The present invention relates to a new composition of matter which improves the properties of mineral oil lubricants when added thereto in small amounts.

The new additive of the present invention is a monocyclic terpene which has been modified by combining therewith both sulfur and phosphorus. The product has the property of inhibiting oxidation in mineral oils and in imparting to such oils improved load bearing characteristics.

The modification of terpenes by the process of sulfurization is known in the prior art. Thus, in the Kobbe U. S. Patent Number 1,845,495, there is described a cutting oil composition comprising a mineral oil to which is added a sulfurized terpene such as sulfurized pine oil, turpentine, pinene, and the like. Terpinol, which contains a hydroxyl group, is also mentioned. According to this patent, the terpene is cooked with sulfur at rather high temperatures, e. g., about 200° to 210° C., for a period of half an hour or more.

While sulfurized terpenes such as those described above have utility in cutting oils, they appear to be too corrosive for use in lubricants such as gear oils and the like, where they must remain in contact with the metal parts to be lubricated over long periods of time, and they are too corrosive for use in internal combustion engine lubrication. Apparently, the drastic sulfurization of such materials incorporates a large amount of sulfur which is beneficial in imparting load bearing properties to lubricating oil but is objectionably corrosive to metals. At any rate, the sulfurized terpenes such as those described by Kobbe have been found to be strongly corrosive to metals, especially those containing copper.

It has been suggested in several prior art patents, e. g., the Angel et al. U. S. Patent Number 2,381,377, the Berger et al. U. S. Patent Number 2,416,281, and the Fuller et al. U. S. Patent Number 2,455,658, that cyclic terpenes, distinguished from the acyclic and monocyclic terpenes, may be treated with phosphorus sulfides to obtain useful oil additives such as oxidation inhibitors and the like. These prior art patents emphasize the exclusion of monocyclic terpenes such as dipentene and its monocyclic isomers, e. g., terpinolene, probably for the reason that the phosphorus sulfide reaction products of the monocyclic terpenes contain large amounts of carbonized material and other oil insoluble degradation products. Apparently, the monocyclic terpenes react so violently with the phosphorus sulfides that some cracking, carbonization, or other molecular degradation ensues. In any event, the prior art appears to have considered it impracticable to react the phosphorus sulfide (P₂S₅, P₄S₇, etc.) with monocyclic terpenes to obtain useful additives for lubricating oils.

It is an object of the present invention to prepare a new composition which, when it is employed for use in the manner set forth, will not have the inhibiting of metal corrosion and of oil oxidation. In larger quantities, the new composition may be added to mineral base lubricants to improve their load bearing properties. By "mineral base lubricants" is meant the usual crankcase oils, gear oils, greases, etc., which contain major proportions of mineral lubricating oil fractions as the basic lubricant.

According to the present invention, it has now been found that highly useful addition agents may be obtained from the monocyclic terpenes, especially those of the empirical composition C₉H₈, illustrated by dipentene and its monocyclic isomers, e. g., terpinolene, which has the closely related structural formula:

\[
\begin{align*}
\text{CH} \rightarrow \text{CH} & \quad \text{CH} \rightarrow \text{CH} \\
\text{CH} & \quad \text{CH}
\end{align*}
\]

and its monocyclic isomers, e. g., terpinolene, which has the closely related structural formula:

\[
\begin{align*}
\text{CH} \rightarrow \text{C} & \quad \text{CH} \rightarrow \text{C} \\
\text{CH} \rightarrow \text{CH} & \quad \text{CH} \rightarrow \text{CH}
\end{align*}
\]

and other closely related materials, e. g., limonene, etc., by reacting the same simultaneously with elemental sulfur and with a sulfide of phosphorus.

It has been found that one molecular proportion of the monocyclic terpene will absorb about 2 atomic proportions of elemental sulfur in this reaction, and this proportion of sulfur is accordingly a preferred maximum proportion to use in the reaction. Somewhat lesser proportions of sulfur, i. e., down to 1.5 atomic proportions to one molecular proportion of terpene, can be used in order to ensure more or less complete reaction of the sulfur, but the final product will contain less sulfur and be somewhat less potent. If greater proportions of sulfur are used, the
2,654,711

product may contain unreacted sulfur in solution which has the disadvantages that it is corrosive and tends to crystalize out of solution on standing. On the other hand, the use of a small excess of sulfur will not be harmful, since a small amount of sulfur is lost in the form of hydrogen sulfide during the reaction.

