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AGENT AND MINERAL OIL LUBRICANT COMPOSITIONS CONTAINING THE SAME

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This invention relates to improvement agents and mineral oil lubricant compositions containing the same and, more particularly, it is concerned with improvement agents which confer improved anti-oxidant, corrosion-inhibiting and pressure-carrying properties on mineral oil lubricants.

It is recognized in the art that mineral oil lubricants are readily oxidized under service conditions thereby reducing the service life of internal combustion engines and steam turbines. A concomitant effect is corrosion of bearing surfaces. These problems become particularly acute when a highly refined paraffinic base mineral oil is employed as the lubricant.

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 thereby causing failure of the engine. 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 the 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 gums, varnishes and sludges is detrimental for many reasons. These substances tend to increase ring sticking and accelerate the formation of further deposits on piston surfaces and in fixed parts of the combustion chamber. The sludges formed in the crank case of the engine increase the rate of corrosion of bearing surfaces, especially of bearing alloys of the types now in use.

In steam turbines, the corrosion problem is particularly acute because of the presence of water in the mineral oil lubricant and in addition to bearing corrosion, rusting may also be encountered.

It is an object of this invention, therefore, to prepare an improvement agent which will obviate the oxidation and corrosion difficulties encountered in the use of mineral oil lubricants.

It is a further object of this invention to provide improved mineral oil lubricant compositions which are stable in storage and use and in which oxidation and corrosion effects are materially inhibited.

It is also an object of this invention to provide

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mineral oil lubricant compositions which have excellent pressure-carrying properties.

In our copending application Serial No. 718,902, filed December 27, 1946, there is disclosed and claimed an improvement agent for mineral oil lubricants which confers excellent antioxidant, corrosion-inhibiting and pressure-carrying properties on mineral oil lubricants. Such improvement agent is prepared by heating an essentially paraffinic base lubricating oil with anhydrous aluminum chloride, removing aluminum chloride from the reaction product and reacting said product with phosphorous pentasulfide at an elevated temperature to incorporate phosphorus and sulfur therein.

The objects of the present invention are accomplished by providing an improvement agent for mineral oil lubricants by reacting an essentially paraffinic base lubricating oil with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst to incorporate phosphorus and sulfur in said lubricating oil, and recovering the reaction product. The reaction product so obtained is an excellent light-colored improvement agent for mineral oil lubricant compositions, which is remarkably effective for inhibiting oxidation and corrosion and which in addition confers excellent pressure-carrying properties. Such improvement agents, as well as the mineral oil lubricant compositions containing them, are believed to be novel and are considered parts of our invention.

In one aspect, the present invention is an improvement over the invention disclosed in our above-identified copending application. As shown in said application, if the treatment of an essentially paraffinic base lubricating oil stock with anhydrous aluminum chloride is omitted prior to reacting the oil with phosphorus pentasulfide, there is obtained a black sludge-like product which is poorly soluble in mineral lubricating oils and which imparts such a degree of color to mineral oil lubricant compositions as to render them unmarketable. However, in accordance with the present invention, the aluminum chloride treatment may be omitted without obtaining the above-described black sludge-like product, provided that the reaction of the essentially paraffinic base lubricating oil with phosphorus pentasulfide takes place in the presence of a surface active silica-containing solid catalyst. It is still necessary to employ an essentially paraffinic base lubricating oil as the initial material, however, because other hydrocarbon materials produce the black, sludge-like, difficultly soluble product regardless of the

use of the surface active silica-containing solid catalyst. The reasons for the advantageous effects of the surface active silica-containing solid catalyst on the reaction are not fully understood. However, the use of such a catalyst is essential for the practice of our invention, since, if the catalyst is omitted, the advantageous results of our invention are not obtained. In order to obtain the results of our invention, therefore, it is necessary (1) to employ an essentially paraffinic base lubricating oil, and (2) to conduct the reaction with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst.

