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MINERAL OIL LUBRICATING COMPOSITION, AND AN IMPROVEMENT AGENT THEREFOR AND ITS METHOD OF PREPARATION

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This invention relates to improvement agents for lubricating oils and methods of making the same.

In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, plain mineral oils often prove unsatisfactory due to the attendant deposition on the engine surfaces, such as cylinder walls, pistons and rings of "varnish," gum or "sludge." This effect is particularly serious in modern engines operating under severe conditions, such as Diesel engines, aviation, truck and tank engines. The problem has become increasingly serious due to the trend toward higher efficiency, or higher power output per unit weight per engine, reduction in the amount of oil employed in the lubricating system of the engine and other conditions which tend to accelerate the deteriorating influences on mineral lubricating oil.

The formation of so-called varnishes or sludges on engine surfaces is due to oxidation or polymerization effects (or both) on the lubricating oils, as well as to like effects on or from the products of combustion of the fuels, which find their way by leakage into the engine crank case and other parts of the engine.

The presence of these substances is disadvantageous for many reasons. In particular the oil and fuel oxidation products tend to increase ring sticking and production of deposits on piston surfaces and in fixed parts of the combustion chamber. Sludges are formed in the crank case of the engine and the rate of corrosion of bearing surfaces is increased especially with bearing alloys of the types now in use.

Petroleum oils intended for use under the severe conditions described are almost always compounded with a mixture of substances each intended to counteract one or more of the undesirable effects noted. These substances, which fall into a wide variety of chemical classifications are known by the general term "improvement agents" or addition agents. Preparation of satisfactory compounded lubricants is a matter of considerable difficulty. Some of the agents are of low potency in that a rather large amount has to be added to achieve certain desired results. Often two or more agents are more or less incompatible with each other; and their rather low solubility in general further adds to the difficulties in preparing a useful lubricant.

One object of the present invention is the provision of an improvement agent for engine oils which can be incorporated in petroleum oils in effective proportions and which imparts to the oil a plurality of functions.

Another object is the provision of such an agent, in the form of a solution in petroleum lubricating oils, which serves the functions of (1) acting as a negative catalyst to suppress the formation of deterioration or oxidation products, such as varnish, sludge and gum, (2) acting as a loosening or suspending agent (detergent) to prevent ring sticking, "varnishing," coating of metallic surfaces by such reduced amounts of deterioration products as may be formed and (3) acting as a supending or dispersing agent for retaining very small particles of solid deterioration or contaminating materials in the oil; for example, particles of carbonaceous matter that find their way into the crank case oil by passing the piston rings which cannot possibly be made absolutely tight. Another object is the provision of a new improvement agent capable of increasing the solubility or dispersibility of other agents such as straight soaps or the like, when it is desired also to add such compounds to the oil.

According to this invention, new improvement agents for lubricating oils capable of achieving these and other objects are prepared from certain alkylated phenols (olefine-phenol reaction products) by simultaneously reacting phosphorus oxychloride ($POCl_3$) and phosphorus sesquisulfide (P_4S_3) with the alkylated phenols to form complex acid reaction products, which in turn are treated with lime (or other metal oxide or hydroxide), producing stable complex metallo-compounds of alkylated phenol esters of phosphorus acids, of the character described in more detail below. That is, as shown post, the new agents are prepared from alkylated phenols containing at least one branched chain alkyl group. Likewise, as there shown, in preparing the new agents, such alkylated phenols are simultaneously reacted with phosphorus oxychloride and phosphorus sesquisulfide under controlled conditions to produce acid reaction products thereof, and the acid reaction products so obtained are heated with polyvalent metal oxides and hydroxides until stable, substantially neutral metallo derivatives thereof are obtained; the stable, oil-soluble improvement agent so obtained being separated from the unreacted metal oxides and hydroxides and other insoluble compounds. The polyvalent metal compounds so obtained, particularly the di- and tri-valent metal compounds and mixtures thereof, are useful for the present purposes.