A much smaller amount of the sulfide of phosphorus, preferably of the order of about 0.01 to about 0.25 molecular proportions for each molecular proportion of terpene, has been found to be sufficient for the purpose of imparting the desirable antioxidant properties and for removing the copper-staining tendency of the product which results from the reaction of the terpene with sulfur alone. Accordingly, the monocyclic terpene is simultaneously reacted with the above stated proportions of sulfur and sulfide of phosphorus.

The reaction is preferably conducted in the presence of a liquid medium, and since the additive is preferably to be employed in a mineral lubricating oil base, such an oil serves conveniently as the medium of the reaction. The temperature at which the reaction is carried out should be at least about 120°C, the melting point of sulfur, and generally should be of the order of 140° to 200°C, more preferably from 150° to 170°C. The reaction is continued at least until the tendency of the reaction mixture to stain copper, as measured by a modified C. R. C. Copper Strip Test (see Example 3), has been substantially reduced. Normally, it is preferred to conduct the reaction to substantial completion which requires a period of one-half to 20 hours, depending on the temperature of the reaction and more usually for a period of 2 to 10 hours. No catalyst is required.

Where large amounts of the sulfide of phosphorus are used, it is generally desirable to employ a plasticizer for the reaction, such as an aliphatic alcohol containing at least eight carbon atoms per molecule. However, when the amount of the sulfide of phosphorus is low, i.e., of the order of 0.02 mol or less per mol of terpene, no plasticizer is necessary.

The sulfur may be employed in the form of ordinary flowers of sulfur. The phosphorus sulfide may be any phosphorus sulfide, phosphorus trisulfide (P4S3) being somewhat preferable because of its high phosphorus content. It is ordinarily convenient to mix the sulfur and sulfide of phosphorus and heat the same to the reaction temperature, after which the dipentene or other monocyclic terpene is gradually added, preferably in admixture with a diluent such as a lubricating oil fraction. Heating is then continued until the reaction is complete, and the product is then preferably blown with nitrogen or other inert gas to remove any hydrogen sulfide present.

In place of a sulfide of phosphorus, there may be employed an organo-substituted thio phosphoric acid, prepared by reacting a sulfide of phosphorus with an alcohol or phenol. Typical of such compounds are di-n-butyl dithiophosphoric acid, di-(ethylhexyl) dithiophosphoric acid, di-(tert-octylphenyl) dithiophosphoric acid, and the like.

The exact chemical structure of the product obtained by the reaction of the terpene with sulfur and sulfide of phosphorus is not known. Presumably, the fundamental character of the monocyclic terpene molecule is not greatly altered, the sulfur and phosphorus serving to saturate or largely saturate the double bonds and perhaps uniting two or more terpene molecules together. The considerable increase in viscosity resulting from the reaction suggests that there is a combining of molecules, probably through sulfur linkages. In any event, the product, when prepared as a mineral oil concentrate, is a viscous oil of reddish cast, clear and free from suspended particles.

It will be understood from the foregoing that the essence of the present invention is the production and use of terpene derivatives made by reacting a monocyclic terpene simultaneously with sulfur and a phosphorus sulfide, such derivatives being useful either alone or in combination with other additives as addition agents for mineral lubricating oils and greases. The invention is preferably and specifically applicable to dipentene and its isomers, e.g., terpinolene, but it also has application to the substituted terpenes, such as terpinol, diterpinyl ethylene ether, and similar compounds. The alcohol and aldehyde derivatives of dipentene and terpinolene are useful for some purposes, but their resistance to oxidation and their tendency to inhibit corrosion are not as satisfactory as the products derived from the hydrocarbons.

As mentioned above, the sulfurized and phosphorus sulfide treated terpenes may also be used as extreme pressure additives. For this purpose they may be used alone or they may be used in combination with other extreme pressure additives, especially in combination with the sulfurized and/or chlorinated long chain hydrocarbons, fatty materials, and aliphatic esters such as chlorinated wax, sulfurized and phosphorus sulfide treated fatty acids and fatty oils of 12 to 22 carbon atoms, sulfurized and/or phosphorus sulfide treated abietic acid and its lower alcohols and esters, and the like. The latter materials are well known extreme pressure additives of the prior art.

