water saturated with carbon dioxide so that the steel was approximately ½'' below the surface of the water and allowed to stand open to the air, the level being kept approximately constant.

After standing for one month, the plates were removed, freed from loose rust by rubbing with muslin, and weighed.

The following results were obtained:

Test No.	Oil used	Loss in weight of plate (milligrams)
23	Oil "B"	41.7
24	Oil "B"+0.5% Zinc di(α-methyl isoamyl) dithiophosphate. 0.2% Chromium di(octyl cresyl) dithiophosphate "B". 0.2% Tin Petroleum sulphonate. 0.05% di(3-carbomethoxy-4-hydroxyphenyl)thioether cresyl phosphite.	3.1

Test 5.—Lauson engine tests

Tests were carried out in standard H–2 type Lauson engines, under the following conditions:

Jacket temperature	210°±2° F.
Oil sump temperature	280°±2° F.
Test Duration	60 hours

Test results were as follows:

Test No.	Lubricant	Piston lacquer rating (C. R. C. visual rating)	Used Oil Analysis: Bearing weight loss (mgs.)	Used Oil Analysis: Per cent visc. inc.	Used Oil Analysis: Per cent insol. in pet. ether (B. P. below 40° C.)	Used Oil Analysis: Acidity
28	Oil "B" (average of over 20 tests)	6.2	92	39.9	0.94	1.04
29	Oil "B"+0.6% chromium di(octyl cresyl) dithiophosphate "B."	7.3	5	20.4	0.64	0.28
30	As test 29+0.2% tin petroleum sulphonate	8.4	10	28.0	0.62	0.53
31	Oil "B"+0.6% chromium di(octyl cresyl) dithiophosphate "A"+0.2% tin petroleum sulphonate.	8.5	39	33.3	0.70	0.60
32	As test 31+0.2% di(3-carbomethoxy-4-hydroxyphenyl)thioether cresyl phosphite.	7.9	7	33.8	0.61	0.63
33	As test 31+0.1% di(3-carbomethoxy-4-hydroxyphenyl)polysulphide.	8.5	17	34.5	0.94	0.39
34	Oil "B"+0.5% zinc di(α-methyl isoamyl) dithiophosphate.	7.5	5	16.0	0.41	0.28
35	As test 34+0.5% tin petroleum sulphonate	9.0	8	23.6	0.10	0.28
36	As test 34+1.0% tin petroleum sulphonate	9.5	17	19.0	0.06	0.45
37	As test 34+0.2% tin petroleum sulphonate+0.2% chromium di(octyl cresyl)dithiophosphate "B."	9.0	6	13.8	0.12	0.21
38	Oil "B"+0.6% zinc octyl cresyl 2-ethyl hexyl dithiophosphate+0.2% tin petroleum sulphonate.	8.7	18	16.4	0.17	0.39
39	Oil "B"+0.6% chromium octyl cresyl 2-ethyl hexyl dithiophosphate+0.2% tin petroleum sulphonate.	8.6	6	20.0	0.14	0.42
40	Oil "B"+0.6% chromium di(2-ethyl hexyl)dithiophosphate+0.2% tin petroleum sulphonate.	7.7	7	25.6	0.05	0.34

The water in test 23 was full of red rust whereas that in test 24 was only slightly affected.

Test 4.—Protection against rusting in presence of hydrobromic acid

The method of British Ministry of Supply specification D. T. D. 698 (Appendix 1) was employed.

This method, in which sand-blasted mild steel strips were immersed first in a solution of hydrobromic acid in kerosine, then in the oil under test (diluted with 15% petroleum ether) and finally suspended for 24 hours in a closed vessel over saturated zinc sulphate solution, was designed to simulate conditions in an internal combustion engine where, after a period of running the engine is allowed to remain idle. Corrosion of the cylinder walls, with consequent loss of power due to unduly large piston clearances, thereupon tends to take place due to the presence of condensed moisture, carbon dioxide, and fuel combustion products, notable among which is hydrobromic acid produced in small quantities from the combustion of the ethylene dibromide normally present in leaded fuel.

The following results were obtained:

Test No.	Oil used	Gain in weight of steel strips due to rust formation (milligrams)
25 [1]	Oil "B"	20.7
26 [1]	Oil "B"+0.6% Chromium di(octyl cresyl) dithiophosphate "B".	12.2
27 [1]	As test 26+0.2% Tin petroleum Sulphonate	5.4

[1] Figures quoted are the mean of at least three tests.

The C. R. C. visual rating was according to the method laid down by the Co-ordinating Research Council for rating piston cleanliness in the standard Chevrolet 36-hour L–4 test, in which a clean piston would have a rating of 10.0.

The majority of the figures quoted were the mean of at least two tests.

It will be seen from the results of tests 29 and and 30 and 34 to 37 that the combination of two additives according to the present invention yielded results superior to those obtained by the use of the metal dithiophosphate only, as regards piston cleanliness.

The advantage of a third addition agent as proposed by this invention is demonstrated by the results of tests 31 to 33, in which the metal dithiophosphate was present in insufficient quantity to effect by itself adequate protection of the bearings against corrosion.

The result of test 37 confirmed the results of oxidation tests already quoted, that a certain additional improvement as regards oil oxidation might be expected from the employment with tin petroleum sulphonate of both a metal dialkyl dithiophosphate and a metal alkylated aryl dithiophosphate.

