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UNITED STATES PATENT OFFICE

2,654,712

SULFURIZED MONOCYCLIC TERPENES AND OIL COMPOSITIONS CONTAINING THEM

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17 Claims. (Cl. 252—46.6)

1

The present invention relates to sulfurized monocyclic terpenes and oil compositions containing them. It relates more particularly to sulfurized and/or phospho-sulfurized monocyclic terpenes which are so treated as to become valuable additives for lubricating oil, the treatment being such as to avoid substantially the production of oil insoluble products and also to avoid the production of copper corrosive products. The invention relates both to an improved process for the sulfur and/or phosphorus sulfide treatment of terpene hydrocarbons and also to an improved product of such process, as well as relating to an improved oil composition containing such product as a modifying agent.

In the prior art, numerous patents have been issued relating to the sulfurization of terpenes. Thus, in the patent to Kobbe, No. 1,844,400, there is disclosed a cutting oil composition comprising mineral oil to which is added a sulfurized terpene such as pine oil, terpentine, pinene, and the like. Terpineol, which contains a hydroxyl group, also is mentioned. According to this reference, the terpene is cooked with sulfur at rather high temperatures, e. g., around 200° to 210° C. (around 400° F.), for a period of half an hour or so.

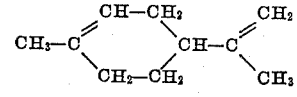
While sulfurized terpenes such as described above have utility in cutting oils, they appear to be too corrosive for use even in lubricants such as gear oils, and the like, where they must remain in contact with the parts to be lubricated, especially parts which contain copper, such as brass or bronze, over long periods of time. They are much too corrosive also for use in internal combustion engine lubrication. Apparently, the sulfurization of such materials incorporates a large amount of sulfur which is beneficial in imparting load bearing properties to lubricating oil, but loosely combined sulfur is objectionably corrosive to metals where the lubricants are used over extended time periods. It is believed that in the case of drastically sulfurized terpenes, and the like, the sulfur is rather loosely attached to the hydrocarbon, part of it being attached to other sulfur atoms which have become incorporated into the hydrocarbon structure, so that it is over-active and hence corrosive to metals. To some extent, the corrosive property may be due simply to the presence of dissolved sulfur. At any rate, the drastically sulfurized terpenes of the general type described by Kobbe, have been found to be too strongly corrosive to metals, especially those containing copper, to be of utility for gear lubricants.

2

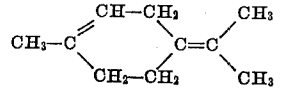
It has also been suggested in several prior art patents, e. g., Angel et al., No. 2,381,377, Berger et al., No. 2,416,281, and Fuller et al., No. 2,455,668, that dicyclic terpenes, as distinguished from the acyclic and monocyclic terpenes, may be treated with phosphorus sulfides to obtain useful oil additives such as oxidation inhibitors, and the like. These prior art references emphasize the exclusion of monocyclic terpenes such as dipentene and its monocyclic isomers, e. g., terpinolene, probably for the reason that in such prior art 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 takes place. In any event, the prior art appears to have considered it impracticable to react the phosphorus sulfides P_4S_3 and P_2S_5, etc., with monocyclic terpenes to obtain useful oxidation inhibiting additives for lubricating oils.

It is an object of the present invention to prepare a new composition which has highly useful properties such as the inhibiting of metal corrosion, and of oil oxidation. In larger quantities, the new composition may be added either to mineral base lubricants or to syntheic lubricants such as branched chain esters, and the like, 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 base lubricating oils. The present invention has primary application to the mineral base products although not limited thereto.

According to the present invention, it has now been found that highly useful oil addition agents may be obtained by first sulfur-treating and thereafter treating with a phosphorus sulfide the monocyclic terpenes $C_{10}H_{16}$, especially dipentene