The so-prepared agents or metallo-compounds, in solution in lubricating oils provide four functions which are useful and advantageous in lubricants. (1) By virtue of the combined polyvalent metal (e. g. calcium, etc.) suspending or detergent properties are imparted, as well as resistance to ring sticking, (2) the combined phosphorus imparts anti-bearing-corrosion and anti-ring-sticking properties as well as pressure-carrying properties, (3) the combined sulfur

serves to give pressure carrying properties to the oil and to retard corrosion of alloy bearings, and (4) by virtue of the organic nucleus, the alkylated phenol groups, the oil has good antioxidant and oiliness properties and suspending and solubilizing functions.

Thus according to the invention there is provided a compound which, dissolved in oil, imparts thereto all the many desirable features which we wish to obtain. It is in a form which is so soluble in motor oils of all types and degrees of refinement that we can incorporate any desired proportions to form a clear solution in lubricating oils, even in most highly refined and most paraffinic of the heavy aviation oils, such as are specified for the most severe and exacting aviation service.

It is known that highly paraffinic oils, refined to the high degree desired to secure such desired properties as low carbon-forming effects and high viscosity indices (improved viscosity temperature relationships) are relatively poor solvents for decomposition products formed in use. Also there is increased tendency to induce bearing corrosion. In this invention these undesirable properties of such oil are done away with by the use of moderate amounts of our new compounding agent having cumulatively all the desired properties in the way of ready solubility in the oils and other advantageous effects mentioned above. We can employ very highly refined paraffinic-type aviation oils that have the desired superior physical characteristics as regards the particular property, and, at the same time avoid any undesirable effects whatever from the use of such oils. In other words, the addition of our compound which is soluble in all proportions in the heavy highly refined paraffinic oils enables us to secure all the properties desired in the way of the oils of superior performance characteristics, as well as the effects of detergency, avoidance of ring sticking, varnish formation, sludge formation and corrosion of alloy bearings that might otherwise be encountered, as well as secure the desired effect of retarding oxidation due to the use of more highly refined oils of less tendency to oxidize combined with the use of a compound which actually retards oxidation.

Another important field of utility for the invention is in Diesel lubricating oils. Heretofore it has been considered best to use naphthene-type oil dosed with certain compounding agents which are of undesirably low efficiency and which moreover are not readily soluble even in the most naphthenic type of Coastal oils. This has often been necessary to make a compromise even for the Coastal oils of greater solubility effect for compound agents between the degree of refining and the solubility effect for the addition agents. It is quite unsatisfactory for most of these agents to use even a moderately refined paraffin type oil, as all or part of the addition agents heretofore used will often separate from the oil upon standing. For these reasons Diesel lubricating oils hitherto prepared have been rather unsatisfactory in that they employ low grade oils of less degree of resistance to oxidation than would otherwise be desirable. With the present invention, we prepare an improved oil which performs satisfactorily in Diesel engines by employing a highly refined paraffin-type of oil with control of ring sticking effects and sludge formation and detergency effects by incorporation of the present compound in any desired proportion.

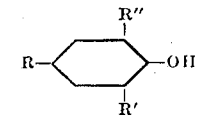
The new improvement agent has another important advantage in that in addition to being very oil-soluble itself, it acts to disperse in mineral oils other improvement agents which are of themselves relatively insoluble. For example, in accordance with the present invention 1 per cent or more of calcium oleate or aluminum stearate can be dissolved in oil to form a stable and common dispersion with the aid of an equal quantity of the new agent. Thus the new agent is sometimes useful when and where its own antioxidant and dispersing properties are not required for its value in dissolving other agents.

The new agent is conveniently prepared in the form of a concentrated oil solution which can readily be stirred into an oil to prepare a compound lubricant.

