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PROCESS FOR PREPARING ADDITION AGENTS FOR MINERAL OIL LUBRICANTS, THE AGENTS SO OBTAINED, AND MINERAL OIL LUBRICANTS CONTAINING THEM

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This invention relates to addition agents for mineral oil lubricants and compositions containing the same, and more particularly it relates to addition agents which confer improved pressure-carrying, bearing corrosion-inhibiting and detergent properties on mineral oil lubricants.

In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, plain mineral lubricating oils often prove unsatisfactory in service because of the attendant deposition on the engine surfaces, such as the cylinder walls, pistons and rings, of "varnish," "gum," or "sludge." These effects are particularly serious in modern engines operating under severe conditions, such as Diesel engines and aviation, truck, and tank engines. The problem has become increasingly serious due to the trend toward (1) higher efficiency, or higher power output per unit weight per engine, (2) reduction in the amount of oil employed in the lubricating system of the engine, and (3) other conditions which tend to accelerate deteriorating influences on mineral lubricating oils.

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 generally known as "improvement agents" or "addition agents." However, preparation of satisfactory compounded lubricants is a matter of considerable difficulty. Some of the agents are of low potency, that is, 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 since the addition agents heretofore employed usually have a rather low solubility the difficulties of preparing a useful lubricant are enhanced.

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It is also a frequent characteristic of prior art addition agents that they are extremely dark in color. When such dark-colored addition agents are added in effective amounts to a highly refined light-colored mineral oil, they often impart such a degree of color to the oil as to render the oil unmarketable.

It is an object of this invention, therefore, to provide an addition agent for mineral oil lubricants which serves the functions of (1) inhibiting the corrosion of bearings, (2) acting as a loosening or suspending agent (detergent) to prevent ring-sticking, varnishing or coating of the metallic surfaces of internal combustion engines, and (3) acting as a suspending or dispersing agent for dispersing very small particles of deterioration products or contaminating materials in the oil.

Another object of this invention is to provide an addition agent for mineral oil lubricants which is readily soluble and extremely light-colored, and which may be added to any light-colored mineral oil lubricant without materially affecting the color thereof.

It is a further object of this invention to provide an addition agent for mineral oil lubricants which confers markedly improved extreme pressure characteristics on such mineral oil lubricants.

These and other objects are attained by the present invention wherein an addition agent for mineral oil lubricants is prepared by reacting an octyl phenol with a sulfur chloride and a relatively small amount of phosphorus sesquisulfide. The reaction product so obtained is a light colored product which, when added to mineral oil lubricants, does not materially affect the color thereof. At the same time our new addition agent imparts improved pressure-carrying, bearing corrosion-inhibiting and detergent properties to mineral oil lubricants.

While we do not desire to be bound by any theory as to the effect of the individual reactants, it is our present belief that the use of phosphorus sesquisulfide results in a light-colored reaction product and also enhances the pressure-carrying characteristics of the product. We are led to this conclusion by the fact that a reaction product of an octyl phenol and a sulfur chloride prepared without phosphorus sesquisulfide tends to be dark in color and of poorer pressure-carrying characteristics. We have also found that when our new addition agents are prepared in the presence of a volatile solvent, the formation of light-colored products is promoted.

In the production of our new addition agents, we react an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of a sulfur

chloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide. The reaction may take place at room temperature, and it usually is preferred to initiate the reaction at such temperature and then raise the temperature to no higher than 350° F. to complete the reaction. However the reaction may take place at any temperature ranging from room temperature to 350° F., provided care is taken that the latter temperature is not exceeded. If the temperature of 350° F. is exceeded to any great extent, especially in the initial stages of the reaction, the reaction product formed will tend to be dark-colored and insoluble in mineral oil lubricants.

As has been stated, it is desirable to use a volatile solvent in the preparation of our new addition agents. A wide variety of solvents may be employed such as benzene, toluene, hexane, carbon tetrachloride, chloroform, cyclohexane and others. The solvent should be inert in the reaction and for this reason materials containing reactive hydroxyl and sulfhydryl groups, such as alcohols, mercaptans and the like should not be employed. Since the solvent is removed from the reaction product after the reaction has been completed, it is desirable that the solvent be relatively volatile and therefore a solvent having a boiling point above 320, F. should not be used. When the temperature of the reaction, as set forth in the preceding paragraph, is above the boiling point of the solvent employed, the reaction is carried out in a closed vessel, as will be obvious to those skilled in the art.