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



and other closely related materials, e. g., limo-

nene, etc., having the same general reactivity with elemental sulfur and with the phosphorus sulfides. These products are obtained by first reacting the monocyclic terpene with elemental sulfur at a moderate temperature above the melting point of sulfur, e. g., within the approximate range of about 250° to 400° F., preferably about 300° to 350° F., until the reaction is complete or substantially complete. This product, like the product of Kobbe, mentioned above, appears to lack some of the characteristics desired, such as substantial freedom from corrosivity towards copper. It is, therefore, further reacted, after the substantially complete mild sulfurization, with a phosphorus sulfide which will reduce its corrosive tendencies. This treatment appears to incorporate some phosphorus into the final product and either to remove the more reactive sulfur or to "fix" the sulfur which remains in the molecule to some extent so as to reduce the activity of the treated terpene product toward metals, such as copper, especially at normal lubricating temperatures. This treatment with phorphorus sulfide is carried out at a temperature within the range of about 170° to 350° F., preferably 200° to 330° F., for a period of time sufficient to bring the reaction to substantial completion. A temperature of about 200° to 250° F. is especially preferred. High temperatures tend to promote fuming of the phosphorus. Ordinarily, the time required for the sulfurization step is about one-half to four hours, or more, and the time required for the phosphorus sulfide treatment is about 1 to 20 hours, preferably about 2 to 5 hours, depending largely upon the reaction temperatures, the amount of sulfur to be added, the activity toward copper that can be tolerated, etc.

For the sulfurization step, it is preferred to use ordinary flowers of sulfur in proportions of about 20 to 35 parts by weight, especially about 25 to 30 parts, of sulfur for each 100 parts of the reaction mixture, or about 25 to 54%, based on the weight of terpene. The sulfur preferably is first melted and the terpene is added gradually thereto, followed by further heating to about 300° to 375° F. However the ingredients may be combined without prior heating and thereafter heated together to a temperature above the melting point of the sulfur. In this case, care should be taken to avoid boiling over. In some cases the sulfur may be added to terpene preliminarily heated to 200°–350° F. but the reverse procedure gives good results. For the phosphorus sulfide treatment, any of the phosphorus sulfides may be used but P_4S_3 which tends to combine with the maximum sulfur from the terpene is preferred. This compound incorporates more phosphorus and reduces corrosivity to copper better than P_2S_5 which is less satisfactory for this reason. The proportions of phosphorus sulfide used should be within the range of about 0.2 to about 10.0%, based on the weight of the sulfurized terpene being treated. Smaller quantities of phosphorus sulfide are used, e. g., 0.2 to about 2% by weight of the sulfurized terpenes, where good load bearing properties are desired. Larger quantities of phosphorus sulfide, preferably at least 1% and up to 10% are preferred where the treated terpene is intended for use as an antioxidant since the larger quantities tend to incorporate more phosphorus into the product and to reduce corrosivity toward metals. They tend, however, to reduce the active sulfur content of the terpene and hence reduce its load bearing potency. Smaller amounts than about 0.2% are not sufficient to overcome the corrosive deficiencies of the sulfurized product and quantities less than 1% are useful chiefly when extreme pressure properties are required.

The exact chemical structure of the sulfurized and phosphorus sulfide treated terpene product is not known. Presumably, the fundamental character of the monocyclic terpene molecule is not greatly altered in the present process, the sulfur and phosphorus saturating or largely saturating the double bonds and perhaps uniting two or more terpene molecules together. By contrast, prior art processes altered the structure considerably, probably due in part to high sulfurizing temperatures. Paracymene may be formed if temperature is too high.

The increase in viscosity resulting from the phosphorus sulfide treatment of the present invention suggests that there may be some combining of molecules, probably through sulfur linkages. In any event, the final treated terpene product is a viscous oil of reddish-brown cast, clear and free from apparent suspended particles.

It will be understood from the foregoing, that the essence of the present invention is the use and production of terpene derivatives made by reacting monocyclic $C_{10}H_{16}$ terpenes, first with sulfur and thereafter with phosphorus sulfides, to prepare additives which may be used either alone or in combination with other additives in lubricating oils and greases. The invention is preferably and specifically applicable to dipentene and its isomers such as terpinolene, but it also has application to the substituted monocyclic terpenes such as terpineol, diterpinyl ethylene ether, and similar compounds.

The sulfurized and phosphorus sulfide treated monocyclic terpenes may be used in combination with conventional extreme pressure additives, especially 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 alkyl esters, such as "Abalyn," hydrogenated derivatives such as "Hercolyn," and the like. The latter materials are well known extreme pressure additives of the prior art.

The invention will be more fully understood by reference to the following specific examples.

Example I

A sulfurized dipentene containing about 32% by weight of sulfur and obtained commercially was treated with P_4S_3 for 12 hours at a temperature of 215° F. Three different samples were made using, respectively, 0.5% P_4S_3, 0.75% P_4S_3, and 1.0% P_4S_3. The two latter products were found to be corrosive to copper, turning a copper strip black in one hour at 250° F. when used as 5% blends in a standard extreme pressure base lubricant consisting of a mixture of 45% heavy mineral oil (220 S. S. U. at 210° F.) and 55% of a lighter oil (50 S. S. U. at 210° F.). However, the product prepared by heating 0.5% P_4S_3 with the sulfurized dipentene did not blacken copper, and a blend of not more than 2% of this product in oil was found to be very satisfactory.

