

## UNITED STATES PATENT OFFICE

2,603,601

ADDITION AGENTS AND MINERAL OIL  
LUBRICANT COMPOSITIONS CON-  
TAINING THE SAMEHerschel G. Smith, Wallingford, and Troy L.  
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PennsylvaniaNo Drawing. Application July 6, 1948,  
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20 Claims. (Cl. 252—46.6)

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This invention relates to addition 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 detergency 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 crankcase 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.

In our copending application Serial No. 718,902, filed December 27, 1946, there is disclosed and

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claimed an addition 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 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.

In our copending application Serial No. 736,618, filed March 24, 1947, now U. S. Patent No. 2,456,336, there is disclosed and claimed an improvement agent for mineral oil lubricants which is prepared by heating an essentially paraffinic base lubricating oil with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst. It is shown in that application 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 application Serial No. 718,902 may be omitted. It is also shown in our latter filed application that when the prior aluminum chloride treatment of the paraffinic base lubricating oil is combined with reaction of the aluminum chloride treated product with phosphorus pentasulfide in the presence of a surface active silica-containing catalyst, lighter colored products are obtained.

The objects of the present invention are accomplished by providing improvement agents for mineral oil lubricants by reacting an essentially paraffinic base lubricating oil or the aluminum chloride treated product thereof with phosphorus pentasulfide, through the use of any of the methods disclosed in our copending applications Serial Nos. 718,902 and 736,618, now U. S. Patent No. 2,456,336, and with an alkylated phenyl phosphite prepared in accordance with U. S. Patent 2,253,227 to Cantrell and Turner. 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.

The present invention may be regarded as an improvement over the inventions disclosed in our above-identified copending applications. While the addition agents disclosed therein confer excellent antioxidant, corrosion-inhibiting and pressure-carrying properties on mineral oil lubricants, they sometimes fail to pass the well known Copper Strip Test (Method 530.31, Federal Speci-

fication VV-L-791c, May 12, 1945, page 259) thus indicating the presence of elementary sulfur or the so-called "corrosive" sulfur. While we do not wish to be bound by any theory as to the exact nature of the phosphorus pentasulfide reaction products with an essentially paraffinic base lubricating oil, it is our present belief that either elementary sulfur or incompletely bound sulfur or both are formed in the reaction. In accordance with the present invention, such elementary or incompletely bound sulfur is "neutralized" or "accepted" by combination with the alkylated phenyl phosphite added in the preparation of the phosphorus pentasulfide reaction product.

It is still necessary for the purposes of the present invention to employ an essentially paraffinic base lubricating oil as the initial material, because other hydrocarbon materials produce a black, sludge-like, difficultly soluble product regardless of whether the prior aluminum chloride treatment or reaction in the presence of a surface active silica-containing solid catalyst are employed. The reasons for the advantageous effects of the prior aluminum chloride treatment or of the surface active silica-containing solid catalyst on the reaction when an essentially paraffinic base lubricating oil is employed are not fully understood. However, the use of at least one of these methods is essential for the practice of our invention since, if the prior aluminum chloride treatment or the use of a surface active silica-containing 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 of the oil and alkylated phenyl phosphite with phosphorus pentasulfide only after aluminum chloride has been reacted with the oil and/or the reaction with phosphorus pentasulfide is conducted 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. 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, Serial No. 718,902. 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 the mixture is vigorously agitated. 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 four or five hours. After the treatment is completed, agitation is stopped and the 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. 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 essentially paraffinic base lubricating oil treated with aluminum chloride as disclosed hereinabove may then be reacted with the alkylated phenyl phosphite and phosphorus pentasulfide. This may be accomplished either by reacting with phosphorus pentasulfide per se, as disclosed in our pending application Serial No. 718,902, or in the presence of a surface active silica-containing solid catalyst as disclosed in our copending application, Serial No. 736,618, now U. S. Patent No. 2,456,336.

If it is desired to react the aluminum chloride treated oil and the alkylated phenyl phosphite with phosphorus pentasulfide per se, this reaction is accomplished by adding from 2 to 20 per cent by weight of  $P_2S_5$  on the mixture of oil and phosphite, preferably 5 to 10 per cent, 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 begins. Hydrogen sulfide is evolved and 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 the completion of the reaction.

