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2,767,165

ADDITION AGENTS

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This invention relates to addition agents for mineral oil lubricant compositions and, more particularly, it is concerned with addition agents which confer improved anti-oxidant, detergent and/or corrosion-inhibiting 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. A concomitant effect is corrosion of bearing surfaces. In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, uncompounded 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 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 type now in use.

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

It is also an object of this invention to provide mineral oil lubricant compositions which have excellent detergency properties.

In our copending application Serial No. 718,902, filed December 27, 1946, now U. S. Patent No. 2,603,603, of which this application is a continuation-in-part, there is disclosed and claimed an improvement agent for mineral oil lubricants which is prepared by treating an essentially paraffinic base lubricating oil with aluminum chloride and reacting the treated oil with phosphorus pentasulfide to incorporate phosphorus and sulfur therein.

As shown in our copending application, the agent is prepared by heating an essentially paraffinic base lubricating oil, such as may be derived from Pennsylvania, Mid-Continent, or other paraffinic base crudes, with anhydrous aluminum chloride, removing aluminum chloride from the reaction product and reacting said product with phosphorus pentasulfide at an elevated temperature to incorporate phosphorus and sulfur therein. Briefly, treatment with aluminum chloride is accomplished by heating the essentially paraffinic base lubricating oil with from 1 to 20 percent of anhydrous aluminum chloride at a temperature of from 150° to 300° F. while vigorously agitating, with the time of treatment varying in accordance with the amount of aluminum chloride used and the temperature of treatment, longer times being required with

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less aluminum chloride and lower temperatures. In general, however, the treatment will be completed after four or five hours. In any event, treatment is continued until a product is obtained which, when freed of aluminum chloride, will not form a black, difficultly soluble sludge-like product upon subsequent reaction with phosphorus pentasulfide. If desired, the aluminum chloride treated oil may be blended with some of the untreated charge stock without deleteriously affecting the subsequent reaction with phosphorus pentasulfide, but ordinarily not more than about 20 percent of untreated oil should be added to the treated product and, preferably, smaller amounts should be used. The reaction with phosphorus pentasulfide is accomplished by adding 2 to 20 percent by weight of P_2S_5 , preferably from 5 to 10 percent, to the aluminum chloride treated oil, or the blend with untreated oil disclosed above, and heating with agitation at a minimum reaction temperature of 450° F. and a maximum reaction temperature below the temperature where cracking of the oil, that is, pyrolytic decomposition of the treated oil begins. Generally, the minimum cracking temperature of the oil will vary between 490° to 530° F. depending on the particular oil used. During the course of the reaction with P_2S_5 , hydrogen sulfide is evolved and phosphorus and sulfur become incorporated in the aluminum chloride treated 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.

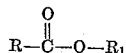
As shown in the aforesaid copending application, if the prior aluminum chloride treatment of the oil is omitted, a black, poorly soluble, sludge-like product is obtained upon subsequent reaction with the phosphorus pentasulfide. Similar unsuitable products are obtained if a hydrocarbon other than an essentially paraffinic base oil is employed as the initial material, regardless of prior treatment with aluminum chloride.

In our U. S. Patent No. 2,456,336, granted December 14, 1948, there is disclosed and claimed an improvement agent for mineral oil lubricants which is prepared by reacting an essentially paraffinic base lubricating oil, of the type described above, with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst. It is shown in the patent that when phosphorus pentasulfide is reacted with an essentially paraffinic base lubricating oil in the presence of a surface active silica-containing solid catalyst, the prior aluminum chloride treatment of the lubricating oil, as disclosed in our copending application Serial No. 718,902, may be omitted. It is also shown in the patent that when the prior aluminum chloride treatment of the oil is combined with reaction of the treated product with phosphorus pentasulfide in the presence of the silica-containing catalyst, lighter colored products are obtained. The reaction of the essentially paraffinic base lubricating oil, whether or not treated with aluminum chloride, with phosphorus pentasulfide in the presence of the silica-containing catalyst is accomplished by adding from 2 to 20 percent by weight of P_2S_5 , preferably from 5 to 10 percent, 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 begins. The surface-active, silica-containing solid catalyst is employed in an amount of from 2 to 25 percent of the oil, and preferably in an amount of 10 percent by weight. Larger amounts than 10 percent 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 tem-

perature 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 surface-active, silica-containing solid catalysts may comprise activated clays, silica-alumina cracking catalysts and the like, as more fully disclosed in the patent.