We may use any octyl phenol in the preparation of our new addition agents. The octyl phenols may be prepared by any method known to the art, but they are preferably made in accordance with the procedure shown in U. S. Patent No. 2,149,759. In accordance with the procedure of said patent, phenol is reacted with a mixture of isomeric octenes, such as is available at the refinery in commercial diisobutylene polymer, in the presence of a condensing agent such as concentrated sulfuric acid. The octyl phenol prepared in this manner is a mixture of isomeric octyl phenols, but it is believed to contain a preponderant amount of tetramethyl butyl phenol (para-iso-octyl phenol). However, our invention is not limited to the use of any specific octyl phenol or to octyl phenols derived from any specific source. Thus any one of the isomeric octyl phenols or mixtures thereof may be employed with good results in accordance with our invention.

The sulfur chloride used in accordance with our invention is preferably sulfur monochloride. However, other sulfur chlorides such as sulfur dichloride and sulfur tetrachloride or mixtures thereof may be employed. When sulfur tetrrachloride is employed alone, it is preferred to use smaller proportions thereof within the range given because the larger proportions tend to produce products which are darker in color than when the other sulfur chlorides are employed. As previously stated, the sulfur chloride is reacted with the phenol in an amount ranging from 0.5 to 30 per cent by weight on the octyl phenol.

Example I.—As an example of the preparation of an addition agent in accordance with our invention, 1374 pounds of an octyl phenol, 13 pounds of phosphorus sesquisulfide (P_4S_3) and 1331 pounds of benzene were placed into a reaction vessel equipped with an agitator, means

for heating and cooling, and a reflux condenser. Then 270 pounds of sulfur monochloride (S_2Cl_2) were added slowly while keeping the reaction mixture at a temperature of 60° F. The addition of the sulfur monochloride required approximately 4 hours. At this time the temperature was raised to 180° F. and the mixture was refluxed for 20 hours at this temperature in order to complete the reaction. At the end of this time the benzene was distilled off and the residue was heated to 250° F. under a vacuum of approximately 15 inches of mercury in order to strip off all of the benzene. The residue was then diluted with 1500 pounds of an oil having the following properties:

Gravity, °API	32.0
Viscosity, SUV:	
100° F.	72.4
Flash, OC, °F.	345
Fire, OC, °F.	395
Pour, °F.	+20
Color, NPA	1.5
Carbon residue, per cent	0.01
Neutralization No.	0.02

The solution of addition agent in the mineral oil had the following properties:

Gravity, °API	17.3
Viscosity, SUV:	
100° F.	1103
Flash, OC, °F.	385
Fire, OC, °F.	450
Pour, °F.	+5
Color, NPA	2.50
Sulfur, per cent	5.42

The reaction products obtained from octyl phenol, a sulfur chloride and phosphorus sesquisulfide are excellent addition agents for mineral oil lubricant compositions. They are readily soluble in all types of mineral oils, that is, paraffinic, naphthenic or mixed base mineral oils, and can be blended with mineral oils in high proportions as is shown in the preceding example. This excellent solubility of our new addition agents enables the preparation of concentrated solutions thereof which may then be diluted down to the proportions desired in the final mineral oil lubricant composition. As stated, our new addition agents confer excellent pressure-carrying, bearing corrosion-inhibiting and detergent properties on the mineral lubricating oils with which they are incorporated. For these purposes our new addition agents are generally added to mineral oils in minor amounts, say from 0.1 to 15 per cent by weight on the mineral oil. Ordinarily small amounts as low as 0.1 per cent by weight are sufficient to effect the desired improvement. However, when extreme pressure properties are to be conferred on a mineral lubricating oil composition, it will ordinarily be desirable to use higher amounts, as high as 15 per cent.

