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AGENT FOR MINERAL OILS AND MINERAL
OIL COMPOSITION CONTAINING THE
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This invention relates to improvement agents for mineral oils and mineral oil compositions containing 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, higher power out-put per unit weight per engine, reduction in the amount of oil employed in the lubrication system of the engine, and other conditions which tend to accelerate the deteriorating influences on mineral lubricating oil.

Formation of so-called varnishes and 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 products of combustion of the fuels, which find their way by leakage into the engine crankcase or 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 crankcase 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 so that a rather large amount has to be added to achieve the desired result. 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 improvement agents for engine oils which can be incorporated in petroleum oils in

effective proportions and which impart to the oil a plurality of functions.

Another object is the provision of addition agents which function (1) as negative catalysts to suppress the formation of deterioration or oxidation products, such as varnish, sludge and gum, (2) as loosening or suspending agents (detergents) to prevent ring sticking, "varnishing," or coating of metallic surfaces by such reduced amounts of deterioration products as may be formed and (3) as suspending or dispersing agents 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 crankcase oil by passing the piston rings which cannot possibly be made absolutely tight.

Another object is the provision of new improvement agents capable of increasing the solubility or dispersibility of other agents, such as straight soaps or the like, when it is desirable also to add such compounds to an oil in which said soaps and like agents are difficultly soluble.

According to this invention, new improvement agents for mineral oils capable of achieving these and other objects are prepared by a series of steps which include: (1) forming a diaryl-chloro-phosphite by esterifying an alkylated phenol which contains at least one alkyl group having from 3 to 5 carbon atoms with phosphorus trichloride; (2) reacting said diaryl-chloro-phosphite with ricinoleic acid; (3) sulfurizing said ricinoleic acid reaction product; and (4) converting said sulfurized product to a metal salt.

These addition agents in solution in mineral oils perform four functions which are useful and advantageous in lubricants: (1) by virtue of their combined 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 alkylated phenyl groups carrying at least one alkyl group having from 3 to 5 carbon atoms, the improved oil has good anti-oxidant and oiliness properties and suspending and solubilizing characteristics.

Thus, according to the invention, there are provided new improvement agents which dissolved in the oil, impart thereto all the many desirable features which we wish to obtain, including the several advantages, virtues and properties de-

scribed hereinbefore. Furthermore, our new improvement agents are so soluble in motor oils of all types and degrees of refinement that we can incorporate them in any desired proportions to form clear solutions in lubricating oils, even in the most highly refined and most paraffinic of the heavy aviation oils, such as are specified in the most severe and exacting aviation services.

It is known that highly paraffinic oils, refined to the high degree necessary to secure such desirable 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 eliminated by the use of moderate amounts of our new compounding agents having cumulatively all the desired properties in the way of ready solubility in the oils and the other advantageous effects mentioned above. We can employ very highly refined paraffinic-type aviation oils that have the desired superior physical characteristics as regards these particular properties, and, at the same time, avoid any undesirable effects whatever from the use of such oils. In other words, the addition of our improvement agents, which are soluble in all proportions in the heavy highly refined paraffinic oils, enables us to secure all the properties desirable in the way of oils of superior performance characteristics, as well as the effects of detergency, avoidance of ring sticking, sludge formation and corrosion of alloy bearings that might otherwise be encountered, and also to 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 oils 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. Thus it has often been necessary to make a compromise even for the Coastal oils of greater solubility effect for compounding 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, employing a highly refined paraffin-type of oil with control of ring sticking effects, sludge formation and detergency effects by mixing therewith any desired proportion of the new improvement agents disclosed herein.

The new improvement agents have another important advantage in that, in addition to being very oil-soluble, they act 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 dispersion with the aid of an equal quantity of one of our new

agents. Thus, our new addition agents are sometimes useful where their own antioxidant and dispersing properties are not required for their value in dissolving other agents.

The new addition agents are conveniently prepared in the form of concentrated oil solutions which can readily be stirred into an oil to prepare a compound lubricant.

In preparing our new addition agents, we advantageously employ as a starting material an alkylated phenol or a mixture of alkylated phenols that contain one or more alkyl groups having from 3 to 5 carbon atoms. In other words, we may employ as our starting material a mono-, di-, or tri-alkyl phenol wherein said alkyl group is a propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, amyl, isoamyl, secondary amyl, or another isomeric pentyl radical. These higher alkylated phenols may not only be derived from phenol itself but also from any of the phenols containing short chain alkyl groups such as the cresols and xylenols.