In our U. S. Patent 2,593,496 and in our copending applications Serial No. 31,598, filed June 7, 1948, now U. S. Patent No. 2,603,600, Serial No. 37,308, filed July 6, 1948, now U. S. Patent No. 2,603,601, and Serial No. 73,218, filed January 27, 1949, now U. S. Patent No. 2,603,602, we have disclosed and claimed improvements over the inventions set forth in our copending application Serial No. 718,902 and our U. S. Patent 2,456,336. Mineral oil lubricants containing the addition agents disclosed in application Serial No. 718,902 and Patent 2,456,336 sometimes fail to pass the well-known Copper Strip Test (Method 530.31, Federal Specification VV-L-791c, May 12, 1945, page 259), thus indicating the presence of elementary sulfur or the so-called "corrosive" sulfur. In accordance with our U. S. Patent 2,593,496 and our copending applications Serial No. 31,598, Serial No. 37,308 and Serial No. 73,218, we found that the incorporation of a sulfur acceptor in the preparation of the agents of Serial No. 718,902 and Patent 2,456,336 resulted in new addition agents passing the Copper Strip Test and otherwise improved.

In our Patent 2,593,496, the sulfur acceptor is an ester having the formula:



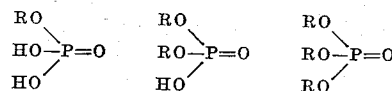
wherein R and R₁ represent aliphatic hydrocarbon radicals, at least one of said radicals containing olefinic unsaturation, and the sum of the carbon atoms of both R and R₁ being not less than 16. The ester is ordinarily added in proportions ranging from 1.0 to 10 percent by weight of the reaction mixture, sufficient to combine with free or "corrosive" sulfur from the phosphorus pentasulfide reaction product. Among the esters which are used are those in which both R and R₁ have olefinic unsaturation, particularly sperm oil which provides an excellent source of this type of ester. Other specific esters are disclosed in the patent.

In our copending application Serial No. 31,598, the sulfur acceptor is a monohydric alkylated phenol having at least 4 carbon atoms in an alkyl group. The alkylated phenol is ordinarily added in proportions ranging from 5 to 50 percent by weight of the paraffinic base lubricating oil, or the aluminum chloride treated product thereof, sufficient to remove free or "corrosive" sulfur from the phosphorus pentasulfide reaction product. The preferred alkylated phenols are the monohydric alkylated phenols having from 4 to 12 carbon atoms in a branched chain alkyl group, particularly paratetramethylbutyl phenol, other specific alkylated phenols being shown in the application.

In our copending application Serial No. 37,308, the sulfur acceptor is an alkylated phenyl phosphite which may be prepared according to U. S. Patent 2,253,227 to Cantrell and Turner. The alkylated phenyl phosphite is ordinarily added in proportions ranging from 10 to 75 percent by weight of its mixture with the paraffinic base lubricating oil, or the aluminum chloride treated product thereof, sufficient to remove free or "corrosive" sulfur from the phosphorus pentasulfide reaction product. The alkylated phenyl phosphites employed are preferably those having from 4 to 8 carbon atoms in a branched chain alkyl group and containing from 1 to 5 percent by weight of combined phosphorus. Paratetramethylbutyl phenyl phosphite is a preferred material; other specific phosphites are shown in the application.

In our copending application Ser. No. 73,218, the sulfur acceptor is an alkyl orthophosphate having at least 5

carbon atoms in the alkyl group. The alkyl orthophosphate is ordinarily added in proportions ranging from 10 to 75 percent by weight of its mixture with the paraffinic base lubricating oil or the aluminum chloride treated product thereof, sufficient to remove free or "corrosive" sulfur from the phosphorus pentasulfide reaction product. The alkyl orthophosphate can be a mono-, di-, or tri-alkyl ester of orthophosphoric acid having the following general formulas:



wherein R represents a saturated aliphatic hydrocarbon radical of at least 5 carbon atoms, preferably 8 to 18 carbon atoms. The upper limit of 18 carbon atoms is not critical, it being dictated by considerations of commercial availability. In the di- and tri-alkyl esters the R's may be the same or different alkyl radicals. A preferred ester is trioctyl phosphate; other specific esters are shown in the application.