In another aspect of our invention, we have found that the properties of mineral oil lubricating compositions containing our new addition agent described above may be still further enhanced, particularly in regard to inhibiting bearing corrosion, if such mineral oil lubricating compositions contain in addition a condensation derivative of the above described reaction product. More particularly, the reaction product of an octyl phenol with a sulfur chloride and phosphorous sesquisulfide prepared in accordance with the preceding disclosure is substantially neutralized with an oxide or hydroxide of a

metal of group II of the periodic table selected from the group consisting of magnesium, calcium, barium and zinc to form a substantially neutral metal salt of said reaction product. The resulting salt is condensed with formaldehyde or a formaldehyde-yielding compound. When the resulting condensation derivative and the original reaction product are both added to a mineral oil lubricant composition, the properties of the composition are still further improved, particularly in regard to inhibiting bearing corrosion.

The neutralization of the reaction product of an octyl phenol with a sulfur chloride and a phosphorus sesquisulfide may be accomplished in any conventional manner known to the art and preferably by heating of the reaction product and the desired metal axide or hydroxide. Calcium hydroxide is preferred for the neutralization.

The condensation of the substantially neutral metal salt of the above disclosed reaction product with formaldehyde or a formaldehyde-yielding compound is accomplished by heating to a temperature not in excess of 275° F. Useful formaldehyde-yielding compounds are trioxymethylene, paraformaldehyde and the like. The amount of formaldehyde used ranges from 0.5 to 2 mols per mol of octyl phenol used in making the reaction product of an octyl phenol with a sulfur chloride and phosphorus sesquisulfide. Formaldehyde-yielding compounds are employed in amounts equivalent to the amount of formaldehyde yielded by such compounds within the range above stated. Following condensation with the formaldehyde or formaldehyde-yielding compound, the condensation product is dehydrated.

The following example illustrates the preparation of the condensation derivative of our invention.

Example II.—Seven hundred sixty one pounds of an octyl phenol, 7.2 pounds of phosphorus sesquisulfide and 736 pounds of benzene were placed into a reaction vessel equipped with an agitator, means for heating and cooling, and a reflux condenser. Then 150 pounds of sulfur monochloride were added slowly at a temperature of 60° F. The mixture was then heated to 180° F. and refluxed at this temperature for 20 hours. The benzene was then distilled off and the residue was heated to 280° F. under a vacuum of about 15 inches of mercury. The resulting reaction product was then diluted with 850 pounds of a mineral oil having the same properties shown in Example I, and then 117 pounds of hydrated lime and 249 pounds of 37 per cent formaldehyde solution were added. The mixture was then heated with agitation to a maximum temperature of 275° F. for about 2 hours. Thereafter, the water was allowed to distill off. The product was then dried under a vacuum of 15 inches of mercury at a temperature of 300° F. The product obtained had the following properties:

Gravity, °API	14.4
Viscosity, SUV:	
100° F.	837
210° F.	58.3
Color, NPA	3.25
Sulfur, per cent	5.88
Neutralization No.	2.20
Ash, per cent	10.8

The above described condensation derivative

is also readily soluble in mineral lubricating oils, and as disclosed in Example II may conveniently be prepared as a concentrate in mineral lubricating oils. When both the above described reaction product and the condensation derivative thereof are incorporated in a mineral oil lubricant composition as previously disclosed, minor amount of both agents are ordinarily sufficient to effect the desired improvement in pressure-carrying, bearing corrosion-inhibiting and detergent properties. The total amount of both agents will generally range from 0.1 to 15 per cent by weight on the mineral lubricating oil. Within this range, it is preferred to employ equal amounts by weight of the two agents, but the proportions of the two agents with respect to each other may vary from 10 to 90 per cent by weight of the reaction product, and from 90 to 10 per cent by weight of the condensation derivative.

The following table illustrates the improved mineral oil lubricant compositions obtained by the use of our new addition agents. In the table, composition A is a good grade uncompounded SAE 30 motor oil, composition B is composition A blended with 1 per cent by weight of the reaction product prepared in accordance with Example I, and composition C is composition A blended with 1 per cent by weight of the reaction product perpared in accordance with Example I and 1 per cent by weight of the condensation derivative prepared in accordance with Example II.