If desired, the aluminum chloride treated paraffinic base lubricating oil and the alkylated phenyl phosphite may be reacted with phosphorus pentasulfide in the presence of a surface active silica-containing catalyst; or, the prior aluminum chloride treatment may be omitted and the essentially paraffinic base lubricating oil and alkylated phenyl phosphite may be reacted with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst. The reaction of the essentially paraffinic base lubricating oil and alkylated phenyl phosphite, whether or not pretreated with aluminum chloride, with phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst is accomplished by adding 2 to 20 per cent by weight of  $P_2S_5$ , preferably from 5 to 10 per cent, to the mixture of essentially paraffinic base lubricating oil and alkylated phenyl phosphite and heating with agitation at a temperature in the range from 300° F. to a maximum 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 varies between 490° to 530° F., depending upon the particular oil used. The surface-active silica-containing solid catalyst is employed in amounts of from 2 to 25 per cent by weight of the reaction mixture 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 the phosphorus and sulfur become incorporated in the reaction product. When the evolution of hydrogen sulfide has nearly ceased, the temperature of the reaction mixture may be

increased within the maximum temperature mentioned 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. Thus, activated clays, that is, natural clays such as bentonite, smectite, floridin, fuller's earth and the like which have been treated with acid, such as are 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, examples of which are described in U. S. Patent No. 2,078,945 and U. S. Patent No. 2,283,173, 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.

In accordance with the present invention, an alkylated phenyl phosphite is admixed with the essentially paraffinic base lubricating oil and the mixture reacted with phosphorus pentasulfide as disclosed hereinabove; or the alkylated phenyl phosphite may be added to the mixture of the phosphorus pentasulfide and the essentially paraffinic base lubricating oil during the reaction after the evolution of hydrogen sulfide has substantially ceased, but prior to completion of the reaction. The alkylated phenyl phosphite is ordinarily added in proportions ranging from 10 to 75 per cent by weight of its mixture with the paraffinic base lubricating oil, sufficient to remove free or "corrosive" sulfur in the phosphorus pentasulfide reaction product. Ordinarily not more than 50 per cent of the alkylated phenyl phosphite is sufficient for most purposes.

The alkylated phenyl phosphite used in our invention is prepared in accordance with U. S. Patent 2,253,227 from phosphorus trichloride and an alkylated phenol. As disclosed in said patent the alkylated phenols from which the alkylated phenyl phosphites are prepared are water-insoluble branched chain alkyl phenols having from 4 to 8 carbon atoms in an alkyl group. These alkylated phenols, in turn, are conveniently prepared by alkylating a simple phenol, such as phenol itself, the cresols or xylenols, with a suitable olefin in the presence of concentrated sulfuric acid as a catalyst in accordance with U. S. Patent 2,149,759 to Cantrell. Olefins such as butene-1, isobutylene, the amylenes (or mixtures of the preceding in refinery gas) and diisobutylene may be employed to produce the alkylated phenol. It is preferred to employ diisobutylene for the alkylation of the phenol since the resulting octyl (diisobutyl) phenol is primarily para-(alpha, alpha, gamma, gamma) tetramethylbutyl phenol. The phenols may be employed either singly or as a mixture. Representative alkyl phenols which may be employed to prepare the alkylated phenyl phosphite used in accordance with our invention include:

4-tertiary-butyl phenol  
2-tertiary-butyl, 4-sec-butyl phenol  
2,4-di-tertiary-butyl phenol  
2,6-di-tertiary-butyl phenol  
2,4,6-tri-tertiary-butyl phenol  
2,6-di-tertiary-butyl, 4-sec-butyl phenol  
2,6-di-tertiary-butyl, 4-methyl phenol  
4,6-di-tertiary-butyl, 2-methyl phenol

2-tertiary-butyl-4,6-dimethyl phenol  
2-tertiary-amyl-4,6-dimethyl phenol  
2,4,6-tri-tertiary-amyl phenol  
2-tertiary-butyl-4,6-di-tertiary-amyl phenol  
diisobutyl phenol

The alkylated phenols are reacted with such an amount of phosphorus trichloride, in accordance with U. S. Patent 2,253,227, that the resulting alkylated phenyl phosphite contains from 1 to 5 per cent by weight of combined phosphorus; i. e., when working with an alkylated phenol having from 4 to 8 carbon atoms in a branched chain alkyl group, the amount of phosphorus trichloride ranges from 5 to 30 per cent of the alkylated phenol. Such phosphites may therefore be defined as alkylated phenyl phosphites having from 4 to 8 carbon atoms in a branched chain alkyl group and containing from 1 to 5 per cent by weight of combined phosphorus.

