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LUBRICATING COMPOSITION

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1

This invention relates to lubricating oil addition agents designed to improve the lubricating properties of lubricating oils for use under conditions of severe service such as those encountered in Diesel engines, and the like, and to lubricating oils containing these addition agents.

Primarily, the object of this invention is to produce, for use under such severe service conditions as are encountered in Diesel engines, lubricating oils which will be non-corrosive to corrosion-sensitive bearings, such as the copper-lead or cadmium-silver type, and which will also avoid the deposition of lacquer and varnish-like materials upon pistons and overcome carbon deposition behind the rings.

Other objects of this invention will be apparent from the description contained hereinafter.

It is well known that ordinary mineral lubricants are effective only within certain limits of engine operating conditions and when these limits are exceeded deterioration of the lubricating oils results causing undesirable ring sticking, bearing corrosion, sludge formation, piston lacquering, and the like. Addition agents have been developed and used in lubricating oils to minimize this deterioration and to reduce its deleterious effects if it does occur.

Addition agents which have been proposed for the improvement of lubricating properties of lubricating oils are many in number. In general these agents are designed to function in some specific manner; for example, an addition agent to which is attributed detergent properties is one which tends to keep pistons, rings and valves free of lacquer and varnish-like deposits. Oil-soluble metal salts of sulfonic acids are perhaps the most used addition agents to improve the detergent properties of a lubricating oil and their use is well known in the art. Prevention of bearing corrosion is another specific function for which lubricating oil addition agents have been designed. Addition agents which perform this function include phenolic compounds, metal salts of the reaction products of a sulfide of phosphorus and an alcohol, metal salts of the reaction products of a sulfide of phosphorus and a hydrocarbon, such as those disclosed in U. S. Patent 2,316,082 to Loane et al., and many others.

The present invention resides in lubricating oils, preferably mineral lubricating oils, containing oil-soluble metal salts of the reaction products of phosphorus pentasulfide, or other sulfides of phosphorus, or even oxides of phosphorus and a particular hydrocarbon fraction, to be described hereinafter, obtained in the refining of

2

lubricating oils. The invention also resides in lubricating oils, preferably mineral lubricating oils, containing oil-soluble metal salts of the reaction products of sulfides or oxides of phosphorus and a hydrocarbon together with oil-soluble metal salts of sulfonic acids, phenols, the reaction product of phosphorus pentasulfide and an alcohol, the reaction product of phosphorus pentasulfide and a phenol and synthetic organic acids prepared by oxidizing high molecular weight mineral oil and paraffin wax fractions.

We have discovered that the performance of internal combustion engines under severe service conditions such as those encountered in Diesel engines can be markedly improved by the use of a lubricating oil to which has been added small amounts of an oil-soluble metal salt of the reaction product of a sulfide or oxide of phosphorus with the particular hydrocarbon fraction referred to above.

We have also discovered that the lubricating properties of a lubricating oil can be markedly improved by the addition of these same small quantities of an oil-soluble metal salt of the reaction product of a sulfide or oxide of phosphorus and a hydrocarbon or hydrocarbon fraction together with small quantities of an oil-soluble metal salt of a sulfonic acid.

Not only may an oil-soluble metal salt of the reaction product of a sulfide of phosphorus and a hydrocarbon be used in conjunction with an oil-soluble metal salt of a sulfonic acid as described hereabove, but it may also be used in conjunction with other lubricating oil addition agents. Such other addition agents which may be used in conjunction with the oil-soluble metal salt of the reaction product of a phosphorus sulfide or oxide and a hydrocarbon include oil-soluble metal salts of phenols and particularly alkyl or cycloalkyl substituted phenols such as those having more than about 12 carbon atoms per molecule; oil-soluble metal salts of phenol sulfides or alkyl or cycloalkyl substituted phenol sulfides and particularly those having alkyl substituents containing at least about 4 carbon atoms; oil-soluble metal salts of fatty acids, halogenated fatty acids or substituted fatty acids such as dichlorostearic acid, phenyl stearic acid and the like; oil-soluble metal salts or soaps of rosin acids such as abietic acid, hydrogenated rosin acids and the like; oil-soluble metal salts or soaps of acids produced by oxidizing hydrocarbons or hydrocarbon fractions such as paraffin wax, paraffinic lubricating oil fractions and the like; oil-soluble metal salts of the reaction products formed by reacting a

sulfide or oxide of phosphorus with an alcohol or with a phenol; oil-soluble metal salts of phosphonic or phosphinic acids obtained by reacting elemental phosphorus with hydrocarbons as described in U. S. Patent 2,311,305 to Ritchey and in fact many others.

We have discovered further that not only does the combination of an oil-soluble metal salt of the reaction product of a phosphorus sulfide and/or oxide and a hydrocarbon with one of the other agents mentioned improve the lubricating qualities of a lubricating oil, but that any of these indicated combinations may be used in conjunction with a third lubricating oil addition agent which may be any one of those described as the second component of our combination addition agent to impart specific desirable properties to lubricating oils.