The essentially paraffinic base lubricating oil used as a starting material in accordance with our invention may be derived from any paraffinic crude, such as Pennsylvania, Mid-continent or other paraffinic base crudes. The lubricating oil is manufactured from such crudes in accordance with conventional methods and may be refined in accordance with methods known in the art.

Although, in accordance with the present invention, it is not necessary to treat the paraffinic base lubricating oil with aluminum chloride, if desired, the paraffinic base lubricating oil may be treated with aluminum chloride as disclosed in our copending application, and the treated oil reacted with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst. The products so obtained have a color which is lighter than that obtained when the aluminum chloride treatment is omitted. If it is desired to treat the essentially paraffinic base lubricating oil with aluminum chloride, such treatment is accomplished as described in our copending application. Briefly, such treatment comprises heating the essentially paraffinic base lubricating oil with from 1 to 20 per cent by weight of anhydrous aluminum chloride at a temperature of from 150° to 300° F. while vigorously agitating. The time of treatment may vary in accordance with the amount of aluminum chloride used and the temperature of treatment, longer times being required with less aluminum chloride and lower temperatures. In general, the treatment will be completed after 4 or 5 hours. After the treatment is completed, agitation is stopped and a sludge containing most of the aluminum chloride settles out from the main body of the oil and is drawn off. The supernatant body of the treated oil may contain further quantities of aluminum chloride finely dispersed therethrough and, in order to insure the removal of all aluminum chloride from the treated oil, agitation with an adsorbent clay followed by filtration may be employed. At the higher temperatures of treatment with aluminum chloride some conversion of the paraffinic base oil to lower boiling products may take place and, although such conversion is slight, the product may be topped, if desired; that is, distilled to remove the lower boiling products overhead and to recover as a residue the bulk of the aluminum chloride treated oil having a minimum initial boiling point in the range 490° to 530° F.

The reaction of the essentially paraffinic base lubricating oil, whether or not treated with aluminum chloride, with phosphorus pentasulfide in the presence of the catalyst is accomplished by adding from 2 to 20 per cent by weight of P_2S_5, preferably from 5 to 10 per cent, to the essentially paraffinic base lubricating oil and heating with agitation at a temperature in the range from 300° F. to a maximum reaction temperature below the temperature where cracking of the oil, that is,

pyrolytic decomposition of the oil begins. Generally the minimum cracking temperature of the oil will vary between 490° to 530° F. depending upon the particular oil used. The surface-active silica-containing solid catalyst is employed in an amount of from 2 to 25 per cent by weight of the oil charged, and preferably in an amount of 10 per cent by weight. Larger amounts than 10 per cent are ordinarily not necessary, but larger amounts will produce a product having a lighter color. During the course of the reaction, hydrogen sulfide is evolved and phosphorus and sulfur become incorporated in the oil. When the evolution of hydrogen sulfide has nearly ceased, the temperature of the reaction mixture may be increased within the maximum temperature disclosed above, say to about 500° F., for completion of the reaction. The mixture is then filtered to remove the catalyst. The products so obtained are excellent improvement agents for mineral oil lubricants.

The surface active silica-containing solid catalysts may comprise activated clays, silica-alumina cracking catalysts and the like. Thus, activated clays, that is, natural clays such as bentonite, smectite, floridin, fuller's earth and the like which have been treated with acid, as described in U. S. Patent No. 1,898,165, for example, may be advantageously employed. Synthetic silica-alumina catalysts of the type used for the cracking of hydrocarbon oils and which are described in U. S. Patent No. 2,078,945 and U. S. Patent No. 2,283,173, for example, may also be employed. Activated silica gel is also suitable. As may be seen, the term "surface active silica-containing solid catalyst" comprises a wide variety of materials, the predominant characteristic of which is the presence of silica in a surface active, that is, activated form.