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

#### Example I

Into a reaction vessel, there were placed 50 parts by weight of an essentially paraffinic base lubricating oil, which had been treated with aluminum chloride in accordance with our copending application Serial No. 718,902, and 50 parts by weight of an octyl (paratetramethylbutyl) phenyl phosphite. Then 12.5 parts by weight of phosphorus pentasulfide were added thereto. The mixture was agitated and heated to 490° F. in the course of one hour. After about 2 hours at this temperature, the evolution of hydrogen sulfide had substantially subsided. The temperature of the reaction mass was then raised to 520° F., and the mass agitated at this temperature for about 6 hours. The mixture was then cooled. The product had the following properties:

|                      |       |
|----------------------|-------|
| Gravity, °API        | 8.4   |
| Sulfur, per cent     | 4.6   |
| Phosphorus, per cent | 4.8   |
| Neutralization No.   | 10-12 |

#### Example II

Into a reaction vessel, there were placed 45 parts by weight of an essentially paraffinic base lubricating oil which had been treated with aluminum chloride in accordance with our copending application Serial No. 718,902, and 50 parts by weight of an octyl (paratetramethylbutyl) phenyl phosphite. Then 5 parts by weight of phosphorus pentasulfide were added thereto and the mixture agitated and heated to 490° F. in the course of one hour. The mixture was held at this temperature for 2 hours, and then the temperature was raised to 520° F. and held there for 6 hours. The product was then cooled and had the following properties:

|                        |       |
|------------------------|-------|
| Gravity, °API          | 15    |
| Viscosity, SUV 210° F. | 133.3 |
| Color, NPA             | 2.5   |
| Phosphorus, per cent   | 3.28  |
| Sulfur, per cent       | 3.0   |
| Neutralization No.     | 11.4  |

#### Example III

An additive was prepared in accordance with the procedure of Example I by reacting 37.5 parts by weight of an aluminum chloride treated essentially paraffinic base lubricating oil and 50 parts by weight of an octyl phenyl phosphite with 12.5 parts by weight of phosphorus pentasulfide.

The additive thus prepared had the following properties:

|                        |       |
|------------------------|-------|
| Gravity, °API          | 9.1   |
| Viscosity, SUV 210° F. | 413   |
| Color, NPA             | 5.0   |
| Sulfur, per cent       | 6.69  |
| Phosphorus, per cent   | 4.63  |
| Neutralization No.     | 38.27 |

#### Example IV

An additive was prepared in accordance with the procedure of Example I by reacting 81 parts by weight of an aluminum chloride treated essentially paraffinic base lubricating oil and 10 parts by weight of an octyl phenyl phosphite with 9 parts by weight of phosphorus pentasulfide. The additive thus prepared had the following properties:

|                        |      |
|------------------------|------|
| Gravity, °API          | 20.6 |
| Viscosity, SUV 210° F. | 89.0 |
| Color, NPA             | 5.5  |
| Sulfur, per cent       | 3.0  |
| Phosphorus, per cent   | 2.7  |
| Neutralization No.     | 13.0 |

#### Example V

An additive was prepared in accordance with the procedure of Example I by reacting 68.4 parts by weight of an aluminum chloride treated essentially paraffinic base lubricating oil and 25 parts by weight of an octyl phenyl phosphite with 8.6 parts by weight of phosphorus pentasulfide. The additive had the following properties:

|                        |       |
|------------------------|-------|
| Gravity, °API          | 17.3  |
| Viscosity, SUV 210° F. | 105.3 |
| Color, NPA             | 3.25  |
| Sulfur, per cent       | 3.0   |
| Phosphorus, per cent   | 3.1   |
| Neutralization No.     | 12.0  |

#### Example VI

Into a reaction vessel were placed 50 parts by weight of a solvent refined paraffinic base lubricating oil which had not been treated with aluminum chloride and 50 parts by weight of an octyl (paratetramethylbutyl) phenyl phosphite. Ten parts by weight of activated clay and 12.5 parts by weight of phosphorus pentasulfide were added and the mixture was heated and agitated at 400° F. The mixture was held at this temperature for 2 hours, and then the temperature was raised to 520° F. and held there for 6 hours. The mixture was then cooled. The product had the following properties:

|                  |     |
|------------------|-----|
| Gravity, °API    | 7.9 |
| Sulfur, per cent | 3.8 |

|                      |     |
|----------------------|-----|
| Phosphorus, per cent | 3.9 |
| Neutralization No.   | 6.0 |