An extreme pressure lubricant was prepared from the following ingredients:

90% base lubricating oil of light and heavy fractions as described above.

1% of the 0.5% P_4S_3 treated sulfurized dipentene.
6% of a prior art E. P. additive (composed of 60% P_4S_3 treated sulfurized "Abalyn" and 40% P_4S_3 treated sulfurized sperm oil).
3% caustic washed sodium polysulfide treated chlorinated wax.

The 0.5% P_4S_3 treated sulfurized dipentene is referred to in the table below as "A." The conventional extreme pressure additive, sulfurized "Abalyn" etc., is referred to as "B" and the conventional sodium polysulfide chlorinated hydrocarbon is referred to as "C." As indicated in Table I, the combination of "A," "B" and "C" in the proportions indicated, gave very good results on both the Timken machine and the S. A. E. machine. It has been found difficult in the past to prepare lubricating compositions which give good readings on both machines, and the product of this invention, when used in proportions of 1%, shows superiority.

TABLE I

EXTREME PRESSURE LUBRICANT TESTS

Composition	Timken Machine			SAE Machine Scale, Lbs.
	Loads, Lbs.	Scar in 1/64"	Lbs./Sq. In.	
1% "A" 6% 3% "C"	33	1.65	25,600	185
7% "B" 3% "C"	33	1.65	25,600	170
10% "B"	33	1.2	35,200	100
10% "C"	33	Gouged		325
Base Oil Only	10	1.35	9,500	<20

As indicated above, when it is desired to impart oxidation inhibiting and corrosion preventing properties to oils used in the crankcases of internal combustion engines, the additives of the present invention have outstanding properties in very small proportions. In general, the proportions used for preventing oxidation and corrosion are about 0.01 to 5.0%, proportions of 0.2 to about 1.0% being specifically preferred.

Several examples of the preparation of phosphorus sulfide treated sulfurized terpenes suitable for use as oxidation and corrosion inhibitors for motor oils are shown below. For convenience, commercial terpenes, predominantly dipentene, may be used. Sulfurized products are also available commercially, including a sulfurized mixture which predominates in dipentene.

Example II

2520 grams of a commercial grade of dipentene were slowly added to 948 grams of molten sulfur and heated at 329°–347° F. for 3 hours with agitation and reflux condensing throughout. The product at this point had an acid number of 14.03 mg. KOH per gram.

500 grams of the above sulfurized dipentene were blended with 442 grams of mineral oil (acid treated naphthenic distillate of 55 S. S. U. viscosity at 210° F.) and 38 grams of P_4S_3 and heated at 257°–302° F. for 2½ hours. 51 grams of C_3 oxo alcohol were then added and heating continued for ½ hour more. The product was then blown with nitrogen at 257°–302° F. for 1½ hours, cooled and filtered. Yield of product=83%.

The product had the following characteristics:

	Percent
Sulfur	14.55
Phosphorus	2.06

Example III

208 grams of sulfurized dipentene prepared as in Example II and 184 grams of mineral oil (same as in Example II) were added to 15.8 grams of P_4S_3 and heated for 3 hours at 257°–302° F. with stirring and reflux condenser. 26 grams of "Lorol B" alcohol were then added and heating and stirring continued for ½ hour more. The product was a clear liquid which remained clear after cooling overnight. This was blown with nitrogen for ½ hour at 257° F. Yield of product=85%. "Lorol B" alcohol is a plasticizer.

The product had the following characteristics:

	Percent
Sulfur	14.99
Phosphorus	2.14
Acid No. 20.5	
Saponification No. 110	

Example IV

1657 grams of sulfurized dipentene prepared as in Example II were blended with 1500 grams of an acid-treated naphthenic petroleum distillate of 55 S. S. U. viscosity at 210° F. and added to 126 grams of P_4S_3. The mixture was stirred and heated under a reflux condenser for 3 hours at 257°–302° F. 170 grams of "Lorol B" alcohol, a commercial mixture of aliphatic alcohols predominating in C_{12} alcohols, were then added and heating continued for 30 minutes more. The product was vacuum stripped at 75 mm. pressure and 212°–230° F., cooled and filtered.

The resulting product was a clear reddish-brown liquid showing the following analysis:

	Percent
Sulfur	12.99
Phosphorus	1.90

This product contains approximately 50% active ingredient.