The following examples illustrate the preparation of our new improvement agents:

Example I

Eight thousand five hundred fifty parts by weight of an SAE 30 grade paraffinic lubricating oil were placed into a reaction vessel equipped with an agitator and means for heating and cooling. Then 450 parts by weight of phosphorus pentasulfide and 900 parts by weight of an activated clay catalyst were added with stirring at a temperature of 400° F. The temperature was held at 400° F. until evolution of hydrogen sulfide had nearly ceased, and then the temperature was raised to 500° F. and held at that point for 2 hours with agitation. The reaction with the P_2S_5 from the time of its addition to the completion of the reaction took 8 hours. The product was then cooled and filtered. The product had the following properties:

Gravity, °API	25.9
Viscosity, SUV:	
100° F.	670
210	75.1
Color, NPA	5.0
Sulfur, percent	1.64
Phosphorus, percent	1.08
Neutralization No.	9.0

Example II

Ten thousand parts by weight of a solvent treated dewaxed lubricating oil stock, 1000 parts by weight of phosphorus pentasulfide and 1000 parts by weight of an activated clay catalyst were placed in a reaction vessel. The mixture was

maintained at 400° F. with stirring until the evolution of hydrogen sulfide had subsided. The temperature was then raised to 500° F. to complete the reaction. The product was then cooled and filtered. It had the following properties:

Gravity, °API	20.9
Viscosity, SUV: 100° F.	1200
Color, NPA	5.0
Sulfur, percent	1.20
Phosphorus, percent	2.65
Neutralization No.	19.4

Example III

Ninety-five parts by weight of a paraffinic base lubricating oil, 5 parts by weight of P_2S_5 and 5 parts by weight of an activated clay catalyst were reacted under the conditions set forth in Example I. The filtered product had the following properties:

Gravity, °API	25.9
Viscosity, SUV:	
100° F.	670
210	75.1
Color, NPA	6.0
Sulfur, percent	1.64
Phosphorus, percent	1.08
Neutralization No.	9.0

Example IV

Ninety-five parts by weight of a paraffinic base lubricating oil which had been treated with aluminum chloride as disclosed hereinabove, 5 parts by weight of P_2S_5 and 20 parts by weight of an activated clay catalyst were reacted under the conditions set forth in Example I. The filtered product had the following properties:

Gravity, °API	26.0
Viscosity, SUV:	
100° F.	675
210	75.2
Color, NPA	3.0
Sulfur, percent	1.67
Phosphorus, percent	1.10
Neutralization No.	8.0

The phosphorus pentasulfide reaction products obtained in accordance with the preceding examples are excellent improvement agents for mineral oil lubricant compositions. They are light-colored and 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 improvement agents enables the preparation of concentrated solutions, which may then be diluted down to the proportion desired in the final mineral oil lubricant composition. As stated, our new improvement agents confer excellent pressure-carrying, antioxidant and corrosion-inhibiting properties on the mineral lubricating oils with which they are incorporated. For these purposes, our new improvement agents are generally added to mineral oils in minor amounts, say from 0.1 per cent to 20 per cent by weight of the mineral oil, sufficient to confer improved pressure-carrying, antioxidant and corrosion inhibiting properties on the mineral lubricating oils with which they are incorporated. When our new improvement agents are to be used for their antioxidant and corrosion-inhibiting effects, small proportions as low as 0.1 per cent by weight are sufficient to effect the improvement. When extreme pressure properties are to be conferred on a lubricating oil, higher proportions, as high as 20 per cent, may conveniently be used.

The following examples illustrate the use of our new improvement agents to obtain improved mineral oil lubricant compositions:

Example V

An excellent motor oil, SAE 30 grade, was prepared by blending 1 part by weight of the improvement agent prepared in accordance with Example I with 99 parts by weight of a highly refined paraffinic SAE 30 grade motor oil. The properties of the improved and unimproved motor oils were as follows:

	Unimproved Motor Oil	Improved Motor Oil
Gravity, °API	29.0	29.1
Viscosity, SUV: 100° F	520	520
Color, NPA	1.75	1.75
Oxidation and Bearing Corrosion Test Method 257, Gulf:		
Duration of Test, Hr	48	48
Oil Bath Temperature, °F	347	347
Air Rate, Cc./Hr.	2,000	2,000
Quantity of Oil, Cc	300	300
Bearing Type	Cd-Ag	Cd-Ag
Wt. Change—		
Grams	−0.1744	−0.047
Per cent	−0.96	−0.01