#### Example VII

An additive was prepared in accordance with the procedure of Example I by reacting 37.5 parts by weight of an aluminum chloride treated paraffinic base lubricating oil, 50 parts by weight of an octyl phenyl phosphite and 12.5 parts by weight of phosphorus pentasulfide, in the presence of 10% activated clay. The additive thus prepared had the following properties:

|                        |      |
|------------------------|------|
| Gravity, °API          | 9.4  |
| Viscosity, SUV 210° F. | 421  |
| Color, NPA             | 1.0  |
| Sulfur, per cent       | 3.7  |
| Phosphorus, per cent   | 4.0  |
| Neutralization No.     | 37.0 |

The 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 antioxidant and corrosion-inhibiting properties on the mineral lubricating oils with which they are incorporated, and are characterized by a high degree of potency at high temperatures. For these purposes, our new improvement agents are generally added to mineral oils in minor amounts, say from 0.1 to 20 per cent by weight of mineral oil, sufficient to confer improved antioxidant and corrosion-inhibiting properties on the mineral lubricating oils with which they are incorporated. Lubricating oils containing our new improvement agents successfully pass the Copper Strip Test.

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

#### Example VIII

An improved motor oil was prepared by blending 1 per cent by weight of the additive of Example II with 99 per cent by weight of a solvent refined paraffinic motor oil (S. A. E. 30). A comparison of the properties of the improved lubricant and the base lubricant follows:

|                                      | Unimproved Lubricant | Improved Lubricant |
|--------------------------------------|----------------------|--------------------|
| Gravity, °API                        | 28.1                 | 28.1               |
| Viscosity, SUV: 100° F.              | 549                  | 561                |
| Viscosity Index                      | 104                  | 102                |
| Flash, °C: °F                        | 455                  | 470                |
| Color, NPA                           | 4.25                 | 4.25               |
| Copper Strip Test                    | passes               | passes             |
| Oxidation and Bearing Corrosion Test |                      |                    |
| Method 257, Gulf:                    |                      |                    |
| Duration of Test: Hrs.               | 48                   | 48                 |
| Oil Bath Temperature: °F             | 347                  | 347                |
| Quantity of Oil: cc                  | 300                  | 300                |
| Air Rate: cc/hr                      | 2,000                | 2,000              |
| Bearing Type                         | Cd-Ag Cu-Pb          | Cd-Ag Cu-Pb        |
| Wt. Change: Grams                    | -0.2040 -0.3150      | +0.0021 +0.0623    |
| Wt. Change: Per Cent                 | -0.93 -1.42          | +0.01 +0.31        |
| Appearance                           | pitted pitted        | bright coated      |
| Chevrolet 36 Hour, Engine Test CRC   |                      |                    |
| Designation L-4:                     |                      |                    |
| Engine Condition Rating              | 75                   | 94                 |
| Bearing Loss: Mg./Whole Bearing      | 541                  | 54                 |

*Example IX*

An improved motor oil was prepared by blend-

the improved motor lubricant and the base lubricant follows:

|                                                    | Unimproved Lubricant | Improved Lubricant |
|----------------------------------------------------|----------------------|--------------------|
| Gravity: °API.....                                 | 28.1                 | 28.3               |
| Viscosity, SUV: 100°F.....                         | 549                  | 558                |
| Viscosity Index.....                               | 104                  | 102                |
| Flash, OC: °F.....                                 | 455                  | 460                |
| Color, NPA.....                                    | 4.25                 | 4.5                |
| Copper Strip Test.....                             | passes               | passes             |
| Neutralization No.....                             |                      | 0.06               |
| Oxidation and Bearing Corrosion Test               |                      |                    |
| Method 257, Gulf:                                  |                      |                    |
| Duration of Test: hr.....                          | 48                   | 48                 |
| Oil Bath Temperature: °F.....                      | 347                  | 347                |
| Quantity of Oil: cc.....                           | 300                  | 300                |
| Air Rate: cc./hr.....                              | 2,000                | 2,000              |
| Bearing Type.....                                  | Cd-Ag Cu-Pb          | Cd-Ag Cu-Pb        |
| Wt. Change: Grams.....                             | -0.2040 -0.3150      | +0.0023 +0.0614    |
| Wt. Change: Per Cent.....                          | -0.93 -1.42          | +0.01 +0.032       |
| Appearance.....                                    | pitted pitted        | bright coated      |
| Chevrolet 36 Hr. Engine Test, CRC Designation L-4: |                      |                    |
| Engine Condition Rating.....                       | 75                   | 95                 |
| Bearing Loss: Mg./Whole Bearing.....               | 541                  | 26                 |