On the basis of Examples II, III and IV, the final reaction product contains approximately 25 to 30% sulfur and 3.8 to 4.3% phosphorus by weight, aside from the oil content.

The performances of these examples in two different types of mineral oil base stocks are shown in Table II. Test oil A is a solvent extracted Mid-Continent motor oil stock of SAE 30 grade. Test oil B is a high quality motor oil stock of SAE 20–10W grade and a viscosity index of 125.

It will be observed that in each case the dipentene derivative of the present invention shows a very marked improvement in bearing weight loss in the 36-hour Chevrolet engine test over the untreated oil. While the overall demerit is increased somewhat, this is not considered serious inasmuch as this phenomenon is common to most corrosion inhibitors, and can be readily corrected by the addition of a small amount of conventional detergent additive. In all cases, the copper strip test is entirely satisfactory.

A sulfurized dipentene derivative of the prior art (not subjected first to sulfur and later to phosphorus sulfide treatment) is shown for comparison in the last line of Table II. While this product is satisfactory in the copper strip test, it is markedly deficient in corrosion inhibition as shown by the bearing weight loss of 0.93 gram per bearing.

TABLE II

PERFORMANCE OF P_4S_3 TREATED SULFURIZED DIPENTENE

36-Hour Chevrolet Engine Test (CRC-L-4)				Copper Strip Test [2]
Test Oil	Sulfurized Dipentene [1] P_4S_3 Treated	Cu-Pb Bearing Wt. Loss, Gm./ Bearing	Overall Demerit	
A	None	0.87	0.5	
A	Example II (0.85%)	0.36	0.6	4
A	Example II (1.0%)	0.10	0.7	4
B	None	2.06	0.5	
B	Example III (1.0%)	0.11	0.7	5
B	Prior Art Sulfurized Dipentene [3] (1.0%).	.092	0.6	6

[1] Volume percent of a 50% (approx.) concentrate of dipentene derivative in mineral oil.
[2] Copper strip test consists of heating a polished copper strip for 3 hours at 212° F. in a blend of 1.0% by weight of the dipentene derivative in an extracted Mid-Continent neutral oil of 150 S. S. U viscosity at 100° F.
[3] Sulfurized dipentene heated with solid sodium hydroxide to reduce copper strip corrosion.

In Table III are presented performance data for the products of the invention in combination with detergent additives of several well-recognized types. It will be noted that in each case the products of the invention allow only a very small amount of bearing corrosion, and at the same time are entirely satisfactory with respect to overall demerits and copper strip test.

The last three lines of Table III show the performance of sulfurized dipentene derivatives of the prior art. Two of these products, made by caustic washing the sulfurized dipentene, are satisfactory bearing corrosion inhibitors, but are extremely bad in the copper strip test. A rating of 10 indicates a black strip with removable deposit. A rating of 8 in this test is the absolute maximum numerical value that can be tolerated for an engine oil in order to protect copper and bronze parts of the engine. A rating of 7 or less is considered essential for a high quality additive for use in engine oils.

The last prior art product shown in the table is satisfactory in the copper strip test, but has lost most of its inhibiting power. The examples of the present invention, on the other hand, have been rendered innocuous in the copper strip test without any loss in bearing corrosion or oxidation inhibiting potency.

treated first with 25% to 54% of its weight of sulfur at a temperature range between 220° and 400° F. for a period of time sufficient to substantially complete its sulfurization and treated thereafter with 0.2 to 10%, based on the weight of the sulfurized terpene, of a phosphorus sulfide at a temperature within the range of 170° to 350° F. for a period of 1 to 20 hours, and 0 to 10% of an extreme pressure additive selected from the group consisting of chlorinated and sulfurized long chain hydrocarbons, sulfurized and phosphorized fatty oils, and sulfurized and phosphorized aliphatic esters.

2. A lubricating composition consisting essentially of a mineral base lubricant containing 0.1% to 2%, based on the total composition, of the reaction product of a monocyclic terpene $C_{10}H_{16}$ reacted first with about 25 to 54% of its weight of sulfur at a temperature within the range of 220° to 400° F. to substantial completion, and thereafter reacted with about 0.2 to 10%, based on the weight of the sulfurized terpene, of a phosphorus sulfide at a temperature within the range of 170° to 350° F. for 1 to 20 hours.

3. As a new composition of matter, the reaction product of a monocyclic terpene $C_{10}H_{16}$ treated first with about 25 to 54% of its weight of sulfur at a temperature within the range of 220° to 400° F. until substantial completion of reaction and treated subsequently with about 0.2 to 10%, based on the weight of the sulfurized terpene, of a phosphorus sulfide at a temperature within the range of 170° to 350° F. for 1 to 20 hours.