In general, the proportions of the additives of the present invention which are useful for preventing oxidation and corrosion are of the order of about 0.03 to 2.0%, proportions of 0.1 to 0.4% being especially preferred. For the purpose of increasing the load bearing properties of a lubricant, it is desirable to employ proportions of the order of 1% to 15% when the treated terpenes are used alone. They may be used in smaller proportions for this purpose when combined with other conventional extreme pressure additives such as those previously mentioned. For convenience in handling and storage, it is advantageous to prepare concentrates of the additives in mineral oil solution, in which the solution contains amounts of the order of 40% to 50% by weight of the additive. These concentrated solutions may be produced by using a lubricating oil as the diluent in the process of preparation of the additives, in an amount sufficient to produce these concentrations. It is only necessary to dilute these concentrated solutions with a base oil to produce a lubricant containing the desired amount of additive. Hence, the proportions used in the mineral base lubricant may vary from as little as 0.05% to as much as 50% of the weight of the total composition, depending upon the purpose.

The invention will be more fully understood by reference to the following examples, in which are described in detail the preparation and testing of additives of the type described above, but it is to be understood that these examples are given by way of illustration only and are not intended to restrict the scope of the invention in any way.
6 EXAMPLE 2

A mixture of 96 grams (3 mols) of sulfur and 6.95 grams (0.632 mol) of FeS was heated to about 150°C, after which a mixture of 262 grams (1.85 mol) of "Special Dipentene" and 300 grams of the lubricating oil diffusely employed in Example 1 was slowly added. The mixture was then heated for 3 hours at 150-170°C, and then the product obtained was an oil concentrate containing about 50% active ingredient, the final analysis: sulfur 12.72%, phosphorus 2.56%.

EXAMPLE 3

Each of the products of Examples 1 and 2 (each containing about 50% of active ingredients) was blended in 1% (by weight) concentration in a lubricating oil base consisting of a well refined, solvent extracted paraflinic type mineral lubricating oil of SAE 20 viscosity grade and the solutions thus formed were submitted to a copper strip corrosive test, which was a modification of C.R.C. Method L-16-445. This method comprises essentially immersing a polished metallic copper strip in the oil blend for 3 hours at 212°F, and noting the extent of staining. Numerical ratings from 1 to 10 denote discolorations from no staining to a black surface film, respectively. For comparison, similar tests were made on a sample of the unblended lubricating oil base and a blend of this base oil with 0.5% of a product obtained by heating the "Special Dipentene" with sulfur, whereby a product containing about 30% by weight of sulfur was obtained. The results were as follows:

<table>
<thead>
<tr>
<th>Oil Blend</th>
<th>Copper Strip Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil base (no additive)</td>
<td>9</td>
</tr>
<tr>
<td>Blend containing product of Ex. 1</td>
<td>6</td>
</tr>
<tr>
<td>Blend containing product of Ex. 2</td>
<td>5</td>
</tr>
<tr>
<td>Blend containing sulfurized dipentene (no FeS added)</td>
<td>40</td>
</tr>
</tbody>
</table>

6 EXAMPLE 4

Blends containing 1/2% (by weight) each of the products of Examples 1 and 2 in the same base oil as that employed in Example 3 were prepared and submitted to a corrosion test designed to test the effectiveness of the additive in inhibiting corrosion of a typical copper-lead bearing.

In this test 500 cc. of the oil was placed in a glass oxidation tube (13 inches long and 2 inches in diameter) fitted at the bottom with a 1/4 inch air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 225°F during the test. Two one-quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated at 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each 4-hour period the bearings were removed, washed with naptha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional 4-hour periods in like manner. The results are given in the following table as "corrosion life," which indicates the number of hours required for the bearing to lose 100 mg. in weight, determined by interpolation of the data obtained in the various periods.

<table>
<thead>
<tr>
<th>Oil Base</th>
<th>Bearing Corrosion Life (Hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td>10</td>
</tr>
<tr>
<td>Base oil + 1.5% product of Ex. 1</td>
<td>35</td>
</tr>
<tr>
<td>Base oil + 1.5% product of Ex. 2</td>
<td>34</td>
</tr>
</tbody>
</table>

EXAMPLE 5

In order to test the load bearing or extreme pressure effects of the additives of the present invention, and to compare the effectiveness of these additives with other extreme pressure agents of known value, tests were made with the Timken machine and the S. A. E. machine, using a base oil consisting of a mixture of 45% of a heavy mineral oil (220 S. S. U. at 210°F) and 55% of a lighter oil (50 S. S. U. at 210°F), alone and in admixture with various extreme pressure agents. The results are shown in the following table, in which the loads or scale readings indicate the maximum readings obtained before failure of the lubricant. All percentages are by weight.