Example VI

An SAE 30 grade motor oil was blended with 1 per cent by weight of the improvement agent prepared in accordance with Example III. The properties of the unimproved and improved motor oils were as follows:

	Unimproved Motor Oil	Improved Motor Oil
Gravity, °API	29.0	29.1
Viscosity, SUV: 100° F	520	520
Color, NPA	1.75	2.25
Oxidation and Bearing Corrosion Test Method 257, Gulf:		
Duration of Test, Hr	48	48
Oil Bath Temperature, °F	347	347
Air Rate, Cc./Hr.	2,000	2,000
Quantity of Oil, Cc	300	300
Bearing Type	Cd-Ag	Cd-Ag
Wt. Change—		
Grams	−0.1744	−0.052
Per cent	−0.96	−0.01

Example VII

An SAE 30 grade motor oil was treated with 1 per cent by weight of the improvement agent prepared in accordance with Example IV. The properties of the unimproved and improved motor oils were as follows:

	Unimproved Motor Oil	Improved Motor Oil
Gravity, °API	29.0	29.3
Viscosity, SUV: 100° F	520	514
Color, NPA	1.75	1.75
Oxidation and Bearing Corrosion Test Method 257, Gulf:		
Duration of Test, Hr	48	48
Oil Bath Temperature, °F	347	347
Air Rate, Cc./Hr.	2,000	2,000
Quantity of Oil, Cc	300	300
Bearing Type	Cd-Ag	Cd-Ag
Wt. Change—		
Grams	−0.1744	−0.038
Per cent	−0.96	−0.01

Example VIII

An improved turbine oil was prepared by blending 0.3 parts by weight of the improvement agent

prepared in accordance with Example I and 99.7 parts by weight of a well refined turbine oil base. The properties of the improved and unimproved turbine oils are as follows:

	Unimproved Turbine Oil	Improved Turbine Oil
Gravity, ° API	29.0	28.9
Viscosity, SUV: 130° F.	192.7	190.6
Color, NPA	2.75	3.0
Oxidation and Bearing Corrosion Test Method 257, Gulf:		
Duration of Test, Hr.	48	48
Oil Bath Temperature: ° F.	347	347
Air Rate, Cc./Hr.	2,000	2,000
Quantity of Oil, Cc.	300	300
Bearing Type	Cd-Ag	Cd-Ag
Weight Change—Grams	−0.1744	−0.0006
Per cent	−0.96	−0.01
Corrosion Test, ASTM D665-44T: Distilled Water, Steel Rd.	rusts	passes

Example IX

A lubricating oil having excellent extreme pressure properties was prepared by blending 15 parts by weight of the improvement agent made according to Example I and 85 parts by weight of a highly refined motor oil. A comparison of the properties of the improved lubricant and the base lubricant follows:

	Unimproved Lubricant	Improved Lubricant
Gravity, ° API	29.3	28.8
Viscosity, SUV: 100° F.	246	245
Color, NPA	1.75	1.75
Falex Wear Test:		
1000 Lb. Guage Load, 15 Min. Wear, No. of Teeth	fails	0
Guage Load at Seizure, Lb.		1,750

The "Oxidation and Bearing Corrosion Test, Method 257, Gulf," referred to in the foregoing examples, is conducted as follows:

An alloy bearing shell of certain commonly used standard dimensions is submerged in 300 cc. of the oil or oil composition to be tested in a 400 cc. Pyrex beaker and heated in a thermostatically controlled oil bath to 347° F. Air is then bubbled through the oil in contact with the bearing shell at a rate of 2000 cc. per hour. At the end of 48 hours, the loss of weight and condition of the bearing shell are determined, the bearing shell being washed free of oil and dried before weighing. When determining the effectiveness of various improvement agents, the usual procedure is to run a blank test simultaneously with the oil composition being tested, employing for that purpose a sample of the untreated oil. In this test it is advantageous to employ commercial bearing shells. These shells comprise a suitable metal backing faced with the alloy bearing metal. In this way the actual bearing face is subjected to severe deterioration conditions. By comparison of the results of such tests with actual service tests, we have found them to be in substantial agreement as to suitability of particular lubricants.