4. Composition according to claim 2 wherein the phosphorus sulfide is P_4S_3.

5. Composition according to claim 3 wherein the phosphorus sulfide is P_4S_3.

6. As a new composition of matter, the reaction product of a monocyclic terpene $C_{10}H_{16}$ treated first with 25 to 54% by weight, based on the terpene, of sulfur at a temperature between about 220° and 400° F. for a time sufficient substantially to complete the sulfurization reaction, said sulfurized product being subsequently treated with 0.2 to 10 percent by weight, based on the sulfurized terpene, of a phosphorus sulfide at a temperature between about 170° and 350° F. for 1 to 20 hours, said final reaction product having a sulfur content of approximately 25 to 30% and a phosphorus content of approximately 3.8 to 4.3% by weight.

7. Composition according to claim 6 wherein the phosphorus sulfide is P_4S_3.

8. Composition according to claim 6 wherein

TABLE III

PERFORMANCE OF P_4S_3 TREATED SULFURIZED DIPENTENE IN THE PRESENCE OF DETERGENTS

36-Hour Chevrolet Engine Test					Copper Strip Test [2]
Test Oil	Detergent (Vol. Percent)	Sulfurized Dipentene [1]	Cu-Pb Brg. Wt. Loss, Gm./Brg.	Overall Demerit	
B	D (1.5%)	None	0.73	0.8	
B	D (1.5%)	P_4S_3 Treated, Ex. IV (0.3%)	0.12	0.5	6
			0.14	0.6	6
C	E (2.5%)	P_4S_3 Treated, Ex. IV (0.3%)	0.12	0.6	6
B	F (1.5%)	None	2.11	0.4	
	F (1.5%)	NaOH Washed [3] (0.4%)	0.08	0.5	10
	F (1.5%)	NaOH Washed [4] (0.4%)	0.08	0.4	10
	F (1.5%)	Na_2S Washed [3] (0.4%)	1.23	0.3	3

[1] Volume percent of a 50% (approx.) concentrate of sulfurized dipentene in oil treated as shown.
[2] Copper strip test same as in Table II.
[3] Commercial product.
[4] Laboratory product.

What is claimed is:

1. A lubricating oil composition comprising about 88 to 99.99% by weight of a mineral base oil of lubricating grade, 0.01 to 5.0% of the reaction product of a monocyclic terpene $C_{10}H_{16}$

the sulfurization temperature range is between 300° and 350° F.

9. Composition according to claim 6 wherein the temperature for treatment with phosphorus sulfide is between 200° and 250° F.

10. Composition according to claim 6 wherein the terpene is predominantly dipentene.

11. The process of preparing an oxidation and corrosion inhibitor for mineral base lubricants which comprises treating 100 parts by weight of a $C_{10}H_{16}$ monocyclic terpene with 25 to 54 parts of sulfur at a temperature within the range of 220° to 400° F. for a period of time sufficient to substantially complete sulfurization; and thereafter treating the sulfurized terpene with 0.2 to 10%, based on the weight of the sulfurized terpene, of a phosphorus sulfide at a temperature of 170° to 350° F. for 1 to 20 hours.

12. Process according to claim 11 wherein the phosphorus sulfide is P_4S_3.

13. Process according to claim 11 wherein the sulfurization temperature is between 300° and 350° F.

14. Process according to claim 11 wherein the temperature of treatment with phosphorus sulfide is between 200° and 250° F.

15. Process according to claim 11 wherein the terpene is predominantly dipentene.

16. The process of preparing an oxidation and corrosion inhibitor, for use in lubricating oil and the like, which comprises gradually adding a $C_{10}H_{16}$ monocyclic terpene composed predominantly of dipentene to 25 to 54% by weight of the terpene of molten sulfur, continuing heating the mixture at a temperature between 300 and 375° F., until sulfurization is substantially completed, adding 0.2 to 10% of phosphorus sesqui sulfide, based on the weight of the sulfurized terpene and maintaining a temperature between 200 and 250° F., until reaction is substantially complete.

17. Composition made by the process of claim 16.

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Certificate of Correction

Patent No. 2,654,712 October 6, 1953

Elmer B. Cyphers et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 32, in the table, second line, under the heading "Composition" for "6%" read *6% "B"*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of November, A. D. 1953.

[SEAL]

ARTHUR W. CROCKER,
Assistant Commissioner of Patents.