In preparing the new agent, the base material is advantageously alkylated phenols which themselves have good antitoxidant properties. A convenient source for this base material or principal reactant is the phenol-olefin reaction products prepared as described in U. S. Patent 2,149,759 issued March 7, 1939, to Troy Lee Cantrell. For instance, an advantageous material is a "heart-cut" of such phenol-olefin reaction products, prepared from the 20–80 per cent cut separated by steam or vacuum distillation; vacuum distillation being preferred. This heart-cut is a mixture of liquid, semi-liquid and crystalline alkylated phenols. It is soluble in all proportions in lubricating oils and gasoline, and soluble in most organic solvents and insoluble in water and NaOH solutions. It has the following properties:

Gravity, °A. P. I.	18.0–24.0
Sp. gr., 60°/60° F.	0.9465–0.9100
Viscosity, S. U. V.:	
100° F.	60–000
Pour, °F.	−30 to +15
Color, N. P. A.	1.0–1.5
Free phenol, percent	Nil
Mineral acidity,	
SO_3 equivalent, percent	Nil
Distillation, A. S. T. M. D 86–38:	
Over point, °F.	375–380
End point, °F.	525–540
10% at, °F.	415–450
50	470–495
90	495–525

This phenol-olefin reaction product contains varying amounts of 4-tertiary-butyl-phenol, 2-tertiary-butyl-4-secondary-butyl phenol, 2,4-di-tertiary - butyl - phenol, 2,6 - di-tertiary-butyl-4-secondary - butyl phenol, 2,4,6-tri-tertiary-butyl phenol, 2,6-di-tertiary-butyl - 4 - methyl phenol, 4,6-di-tertiary-butyl-2-methyl phenol, 4,6-di-tertiary-butyl-2-methyl phenol and other alkylated phenols containing a branched chain alkyl group attached to the phenyl nucleus thereof. All these alkylated phenols have good antioxidant properties and are useful in making our new improvement agents. As a class they may be represented by the following general formula:



wherein R, R' and R'' represent hydrogen or an alkyl group, at least one branched chain alkyl group being present. Those containing secondary or tertiary alkyl groups are particularly advantageous for the present purposes.

In proceeding in accordance with the first stage

of the present invention, such alkylated phenols are brought into reaction with phosphorus oxychloride and phosphorus sesquisulfide in the desired proportions, the mixture of reactants being heated to facilitate reaction. Upon heating the mixture, the three reactants vigorously interact, forming complex alkylated phenyl esters of phosphorus acids, wherein the alkylated phenyl groups thereof contain at least one branched chain alkyl substituent. Advantageously, the reaction may be effected at temperatures between 280 and 550° F., and is usually carried out at about 450° F. Likewise, the proportions of the reactants, namely the alkylated phenols, $POCl_3$ and P_4S_3, may be varied and controlled to produce reaction products advantageously for the present purposes. Usually we employ 15 to 25 parts of phosphorus oxychloride and 1 to 5 parts of phosphorus sesquisulfide per 100 part of the alkylated phenol. The reaction products so obtained readily react with metal oxides and hydroxides, forming metal salts of these alkylated phenol esters.

In forming such metal salts, the reaction products or esters described ante may be treated with various metal compounds. For instance, valuable improvement agents are readily obtained by heating such products with lime. In doing so, lime (quick or hydrated) is added in the proportions of about 5 to 25 parts (figured as CaO) per 100 parts of the reaction product and the mixture heated at a temperature of 220–400° F. for about three hours. The reaction mixture is filtered and is then ready for use.

In lieu of ordinary lime, dolomitic limes, magnesia or magnesium hydroxide can be employed. Likewise other polyvalent metallic oxides or hydroxides, such as alumina or zinc oxide may be employed in preparing our metallo-derivatives or metal salts of these alkylated phenyl esters of phosphorus acids. That is, various metal compounds may be employed in the practice of this invention.

The improvement agents so obtained are of complex constitution, even when a single alkylated phenol, such as 2,6-di-tertiary-butyl-4-methyl phenol, etc., is employed. Further, using mixtures of alkylated phenols, such as the "heart-cut" of the olefin-phenol reaction products described ante, mixtures of metallo-derivatives of alkylated phenyl esters are obtained. As stated, these are advantageous in the practice of this invention.