<table>
<thead>
<tr>
<th>Lubricant Composition</th>
<th>Timken Machine (Lbs.)</th>
<th>S. A. E. Machine (Scale Reading)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil only</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>90% Base oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Unchlorinated wax (40% CI)</td>
<td>41</td>
<td>282</td>
</tr>
<tr>
<td>90% Base oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Chlorinated wax (40% CI)</td>
<td>43</td>
<td>265</td>
</tr>
<tr>
<td>90% Base oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5% Balanced Sulfur (20% S, 15% P)</td>
<td>45</td>
<td>353</td>
</tr>
<tr>
<td>90% Base oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5% Chlorinated wax (40% CI)</td>
<td>45</td>
<td>353</td>
</tr>
</tbody>
</table>

It will be seen from the above data that a base
oil containing 10% of chlorinated wax is markedly superior to the base oil alone in both types of tests, that when a portion of the chlorinated wax is substituted by a product of the present invention, the load bearing characteristic of the lubricating oils is distinctly better as measured by the S. A. E. test, although slightly inferior on the Timken scale, and that when the product of the present invention is substituted for sulfurized degras, a well known extreme pressure agent, the result is a measurable improvement as measured on the S. A. E. scale. Although slightly inferior, the Timken rating is quite satisfactory for most purposes.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenoates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphates and thiophosphates, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, re- action products of metal phenates and sulfur, re- action products of metal phenates and phosphorus sulfides, metal phenol sulfonates, and the like. Thus the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert. octyl- phenol sulfide, calcium tert.-amylnaphthalensulfide, caesium octylate, nickel octanoate, barium octadecyl- calcium phenyl stearate, zinc dispropoxy- salicylate, aluminum naphthenate, calcium octyl- phosphate, barium di-tert.-amylphenol sulfide, calcium petroleum sulfonate, zinc methylcyclo- hexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives, such as phenols and phenol sulfides, may be employed.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crude, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodi-ethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or volatized products may be employed in admixture with mineral oils.

For the best results the base stock chosen should normally be an oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however, they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds (Saybolt) viscosity at 210° F. For the lubrication of certain low and medium speed diesel engines, the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used such as dyes, pour point depressants, heat thickened fatty oils, sulfonated fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, volatilized fats, volatilized mineral oils, and/or volatilized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8 to 20 carbon atoms, e.g., octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

What is claimed is:

1. A minerallubricating oil composition containing 0.5 to 50% by weight of a product obtained by simultaneously reacting one molecular proportion of a monocyclic terpene with about 1.5 to about 2 atomic proportions of sulfur and with about 0.01 to about 0.25 molecular proportions of a sulfide of phosphorus at a temperature of at least 120° C. and up to a temperature of about 200° C.

2. A composition according to claim 1 in which the sulfide of phosphorus is PO₄S₂.

3. A composition according to claim 2 in which the reaction is conducted at a temperature of 140° to 200° C.

4. A mineral lubricating oil composition containing about 40% to about 50% by weight of a product obtained by simultaneously reacting one molecular proportion of a monocyclic terpene with about 2 atomic proportions of sulfur and with about 0.01 to about 0.25 molecular proportions of a sulfide of phosphorus at a temperature of at least 120° C. and up to a temperature of about 200° C.

5. A mineral lubricating oil composition containing about 40% to about 50% by weight of a product obtained by simultaneously reacting one molecular proportion of a monocyclic terpene with about 2 atomic proportions of sulfur and about 0.01 to about 0.25 molecular proportions of PO₄S₂ at a temperature of 140° to 200° C.

6. As a new composition of matter the product obtained by simultaneously reacting one molecular proportion of a monocyclic terpene with about 2 atomic proportions of sulfur and about 0.01 to about 0.25 molecular proportions of a
sulfide of phosphorus at a temperature of at least 120° C. and up to a temperature of about 200° C. 7. A composition according to claim 6 in which the sulfide of phosphorus is P₄S₃.

8. The process which comprises simultaneously reacting one molecular proportion of a monocyclic terpene with about 2 atomic proportions of sulfur and about 0.01 to about 0.25 molecular proportions of a sulfide of phosphorus at a temperature of at least 150° C. and up to a temperature of about 200° C.

9. A process according to claim 8 in which the sulfide of phosphorus is P₄S₃.

10. A process which comprises heating a mixture of about one molecular proportion of a monocyclic terpene consisting essentially of a mixture of dipentene and terpinolene, about 2 atomic proportions of sulfur and about 0.02 molecular proportions of P₄S₃ in the presence of a mineral lubricating oil diluent at a temperature of about 150–170° C. for a period of about 3 hours.

ABRAHAM D. KIRSHENBAUM.
HARRY W. RUDEL.

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<table>
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<th>Name</th>
<th>Date</th>
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