ing 1 per cent by weight of the additive of Example III with 99 per cent by weight of an S. A. E. 30 motor oil. A comparison of the properties of the improved lubricant and the base lubricant follows:

*Example XI*

25 An improved motor oil was prepared by blending 1 per cent by weight of the additive of Example V with 99 per cent by weight of an S. A. E. 30 motor oil. A comparison of the properties

|                                                   | Unimproved Lubricant | Improved Lubricant |
|---------------------------------------------------|----------------------|--------------------|
| Gravity °API.....                                 | 28.1                 | 28.3               |
| Viscosity, SUV: 100°F.....                        | 549                  | 558                |
| Viscosity Index.....                              | 104                  | 102                |
| Flash, OC: °F.....                                | 455                  | 460                |
| Color, NPA.....                                   | 4.25                 | 4.5                |
| Copper Strip Test.....                            | passes               | passes             |
| Neutralization No.....                            |                      | 0.06               |
| Oxidation and Bearing Corrosion Test              |                      |                    |
| Method 257, Gulf:                                 |                      |                    |
| Duration of Test: hr.....                         | 48                   | 48                 |
| Oil Bath Temperature: °F.....                     | 347                  | 347                |
| Quantity of Oil: cc.....                          | 300                  | 300                |
| Air Rate: cc./hr.....                             | 2,000                | 2,000              |
| Bearing Type.....                                 | Cd-Ag Cu-Pb          | Cd-Ag Cu-Pb        |
| Wt. Change: Grams.....                            | -0.2040 -0.3150      | +0.0019 +0.0599    |
| Wt. Change: Per Cent.....                         | -0.93 -1.42          | +0.01 +0.31        |
| Appearance.....                                   | pitted pitted        | bright coated      |
| Chevrolet 36 Hr. Engine Test CRC Designation L-4: |                      |                    |
| Engine Condition Rating.....                      | 75                   | 92                 |
| Bearing Loss: Mg./Whole Bearing.....              | 541                  | 74                 |

*Example X*

An improved motor oil was prepared by blend-

of the improved motor lubricant and the base lubricant follows:

|                                                    | Unimproved Lubricant | Improved Lubricant |
|----------------------------------------------------|----------------------|--------------------|
| Gravity: °API.....                                 | 28.1                 | 28.3               |
| Viscosity, SUV: 100°F.....                         | 549                  | 558                |
| Viscosity Index.....                               | 104                  | 102                |
| Flash, OC: °F.....                                 | 455                  | 465                |
| Color, NPA.....                                    | 4.25                 | 4.5                |
| Copper Strip Test.....                             | passes               | passes             |
| Neutralization No.....                             |                      | 0.06               |
| Oxidation and Bearing Corrosion Test               |                      |                    |
| Method 257, Gulf:                                  |                      |                    |
| Duration of Test: Hr.....                          | 48                   | 48                 |
| Oil Bath Temperature: °F.....                      | 347                  | 347                |
| Quantity of Oil: cc.....                           | 300                  | 300                |
| Air Rate: cc./hr.....                              | 2,000                | 2,000              |
| Bearing Type.....                                  | Cd-Ag Cu-Pb          | Cd-Ag Cu-Pb        |
| Wt. Change: Grams.....                             | -0.2040 -0.3151      | +0.0028 +0.0587    |
| Wt. Change: Per Cent.....                          | -0.93 -1.42          | +0.01 +0.29        |
| Appearance.....                                    | pitted pitted        | bright coated      |
| Chevrolet 36 Hr. Engine Test, CRC Designation L-4: |                      |                    |
| Engine Condition Rating.....                       | 75                   | 93                 |
| Bearing Loss: Mg./Whole Bearing.....               | 541                  | 67                 |

ing 1% by weight of the additive of Example IV with 99 per cent by weight of an S. A. E. 30 motor oil. A comparison of the properties of

