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ADDITION AGENTS FOR MINERAL OIL LUBRICANTS

Herschel G. Smith, Wallingford, and Troy L. Cantrell, Lansdowne, Pa., and John G. Peters, Audubon, N. J., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

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This invention relates to addition agents for mineral oil lubricants, and more particularly, it is concerned with an addition agent with confers improved bearing corrosion inhibiting and detergent properties on mineral oils.

In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, mineral lubricating oils frequently prove unsatisfactory because they tend to deposit varnish, gum and sludge on the engine surfaces, such as the cylinder walls, pistons and rings, and also to induce corrosion of bearing materials. These problems have become increasingly serious because of the trend toward higher efficiency or higher power output per unit weight of engine, which results in conditions tending to accelerate deteriorating influences on the mineral oil lubricant.

The formation of so-called varnishes and sludges on engine surfaces is a result of oxidation effects on the lubricating oils. The presence of such engine deposits is detrimental for many reasons. These substances increase ring sticking and accelerate the formation of further deposits on piston surfaces and fixed parts of the combustion chamber. The sludges formed in the crankcase of the engine increase the rate of corrosion of bearing surfaces, especially of bearing alloys of the type now in use.

In the lubrication of steam turbines, the problems become more acute because of the presence of water in the mineral oil lubricant. Therefore, in addition to bearing corrosion, rusting may also be encountered.

Heretofore, addition agents serving the function of retarding bearing corrosion and acting as a detergent in mineral oil lubricants have ordinarily been organic sulfur or phosphorus compounds. While these compounds have been generally useful, for some applications they are not entirely satisfactory. Thus, in compounded aviation lubricating oils which are subject to the high temperatures incident to air cooled engine conditions, the presence of addition agents containing organic sulfur or phosphorus compounds tends to corrode bronze exhaust valves.

It is an object of this invention, therefore, to provide an addition agent for mineral oil lubricants which will prevent the formation of the engine deposits encountered in the use of mineral oil lubricants.

It is a further object of this invention to provide addition agents for mineral oil lubricants which serve the functions of (1) inhibiting the corrosion of bearings, (2) inhibiting rusting, and

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(3) acting as a detergent to prevent ring sticking, the formation of engine deposits and to suspend or disperse very small particles of deterioration products or contaminating materials in the lubricant.

It is a further object of this invention to provide addition agents for mineral oil lubricants which serve the functions above noted, but which do not contain sulfur or phosphorus in the molecule.

These and other objects are accomplished by the present invention wherein we provide as an addition agent for mineral oil lubricants a metallo compound obtained by reacting in aqueous slurry of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with formaldehyde and condensing the resulting product with aniline and a mono-alkyl phenol having from 4 to 12 carbons atoms in the alkyl substituent. The resulting metallo compound is an excellent detergent and is also effective for inhibiting bearing corrosion and rusting. Such metallo compounds, as well as the mineral oil lubricant compositions containing them, are believed to be novel and are considered parts of our invention

The metallo compound of our invention is prepared by reacting an aqueous slurry of the metal hydroxide and formaldehyde at a mildly elevated temperature, say 160° F., but not exceeding 200° F. The exact nature of the reaction product is unknown, but the reaction product contains combined therein the metal of the metal hydroxide. This product is then condensed with aniline and a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent. The condensation between the reaction product of the metal hydroxide and formaldehyde, and the aniline and phenol proceeds spontaneously upon mixing the reactants. Since the reaction is exothermic, care should be taken not to allow the temperature to exceed about 200° F., otherwise dark-colored, highly resinous, insoluble products may result. After the condensation is completed, the temperature is raised to distill off all water, both that formed in the condensation and added with the reactants. The reactants are preferably employed in the proportions of one mol of metal hydroxide, 2 to 4 mols of formaldehyde, 0.5 to 1.0 mol of aniline and 2 to 4 mols of the mono-alkyl phenol.

As stated, the mono-alkyl phenols have from 4 to 12 carbon atoms in the alkyl substituent. Thus, the alkyl substituent may include normal or branched chain butyl, amyl, hexyl, heptyl,

octyl, decyl and do-decyl radicals. A preferred alkyl substituent is the tetramethylbutyl radical. The mono-alkyl phenols are preferably obtained by alkylating in known manner, in the presence of concentrated sulfuric acid, phenol with olefins having from 4 to 12 carbon atoms. Olefins such as butene-1, isobutylene, the amylenes, di-isobutylene and tri-isobutylene may conveniently be employed. It is preferred to conduct the alkylation with di-isobutylene since the resulting product is primarily para tetramethylbutyl phenol.