	A	B	C
Gravity, °API	29.3	29.0	28.9
Viscosity, SUV:			
100° F	535	533	529
210° F	67.5	67.1	66.6
Viscosity Index	104	103	104
Flash OC, °F	465	490	495
Fire, OC, °F	525	545	535
Cloud, °F	-------	none	−5
Pour, °F	+5	−5	0
Aging Test, 32° F., 24 Hr.	bright	bright	bright
Room Temp., 15 Days	bright	bright	bright
Color, NPA	1.75	1.75	1.75
Appearance	bright	bright	bright
Sulfur, B, Per Cent	0.12	0.19	0.26
Carbon Residue, Per Cent	0.11	0.13	0.19
Precipitation No.	-------	nil	nil
Centrifuge Test, Separation, Per Cent:			
1500 R. P. M., Room Temp., 2 Hr.	-------	nil	nil
Neutralization No.	0.02	0.02	0.02
Chevrolet 36 Hour Engine Test:			
CRC Designation L-4—			
Engine Rating	75-541	95-49	95-14
Falex Wear Test:			
1000 Lb. Gauge Load, 15 min.—			
Wear: No. of Teeth	fails	0	0
Gauge Load at Seizure: Lb.	-------	1,100	1,800

As may be seen from the above data, the color of the base lubricating oil remains unchanged and bright notwithstanding the addition of our new addition agents. As shown by the data on the Falex wear test, even small amounts of our new addition agents effectively improve the pressure carrying properties of the base oil. When larger amounts are used the improvements obtained in pressure-carrying properties are even more striking. The remarkably effective detergent and bearing-corrosion inhibiting properties imparted to the base oil are shown by the data on the Chevrolet 36 hour engine test. In the hyphenated figures shown thereunder, the figure to the left of the hyphen indicates the freedom from engine deposits expressed in per cent, the larger the per cent (approaching 100 as a limit) the cleaner the engine. The marked improvement in detergent effects obtained from the use of our new addition agents is clear. The figure

to the right of the hyphen indicates the amount of bearing corrosion expressed in milligrams loss in weight of a standard bearing. As shown under composition B, a mineral oil lubricant composition containing the reaction product of an octyl phenol with a sulfur chloride and phosphorus sesquisulfide in accordance with our invention, reduces the loss in weight of the bearing from 541 milligrams to 49 milligrams. As shown under composition C, when the mineral oil lubricant composition contains both the aforesaid reaction product and the condensation derivative thereof, a still further improvement is obtained, the loss in weight of the bearing being only 14 milligrams. Our new addition agents clearly confer excellent bearing corrosion-inhibiting properties. Finally, the above data show the excellent stability and solubility of our new addition agents.

The Chevrolet 36 hour engine test referred to above is an accepted standard test designed to determine the oxidation and bearing corrosion characteristics of engine crank case oils designed for use under heavy duty service conditions. In this procedure, the crank case 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 examples the preparation of compounded lubricating oils, our invention is not limited thereto, but comprises all mineral oil lubricant compositions containing our new addition agents, such as greases and the like.

As used in the appended claims, the term "formaldehyde" includes formaldehyde-yielding compounds as well as formaldehyde itself.

We claim:

1. The process of preparing an addition agent for mineral oil lubricants which comprises simultaneously reacting at a temperature ranging from room temperature to 350° F. an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of a sulfur chloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide.

2. The process of preparing an addition agent for mineral oil lubricants which consists of simultaneously reacting at a temperature ranging from room temperature to 350° F. and in the presence of a solvent an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of a sulfur chloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide, and distilling off the solvent.

3. The process of claim 2, wherein the solvent is a volatile solvent having a maximum boiling point of 320° F.

4. The process of preparing an addition agent for mineral oil lubricants which comprises simultaneously reacting at a temperature ranging from room temperature to 350° F. and in the presence of a volatile solvent having a maximum boiling point of 320° F. an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of sulfur monochloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide, and distilling off the solvent.