The objects of the present invention are accomplished by providing salts of the phosphorus pentasulfide-essentially paraffinic base lubricating oil reaction products of our copending application Serial No. 718,902 and our Patent 2,456,336, whether or not these products have been treated with sulfur acceptors in accordance with our Patent 2,593,496 and our copending applications Serial No. 31,598, Serial No. 37,308 and Serial No. 73,218. We have found that the foregoing reaction products possess sufficient acidity to enable their neutralization with bases and that the salts so obtained are effective improvement agents for mineral oil lubricants. The desired salts can also be obtained by metathesis of an alkali metal salt of such reaction products and a water-soluble salt of a metal other than an alkali metal.

The salts of the present invention are easily prepared by simple neutralization with an inorganic base or an organic nitrogen base, or by metathesis, if desired. For example, alkali metal and ammonium salts can be prepared by neutralizing the reaction products of our patents and copending applications, referred to above, with a hydroxide or carbonate of an alkali metal such as sodium, potassium, lithium, ammonium, etc. The alkaline earth metal hydroxides, i. e., calcium, barium, magnesium and strontium hydroxides, yield a particularly preferred group of salts. Aluminum hydroxide is also suitable. Salts of these metals as well as salts of zinc, copper, tin, lead, iron, cobalt, nickel, manganese, cadmium, mercury, bismuth, vanadium, chromium, and the like can conveniently be prepared by metathesis of a water-soluble salt of such metal with an alkali-metal salt of the desired phosphorus pentasulfide reaction product.

Organic nitrogen bases yield valuable addition salts. Such bases include primary, secondary and tertiary aliphatic and aromatic amines and heterocyclic nitrogen bases. Primary alkyl amines such as ethyl, butyl, amyl, hexyl, cyclohexyl, heptyl, octyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl and eicosyl are suitable. Mixtures of primary alkyl amines, such as are present in commercially available amines derived from fatty acids by well known methods, make desirable salts. For example, cocoamine, derived from coconut oil fatty acids and containing primarily dodecyl amine with smaller amounts of homologues, yields a preferred salt. Primary alkenyl amines corresponding to the primary alkyl amines, such as undecenyl, oleyl, etc., can also be employed. A preferred group is the primary alkyl or alkenyl amines having from 8 to 22 carbon atoms. Salts derived from secondary and tertiary amines, whether aliphatic or aromatic, such as the di- and tri-ethanolamines, dicyclohexylamine, N-alkyl and N-dialkylarylamines, e. g., N-ethylaniline, N-dimethylaniline are satisfactory, as are primary aryl, aralkyl and cycloalkyl amines such as ani-

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line, benzylamine and cyclohexylamine. A valuable class of salts is derived from heterocyclic nitrogen bases, such as pyridine, picoline, ethyl pyridine, lutidine, aldehydine, parvoline, quinoline, quinaldine, lepidine, isoquinoline, nicotine, piperidine, morpholine, N-phenyl morpholine, and the like.

The following examples illustrate the preparation of our new improvement agents. Unless otherwise stated, all parts are by weight.