The oil-soluble metal salt of the reaction product of a sulfide of phosphorus and a hydrocarbon to be used in the practice of our invention is generally prepared by first reacting a sulfide or oxide of phosphorus with a hydrocarbon and then preparing a metal salt of the reaction product. Thus a phosphorus sulfide or oxide, preferably phosphorus pentasulfide, in amounts in the order of about 3% to 50%, preferably 10% to 20%, by weight of the hydrocarbon used is reacted with a hydrocarbon such as naphthalene, acenaphthene, lauryl benzene or the like or with a petroleum fraction such as one described hereinbelow, for one to twelve hours at temperatures of about 200° F. to 600° F., preferably at about 400° F. This reaction, when carried out with a sulfide of phosphorus, proceeds with the evolution of hydrogen sulfide and is generally continued until such evolution ceases. Moreover, it has been observed that when the reaction is effected with phosphorus pentasulfide elemental sulfur is sometimes one of the reaction products. When phosphorus pentoxide is employed water is one of the reaction products.

The reaction product is acidic and capable of forming salts with basically reacting compounds. Salts may be prepared directly from the crude reaction product or the reaction mixture may first be blown with nitrogen, fuel gas, steam or other gas to remove volatile reaction products from the mass. The desired oil-soluble metal salt is usually prepared by direct neutralization of the above reaction mixture with a basic compound of the desired metal such as the oxide, hydroxide or carbonate, but it may also be prepared by first neutralizing the reaction mixture with a hydroxide or oxide of an alkali metal, such as sodium or potassium, and then preparing the desired metal salt from the alkali metal salt by metathesis. For example, a heavy metal salt, such as the nickel salt, may be prepared by metathesizing the sodium salt of the reaction product with a nickel salt using conditions well known in the art for effecting reactions of this type. When direct neutralization of the reaction mixture with a metal hydroxide, oxide, or carbonate is carried out it is sometimes advantageous to dilute the reaction mixture with about an equal volume of a lower boiling hydrocarbon or hydrocarbon fraction such as a low boiling gasoline or naphtha fraction or the like, and to use a small amount of water along with the metal hydroxide, oxide, or carbonate. Under such conditions and particularly if slightly elevated temperatures are employed, the neutralization proceeds to completion in a rather short period of time.

Phosphorus sulfides or oxides which may be

employed include phosphorus pentasulfide, phosphorus trisulfide, phosphorus pentoxide and phosphorus trioxide as well as mixtures of these sulfides and/or oxides. In place of phophorus sulfides and oxides we may employ mixtures of elemental phosphorus and elemental sulfur as phosphosulfurization agents. In carrying out the reaction between a hydrocarbon or hydrocarbon fraction and phosphorus and sulfur, white phosphorus and powdered sulfur are added to the hydrocarbon or hydrocarbon fraction and the mixture is heated to at least about 300° F. and preferably to at least about 400° F. for a period of 2 hours or until the reaction is complete. The reaction product is then treated in the manner described for treatment of the product obtained when a sulfide or oxide of phosphorus is reacted with a hydrocarbon or hydrocarbon fraction.

In the following description the term "phosphosulfurization" will be employed to indicate the reaction between a phosphorus sulfide, a phosphorus oxide or phosphorus and sulfur with a hydrocarbon. The reaction product will be described generically as an acid of phosphorus having an organic substituent. More specifically, the product obtained by reacting a hydrocarbon with a phosphorus sulfide will be designated as a sulfur-containing acid of phosphorus having an organic substituent.

Although many hydrocarbons and hydrocarbon fractions may be used in the preparation of acidic phosphorus compounds by treatment with phosphorus sulfides or oxides, there appear to be great differences in their reactivity, i. e., in the ability of the hydrocarbons or hydrocarbon fractions to form the desired phosphorus compounds. Thus, although petroleum distillates boiling in the lubricating oil range may generally be employed as the phosphosulfurization stock, the yields of the desired acidic products are usually low and the products are contaminated with undesirable polymerized or resinified bodies which are objectionable and which are difficultly separable from the desired reaction products.

We have found that by various means described herebelow it is possible to separate from lubricating oil fractions of petroleum, such as lubricating oil distillates, fractions which phosphosulfurize readily to produce relatively high yields of the desired reaction products without the formation of the undesirable polymerized or resinified materials described above. The preferred fraction is one which contains hydrocarbons that are not highly paraffinic and yet not highly aromatic. Thus it is desirably one obtained as an intermediate fraction or heart cut from a lubricating oil distillate by fractionation of the lubricating oil distillate with a selective solvent.