That is, our improvement agent is probably a mixture of similar or analogous compounds and may contain varying proportions of the several constituents, namely combined phosphorus, sulfur, metal, etc., combined in a complex metallo compound. As a matter of fact, we vary the relative proportions of the reactants, depending upon the particular properties desired. There is considerable flexibility in the proportion of calcium or other metal added and combined for securing a range of detergency, anti-ring sticking, and solid suspension effects; or in the amount of combined phosphorus as required to obtain the desired anti-ring sticking and anti-corrosion effects. That is, these constituents of our improvement agents can be varied at will. For instance, the metal content can be made to vary over relatively wide limits.

That is, in practice we vary the proportions of the several reactants in accordance with the particular properties desired. After the desired combinations have been effected, the reaction product is filtered to remove insoluble compounds and is then ready for use. The filtered materials are readily soluble in lubricating oil.

In preparing improved lubricants, the optimum proportion of the agent to be introduced into lubricating oils depends on the severity of the service conditions and the degree to which the oil itself tends to form gum or varnish. Ordinarily from 0.25 to 5.0 per cent by weight of the improvement agent on the oil is suitable. The improved lubricants so obtained have the advantageous properties described ante and are superior lubricants.

The preparation and use of our improvement agents is further illustrated in the following illustrative examples which are typical but not limitative of this invention.

Example I.—In a specific example illustrative of one advantageous way of preparing an agent within the purview of the invention, 1684 pounds of the above described phenol-olefin reaction product were mixed with 50 lbs. of P_4S_3 and 614 pounds of $POCl_3$. The mixture was agitated and heated at 450° F. for a period of 4½ hours.

The reaction product so obtained was a mixture of alkylated phenyl esters of phosphorus acids, which readily react with metal oxides and hydroxides. This particular reaction product had the following properties:

Gravity	°A. P. I.	0.6
Specific gravity, 60°/60° F		1.0711
Viscosity, S. U. V.:		
100° F		908
Color, N. P. A		6.5
Sulfur, Carius	per cent	0.50
Phosphorus, Carius	do	6.92
Chlorine, Carius	do	10.80
Ash as sulfate	do	0.475

This reaction product was diluted with approximately an equal weight of mineral lubricating oil, namely, a Texas oil having a Saybolt viscosity of 104 at 100° F. The mixture containing 85.7 pounds of the reaction product and 86.7 pounds of mineral oil was stirred in an open iron vessel and 7.1 pounds of hydrated lime added. This mixture was agitated and heated to 350° F. for 3 hours. The solution of improvement agent in oil so obtained was then admixed with a filter aid and filtered. The filtrate had the following identifying properties:

Gravity	°A. P. I.	14.9
Sp. gr., 60°/60° F		0.9665
Viscosity, S. U. V.:		
100° F		567
210° F		57.0
Pour	°F.	−30
Color, N. P. A		3.5
Sulfur, B	per cent	0.27
Chlorine, Carius	do	0.17
Phosphorus, Carius	do	3.44
Carbon residue	do	6.11
Ash as sulfate	do	6.13

It is an excellent improvement agent for lubricating oils; it being a concentrated solution of the effective agent in oil.

By adding varying proportions of this concentrate to commercial lubricating oils, a large range of improved lubricants is readily obtained.

Example II.—A metallo-derivative containing nickel in lieu of calcium may be prepared by substituting a molecular equivalent proportion of nickel carbonate for the hydrated calcium lime in the above example.

New improvement agents or concentrates

thereof containing other divalent metal salts or derivatives can be prepared in a similar manner by selecting a suitable reactive divalent metal compound for reaction with the alkylated phenol esters of the phosphoric acids. For instance, tin salts of these esters are effective improvement agents. In general, polyvalent metal derivatives of the alkylated phenyl esters of the phosphorus acids prepared by the methods described ante, are useful and advantageous improvement agents for lubricating oils.