*Example XII*

An improved motor oil was prepared by blending 1 per cent by weight of an additive, prepared

according to Example VI with 99 per cent by weight of a solvent refined paraffinic motor oil S. A. E. 30. The properties of the improved and unimproved motor oils were as follows:

|                                                        | Unimproved Motor Oil | Improved Motor Oil |
|--------------------------------------------------------|----------------------|--------------------|
| Gravity: °API.....                                     | 28.1                 | 27.9               |
| Viscosity, SUV: 100°F.....                             | 549                  | 556                |
| Viscosity Index.....                                   | 104                  | 100                |
| Flash, OC: °F.....                                     | 455                  | 465                |
| Color, NPA.....                                        | 4.25                 | 5.75               |
| Copper Strip Test, 212°F., 3 Hr.....                   | passes               | passes             |
| Oxidation and Bearing Corrosion Test Method 257, Gulf: |                      |                    |
| Duration of Test: Hr.....                              | 48                   | 48                 |
| Oil Bath Temperature: °F.....                          | 347                  | 247                |
| Quantity of Oil: cc.....                               | 300                  | 300                |
| Air Rate: cc./hr.....                                  | 2,000                | 2,000              |
| Bearing Type.....                                      | Cd-Ag Cu-Pb          | Cd-Ag Cu-Pb        |
| Wt. Change: Grams.....                                 | -0.2040 -0.3150      | -0.042 +0.752      |
| Wt. Change: Per Cent.....                              | -0.93 -0.42          | -0.02 +0.33        |
| Appearance.....                                        | pitted pitted        | bright coated      |

Example XIII

An improved motor oil was prepared by blending 1 per cent by weight of the additive, prepared according to Example VII, with 99 per cent by weight of a solvent refined paraffinic motor oil S. A. E. 30. Comparison of the improved and unimproved motor oils are as follows:

|                                                        | Unimproved Motor Oil | Improved Motor Oil |
|--------------------------------------------------------|----------------------|--------------------|
| Gravity: °API.....                                     | 28.1                 | 28.3               |
| Viscosity, SUV: 100°F.....                             | 549                  | 560                |
| Viscosity Index.....                                   | 104                  | 104                |
| Flash, OC: °F.....                                     | 455                  | 475                |
| Color, NPA.....                                        | 4.25                 | 4.25               |
| Copper Strip Test, 212°F., 3 Hr.....                   | passes               | passes             |
| Oxidation and Bearing Corrosion Test Method 257, Gulf: |                      |                    |
| Duration of Test: hr.....                              | 48                   | 48                 |
| Oil Bath Temperature: °F.....                          | 347                  | 347                |
| Quantity of Oil: cc.....                               | 300                  | 300                |
| Air Rate: cc./hr.....                                  | 2,000                | 2,000              |
| Bearing Type.....                                      | Cd-Ag Cu-Pb          | Cd-Ag Cu-Pb        |
| Wt. Change: Grams.....                                 | -0.2040 -0.3150      | +0.004 +0.0323     |
| Wt. Change: Per Cent.....                              | -0.93 -1.44          | +0.03 +0.15        |
| Appearance.....                                        | pitted pitted        | bright coated      |

Example XIV

In order to determine the comparative improvement in properties obtained by using the additive of the present invention, additives prepared in accordance with the disclosures of Serial No. 718,902, Serial No. 736,618, now U. S. Patent No. 2,456,336, and the present invention were subjected to the well known Copper Strip Test. In each instance 1 part by weight of the additive was compounded with 99 parts by weight of a highly refined motor oil. The uncompounded oil is included for purposes of comparison.

|                            | Uncompounded Lubricant | Lubricant of S. N. 718,902 | Lubricant of S. N. 736,618 | Lubricant of Present Invention |
|----------------------------|------------------------|----------------------------|----------------------------|--------------------------------|
| Gravity: °API.....         | 28.1                   | 27.8                       | 28.2                       | 28.3                           |
| Viscosity, SUV: 100°F..... | 549                    | 544                        | 551                        | 554                            |
| Color, NPA.....            | 4.25                   | 4.50                       | 4.50                       | 4.25                           |
| Copper Strip Test.....     | passes                 | tarnished                  | tarnished                  | 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 cc. of the oil or oil composition to be tested in a 400 cc. 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 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 determin-

ing 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.