It is well known that by means of extraction with selective solvents such as phenol, furfural, nitrobenzene, dichloroethyl ether, sulfur dioxide-benzene, benzonitrile, benzaldehyde, chloroaniline, chlorophenol, and the like it is possible to fractionate mineral oil fractions on the basis of the relative paraffinicity or aromaticity of the molecules present. Thus these solvents selectively dissolve the more aromatic hydrocarbon molecules leaving the more paraffinic molecules undissolved. By controlling the amounts of solvent and other conditions of extraction such as temperature it is possible to control the proportion of any given stock which will be dissolved.

Moreover by the use of two extraction steps it is possible to separate the original lubricating

oil fraction into three fractions, i. e., a first extract, a second extract and a final raffinate. In this case the first extract would comprise the most highly aromatic molecules, the final raffinate would comprise the most highly paraffinic molecules and the second extract would comprise molecules which are more aromatic than the molecules present in the raffinate but less aromatic and thus more paraffinic than the molecules present in the first extract. Such a material, i. e., the second extract would constitute a desirable phosphosulfurization stock. Such a fraction may be obtained from substantially any lubricating oil stock whether obtained from naphthene or paraffin type crude oil, but the amount of the desired fraction obtainable will vary with the type of stock employed and with the efficiency of the solvent fractionation used to produce it. Although the physical characteristics of the desired intermediate fraction will vary with the type of crude oil from which it has been produced and with the viscosity of the fraction extracted, in general, the viscosity gravity constant (V. G. C.) should be within the limits of about 0.82 and about 0.90 and preferably within the limits of 0.84 and 0.88. Viscosity gravity constant is a relationship between the viscosity and gravity of an oil and is described by Hill and Coates in the Journal of Industrial and Engineering Chemistry, vol. 20 (1928), page 641. The limits indicated are not the limits for the average V. G. C. of the fraction but rather they represent the practical limits of the V. G. C.'s of the molecules present in the desired fraction. Under any circumstance the desirable fraction will not contain more than about 20% by volume of material having V. G. C.'s outside of the range of 0.82 to 0.90 and preferably 0.84 to 0.88. The presence of undesirable material may be determined by a solvent fractionation involving two or more solvent extractions. Thus, extraction of the particular fraction under conditions such that 5% to 10% of the fraction will be removed as extract should produce an extract oil having a V. G. C. not greater than about 0.90 and preferably not greater than about 0.88. Furthermore, extraction with a solvent which will dissolve 90% to 95% of the fraction should leave 5% to 10% of a raffinate oil having a V. G. C. not less than about 0.82 and preferably not less than 0.84.

In preparing a particularly desirable phosphosulfurization stock, a lubricating oil fraction of a waxy Santa Fe Springs (California) crude oil was prepared by vacuum distillation in the presence of superheated steam. This distillate was dewaxed by diluting with 4 volumes of liquid propane, cooling to −50° F. and filtering to remove the wax. The propane was then removed by a topping distillation. The results of tests on the waxy distillate and on the dewaxed distillate were as follows:

	Waxy Distillate	Dewaxed Distillate
Gravity, ° API	18.6	16.8
Saybolt Universal viscosity, seconds, at—		
100° F.	2,600	5,438
130° F.	799	1,400
210° F.	108.5	139.2
Viscosity Index	30	−10
Viscosity gravity constant	0.876	0.887
Pour Point, ° F.	110	15
Flash point, Cleveland open cup, ° F.	495	505

The dewaxed distillate was extracted with 3 volumes of phenol at 150° F. to produce, after removal of the phenol, a phenol raffinate and a phenol extract. This phenol extract amounted to about 55% by volume, and the phenol raffinate amounted to about 45% by volume, of the dewaxed distillate. The phenol extract was further treated with 7 volumes of furfural at 150° F. to produce, after removal of the furfural, a furfural raffinate and furfural extract. The furfural raffinate amounted to about 35% by volume of the phenol extract or about 19% by volume of the dewaxed distillate. This furfural raffinate is a particularly desirable hydrocarbon fraction for reacting with a phosphorus sulfide or oxide to produce our lubricating oil blending agents.

The characteristics of this furfural raffinate fraction are given below together with the characteristics of the phenol raffinate, phenol extract and furfural extract.

	Phenol Raffinate	Phenol Extract	Furfural Raffinate	Furfural Extract
Gravity, °A. P. I.	28.7		19.7	
Viscosity, SUS at—				
100° F.	729	[1]110,000	3,800	[1]1,400,000
130° F.	305	12,354		87,197
210° F.	73.1	394	131	919
Conradson carbon, percent residue	0.03	2.9	1.4	5.8
Iodine No. (Hanus) Mg. Iodine absorbed per g.	0.62	3.1	1.2	24.4
Sulfur, percent		1.04	0.97	1.05
Carbon, percent	86.00	87.57	85.40	86.82
Hydrogen, percent	14.11	10.87	12.33	9.93
Viscosity Index	90	−270	28.9	−820
Viscosity gravity constant based on viscosity at 210° F.	0.806		0.864	

[1] Extrapolated.