A series of lubricating oil compositions was prepared by dissolving in a straight engine oil various quantities of the improvement agents of the present invention. These compositions were submitted to various tests and all of them gave improved lubricating qualities. Typical compositions and their preparation are illustrated in the following examples:

Example III.—An improved lubricating oil was prepared by dissolving 2.0 per cent of the preparation of Example I in a high grade lubricating oil for use in Diesel engines.

The improved composition containing this calcium derivative gave superior lubrication in such engines under service conditions.

Example IV.—An improved lubricating oil was prepared by dissolving 3.0 per cent of the preparation of Example II in a high grade lubricating oil for use in Diesel engines.

This composition containing the nickel derivative also gave improved lubrication in the Diesel engine under service conditions.

The viscosities and their conventional identifying characters of these improved compositions, together with those of the base oil were as follows:

	Base oil	Improved lubricant	
		Example III	Example IV
Gravity °A. P. I.	26.5	26.5	26.3
Viscosity, S. U. V.:			
100° F.	1,819	1,761	1,764
210° F.	122.3	117.4	115.8
Viscosity index	93	91	89
Flash, OC °F.	525	510	495
Fire, OC °F.	595	585	590
Pour °F.	+5	0	+5
Color, N. P. A.	5.5	5.5	7.5
Sulfur, B percent	------	0.36	0.23
Carbon residue do	0.46	0.43	0.55
Ash as sulfate do	------	0.24	0.388
Copper strip test, 212° F., 3 hrs.	(1)	(1)	(1)

[1] Passes.

In order to evaluate their tendency to cause ring sticking in engines, these compositions were subjected to a motor service test in the laboratory, using a standard Waukesha-CFR crankcase with special L head type cylinder block, coupled to a cradle-type electric dynamometer. This engine has a bore of 3/14 inch, a stroke of 4½ inches, and a compression ratio of 4.7:1. The piston is of cast iron with four compression rings and one oil-control ring, all located above the wrist pin. Three liters of the oil to be tested are placed in the crankcase. The engine is then run at 900 R. P. M. with the spark and the air-fuel ratio adjusted to give maximum power, and the coolant temperature is maintained at 350° F. At the end of 25 hours running, the engine is stopped and dismantled and the piston is examined. The performance of the oil is then rated according to the condition of the piston, in keeping with the following scale, in which the rating number increases as the piston condition becomes worse:

Ratings

No. 1—No ring stick, and no heavy hard deposit.
2—Top or oil ring (or both) stuck on a small part of circumference.
3—Top or oil ring (or both) completely stuck.
4—Top or oil ring (or both) completely stuck, and ring partly stuck.
5—Top, 2nd and oil rings completely stuck.
6—Condition No. 5 with 3rd and 4th rings partly stuck.

In the above test the rating of the several compositions were as follows:

	Composition		
	Base oil	Improved oil	
		Ex. III	Ex. IV
Rating No.	4	1	2

These compositions were also subjected to the well known Almen and Timken lubricating test with the following results:

	Composition		
	Base oil	Improved oil	
		Ex. III	Ex. IV
Almen test pounds	6	16	14
Timken test do	14	44	52

Similar improved results are obtained with lubricating oils containing small amounts of other metal salts of these esters of alkylated phenols.

While the improvement agent of the present invention has been described in reference to compounding engine lubricating oils for the primary purpose of preventing ring sticking, its field of usefulness is not confined to that application. It can be used in oils wherever its properties may be desired. Sometimes it is used for its dispersive powers on other agents, when its own antioxidant and detergent properties are not needed.

That is, another important advantage of the agents of the present invention is that in addition to being highly soluble in oils themselves, they are effective to disperse in mineral oils certain soaps which are of themselves difficultly soluble, for example, calcium oleate or aluminum stearate. Again, sulfurized sperm oil soap is a desirable addition agent to oils, but its low solubility prevents incorporation of more than a rather small quantity in paraffin base oils. By the present invention 1 per cent or more of such soap can be dispersed in oil, to form a stable dispersion by including an equal amount of the new improvement agents of this invention. Thus in the practice of the present invention, our new agents may be used in conjunction with other previously known addition agents, in compounding lubricating oils to improve their properties. Thus in the practice of the present invention, various embodiments thereof may be employed in addition to the illustrative embodiments shown ante.