Example I

Three thousand (3000) gallons of a solvent-refined dewaxed paraffinic base lubricating oil were charged to a vessel equipped with an agitator and means for heating and cooling, and agitated at 275° F. while adding 4 percent by weight of anhydrous aluminum chloride. Agitation was then continued for 4 hours. At the end of this time agitation was stopped and the bulk of the aluminum chloride settled in a sludge at the bottom of the vessel. The sludge was withdrawn; and in order to remove any remaining dispersed aluminum chloride in the body of the oil, there was added 0.2 pound per gallon of oil of an adsorbent clay, such as "Super-Filtrol," and the mixture agitated at 210° F. The mixture was then filtered and there was obtained, in a yield of 84.1 percent by volume of the original charge, an aluminum chloride treated oil free of aluminum chloride and having a viscosity index of 105. To 81 parts by volume of the treated oil, there were added 19 parts by volume of the original untreated oil and, of this mixture, 8550 parts were placed into a reaction vessel equipped with an agitator and means for heating and cooling. Then 450 parts of phosphorus pentasulfide were added with agitation and the temperature was raised to 450° F. A large volume of hydrogen sulfide was evolved and when evolution of hydrogen sulfide had nearly ceased, the temperature was raised to 500° F. to complete the reaction. The reaction with phosphorus pentasulfide from the time of its addition to the completion of the reaction took 8 hours.

Three thousand (3000) parts of the above product were then heated to 150° F. and 102 parts of calcium hydroxide were added in the form of an aqueous slurry. The mixture was heated to 180° F. for half an hour and dried at 280° F. for one hour. The whole was then diluted with 3000 parts of a paraffinic lubricating oil having a viscosity of 70 S.U.S. at 100° F. and filtered through diatomaceous earth. The product had the following properties:

Gravity, °API	25.8
Viscosity, SUS:	
100° F.	262
210	52.6
Color, ASTM Union	Dark
Sulfur, B, percent	1.28
Ash, percent	2.05
Neutralization value, ASTM D974-48T, Strong base No.	1.86

Example II

An identical portion of the phosphorus pentasulfide and aluminum chloride treated mineral lubricating oil, as described in Example I, was reacted with 300 parts of barium hydroxide octahydrate with agitation at 180° F. for 1 hour. Then 3000 parts of a lubricating oil having a viscosity of 70 S. U. S. at 100° F. was added and the whole filtered through diatomaceous earth. The product had the following properties:

Gravity, °API	24.1
Viscosity, SUS:	
100° F.	288
210	55
Color, ASTM Union	Dark
Sulfur, B, percent	1.44
Ash, percent	3.09
Neutralization value, ASTM D974-48T, strong base No.	1.91

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Example III

Three thousand (3000) parts of a phosphorus pentasulfide and aluminum chloride treated mineral lubricating oil, as described in Example I, were reacted with 300 parts of cocoamine in the manner of the preceding examples with respect to reaction with calcium hydroxide and barium hydroxide and diluted with 3000 parts of a lubricating oil having a viscosity of 70 S. U. S. at 100° F. The product had the following properties:

Gravity, °API	27.1
Viscosity, SUS, 210° F.	50.7
Color, ASTM Union	8.0
Sulfur, B, percent	1.17
Neutralization value, ASTM D974-48T, strong base No.	1.6

Example IV

Fifty-one (51) parts of an essentially paraffinic base lubricating oil (SAE 30) which had been treated with aluminum chloride in accordance with our copending application Serial No. 718,902 were placed in a reaction vessel with 5.6 parts of phosphorus pentasulfide. The mixture was then agitated and heated to 450° F. for a period of 2 hours. The temperature was then gradually raised to 525° F. over a period of 4 hours and maintained at that point for 2 hours. The mixture was then cooled to 350° F. and 5.1 parts of sperm oil added. The mixture was held at this temperature for 4 hours, then cooled and diluted with an equal weight of a light lubricating oil, thereby forming a concentrate of the product.

Three thousand parts of the above reaction product were heated to 250° F. and 150 parts of a 5 per cent slurry of lime in water were added, the whole agitated at 180° F. for half an hour, then dried at 280° F. and filtered through diatomaceous earth. The product had the following properties:

Gravity, °API	21.5
Viscosity, SUS, 210° F.	80.1
Color, ASTM Union	Dark
Sulfur, B, percent	2.81
Neutralization value, ASTM D974-48T, strong base No.	1.1
Ash, percent	0.85