The preferred hydrocarbon fraction to be used in the practice of our invention may also be prepared in other ways. For example, the above described procedure may be modified to obtain the desired material. Instead of reextracting the phenol extract with furfural the solution of phenol extract in phenol or the original phenol extract phase may be cooled until the desired raffinate has separated or a sufficient quantity of water may be added to the extract phase to release or reject the desired proportion of raffinate. Also a lower boiling hydrocarbon, such as propane, butane, a light gasoline or naphtha fraction, or the like, may be added to the phenol extract phase to effect the separation of the desired raffinate. Combinations of these treatments may be used as would be understood by one skilled in the art.

It is also possible to produce the same desirable material by using other selective solvents at any or all stages of the process as outlined above in place of phenol and furfural. Thus, the first extraction may be carried out with phenol, furfural, sulfur dioxide, sulfur dioxide-benzene, nitrobenzene, or some other suitable solvent and the second extraction carried out with the same solvent under different conditions of temperature,

solvent ratio, etc. or with a different solvent suitable for effecting the separation of the desired material.

Among other methods of preparing the desired material which will be obvious to those skilled in the art, may be mentioned that of changing the solvent and/or conditions of extraction in such a manner that the desired material will be found in the first raffinate fraction rather than the extract fraction. A second extraction may then be performed on the raffinate from the first extraction using any suitable solvent and adjusting conditions of extraction, temperature, solvent ratio, etc., in such a manner that the desired hydrocarbon fraction will be obtained as a second extract from the first raffinate.

The desirability of employing an intermediate fraction of a lubricating oil distillate which is separated from the lubricating distillate by a solvent fractionation process is illustrated by the results of phosphosulfurization reactions which have been carried out on the various fractions described above which were prepared by first extracting a lubricating distillate with phenol and subsequently extracting the extract oil from the phenol extraction with furfural. Thus the phosphosulfurization reaction was carried out on the phenol raffinate, the phenol extract and on the furfural raffinate from the extraction of the phenol extract as well as on the furfural extract. In each case the hydrocarbon fraction was heated for three hours at about 400° F. with 12.5% by weight of phosphorus pentasulfide. The reaction product was diluted with three volumes of a paraffinic solvent having a boiling range of about 140° F. to about 200° F. and consisting primarily of hexanes and heptanes, the diluted material was filtered to remove insoluble reaction products and the filtrate reacted with an excess of lime, the excess being removed by filtration after neutralization was complete. The filtered product was evaporated to remove the solvent. The yields of oil-soluble products and the percentages of phosphorus, sulfur and calcium in the various products are shown below.

	Dewaxed Distillate	Phenol Raffinate	Phenol Extract	Furfural Raffinate	Furfural Extract
Yield of oil-soluble reaction product, based on total reactants, per cent by weight	85	91	80	95	74
Phosphorus content of oil-soluble product, per cent by weight	0.9	0.2	1.67	2.39	1.48
Sulfur content of oil-soluble product, per cent by weight	1.7	0.4	3.50	4.08	3.30
Calcium content of oil-soluble product, per cent by weight	0.9	0.2	0.89	2.29	0.89

The lower yields of oil-soluble reaction products obtained with the phenol extract and with the furfural extract are due to the production of appreciable quantities, i. e., about 20% and about 30%, respectively, of polymerized material which is insoluble in the solvent employed and in lubricating oil. The desirability of hydrocarbon material for phosphosulfurization depends not along upon the high yields of oil-soluble reactions produced, but also upon the phosphorus, sulfur and metal content of the final reaction product. Thus, phenol raffinate gives a relatively high yield of oil-soluble product, however, very little phosphosulfurization occurs as indicated by the low phosphorus, sulfur and metal contents.

The phosphosulfurized product or the product obtained after reacting a hydrocarbon or hydrocarbon fraction with a sulfide or an oxide of phosphorus will be referred to herein as a concentrate. Such concentrates may contain, depending upon the reactivity of the hydrocarbon or hydrocarbon fraction, upon the amount of phosphorus, sulfide, or oxide employed and upon the conditions of reaction, between about .05% and about 5.0% by weight of phosphorus in the form of an oil-soluble reaction product. These concentrates after neutralization with lime or other metal oxide or hydroxide may be added to lubricating oils in amounts sufficient to produce oils containing the desired proportions of reaction product as determined by their phosphorus content. When these additives are employed as the only addition agents, the final oil will desirably contain between about 0.01% and about 0.5% by weight of phosphorus and preferably between about 0.05% and about 0.2% by weight of phosphorus.