Of the various individual alkylated phenols which contain at least one alkyl group having from 3 to 5 carbon atoms that may be used as starting materials in making our new addition agents there may be mentioned 2-isopropyl phenol; 4-tertiary-butyl phenol; 2-isoamyl phenol; 2-tertiary-amyl phenol; 2,4-ditertiary-butyl phenol; 2-tertiary-butyl-4-secondary-butyl phenol; 2,6-ditertiary-butyl-4-methyl phenol; 4,6-ditertiary-butyl-2-methyl phenol; 2,6-ditertiary-butyl-3-methyl phenol; 2,4,6-tritertiary-butyl phenol; 2,6-ditertiary-butyl-4-secondary-butyl phenol; 2,5-ditertiary-butyl-4-secondary-butyl phenol; etc. These alkylated phenols are conveniently prepared by the reaction of a primary, secondary, or tertiary olefin with a phenol.

As hereinabove mentioned, we may use mixtures of alkylated phenols that contain one or more alkyl groups having from 3 to 5 carbon atoms instead of using individual alkylated phenols such as those mentioned in the preceding paragraph. For instance, we may use any of the alkylated phenols, obtained by reacting phenols with olefins, which are described in U. S. Patent No. 2,149,759. It is normally preferred to use the semi-liquid, light colored products described in said patent. Suitable mixtures of alkylated phenols can be obtained by taking a crude semi-liquid phenol-olefin reaction product, made in accordance with said U. S. Patent No. 2,149,759, by passing a butane-butene gas mixture through 90 per cent phenol at 160-180° F., in the presence of 5 per cent by weight of sulfuric acid, and then securing a 60, 70, or 80 per cent "heart-cut" (20-80, 15-85, or 10-90 per cent) thereof by subjecting it to fire and steam distillation in the presence of adequate caustic soda to insure mild alkalinity during distillation. It is to be understood that unfractionated phenol-olefin reaction products may be used in place of "heart-cuts" separated therefrom in synthesizing satisfactory addition agents comprehended by our invention.

The particular alkylated phenol mixture which was employed as a starting material in the example set forth hereinbelow was a 60 per cent "heart-cut" of a phenol-butene reaction product made in accordance with said U. S. Patent No. 2,149,759 by separately collecting the 20-80 per cent cut obtained by steam or vacuum distillation; vacuum distillation being preferred. This "heart-cut" is a mixture of liquid, semi-liquid and crystalline butylated 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, °API	18.0-24.0
Sp. gr., 60°/60° F	0.9465-0.9100
Viscosity, SUV, 100° F	60-100
Pour, °F	-30 to +15
Color, NPA	1.0-1.5
Free phenol, per cent	nil
Mineral acidity, per cent SO ₃ equivalent	nil
Distillation, ASTM D 86-38:	

Over point, °F	375
End point, °F	538
10% at °F	455
50% at °F	493
90% at °F	524
Recovery, per cent	96

This phenol-butene reaction product contains varying amounts of butylated phenols such as 4-tertiary-butyl-phenol, 2-tertiary-butyl-4-secondary-butyl phenol, 2,4-ditertiary-butyl phenol, 2,6-ditertiary-butyl-4-secondary-butyl phenol, 2,5-ditertiary-butyl-4-secondary-butyl phenol, 2,4,6-tritertiary-butyl phenol, 2,6-ditertiary-butyl-4-methyl phenol, 2,6-ditertiary-butyl-3-methyl phenol, 4,6-ditertiary-butyl-2-methyl phenol and still other phenols containing a butyl group attached to the phenyl nucleus thereof. All of these butylated phenols have good antioxidant properties and are useful in making our new improvement agents. Those containing secondary or tertiary alkyl groups are particularly advantageous for use in preparing the improvement agents of the present invention.

The ricinoleic acid used is purified from castor oil fatty acids. Pure ricinoleic acid with a specific gravity of 0.945, a melting point of 17° C. and a boiling point of 250° C. (15 mm. pressure) may be used, but in the example set forth hereinbelow a technical grade of ricinoleic acid was employed which had the following properties:

Sp. gr., 60°/60° F	0.9398
Acid value	188
Iodine number	87
Saponification number	188
Unsaponifiable matter, per cent	0.5
Acetyl value	150
Freezing point, °C	-6 to -10

The following example which illustrates but does not limit the invention describes the preparation of one of our improved addition agents and an improved lubricating oil containing the same.