5. The process of claim 4, wherein the volatile solvent is benzene.

6. The process of preparing an addition agent for mineral oil lubricants which comprises simultaneously reacting at a temperature ranging from room temperature to 350° F. an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of a sulfur chloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide, neutralizing the reaction product obtained thereby with a member of the class consisting of oxides and hydroxides of a metal selected from the group consisting of magnesium, calcium, barium and zinc to obtain a substantially neutral reaction product, condensing the neutral reaction product with formaldehyde by heating at a temperature not greater than 275° F. the neutralized reaction product and from 0.5 to 2 mols of formaldehyde per mol of octyl phenol used in making said reaction product.

7. The process of preparing an addition agent for mineral oil lubricants which comprises simultaneously reacting at a temperature ranging from room temperature to 350° F. and in the presence of a volatile solvent having a maximum boiling point of 320° F. an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of sulfur monochloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide, distilling off the solvent, diluting the residue with a mineral lubricating oil, neutralizing the residue with a member of the class consisting of oxides and hydroxides of a metal selected from the group consisting of magnesium, calcium, barium and zinc to obtain a substantially neutral reaction product, condensing the neutral reaction product with formaldehyde by heating at a temperature not greater than 275° F. the neutralized reaction product and from 0.5 to 2 mols of formaldehyde per mol of octyl phenol used in making said reaction product, and dehydrating the resulting condensation product.

8. The process of claim 6, wherein calcium hydroxide is employed for the neutralization.

9. The process of claim 7, wherein calcium hydroxide is employed for the neutralization.

10. An addition agent for mineral oil lubricants obtained by the process of claim 1.

11. An addition agent for mineral oil lubricants obtained by the process of claim 2.

12. An addition agent for mineral oil lubricants obtained by the process of claim 6.

13. An addition agent for mineral oil lubricants obtained by the process of claim 7.

14. An addition agent for mineral oil lubricants obtained by the process of claim 9.

15. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer improved pressure-carrying, bearing corrosion-inhibiting and detergent properties on the composition, of a simultaneous reaction product of an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of a sulfur chloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide.

16. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor

amount, from 0.1 to 15 per cent by weight on the oil, of a simultaneous reaction product of an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of sulfur monochloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide, said reaction product having been prepared in the presence of a volatile solvent which is subsequently distilled off.

17. A lubricant composition comprising a major amount of a mineral lubricating oil and minor amounts, sufficient to confer improved pressure-carrying, bearing corrosion-inhibiting and detergent properties on the composition of (1) the simultaneous reaction product of an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of a sulfur chloride and from 0.1 to 5 per cent by weight on the octyl phenol of phosphorus sesquisulfide, and (2) the condensation product of formaldehyde and a substantially neutral metal salt of (1), said metal being a metal selected from the group consisting of magnesium, calcium, barium and zinc, the amount of formaldehyde being from 0.5 to 2 mols per mol of octyl phenol employed to form (1), and the amounts of (1) and (2) with respect to each other ranging from 10 to 90 percent by weight of (1) and from 90 to 10 per cent by weight of (2).

18. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, from 0.1 to 15 per cent by weight on the oil of: (1) the simultaneous reaction product of an octyl phenol with from 0.5 to 30 per cent by weight on the octyl phenol of sulfur monochloride and from 0.1 to 5 per cent by weight on the octyl

phenol of phosphorus sesquisulfide, said reaction product having been prepared in the presence of a volatile solvent which is subsequently distilled off; and (2) the anhydrous condensation product of formaldehyde and a substantially neutral metal salt of (1), said metal being a metal selected from the group consisting of magnesium, calcium, barius and zinc, the amount of formaldehyde being from 0.5 to 2 mols per mol of octyl phenol employed to form (1); and the amounts of (1) and (2) with respect to each other ranging from 10 to 90 per cent by weight of (1) and from 90 to 10 per cent by weight of (2), and totaling from 0.1 to 15 per cent by weight on the mineral oil.

19. A lubricant composition in accordance with claim 17, wherein the metal salt is a calcium salt.

20. A lubricant composition in accordance with claim 17, wherein the metal salt is a calcium salt.

21. A lubricant composition in accordance with claim 17, wherein the amounts of (1) and (2) are equal.

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