In preparing lubricating oils containing the reaction product of a phosphorus sulfide or oxide and a hydrocarbon with other addition agents such as sulfonates, phenates and the like, the proportion of the said reaction product should be such that the phosphorus content due to the presence of said reaction product will also be in the order of from about 0.01% to about 0.5%, and preferably in the range of about 0.05% to about 0.2%, and the second additive, i. e., the sulfonate, phenate, etc., will constitute between about 0.1% and about 5.0% by weight and preferably between about 0.5% and 2.5% by weight of the finished oil.

The amount of phosphorous contained in these oils was determined by a standard analytical procedure consisting of first converting the phosphorous in a weighed quantity of the material to be analyzed to the phosphate form by oxidation with sodium peroxide in a Parr bomb and then finishing the analysis according to the procedure given by Kolthoff and Sandell, Textbook of Inorganic Analysis (1936), page 676, for the determination of phosphorus in steel wherein the phosphorus is weighed as magnesium pyrophosphate.

Oil-soluble sulfonates which may be used in conjunction with our reaction product between an oxide or sulfide of phosphorus and a hydrocarbon include the metal salts of substantially any oil-soluble sulfonic acid. Suitable sulfonic acids are obtainable on the market, generally in the form of their sodium salts, containing about 60% by weight of sodium sulfonates and 40% by weight of mineral oil. The sodium salts may be used directly or they may be converted into other metal salts by processes of metathesis which are well known in the art.

If desired the oil-soluble metal salt of a sulfonic acid may be prepared by direct sulfonation of a suitable material, with fuming sulfuric acid, gaseous sulfur trioxide, chlorosulfonic acid, etc., to form oil-soluble acids followed by the preparation of metal salts either by direct neutralization with a basic metal compound, such as the oxide, hydroxide or carbonate, or by neutralization with a metal oxide, hydroxide or carbonate followed by preparation of the desired metal salt by metathesis. The petroleum fraction described above as furfural raffinate is of particular value as a starting material for the preparation of oil-soluble metal salts or sulfonate acids because this

stock appears to yield large quantities of desirable oil-soluble sulfonic acids. The type of sulfonic acids which are preferably employed are those commonly described as mahogany acids as distinguished from the green acids which are the water-soluble sulfonic acids produced along with the mahogany acids in the sulfonation of petroleum fractions. Although the mahogany acids are the preferred sulfonic acids from which oil-soluble metal salts are produced it is known that relatively large proportions of green acid salts may be solubilized in a mineral oil by the oil-soluble mahogany acid salts and such mixtures of mahogany sulfonates and green sulfonates, the latter solubilized by the mahogany sulfonates, may be employed in our lubricating compositions.

Oil-soluble metal salts of phenols which may be used in the practice of our invention include the oil-soluble metal salts of many phenolic materials such as those of alkyl or cycloalkyl substituted phenols having more than about 12 carbon atoms per molecule as well as phenol sulfides of the alkyl hydroxy phenyl thio ether type. Thus metal phenates such as those described in U. S. Patent 2,281,401 to Wilson and U. S. Patent 2,344,988 to Kavanagh et al. may be employed. Phenol sulfides of the above type which may be employed are described in U. S. Patent 2,139,766 to Mikeska et al. and similar compounds together with their method of preparation are described in U. S. Patent 2,139,321 to Mikeska et al.

Suitable oil-soluble metal salts of synthetic organic acids produced by oxidizing hydrocarbons or hydrocarbon fractions are described in U. S. Patent 2,270,620 to Bray. The synthetic organic acids used in the preparation of oil-soluble metal salts are preferably obtained by oxidizing relatively high molecular weight hydrocarbon fractions such as highly paraffinic lubricating oil fractions and the like or paraffin wax. The acids so produced may be converted into the metal salts directly or they may be chlorinated and the chlorinated acids converted into their metal salts. Preferably the acids will contain in excess of 10 carbon atoms per molecule.

Suitable oil-soluble metal salts of acids produced by the reaction of a phosphorus sulfide or oxide with alcohol or with phenol are preferably those alkyl, aryl, or aralkyl phosphoric or thiophosphoric acid salts prepared by the reaction of P_2S_5 or P_2O_5 on an alcohol or phenol. The method of preparing these salts is fully described in the Freuler U. S. Patent 2,364,284. The preferred alcohols and phenols are the monohydroxy organic compounds where the organic group comprises an alkyl, cycloalkyl, aryl, aralkyl or alkaryl radical.

Metals which may be used to form the desired metal salts or soaps of each of the additive materials described hereinabove include the alkaline earth metals, calcium, strontium, barium and magnesium, and the polyvalvent metals such as zinc, nickel, aluminum, lead, manganese, mercury, copper, iron, tin, chromium, bismuth and thorium. In some instances the alkali metal salts may be employed such as the sodium, potassium or lithium salt.

The products of this invention may be employed to improve the lubricating qualities of any lubricating oil, but we prefer to use mineral lubricating oils, especially mineral lubricating oils having a viscosity index (defined by Dean and Davis, Chemical and Metallurgical Engineering, vol. 36, page 618 (1929)) in the range of about 75 to about 95, such as those produced by solvent treating paraffinic base stocks.

