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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 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.

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 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 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 in that rather large amounts have 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 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 hitherto obtainable only by use of two or more agents. Another object is the provision of such an agent which, in the form of a solution in petroleum lubricating oils, combines 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" or coating of metallic surfaces by such reduced amounts of deterioration products as may be formed, and (3) acting as a suspending or dispersing agent for retaining very small particles or solid particles of deterioration or contaminating materials in the oil; for example, particles of carbonaceous matter that find their way into the oil by passing the rings, which cannot possibly be made absolutely tight. Another object is the provision of an 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 an oil.

According to the invention, agents capable of achieving these and other objects of the invention are prepared by bringing into reaction sulfophospho-derivatives of higher fatty alcohols, with lime (or other metal oxide or hydroxide), under conditions producing a complex metallic compound of such derivatives, of nature described in more detail below.

The compound in solution in a lubricating oil provides four functions, so to speak, in a single molecular structure. (1) By virtue of its combined metal (e. g. calcium) suspending and detergent properties are imparted and resistance to ring-sticking, (2) the combined phosphorus imparts anti-bearing-corrosion and anti-ring-sticking 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 high-molecular-weight fatty alcohol, the oil has good

anti-oxidant 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 stable clear solution in lubricating oils; even in the 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 a known fact that highly paraffinic oils, refined to the high degree desired to secure such properties as low carbon forming effects and the like as well as high viscosity index values (improved viscosity temperature relationships) that are preferred for such service, exhibit in use less solubility for decomposition products encountered in use, while there is increased tendency to induce bearing corrosion, due to the fact that in such highly refined oils less protective effects are developed. In the invention, we attain the desired objective by the use of moderate amounts of the compounding agent having cumulatively all the desired properties, in the way of ready solubility in the oil and the other effects mentioned above. We can employ very highly refined paraffinic type aviation oils that have the desired superior physical characteristics as regards the oil proper, and, at the same time, avoid any undesirable effects whatever from the use of such heavily refined paraffin type 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 of the properties desired in the way of the oils of superior performance characteristics, as well as the effects of detergency, avoiding of ring sticking, varnish formation, sludge formation, and corrosion of alloy bearings, that might otherwise be encountered, as well as 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 heavily with less effective or less concentrated types of compounding agents which are not so readily soluble even in the more naphthenic type of Coastal oils. 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 will often separate from the oil upon standing. For these reasons Diesel lubricating oils hitherto prepared have been rather unsatisfactory in that they employ lower grade oils of less degree of resistance to oxidation than would otherwise be desirable. With the present invention, we prepare an oil which performs satisfactorily in Diesel engines, by employing a highly refined paraffin type oil, with control of ring sticking effects and sludge forming and detergency effects by incorporation of the present compound in any desired proportion.

A convenient source for the principal reactant, the higher molecular weight monohydric alcohols, is sperm oil, the alcohols being obtained therefrom in known ways. As is well known, sperm oil is a liquid wax, and not a fatty oil. It is composed largely of esters of high molecular weight monohydric alcohols, as distinguished from fatty oils which are esters of a polyhydric alcohol (glycerol). The sperm oil esters have the following general formula:

$$R-\overset{\overset{O}{\|}}{C}-O-R'$$

wherein R and R′ are aliphatic chains of high molecular weight each containing a double bond. The acids are mainly oleic acid and homologous acids of the oleic type and the alcohols are monohydric alcohols of the ethylene series—the series of alcohols corresponding to the oleic series of acids. Sperm oil alcohols have the probable formula

$$CH_3-CH_2-(CH_2)_n-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-(CH_2)_n-CH_2OH$$

wherein n is at least 3. Ordinarily the total number of carbon atoms in the alcohol is 10 to 18.

Sperm oil alcohols are pale yellow or white semi-crystalline substances which melt at moderate temperatures to liquids. They are obtained from the sperm oil esters by treatment thereof with an alkaline hydroxide such as calcium hydroxide, followed by a distillation or extraction process to separate the alcohols. A typical batch of sperm oil alcohols had the following identifying properties:

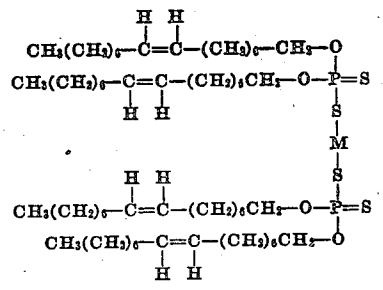
Gravity, °A. P. I.	36.0
Viscosity, S. U. V., 210° F.	37
Pour, °F.	85
Color, N. P. A.	1
Neutralization No.	0.01
Iodine No., Mod. Hanus	55.5
Saponification No.	0.6