Example

1648 parts by weight of the "heart-cut" of the reaction product of butene and phenol hereinbefore described was heated with 500 parts by weight of phosphorus trichloride at 500° F. for 16 hours. The product (I) had the following properties:

Gravity, °API	8.8
Viscosity, SUV 100° F	1743
Neutralization number	135
Phosphorus, per cent	5.4
Chlorine, per cent	5.8

479 parts by weight of product (I) as described above was heated with 300 parts by weight of ricinoleic acid, such as was hereinbefore described, at 400° F. for 4 hours. The product (II) had a neutralization number of 69.5.

200 parts by weight of product (II) described

above was heated with 7 parts by weight of sulfur at 350° F. for 2 hours. The product (III) had a neutralization number of 67.5 and contained 3.2 per cent of sulfur.

200 parts by weight of product (III) was heated with 10 parts by weight of hydrated lime, Ca(OH)₂, plus 2 per cent of water at 350° F. When this reaction was complete, 200 parts by weight of 100 viscosity at 100° F. Texas oil was added. The mixture was filtered through a filtering medium to remove any insoluble material. The concentrate had the following properties:

Gravity, °API	13.6
Viscosity, SUV 100° F	676
Sulfur, per cent	1.74
Phosphorus, per cent	1.69
Ash as sulfate, per cent	4.44

Three per cent of this concentrate was added to motor lubricating oil to improve the antioxidant and detergent properties. A comparison of the oils is as follows:

Description	Base oil	Oil containing addition agent
Gravity, °API	21.4	20.9
Viscosity, SUV:		
100° F	1,455	1,441
210° F	82.5	81.7
Flash, O.C., °F	420	415
Fire, O.C., °F	490	490
Pour, °F	0	+5
Sulfur (B), percent		0.31
Copper strip test 212° F., 3 hr.	Passes	Passes
Ash (as sulfate), percent		0.087
Carbon residue, percent	0.25	0.23
Neutralization No.	0.03	0.13

Our new addition agents possess great oiliness properties, and therefore oils containing the same can be used for some special lubricating services, such as for the break-in of motors and for operation of the same under severe conditions. An oil containing small amounts of the new addition agent described in the example above has superior oiliness and detergent properties, protects bearings from corrosion, and reduces the amount of sludge formation and ring sticking at high temperatures. The tendency of oils to cause ring sticking in engines is conveniently evaluated by the testing method which is described in the paragraph that begins in line 55 in column 1 on page 4 of U. S. Patent No. 2,342,433. When a base oil having the properties set forth in the above example and the same oil containing 3.0 per cent of the new addition agent described in the above example was tested in accordance with the test set forth in U. S. Patent No. 2,342,433, it was found that the piston rating of the base oil was 4 and the piston rating of the oil containing the addition agent was 1.

While in the above example we converted product (III) to a metal salt by heating it with lime, it is to be understood that other metal salts in addition to the calcium salt may be made by reacting product (III) with other metallic oxides and hydroxides, such as those of aluminum and zinc.

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 0.5 to 5.0 per cent by weight of our new improvement agent on the oil is suitable. The improved lubricants so obtained have the advantageous properties described hereinabove.

By adding varying proportions of this improvement agent to commercial lubricating oils, a wide range of improved lubricants is readily obtained.

Furthermore, the improvement agent described in the above example is so soluble in mineral oils that concentrated solutions thereof can be readily prepared. These concentrates are also useful improvement agents in making commercial lubricants and can be readily incorporated and blended with various lubricating oils and bases to produce commercial lubricants.

These concentrates can also be prepared with advantage by incorporating mineral oil with the acid reaction product (III) prior to reacting the same with the metal oxide or hydroxide.

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

Stated otherwise, 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 hereinbefore.

We claim:

1. A suitable additive for mineral oils which comprises a metal salt of a sulfurized derivative of a ricinoleic acid reaction product of a diaryl-chloro-phosphite which has been made by esterifying an alkylated phenol which contains at least one alkyl group having from 3 to 5 carbon atoms with phosphorus trichloride.

2. A calcium salt of a sulfurized derivative of a ricinoleic acid reaction product of a diaryl-chloro-phosphite which has been made by esterifying an alkylated phenol which contains at least one alkyl group having from 3 to 5 carbon atoms with phosphorus trichloride.

3. A calcium salt of a sulfurized derivative of a ricinoleic acid reaction product of a diaryl-chloro-phosphite which has been made by esterifying a butylated phenol which contains at least one butyl group with phosphorus trichloride.

4. A mineral oil composition containing from 0.5 to 5.0 per cent by weight of a product as defined in claim 1.

5. A mineral oil composition containing from 0.5 to 5.0 per cent by weight of a product as defined in claim 2.

6. A mineral oil composition containing from 0.5 to 5.0 per cent by weight of a product as defined in claim 3.

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