Example V

Into a reaction vessel there were placed 50 parts of an essentially paraffinic base lubricating oil which had been treated with aluminum chloride in accordance with our copending application Serial No. 718,902, 50 parts by weight of octyl (paratetramethylbutyl) phenyl phosphite and 12.5 parts of phosphorus pentasulfide. The whole was heated to 400° F. with agitation for 2 hours until the evolution of hydrogen sulfide had substantially subsided. With continued agitation, the temperature of the reaction mass was then raised to 520° F. and held at this point for approximately 6 hours. The reaction product was then cooled to 180° F. and 17 parts of barium hydroxide octahydrate in an aqueous slurry were added. The mixture was slowly heated to 280° F. and held at this temperature for 1 hour to remove formed and added water. The mixture was then diluted with an equal weight of a lubricating oil having a viscosity of 70 S. U. S. at 100° F. and filtered through diatomaceous earth. The product had the following properties:

Gravity, °API	16.0
Viscosity, SUV, sec., 210° F.	69.2
Color, ASTM Union	6.0
Sulfur, B, percent	4.9
Ash, percent	0.9
Neutralization value, ASTM D974-48T, strong base No.	0.4

Example VI

In the presence of 5 parts of an activated montmorillonite as a catalyst, 50 parts of an SAE 30 Mid-Continent paraffinic base lubricating oil and 50 parts of tri-secondary-octyl phosphate were reacted with 10 parts of phosphorus pentasulfide. The mixture was agitated and the temperature raised to 490° F. and held at that temperature for a period of 2 hours. After this time the evolution of hydrogen sulfide had subsided and with continued agitation the temperature was raised to 520° F. and held there for 6 hours to complete the reaction. The mass was then filtered through diatomaceous earth to remove the clay catalyst. The filtrate was then reacted with 2.5 parts of calcium hydroxide in the form of an aqueous slurry. This reaction was carried out by raising the temperature to 250° F. for a period of 30 minutes. The product was then filtered through diatomaceous earth to give a filtrate with the following properties:

Gravity, ° API.....	14.1
Color, ASTM Union.....	8.0
Sulfur, B, percent.....	3.0
Phosphorus, percent.....	2.8
Neutralization value, ASTM D974-48T, strong base No.....	Nil

Although the preceding examples have shown the use of certain bases and reactants in preparing the salts of the present invention, it will be understood that the other bases and reactants disclosed herein may be substituted for the materials of the specific examples to yield satisfactory products.

The salts obtained in accordance with the present invention are excellent improvement 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 such oils in high proportions. This excellent solubility of our new improvement agents permits of the preparation of concentrated solutions which may then be diluted down to the proportion desired in the final mineral oil lubricant composition. The salts of the present invention confer one or more advantageous properties on the mineral lubricating oils with which they are incorporated, such as antioxidant, bearing corrosion-inhibiting and rust inhibiting properties. For these purposes, our new improvement agents are generally added to mineral oils in minor amounts, say from 0.1 to 25 percent by weight of the mineral oil, sufficient to confer the desired effect.

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

Example VII

An improved motor oil, SAE 20, was prepared by blending 2 parts by weight of the agent prepared according to Example I and 98 parts by weight of an SAE 20 grade lubricating oil base. Properties of the improved and unimproved motor oil are as follows:

	Unimproved Lubricant		Improved Lubricant	
Gravity, ° API.....	29.0		28.9	
Viscosity, SUS, 100° F.....	335		339.2	
Color, ASTM Union.....	4.25		4.5	
Oxidation and Bearing Corrosion Test, Method 257, Gulf:				
Duration of Test, Hr.....	48		48	
Oil Bath Temperature, °F.....	347		347	
Air Rate, MI./Hr.....	2,000		2,000	
Quantity of Oil, MI.....	300		300	
Bearing Type.....	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb
Wt. Change, Grams.....	-0.2319	-0.0867	-0.003	-0.0121
Wt. Change, Percent.....	-1.28	-0.38	-0.05	-0.06

Example VIII

An improved motor oil was prepared by blending 2 parts by weight of the additive prepared according to Example II and 98 parts by weight of a solvent refined SAE 20 grade motor oil base. Properties of the improved and unimproved motor oils are as follows:

	Unimproved Lubricant		Improved Lubricant	
Gravity, ° API.....	29.0		28.8	
Viscosity, SUS, 100° F.....	335		342	
Color, ASTM Union.....	4.25		4.50	
Oxidation and Bearing Corrosion Test, Method 257, Gulf:				
Duration of Test, Hr.....	48		48	
Oil Bath Temperature, °F.....	347		347	
Air Rate, MI./Hr.....	2,000		2,000	
Quantity of Oil, MI.....	300		300	
Bearing Type.....	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb
Wt. Change, Grams.....	-0.2319	-0.0867	-0.0032	-0.0109
Wt. Change, Percent.....	-1.28	-0.38	-0.005	-0.05

Example IX

Similarly, an improved motor oil was prepared by blending 2 parts by weight of the additive prepared according to Example III and 98 parts by weight of a solvent refined SAE 20 grade motor oil base. The properties of the improved and unimproved motor oil are as follows:

	Unimproved Lubricant		Improved Lubricant	
Gravity, ° API.....	29.0		29.1	
Viscosity, SUS, 100° F.....	335		337	
Color, ASTM Union.....	4.25		4.0	
Oxidation and Bearing Corrosion Test, Method 257, Gulf:				
Duration of Test, Hr.....	48		48	
Oil Bath Temperature, °F.....	347		347	
Air Rate, MI./Hr.....	2,000		2,000	
Quantity of Oil, MI.....	300		300	
Bearing Type.....	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb
Wt. Change, Grams.....	-0.2319	-0.0867	-0.0071	-0.0317
Wt. Change, Percent.....	-1.28	-0.38	-0.01	-0.15

Example X

An improved motor oil was prepared by blending 2 parts by weight of the additive prepared according to Example IV and 98 parts by weight of a solvent refined motor oil base stock. The properties of the improved and unimproved motor oil are as follows:

	Unimproved Lubricant		Improved Lubricant	
Gravity, ° API.....	29.0		29.0	
Viscosity, SUS, 100° F.....	335		339	
Color, ASTM Union.....	4.25		4.50	
Oxidation and Bearing Corrosion Test, Method 257, Gulf:				
Duration of Test, Hr.....	48		48	
Oil Bath Temperature, °F.....	347		347	
Air Rate, MI./Hr.....	2,000		2,000	
Quantity of Oil, MI.....	300		300	
Bearing Type.....	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb
Wt. Change, Grams.....	-0.2319	-0.0867	-0.0015	-0.0341
Wt. Change, Percent.....	-1.28	-0.38	-0.002	-0.015

Example XI

An improved motor oil was prepared by blending 1 part by weight of the additive prepared according to Example V with 99 parts by weight of a solvent refined paraffinic motor oil base stock. Comparison of the prop-

erties of the improved lubricant and the base lubricant follows:

	Unimproved Lubricant		Improved Lubricant	
Gravity, ° API	28.8		28.6	
Viscosity, SUS, 100° F.	352		342	
Color, ASTM Union	4.0		4.5	
Oxidation and Bearing Corrosion Test, Method 257, Gulf:				
Duration of Test, Hr.	48		48	
Oil Bath Temperature, ° F.	347		347	
Quantity of Oil, MI.	300		300	
Air Rate, MI./Hr.	2,000		2,000	
Bearing Type	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb
Wt. Change, Grams.	-0.2040	-0.3150	-0.0013	-0.026
Wt. Change, Percent.	-0.93	-1.42	-0.01	-0.12
Appearance	pitted	pitted	bright	coated
Chevrolet 36 Hr., Engine Test, CRC Designation L-4				
Engine Condition Rating	75		94	
Bearing Loss, Mg./Whole Bearing	541		54	

Example XII

An improved motor oil was prepared by blending 1 part by weight of the additive prepared according to Example VI with 99 parts by weight of a solvent refined paraffinic motor oil base stock.