The Chevrolet 36 Hour Engine Test referred to above is an accepted standard test designed to determine the oxidation, bearing corrosion, and detergency 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

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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. The detergency characteristics are expressed as "Engine Condition Rating" and indicate the freedom from engine deposits expressed in per cent, the larger the per cent (approaching 100 as a limit) the cleaner the engine. The amount of bearing corrosion is indicated as "Bearing Loss" and is expressed in milligrams loss in weight of the standard bearing.

As shown in the above examples, the addition of our new improvement agents to mineral oil lubricant compositions confers excellent detergency, 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. The lubricants obtained pass the Copper Strip Test.

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, pour point depressants, anti-foam agents and the like may be added without departing from the spirit of the invention.

What we claim is:

1. The process of preparing an improvement agent for mineral oil lubricants which comprises 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 said product and from 10 to 75 per cent by weight of its mixture with said product of an alkylated phenyl phosphite with phosphorus pentasulfide at an elevated temperature not below 300° F. and not in excess of the minimum cracking temperature of said product to incorporate phosphorus and sulfur therein.

2. The process of preparing an improvement agent for mineral oil lubricants which comprises 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 said product and from 10 to 75 per cent by weight of its mixture with said product of an alkylated phenyl phosphite with phosphorus pentasulfide at a temperature of from 450° F. to a maximum temperature below the minimum cracking temperature of said product to incorporate phosphorus and sulfur therein.

3. 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 on said oil of anhydrous aluminum chloride at a temperature of from 150° to 300° F., removing aluminum chloride from the reaction product, and reacting said product and an alkylated phenyl phosphite in an amount of from 10 to 75 per cent by weight of its mixture with said product with from 2 to 20 per cent by weight of said mixture or phosphorus pentasulfide at a temperature of from 450° F. to a maximum temperature below the minimum cracking of said

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product to incorporate phosphorus and sulfur therein.

4. The process of claim 3, wherein the product is dissolved in a mineral lubricating oil.

5. The process of claim 3, wherein the alkylated phenyl phosphite contains from 4 to 8 carbon atoms in a branched chain alkyl group, and contains from 1 to 5 per cent by weight of combined phosphorus.

6. The process of claim 5, wherein the alkylated phenyl phosphite is para-tetramethylbutyl phenyl phosphite.

7. 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 and an alkylated phenyl phosphite having from 4 to 8 carbon atoms in a branched chain alkyl group in an amount of from 10 to 75 per cent by weight of its mixture with said oil 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.

8. The process of preparing an improvement agent for mineral oil lubricants which comprises heating an essentially paraffinic base lubricating oil and an alkylated phenyl phosphite in an amount of from 10 to 50 per cent by weight of its mixture with said oil with from 2 to 20 per cent by weight of said mixture of phosphorus pentasulfide in the presence of from 2 to 25 per cent by weight of the reaction mixture 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 therein.

9. The process of claim 8, wherein the alkylated phenyl phosphite contains from 4 to 8 carbon atoms in a branched chain alkyl group and contains from 1 to 5 per cent of combined phosphorus.

10. The process of claim 9, wherein the alkylated phenyl phosphite is para-tetramethylbutyl phenyl phosphite.

11. 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 said oil 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 on the mixture of said product and the alkylated phenyl phosphite hereinafter described of phosphorus pentasulfide in the presence of a surface active silica-containing solid catalyst and an alkylated phenyl phosphite having from 4 to 8 carbon atoms in a branched chain alkyl group in an amount of from 10 to 75 per cent by weight of its mixture with said product 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.

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

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

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

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

16. The product obtained by the process of claim 11.

17. A lubricant composition 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 1.

18. A lubricant composition 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 3.

19. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer improved antioxidant and corrosion inhibiting properties

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on the composition, of the product obtained by the process of claim 7.

20. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to confer improved antioxidant and corrosion inhibiting properties, of the product obtained by the process of claim 11.

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**REFERENCES CITED**

The following references are of record in the file of this patent:

**UNITED STATES PATENTS**

| Number    | Name                 | Date           |
|-----------|----------------------|----------------|
| 2,253,227 | Cantrell et al. .... | Aug. 19, 1941  |
| 2,449,934 | Giammaria .....      | Sept. 21, 1948 |
| 2,456,336 | Smith et al. ....    | Dec. 14, 1948  |