In preparing high quality lubricating compositions we may add to a lubricating oil a sufficient quantity of the metal salts of the reaction product obtained by reacting phosphorus oxide or sulfide with a hydrocarbon to impart to the finished lubricating oil a phosphorus content in the desired range. We may also add the desired quantities of one or more of the lubricating oil additives described herein to the above composition to impart other and additional specific and desirable properties to the finished composition. The metal salts employed are oil-soluble and require only simple mixing with a lubricating oil to obtain solution. However, the blending is usually effected at slightly elevated temperatures in the range of 100° F. to 200° F. in order to facilitate solution and dispersion of the addition agents in the body of the lubricating oil.

Methods which have been employed to evaluate lubricating compositions of our invention include various accelerated engine tests. These tests have been run on oils without the addition of our agents and on oils containing our addition agents.

Three different engine tests have been employed in the evaluation of our lubricating oils. These tests have been carried out in Lauson single cylinder engines, standard 6 cylinder Chevrolet engines and a single cylinder Caterpillar Diesel standard test engine. The tests are referred to as the Lauson engine test, the Chevrolet engine test and the Caterpillar test, respectively.

In carrying out the Lauson engine test, the engine is operated for a total of 60 hours under a load of about 3.5 horsepower with a coolant temperature of about 295° F. and an oil temperature of about 280° F. This test is employed to determine the lacquering and corrosion tendencies of the oil. At the end of the test the cleanliness of the engine is observed and given a numerical "detergency rating" between 0 and 100%, where 100% indicates a perfectly clean engine. Thus a detergency rating of 100 would indicate that there were substantially no lacquer or varnish-like deposits within the engine. The corrosivity of the oil is measured by determining the loss in weight of corrosion sensitive copper-lead bearings after 20, 40 and 60 hours of operation. In some instances the corrosivity is also determined by measuring the loss in weight of a lead strip suspended in the oil in the crank case of the engine. In those cases in which corrosion was extremely severe and there appeared to be danger of engine failure due to excessive corrosion of the copper-lead bearings as indicated by an examination made at the 40-hour period, these bearings were replaced with Babbitt bearings in order to complete the test.

In the Chevrolet engine test the engine is operated under a load of about 30 horsepower with a coolant temperature of about 200° F. and an oil temperature of about 280° F. This test is used to evaluate corrosivity of the lubricant. The loss in weight of copper-lead bearings is determined after 36 hours of operation.

In the Caterpillar test which is employed to determine the detergency of an oil, i. e., the ability of the oil to prevent lacquering of the engine, the engine is operated for a period of 100 hours under a load of about 19.8 horsepower with a coolant temperature of about 175° F. and an oil temperature of about 145° F. At the end of the test a numerical "detergency rating" is assigned. The

method of rating is similar to that employed in the Lauson engine test and 100% indicates a completely clean engine.

The following specific examples are given to further illustrate our invention, however, they should not be taken as limiting the broad aspects of our invention.

Example I

To 1170 grams of the petroleum fraction described hereinabove as furfural raffinate was added 146 grams of P_2S_5 and the mixture was stirred for about three hours at a temperature of about 400° F. During the early stages of the reaction evolution of hydrogen sulfide was vigorous, but at the end of the reaction period evolution of hydrogen sulfide had practically ceased. The mixture was cooled to room temperature, diluted with about an equal volume of a light paraffinic hydrocarbon solvent having a boiling range of 140° F. to 200° F. and filtered. About one-third of the filtrate was heated on a steam bath to about 60° C. and an excess of $Ca(OH)_2$ added along with a few milliliters of water. When the mixture was neutral it was filtered to remove the excess unreacted $Ca(OH)_2$; the solvent was then removed from the filtrate by evaporation on a steam bath followed by heating to about 140° F. under a vacuum of about 25 inches of mercury. The evaporated product amounting to 484 grams contained 4.08% sulfur, 2.39% phosphorus and 2.29% calcium. This material will be designated hereinafter as product A.

The efficacy of product A in preventing deposition of lacquer and varnish-like materials upon the piston and behind the rings of an internal combustion engine and in preventing corrosion of alloy bearings of the copper-lead type was shown by dissolving 6.7% by weight of the material in a mineral lubricating oil of SAE 30 grade having a gravity of 28.5° API, a viscosity of 746 SSU at 100° F. and a vicosity index of 90 and evaluating the solution for its lubricating properties in the Lauson engine test.

The results are shown in the following table:

	Detergency Rating, Per Cent	Wt. Loss, Mgs.					
		Cu-Pb bearing, hours			Pb strip suspended in crankcase oil, hours		
		20	40	60	20	40	60
Oil (without addition agents) control	58	200	600	(1)	-----	-----	-----
Oil+6.7% product A	75	4	7	8	1	1	2

[1] Cu-Pb bearing replaced by Babbitt bearing at 40 hrs. due to excessive corrosion.