As shown in the above examples, the addition of our new improvement agents to mineral oil lubricant compositions confers excellent pressure-carrying, antioxidant and corrosion-inhibiting properties. At the same time the compositions so obtained are stable in storage and use and have a color which is substantially unaffected by the addition of the improvement agent.

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 improvement agents, such as greases and the like.

1. The process of preparing an improvement agent for mineral oil lubricants which comprises heating an essentially paraffinic base lubricating oil with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst at a temperature of from 300° F. to a maximum temperature below the minimum cracking temperature of said lubricating oil to incorporate phosphorus and sulfur in said lubricating oil, and recovering the reaction product.

2. The process of preparing an improvement agent for mineral oil lubricants which comprises heating an essentially paraffinic base lubricating oil with from 2 to 20 per cent by weight of phosphorus pentasulfide in the presence of from 2 to 25 per cent by weight of a surface active silica-containing solid catalyst at a temperature of from 300° F. to a maximum temperature below the minimum cracking temperature of said lubricating oil to incorporate phosphorus and sulfur in said lubricating oil, and recovering the reaction product.

3. The process of claim 2, wherein the amount of phosphorus pentasulfide is from 5 to 10 per cent.

4. The process of claim 2, wherein the catalyst is an activated clay catalyst.

5. The process of claim 2, wherein the catalyst is a cracking catalyst of the silica-alumina type.

6. The process of preparing an improvement agent for mineral oil lubricants which comprises heating an essentially paraffinic base lubricating oil with from 5 to 10 per cent by weight of phosphorus pentasulfide in the presence of 10 per cent by weight of a surface active silica-containing solid catalyst at a temperature of from 300° F. to a maximum temperature below the minimum cracking temperature of said lubricating oil to incorporate phosphorus and sulfur in said lubricating oil, recovering the reaction product and dissolving it in a mineral lubricating oil.

7. The process of preparing an improvement agent for mineral oil lubricants which comprises heating an essentially paraffinic base lubrication oil with anhydrous aluminum chloride at a temperature of from 150° to 300° F., removing aluminum chloride from the reaction product, heating said product with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst at a temperature of from 300° F. to a maximum temperature below the minimum cracking temperature of the aluminum chloride treated oil to incorporate phosphorus and sulfur therein, and recovering the reaction product.

8. The process of preparing an improvement agent for mineral oil lubricants which comprises heating an essentially paraffinic base lubricating oil with from 1 to 20 per cent by weight of anhydrous aluminum chloride at a temperature of from 150° to 300° F., removing aluminum chloride from the reaction product, heating said product with from 2 to 20 per cent by weight of phosphorus pentasulfide in the presence of from 2 to 25 per cent by weight of a surface active silica-containing solid catalyst at a temperature of from 300° F. to a maximum temperature below the minimum cracking temperature of the aluminum chloride treated oil to incorporate phosphorus and sulfur therein, and recovering the reaction product.

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

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

11. An improvement agent for mineral oil lubricants obtained in accordance with the process of claim 6.

12. The product obtained by the process of claim 7.

13. The product obtained by the process of claim 8.

14. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer improved pressure-carrying, antioxidant and corrosion-inhibiting properties on the composition, of the product obtained by the process of claim 1.

15. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, from 0.1 to 20 per cent by weight, of the product obtained by the process of claim 2.

16. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer improved pressure-carrying, antioxidant and corrosion-inhibiting properties on the composition, of the product obtained by the process of claim 7.

17. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, from 0.1 to 20 per cent by weight, of the product obtained by the process of claim 8.

18. A turbine oil comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer improved antioxidant and corrosion-inhibiting properties on the composition of the product obtained by the process of claim 2.

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