Further tests were carried out in standard H–2 type Lauson engines, under different conditions, as follows:

Jacket temperature °F	350
Oil sump temperature °F	225
Duration hours	100

These tests were designed more particularly to illustrate the effectiveness of the lubricating compositions of this invention under "heavy duty" conditions as in high-speed diesel engines operating under heavy load.

Tests results were as follows:

Test No.	Lubricant	Piston lacquer rating (C. R. C. visual rating)	Piston rings stuck	Bearing Wt. loss (mgs.)	Used Oil Analysis (100 hours)		
					Per cent visc. inc.	Per cent insol. in pet. ether (B. P. below 40° C.)	Acidity
41	Oil "B"	1.5	1	118	176.1	0.32	0.45
42	Oil "B" (repeat test)	1.5	2	109	197.0	0.39	0.45
43	Oil "B"+0.7% di(α-methyl isoamyl) dithiophosphate.	zinc 3.2	1	12	137.1	0.09	0.28
44	Oil "B"+0.5% di(α-methyl isoamyl) dithiophosphate +0.5% tin petroleum sulphonate.	zinc 7.5	None	14	107.6	0.06	0.28

The considerable superiority of the combination of additives of the present invention was thus amply demonstrated.

Test 6—36 hour Chevrolet test

Tests were carried out on a 6-cylinder Chevrolet engine of standard type and according to the standard Co-ordinating Research Council procedure L-4.

Test No.	Oil Composition	Average Corrosion loss per whole brg.	Piston Varnish Rating	Total Varnish Rating	Total Sludge Rating
45	Oil "B"	0.856	8.4	48.4	46.0
46	Oil "B"+0.6% Chromium di(octyl cresyl dithiophosphate) "A"; 0.2% Tin Petroleum Sulphonate. 0.2% di(3-carbomethoxy-4-hydroxyphenyl)thioether cresyl phosphite.	0.109	9.2	49.4	47.4
47	Oil "B"+0.5% Zinc di(α-methyl isoamyl) dithiophosphate. +0.5% tin petroleum sulphonate.	0.192	8.95	48.95	46.4
48	Oil "B"+0.5% Zinc di(α-methyl isoamyl) dithiophosphate. 0.2% tin petroleum sulphonate. 0.2% chromium di(octyl cresyl). dithiophosphate "B"; 0.05% di(3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite.	0.127	8.85	48.85	43.9

Test No.	Used Oil Analysis (36 hours)		
	Per cent viscosity increase	Per cent insoluble in petroleum ether (B. P. below 40° C.)	Acidity (mgs KOH per gram)
45	52.3	0.85	0.62
46	59.1	0.68	0.75
47	24.1	0.37	0.45
48	22.1	0.32	0.22

In all the foregoing examples, the tin petroleum sulphonate employed was prepared as described in Example 6.

It will be understood that in all the foregoing tests the metal dithiophosphate additives were employed as prepared by the methods already illustrated, some being relatively pure organic compounds and others associated with varying minor amounts of other compounds, notably the free dithiophosphoric acids and their sodium salts.

The invention will be understood as including an additive for use in a lubricating oil base, which additive comprises in admixture tin petroleum sulphonate and an oil-soluble metal salt of an organic di-substituted dithiophosphoric acid.

We claim:

1. A lubricating composition, which comprises, a hydrocarbon lubricating oil base in major proportion between 0.05% and 2.0% by weight of said base, a proportion between 0.05% and 2.0% by weight of said base of a tin salt of an oil-soluble petroleum sulphonic acid and a proportion between 0.1% and 2.0% by weight of said base of an oil-soluble chromium salt of an octyl cresyl dithiophosphoric acid.

2. A lubricating composition in accordance with claim 1 in which the chromium salt is from 0.3 per cent to 2 per cent, the tin salt is from 0.05 per cent to 0.5 per cent by weight of the base and the proportion of the tin salt is never more than that of the chromium salt.

3. A lubricating composition in accordance with claim 1 in which there is included, in an amount from 0.1 per cent to 1 per cent by weight of the base, a derivative of a hydroxy substituted aromatic thioether selected from the group consisting of di(3-carbomethoxy-4-hydroxy phenyl) thioether cresyl phosphite and (3-carbomethoxy-4-hydroxy phenyl) polysulphide.

4. A lubricating composition which comprises a hydrocarbon lubricating oil base in major proportion, a proportion between 0.05 per cent and 2 per cent by weight of said base of a tin salt of an oil-soluble petroleum sulphonic acid, and a proportion between 0.1 per cent and 2 per cent by weight of said base of an oil-soluble chromium salt of an organic dithiophosphoric acid selected from the group consisting of; chromium di(octyl cresyl) dithiophosphate, chromium di(p-octyl phenyl) dithiophosphate, chromium di(α-methyl isoamyl) dithiophosphate, chromium di(2-ethyl

hexyl) dithiophosphate, chromium octyl cresyl 2-ethyl hexyl dithiophosphate, and chromium octyl cresyl cresyl dithiophosphate.

5. A lubricating composition in accordance with claim 4 in which the chromium salt is from 0.3 per cent to 2 per cent, the tin salt is from 0.05 per cent to 0.5 per cent by weight of the base and the proportion of the tin salt is never more than that of the chromium salt.

6. A lubricating composition in accordance with claim 4 in which there is included, in an amount from 0.1 per cent to 1 per cent by weight of the base, a derivative of a hydroxy substituted aromatic thioether selected from the group consisting of di (3-carbomethoxy-4-hydroxy phenyl) thioether cresyl phosphite and (3-carbomethoxy-4-hydroxy phenyl) polysulphide.

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