Example II

A 1000 gram portion of the petroleum fraction described hereinabove as furfural raffinate was diluted with two volumes of a petroleum naphtha fraction having a boiling range of about 200° F. to about 300° F. and sulfonated by treatment with 333 ml. of 60% fuming sulfuric acid in a vessel equipped with a continuous stirrer and a thermometer. The fuming sulfuric acid was added at such a rate that the maximum temperature attained during the sulfonation was about 75° F. As soon as all of the fuming sulfuric acid had been added the reaction mixture was stirred into three liters of the same solvent and allowed to stand over night. The solvent solution of the oil-soluble sulfonic acids was then separated from the acid sludge layer by decantation and the acid sludge layer washed free of oil-soluble sulfonic acids by repeated washings with solvent.

The combined original naphtha solution and washings were blown with fuel gas at room temperature to remove SO_2 and an excess of $Ca(OH)_2$ was added along with a small amount of water. When neutralization was complete the mixture was dehydrated by topping to 260° F., on a hot plate and the unreacted $Ca(OH)_2$ filtered off using finely ground diatomaceous earth as a filter aid. The naptha was removed from the filtrate by topping to 400° F. and 644 grams of a calcium sulfonate concentrate were obtained.

This material will be designated hereinafter as product B. The calcium sulfate ash value of product B was about 4.0%; this being the value obtained by heating a weighed sample of the calcium sulfonate concentrate to be tested, in the presence of sulfuric acid, to obtain a residual ash of calcium sulfate, and expressing the result in terms of per cent by weight of the concentrate tested.

A Lauson engine test was made on a lubricating oil consisting of 7.4% product B, 3.3% product A and 89.3% of the mineral lubricating oil described in Example I. The results are shown in the following table:

	Detergency Rating, Per Cent	Wt. Loss, Mgs.					
		Cu-Pb bearing, hours			Pb strip suspended in crankcase oil, hours		
		20	40	60	20	40	60
Oil (without addition agents) control	58	200	600	(1)	-----	-----	-----
Oil+7.4% product B +3.3% product A	82	12	36	44	7	26	52

[1] Cu-Pb bearing replaced by Babbitt bearing at 40 hrs. due to excessive corrosion.

Example III

A lubricating composition was prepared using as addition agents product A described in Example I and calcium sulfonate prepared from a commercial oil-soluble sodium sulfonate. The calcium sulfonate employed was prepared by diluting the sodium sulfonate with an equal volume of mineral lubricating oil described in Example I and adding to the diluted mixture an excess of calcium chloride. The mixture was heated to about 200° F. and when metathesis was complete the product was dehydrated and filtered. This product, which will be referred to as a calcium sulfonate concentrate, contained about 30% by weight of calcium sulfonates.

A lubricating composition was prepared comprising 6.0% by weight of the calcium sulfonate concentrate, 3.3% by weight of product A and 90.7% by weight of the mineral oil employed in Example I. The resulting oil contained approximately 1.8% by weight of calcium sulfonate, and 0.079% by weight of phosphorous in the form of the calcium salt of phosphosulfurized hydrocarbon. This oil had a sulfate ash of 0.6% by weight.

This oil was evaluated as a lubricant in the Caterpillar, Chevrolet and Lauson engine tests. In the Caterpillar test the oil had a detergency rating of 88.5% as compared to 50% for the mineral oil without additives. In the Chevrolet engine test, bearing weight losses of copper-lead

bearings were 137 milligrams and 145 milligrams, respectively, on two different bearings. The bearing weight loss determined with the mineral oil containing no additives was 3,000 milligrams.

The results of the Lauson engine test on the lubricating composition are shown in the following table:

	Detergency Rating, Per Cent	Wt. Loss, Mgs.					
		Cu-Pb bearing, hours			Pb strip suspended in crankcase oil, hours		
		20	40	60	20	40	60
Oil (without addition agents) control	58	200	600	(1)			
Oil+3.3% product A +6.0% calcium sulfonate concentrate	88	5	12	15	2	22	31

[1] Cu-Pb bearing replaced by Babbitt bearing at 40 hrs. due to excessive corrosion.

Example IV

To 301 grams of the hydrocarbon fraction designated hereinabove as phenol extract was added 37.6 grams of P_2S_5 and the mixture was stirred for about three hours at a temperature of about 400° F. The reaction mixture was treated in the manner described in Example I. The yield of oil-soluble product amounted to 269 grams of material having a calcium sulfate ash of about 4.5% and a phosphorus content of 1.67% by weight. This material will be designated hereinafter as product C.