Other high molecular weight monohydric alcohols such as oleyl alcohol and the like can be employed in lieu of sperm oil alcohols. Among other useful alcohols are those derived from wool fat or degras, $C_{10}H_{19}OH$; and from lanolin or purified degras, $C_{12}H_{23}OH$; glutinol, $C_{14}H_{27}OH$ from the wax of the elder leaves; vitol, $C_{17}H_{33}OH$ occurring in grape leaves; and cerosine, $C_{24}H_{47}OH$ recovered from sugar cane bagasse. This invention is not limited to the naturally occurring higher unsaturated type alcohols, but to the use of any higher unsaturated type alcohol regardless of origin. We can also employ high molecular weight saturated alcohols, such as lorol alcohol derived from coconut oil fatty acids.

While these high molecular weight alcohols are relatively inert, by the expedient of treating them with phosphorus pentasulfide, they can in effect be combined in stable form with a rather large proportion of lime or other metal.

In proceeding in accordance with the invention, the sperm oil alcohols or their equivalents are brought into reaction with phosphorus pentasulfide (P_2S_5) in proportion about 10 to 35 parts, and 100 parts of the alcohols, with maintenance of the reaction temperature at 300 to 460° F. When reaction is complete, hydrated lime is mixed in, in proportion between one and 15 parts, and heating is continued at a temperature of 300 to 320° F. for about one hour. The reaction mixture is filtered and is then ready for use.

This product is of complex constitution, even when but a single alcohol is employed. Below is given a probable structural formula for the hexadecylene compound, which may be regarded as a sort of average or typical compound in our mixture. It is to be understood that the invention does not depend on the correctness of the formula.



It seems probable that similar or homologous compounds in our reaction product have varying proportions of the components (combined phosphorus, sulfur, etc.) but the average effect is what might be expected from a molecular structure as above. 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 added for securing a range of degrees of detergency, anti-ring-sticking, or solid suspending effects; or in the amount of combined phosphorus as required for anti-ring-sticking and anti-corrosion effects; or in the amount of combined sulfur for varying the effects as to the pressure carrying and corrosion retarding of alloy bearings. Although the structural formula indicates a quantitative relationship between the various elements, it must be understood that these various constituents can be varied at will; that is, the sulfur content can be made greater or less than the phosphorus content, and the amount of metal can be made to vary over relatively wide limits.

The physical identifying characteristics of our preparation generally fall within the ranges indicated below:

Gravity	° A. P. I.	10–20
Sulfur, B	per cent	2–12
Phosphorus	do	2–10
Ash as sulfate	do	5–20

In lieu of ordinary lime, dolomitic limes or magnesia or magnesium hydroxide can be employed; and other metallic oxides or hydroxides such as alumina or zinc oxide. Mono-, di- and trivalent metal compounds and mixtures thereof are useful.

The optimum proportion of the agent to be put into lubricating oils depends on the severity of the service conditions and the degree to which the oil itself tends to form gum and varnish. Ordinarily from 0.25 to 5.0 per cent is suitable.

Example 1.—In a specific example illustrative of one good way of preparing the agents of the invention, 100 parts by weight of the sperm oil alcohols as described above are placed in a stirring still and heated to 250° F.; while stirring at that temperature 17.7 parts by weight of P_2S_5 are added, and the mixture is heated to 300° F., and agitated one-half hour. A mixture of 10 parts hydrated lime, $Ca(OH)_2$, and 1 part water is added slowly with agitation. The mixture is heated to 300–320° F. for one hour, then filtered to remove excess lime, and impurities. The product had the following properties:

Gravity	° A. P. I.	16.3
Viscosity, S. U. V.:		
100° F		1325
210° F		198 8
Pour	° F.	+45
Color, N. P. A.		2.5
Sulfur, B	per cent	8.55
Phosphorus	do	4.60
Ash as sulfate	do	10.09

It was readily soluble in oil.

Example 2.—An improved lubricating oil was prepared by dissolving 1.0 per cent of the preparation of Example 1 in a high grade lubricating oil for use in Diesel engines.

Tests were run on the straight oil and the compounded oil to compare their behavior under service conditions. For this purpose a test engine in the form of a standard Waukesha-CFR crankcase with special L-head type cylinder block was employed, coupled to a cradle-type electric dynamometer. This engine has a bore of 3¼ inches, a stroke of 4½ inches, and a compression ratio of 4.7:1. The piston is of cast iron (except in test C below) 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 a controlled speed, with the spark and the air-fuel ratio adjusted to give maximum power, and the coolant temperature is maintained at a fixed value. At the end of the test 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:

Piston condition performance rating

No. 1—No ring stuck, 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, end ring partly stuck.
5—Top, 2nd and oil rings completely stuck.
6—Condition No. 5 with 3rd and 5th rings partly stuck.