While we do not desire to be bound by any theory as to the reaction or reactions involved or the chemical composition of the products, we believe that in view of the multiple points of the respective molecules at which the reactants may react, we obtain a mixture of compounds. Our designation of the condensation product as a "metallo compound" is intended to cover all of such compounds.

The following example illustrates the preparation of our new addition agent.

Example I

Into a jacketed iron reaction vessel (No. 1) were charged 12.9 parts by weight of phenol and 16.5 parts by weight of di-isobutylene. The vessel was closed and the mixture agitated. Then 0.6 parts by weight of 94–98% sulfuric acid were added. Cold water was run through the jacket of the reaction vessel in order to maintain a reaction temperature below 220° F. When all of the materials had been added, the temperature was permitted to attain 220° F. and held at that temperature for 4 hours. The resulting para tetramethylbutyl phenol was dissolved in 73 parts by weight of a mineral lubricating oil.

Into an enamel lined reaction vessel (No. 2) were charged 4.6 parts by weight of calcium hydroxide with sufficient water to make a slurry, to which was added 14.9 parts by weight of a 37% by weight aqueous solution of formaldehyde. The reactants were heated to a temperature of 160° F. for 2 hours. Thereafter, the reaction product was added to the mineral oil solution of para tetramethylbutyl phenol in reactor vessel No. 1 with agitation for 15 minutes. Then 4.3 parts by weight of aniline were added and the temperature maintained below 200° F. The condensation product was then dried by increasing the temperature to 280° F., distilling off the water, following which the product was filtered. The additive, thus prepared, had the following properties:

Gravity, °API	20.3
Viscosity, SUV, 210° F	111.4
Color, NPA	4.75
Neutralization No	0.92 alk.
Ash as sulfate, per cent	4.513

The reactants in the above example were in the relative molar proportions of 1.0 mol of calcium hydroxide, 3 mols of formaldehyde, 2.3 mols of para tetramethylbutyl phenol, and 0.7 mol of aniline.

The condensation products obtained in accordance with the above disclosure are excellent addition agents for mineral oil lubricants. They are readily soluble in all types of mineral oils, that is, paraffinic, naphthenic or mixed base mineral oils and, as a matter of fact, can be blended with mineral oils in proportions as high as 50 per cent by weight or higher. This excellent solubility of our new addition agents enables the preparation of concentrated solutions thereof, as shown in Example I, supra, which may then be diluted down to the proportion desired in the final mineral oil lubricant composition. As stated, our new addition agents confer excellent detergent effects on the mineral lubricating oils with which they are incorporated, and also confer in addition excellent bearing corrosion-inhibiting and rust inhibiting properties. For these purposes, our new addition agents are generally added to mineral lubricating oils in minor amounts, say from 0.1 per cent to 5.0 per cent by weight of the mineral oil, sufficient to confer improved detergent and/or bearing corrosion inhibiting properties on the mineral lubricating oils with which they are incorporated. Generally the addition of 1.0 per cent by weight of our new addition agents is sufficient to effect the desired improvement. In view of their high molecular weight and low volatility at high temperatures, as well as the absence of sulfur and phosphorus in the molecule, our new addition agents are particularly advantageous for preparing lubricants which encounter high temperatures, such as aviation lubricating oils.

The following example illustrates the use of our new addition agents to obtain improved mineral oil lubricant compositions.

Example II

A motor lubricating oil SAE 30 was blended with 4.0 per cent by volume of the additive, prepared according to Example I. A comparison of the properties of the base oil and improved oil follows:

	Base Oil	Improved Oil
Gravity: ° API	29.2	28.8
Viscosity, SUV:		
70° F	1384	1475
100° F	518	544
130° F	238	249
210° F	67.2	69.5
Viscosity Index	107	107
Flash, OC, ° F	435	465
Fire, OC, ° F	515	530
Cloud, ° F	----------	+8
Pour, ° F	+10	−25
Aging Test, 32° F., 24 Hr.	----------	bright
Room Temp., 15 Days	----------	bright
Color, NPA	2.5	2.75
Appearance	bright	bright
Sulfur, B, Per Cent	0.13	0.12
Carbon Residue, Per Cent	0.05	0.46
Copper Strip Test, 212° F., 3 Hr.	passes	passes
Corrosion Test, ASTM D 665–46T, Distilled Water:		
Steel Rod, Appearance	rust	bright
Area Rusted, Per Cent	100	0
Neutralization No	0.10	0.39 alk.
U–V Light Stability, Quartz Tube, 8 Hr., Appearance	----------	bright
Ash as Sulfate, Per Cent	----------	0.198
Chevrolet 36 Hour Engine Test, CRC L–4:		
Engine Condition Rating	----------	93
Bearing Loss: Mg./Whole Bearing	----------	30

As shown in the above example, our new addition agents confer remarkably effective detergent properties. Thus the engine condition rating shown under the Chevrolet 36 Hour Engine Test indicates a freedom from engine deposits, expressed in per cent, of 93 per cent, the larger the per cent (approaching 100 as a limit) the cleaner the engine. The marked improvement in detergent properties obtained by the use of our new addition agents is clear. As shown by the data under bearing loss which indicates the amount of bearing corrosion expressed in milligrams loss in weight of a standard bearing, our new addition agents confer excellent bearing corrosion inhibiting properties since only 30 milligrams' loss was observed. In addition to these advantages, our new addition agents also inhibit rusting as is shown under the corrosion test.

The Chevrolet 36 Hour Engine Test referred to above is an accepted standard test designed to determine the oxidation, detergency and bearing corrosion characteristics of engine crankcase oils designed for use under heavy duty service conditions. In this procedure, the crankcase lubricant is evaluated with respect to its stability or resistance to oxidation, bearing corrosion and the deposition of contaminants resulting from decomposition and oxidation or other changes that occur in the lubricant in service. The procedure involves the intermittent operation of a special 6-cylinder automotive test engine at constant speed and load for a total of 36 hours subsequent to a run-in period of 8 hours at graduated speeds and loads. Prior to each test, a complete set of new piston rings is installed and two new weighed copper-lead test bearings are installed in symmetrical location. Performance of the test oil is judged by examination of the power section of the engine for deposits and by ascertaining the weight loss of the test bearings.

While we have shown in the above examples the preparation of compounded lubricating oils, our invention is not limited thereto, but comprises all mineral oil lubricant compositions containing our new agents, such as greases and the like. The use of our new agents in greases is disclosed and claimed in the copending application of Smith and Cantrell, Serial No. 41,706, filed July 30, 1949, and assigned to the same assignee as the instant application.

We claim:

1. The process which comprises reacting an aqueous slurry of 1 mol of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with from 2 to 4 mols of formaldehyde at a temperature not exceeding 200° F. and condensing the resulting product at a temperature not exceeding about 200° F. with from 0.5 to 1 mol of aniline and from 2 to 4 mols of a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent.

2. The process which comprises reacting an aqueous slurry of 1 mol of a metal hydroxide selected from the group consisting of barium, strontium, magnesium and calcium hydroxides with from 2 to 4 mols of formaldehyde at a temperature not exceeding 200° F., condensing the resulting product at a temperature not exceeding 200° F. with a mineral lubricating oil solution of from 2 to 4 mols of a mono-alkyl phenol having from 4 to 12 carbon atoms in the alkyl substituent and from 0.5 to 1 mol of aniline, and recovering a solution of the condensation product in the mineral lubricating oil.

3. The process which comprises reacting an aqueous slurry of 1 mol of calcium hydroxide with 3 mols of formaldehyde at a temperature of about 160° F., and condensing the resulting product with 0.7 mol of aniline and 2.3 mols of para tetramethylbutyl phenol at a temperature not exceeding 200° F.

4. The product obtained by the process of claim 1.

5. The product obtained by the process of claim 2.

6. The product obtained by the process of claim 3.

7. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer bearing corrosion inhibiting and detergent properties on the composition, of the product obtained by the process of claim 1.

8. The composition of claim 7, wherein the said product is present in amount of from 0.1 to 5.0 per cent by weight of the mineral lubricating oil.

9. A lubricant composition comprising a major amount of a mineral lubricating oil and 1.0 per cent by weight on the mineral lubricating oil of the product obtained by the process of claim 3.

HERSCHEL G. SMITH.
TROY L. CANTRELL.
JOHN G. PETERS.

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