What we claim is:

1. A process of preparing an improvement agent for lubricating oils, from alkylated phenols containing at least one branched chain alkyl

group, which comprises heating 100 parts of said alkylated phenols with 10 to 25 parts of phosphorous oxychloride and 1 to 5 parts of phosphorus sesquisulfide, by weight, at temperatures between 280 and 550° F. until substantially all of the phosphorus oxychloride and phosphorus sesquisulfide have reacted and acid reaction produces thereof are obtained, and converting the acid reaction products so obtained into stable, substantially neutral metal derivatives thereof by further heating said acid reaction products with a reactive metal compound of a class consisting of the oxides and hydroxides of a polyvalent metal, the amount of said reactive polyvalent metal compound being sufficient to neutralize the acidity of said reaction products, and the mixture being heated to temperatures between 220 and 400° F. until stable, substantially neutral, metal derivatives thereof are obtained, and separating the unreacted metal oxides and hydroxides and other insoluble compounds from the oil-soluble improvement agent so obtained.

2. The method of claim 1 wherein said reactive metal compound is lime.

3. The method of claim 1 wherein said reactive metal compound is a divalent metal compound.

4. The method of claim 1 wherein the alkylated phenols employed as the starting material are phenol-olefin reaction products comprising a mixture of alkylated phenols containing secondary and tertiary alkyl groups.

5. The method of claim 1 wherein the said acid reaction products of the alkylated phenols are heated with the said polyvalent metal compounds in proportions of 5 to 25 parts of the reactive metal compound per 100 parts of said acid reaction products.

6. The method of claim 1 wherein said acid reaction products are diluted with mineral oil prior to the treatment with the said polyvalent metal compounds, and wherein the oil solution of stable, substantially neutral oil soluble metallo compounds so obtained is filtered to remove unreacted metal oxides and hydroxides and other insoluble compounds.

7. A process of preparing an improvement agent for lubricating oils, from alkylated phenols containing at least one branched chain alkyl group which comprises heating 100 parts of said alkylated phenols with 10 to 25 parts of phosphorus oxychloride and 1 to 5 parts of phosphorus sesquisulfide, by weight, at temperatures between 280 and 550° F. until substantially all of the phosphorus oxychloride and phosphorus sesquisulfide have reacted and acid reaction products thereof are obtained, diluting the acid reaction product so obtained with mineral oil, adding to the so fluxed acid reaction products a reactive metal compound of the class consisting of the oxides and hydroxides of a polyvalent metal in proportions of 5 to 25 parts of said reactive metal compound per 100 parts of said acid reaction products, further heating the mixture to temperatures between 220 and 400° F. until stable, substantially neutral, oil-soluble metallo derivatives thereof are formed in situ in the mineral oil, and filtering the oil concentrate of the improvement agent so obtained to remove unreacted metal oxides and hydroxides and other compounds insoluble in the oil.

8. An improvement agent soluble in petroleum oil and capable of inhibiting formation of gum, varnish, and sludge in engines, comprising the stable, oil-soluble, substantially neutral metallo compounds obtained by the process of claim 1.

9. An improved lubricating composition comprising a major amount of a mineral lubricating oil and a small proportion of the stable, oil-soluble, substantially neutral metallo compounds obtained by the process of claim 1, the amount of said oil-soluble improvement agent being sufficient to inhibit the formation and deposition of gum, varnish and sludge in engines and to disperse such deposits when present.

10. An improvement agent, for lubricating oils, comprising the stable, substantially neutral product of the process of claim 7, said product being readily soluble in petroleum oils and capable of inhibiting formation of gum, varnish and sludge in engines.

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