In test A, the engine is run at 900 R. P. M. for 25 hours, and the coolant temperature is maintained at 350° F. The piston condition is reported for such 25 hours running time.

In test B the speed and temperature are as above, but the engine is not run for a fixed time, but is run until the engine power output as measured by the dynamometer is observed to drop; this being indicative of ring sticking. The test is reported in terms of the number of hours running time until the power output begins to fall off.

Test C is like test B except that the engine speed is maintained at 1200 R. P. M. and the coolant temperature at 375° F., and that an aluminum piston is used.

Test D is like test C except that an iron piston is used as in tests A and B.

In the following table are set forth data obtained in these tests, and other comparative char-

acteristics, of the plain oil and the compounded oil.

	Uninhibited oil	Oil containing 1% additive
Gravity ° A. P. I.	28.9	28.9
Viscosity, S. U. V.:		
100° F.	1,487	1,489
210° F.	117.7	117.3
Viscosity index	104	104
Flash, O. C. ° F.	540	525
Fire, O. C. ° F.	615	615
Pour ° F.	0	0
Color, N. P. A.	2.75	2.75
Carbon residue per cent	0.25	0.33
Falex wear test:		
500 lb. gage load, 15 min.—		
Wear: No. of teeth	22	0
Motor oil service test A:		
Piston rating	4	1
Used oil (after 25 hrs. use)—		
Gravity ° A. P. I.	27.8	27.9
Viscosity, S. U. V.—		
100° F.	1,666	1,678
210° F.	124.2	124.2
Viscosity index	102	101.5
Flash, O. C. ° F.	525	535
Fire, O. C. ° F.	615	630
Pour ° F.	0	0
Color, N. P. A.	[1] 4.25	[1] 5.0
Carbon residue per cent	0.49	0.62
Precipitation under centrifuging	Trace	Trace
Neutralization No.	0.60	0.56
Sludge per cent	0.03	0.02
Falex wear test:		
500 lb. gage load, 15 min.—		
Wear: No. of teeth	13	0
Motor service test B: Oil rating hours	19	68
Motor service test C: Oil rating do	22	58
Motor service test D: Oil rating do	18	72

[1] Dil.

An important advantage of the agents of the present invention is that, in addition to being highly oil soluble themselves, they are effective to disperse in mineral oils certain soaps which are of themselves difficultly soluble; for example calcium oleate and aluminum stearate. Sulfurized sperm oil soap is a desirable addition agent to oils, but its low solubility prevents incorporation of more than a rather small quantity into paraffin base oils. According to the present invention one per cent or more of such soap can be dispersed in oil, to form a stable and permanent dispersion, by including an equal amount of the new agent. While the improvement agent has been described in reference to compounding engine lubricating oils for the 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.

What we claim is:

1. A process of preparing an improvement agent for lubricating oils, from monohydric alcohols of the ethylene series, which comprises heating 100 parts of said alcohols with 10 to 35 parts of phosphorus pentasulfide at temperatures between 300° and 460° F. until substantially all of the phosphorus pentasulfide has reacted and acid reaction products thereof are obtained, and then converting said acid reaction products into substantially neutral metal derivatives thereof by further heating the acid reaction products so obtained with a reactive metal compound of the class consisting of the oxides and hydroxides of a polyvalent metal, the amount of such polyvalent metal compound being in excess of that required to neutralize the acidity of said acid reaction products and the mixture being heated at temperatures between 300° and 320° 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. A process of preparing an improvement agent for lubricating oils, from monohydric alcohols of the ethylene series, which comprises heating 100 parts of at least one such alcohol and 10 to 35 parts of phosphorus pentasulfide at temperatures between 300° and 460° F. until substantially all of the phosphorus pentasulfide is reacted and acid reaction products thereof are obtained, adding to such acid reaction products a reactive metal compound of the class consisting of polyvalent metal oxides and hydroxides in proportions stoichiometrically equivalent to 1 to 15 parts of $Ca(OH)_2$, maintaining this mixture at a temperature of 300 to 320° F. for approximately one hour and filtering the oil-soluble reaction products so obtained to remove unreacted metal oxides and hydroxides and other insoluble compounds.

3. The method of claim 1 wherein the metal compound is lime.

4. The method of claim 1 wherein the alcohols are sperm oil alcohols.

5. An improvement agent soluble in petroleum oils and capable of inhibiting formation of gum, varnish and sludge in engines and of dispersing such deposits when present, comprising the substantially neutral, stable, oil-soluble, metallo compounds obtained by the process of claim 1.

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

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