Comparison of the properties of the improved and the unimproved motor oil are as follows:

	Unimproved Motor Oil		Improved Motor Oil	
Gravity, ° API	29.0		28.9	
Viscosity, SUS, 100° F.	449		453	
Color, ASTM Union	4.25		4.5	
Oxidation and Bearing Corrosion Test, Gulf 257:				
Duration of Test, Hr.	48		48	
Oil Bath Temperature, ° F.	347		347	
Air Rate, MI./Hr.	2,000		2,000	
Quantity Oil Used, MI.	300		300	
Bearing Type	Cd-Ag	Cu-Pb	Cd-Ag	Cu-Pb
Wt. Change, Grams.	-0.204	-0.3150	-0.0013	-0.031
Wt. Change, Percent.	-0.93	-1.42	-0.01	-0.14
Copper Strip Test	passes		passes	

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 ml. of the oil or oil composition to be tested in a 400 ml. Pyrex beaker and heated in a thermostatic oil bath to 347° F. Air is then bubbled through the oil in contact with the bearing shell at a rate of 2000 ml. 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 the suitability of particular lubricants.

As shown in the above examples, the addition of our new improvement agents to mineral oil lubricant compositions confers excellent antioxidant and bearing corrosion inhibiting properties. At the same time, the com-

positions 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. Furthermore, conventional addition agents, such as viscosity index improvers, anti-foam agents, pour point depressants and the like may be added without departing from the spirit of the invention.

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. An addition agent for mineral oil lubricants comprising a salt selected from the group consisting of alkaline earth metal salts and primary aliphatic amine salts, said primary aliphatic amine having from 8 to 22 carbon atoms, of a product prepared by heating an essentially paraffinic base lubricating oil with anhydrous aluminum chloride at a temperature of from 150° to 350° F., removing aluminum chloride from the reaction product, and reacting the latter with phosphorus pentasulfide at a temperature of from 450° F. to a maximum temperature below the minimum cracking temperature of said reaction product to incorporate phosphorus and sulfur therein.

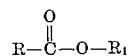
2. The addition agent of claim 1, wherein the phosphorus pentasulfide reaction product has incorporated therein a sulfur acceptor.

3. The addition agent of claim 1, wherein there is additionally employed in the preparation of the phosphorus pentasulfide reaction product a surface active silica-containing soild catalyst.

4. An addition agent for mineral oil lubricants comprising a salt selected from the group consisting of alkaline earth metal salts and primary aliphatic amine salts, said primary aliphatic amine having from 8 to 22 carbon atoms, of a product prepared by heating an essentially paraffinic base lubricating oil with phosphorus pentasulfide in the presence of a surface active silica-containing soild 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 therein.

5. The addition agent of claim 4 wherein the phosphorus pentasulfide reaction product has incorporated therein a sulfur acceptor.

6. An addition agent for mineral oil lubricants comprising an alkaline earth metal salt of a product prepared by heating an essentially paraffinic base lubricating oil with anhydrous aluminum chloride at a temperature of from 150° to 300° F., removing aluminum chloride from the reaction product, reacting said product with phosphorus pentasulfide to incorporate phosphorus and sulfur therein, and then further reacting the resulting product at a temperature of from 300° to 400° F. with an ester having the formula:



wherein R and R₁ represent aliphatic hydrocarbon radicals, at least one of said radicals containing olefinic unsaturation, and the sum of the carbon atoms of both R and R₁ being not less than 16.

7. The addition agent of claim 6, wherein the alkaline earth metal is calcium, and the ester is sperm oil.

8. An addition agent for mineral oil lubricants comprising an alkaline earth metal salt of a product prepared by heating an essentially paraffinic base lubricating oil with anhydrous aluminum chloride at a temperature of from 150° to 300° F., removing aluminum chloride from the reaction product, and reacting the latter with an alkylated phenyl phosphite and phosphorus pentasulfide at

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a temperature of from 300° F. to a maximum temperature below the minimum cracking temperature of said reaction product to incorporate phosphorus and sulfur therein.

9. The addition agent of claim 8, wherein the alkaline earth metal is barium, and the alkylated phenyl phosphite is para-tetramethylbutylphenyl phosphite. 5

10. An addition agent for mineral oil lubricants comprising an alkaline earth metal salt of a product prepared by reacting an essentially paraffinic base lubricating oil and an alkyl orthophosphate having at least 5 carbon atoms in an alkyl group 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 oil to incorporate phosphorus and sulfur therein. 15

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11. The addition agent of claim 10, wherein the alkaline earth metal is calcium, and the alkyl orthophosphate is tri-sec octyl phosphate.

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