A solution of 6.7% by weight of product C, 6.0% by weight of the calcium sulfonate concentrate described in Example III, and 87.3% by weight of the mineral lubricating oil described in Example I was evaluated as a lubricant in the Lauson engine test. This oil contained about 1.8% by weight of calcium sulfonate and about 0.12% by weight of phosphorus. The results are shown in the following table:

	Detergency Rating, Per Cent	Wt. Loss, Mgs.					
		Cu-Pb bearing, hours			Pb strip suspended in crankcase oil, hours		
		20	40	60	20	40	60
Oil (without addition agents) control	58	200	600	(1)			
Oil + 6.7% product C +6.0% calcium sulfonate concentrate	73				4	6	7

[1] Cu-Pb bearing replaced by Babbitt bearing at 40 hrs. due to excessive corrosion.

Example V

To 346 grams of the hydrocarbon fraction described hereinabove as furfural extract was added 43.3 grams of P_2S_5 and the mixture was stirred for about three hours at a temperature of about 400° F. The reaction product was treated in the manner described in Example I. The final oil-soluble product amount to 286 grams of material having a calcium sulfate ash of about 5.0% and a phosphorus content of 1.48% by weight. This material will be designated hereinafter as product D.

A solution of 6.0% by weight of product D, 6.0% by weight of the calcium sulfonate concentrate described in Example III, and 88.0% by weight of

the mineral lubricating oil described in Example I was evaluated as a lubricant in the Lauson engine test. This oil contained about 1.8% by weight of calcium sulfonate and about 0.090% by weight of phosphorus. The results are shown in the following table:

	Detergency Rating, Per Cent	Wt. Loss, Mgs.					
		Cu-Pb bearing, hours			Pb strip suspended in crankcase oil, hours		
		20	40	60	20	40	60
Oil (without addition agents) control	58	200	600	(1)			
Oil+6.0% product D +6.0% calcium sulfonate concentrate	65				4	18	23

[1] Cu-Pb bearing replaced by Babbitt bearing at 40 hrs. due to excessive corrosion.

The foregoing description of our invention is not to be taken as limiting but only as illustrative thereof since many variations may be made by those skilled in the art without departing from the scope of the following claims.

We claim:

1. A composition of matter adapted for addition to lubricating oil comprising an oil-soluble alkaline earth metal salt of the reaction product obtained by phosphosulfurizing a hydrocarbon lubricating oil fraction from which the most highly aromatic and the most highly paraffinic components have been removed, which hydrocarbon lubricating oil fraction is selected from those lubricating oil fractions obtained as solvent raffinate of a solvent extract and a solvent extract of a solvent raffinate, said solvent being a selective solvent of the type which selectively dissolves the more aromatic hydrocarbons, and said selective solvent being chosen from the group consisting of the same solvent used in extract formation and raffinate formation under different conditions of treatment, and a different selective solvent used in extract formation and raffinate formation, said reaction product being obtained by reacting said lubricating oil fraction with between about 3% and 50% of a phosphorus sulfide at temperatures between about 200° F. and 600° F.

2. A composition as set forth in claim 1 in which the phosphosulfurizing agent is phosphorus pentasulfide.

3. A composition as set forth in claim 1 in which the alkaline earth metal salt is calcium.

4. A composition as set forth in claim 1 in which the alkaline earth metal salt is barium.

5. A composition as set forth in claim 1 in which the alkaline earth metal salt is magnesium.

6. A lubricating oil composition containing a major proportion of mineral lubricating oil and a small amount, sufficient to impart detergency and anti-corrosion properties to said oil, of an oil-soluble alkaline earth metal salt of the reaction product obtained by phosphosulfurizing a hydrocarbon lubricating oil fraction from which the most highly aromatic and the most highly paraffinic components have been removed, which hydrocarbon lubricating oil fraction is selected from those lubricating oil fractions obtained as a solvent raffinate of a solvent extract and as a solvent extract of a solvent raffinate, said solvent being a selective solvent of the type which selectively dissolves the more aromatic hydrocarbons, and said selective solvent being chosen from the

group consisting of the same solvent used in extract formation and raffinate formation under different conditions of treatment, and a different selective solvent used in extract formation and raffinate formation, said reaction product being obtained by reacting said lubricating oil fraction with between about 3% and 50% of a phosphorus sulfide at temperatures between about 200° F. and 600° F.

7. A composition as set forth in claim 6 in which the phosphosulfurizing agent is phosphorus pentasulfide.

8. A composition as set forth in claim 6 in which the alkaline earth metal salt is calcium.

9. A composition as set forth in claim 6 in which the alkaline earth metal salt is barium.

10. A composition as set forth in claim 6 in which the alkaline earth metal salt is magnesium.

11. A composition as set forth in claim 6 which includes an oil-soluble metal sulfonate.

12. A composition as set forth in claim 6 in which the phosphosulfurizing agent is phosphorus pentasulfide and the composition includes an oil-soluble metal sulfonate.

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