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SOLUTION OF COPPER MERCAPTIDES FROM TERPENES

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This invention relates to solutions of copper mercaptides derived from terpenes and more particularly to solutions of such mercaptides in lubricating oils.

The production of a satisfactory lubricant, and particularly the production of a suitable lubricating oil for use in internal combustion engines, has presented a very difficult problem and has been the subject of a great deal of research. The problems presented are primarily due to deterioration of the lubricating oil under the conditions of use, which deterioration is primarily the result of oxidation accelerated by heat and the presence of the various metals in contact therewith. The products of such deterioration tend to form sludge, increase the viscosity of the oil, deposit on the parts of the engine and corrode sensitive bearing metals, such as those composed of alloys or mixtures of copper or lead, cadmium and nickel, silver and cadmium, and cadmium and tin. The increase in viscosity, the sludge and the deposits on the parts of the engine impede and may even arrest circulation of the lubricant. Corrosion of the sensitive bearing metals may proceed to such an extent as to cause mechanical failure of the engine. Accordingly, frequent and expensive changes of the oil, reconditioning of the engine and replacement of bearings are necessary. This is particularly true in so called heavy-duty service, that is, in the operation of trucks, buses, stationary and mobile power units and the like, where heavy loads are applied to the engines and deterioration of the oil is accelerated.

Many compounds have been proposed for addition to lubricating oils for the purpose of curing one or more of the defects of the ordinary petroleum lubricating oil. Amongst the materials which have been proposed for addition to lubricating oils are sulfur and sulfur compounds. Sulfur and its compounds are generally added to increase the film strength of the oils. This requires the addition of relatively large proportions of the sulfur and its compounds with sacrifice of other desirable properties of the oil. Usually the sulfur and its compounds tend to increase the corrosion of sensitive bearing metals, and to have other deleterious effects, so that they are not ordinarily used, except where high bearing pressures are encountered and it is essential that the oil have a high film strength. Under these circumstances, the disadvantageous properties of the additions are less important and, in some cases, may be overcome by the addition of other materials.

Those skilled in the art have also proposed the addition of soaps and soap-like materials to lubricating oils so as to take advantage of the detergent properties thereof for removing deposits from the parts of the engines and for maintaining the products of deterioration in suspension in the oils. Some of these materials are alleged to inhibit deterioration of the oils, and others are alleged to inhibit corrosion of sensitive bearing metals. Such soaps and soap-like materials are organic compounds containing metals in chemical combination and may generally be referred to as organo-metallic compounds. Generally, the disclosures of the organo-metallic compounds in the art are quite broad and frequently indicate a large number of different metals as being suitable, some of them even indicating that copper compounds would be suitable. Copper and its compounds are notorious as catalysts for the oxidation of organic compounds. Those skilled in the art have generally found that many copper compounds, when employed in lubricating oils in the proportions ordinarily recommended for organo-metallic compounds, actually accelerate oxidation of the oils and/or corrosion of sensitive bearing metals. In the case of those copper compounds which apparently inhibit the formation of sludge and like deterioration products, it has been generally necessary to add relatively large amounts of the copper compound to the oil in order to obtain practical and optimum results. However, such large amounts of such copper compounds generally accelerate corrosion of sensitive bearing metals. Also, while many compounds appear to have very desirable properties when subjected to some laboratory tests, they do not exhibit such properties when tested in an engine, particularly under conditions of heavy-duty service.

It is an object of this invention to provide new improved and more stable lubricants. Another object is to provide lubricating oils for internal combustion engines and particularly for heavy-duty service. A further object is to provide more stable lubricants which can be employed in internal combustion engines over long periods of time with the formation of less deposits on the engine and less corrosion of sensitive bearing metals. A still further object is to provide concentrated solutions of valuable additive compounds for lubricating oils, which concentrated solutions are particularly valuable for treating lubricating oils. Other objects are to provide new compositions of matter and to advance the art.

The above and other objects of my invention may be accomplished by incorporating, in a hydrocarbon oil, an oil-soluble copper mercaptide derived from a terpene in an amount sufficient to provide at least 50 parts of copper per one million

parts of oil, hereinafter abbreviated P. P. M. I have found that the copper mercaptides, derived from terpenes, are particularly desirable compounds for addition to lubricating oils, as they largely inhibit deterioration of the lubricating oils and corrosion of sensitive bearing metals by the lubricating oils. This is particularly apparent when such lubricating oils are employed in internal combustion engines under heavy-duty service, wherein the copper mercaptides operate to stabilize the oil against deterioration, so that the engines can be operated with such lubricating oils over long periods of time without causing objectionable increase in the viscosity of the oils, objectionable corrosion of sensitive bearing metals and the formation of objectionable amounts of deposits on the engines. I have further found that, some of such copper mercaptides are quite soluble in hydrocarbon oils, whereby they can be dissolved in such oils in high concentration. Such concentrated solutions are liquids and are readily miscible with lubricating oils, and provide a means for incorporating the desired amount of copper mercaptides in a lubricating oil, in a simple and economical manner.

The copper mercaptides, which are to be employed in accordance with my invention, may be prepared by treating mercaptans, derived from terpenes, with copper or a copper salt. Suitable mercaptans may be prepared by treating terpenes with hydrogen sulfide in the presence of a catalyst, in accordance with the method described by J. N. Borglin and E. Ott in Patent 2,076,875. The preferred copper mercaptides, which are to be employed in accordance with my invention, are those prepared by the method disclosed in my co-pending application Serial No. 440,253 filed April 23, 1942. Briefly stated, such co-pending application discloses a method which comprises heating a terpene with sulfur to form a terpene-sulfur complex, hydrogenating the terpene-sulfur complex under pressure in the presence of a sulf-active hydrogenation catalyst to reduce the complex to a mercaptan and then reacting the mercaptan with a copper salt to produce the copper mercaptide. Particularly suitable mercaptides are those prepared in accordance with the process of such co-pending application from

Alpha-pinene
Beta-pinene
Dipentene
Terpinolene
Menthene
Alpha-terpineol
Camphene
Pine oil
Terpentine
Camphor oils
Terpenes obtained as by-products in the manufacture of synthetic camphor

The oil, to be employed as the lubricant, may be any of the usual mineral oils, such as the petroleum lubricating oils ordinarily employed in the lubrication of internal combustion engines. It is not essential that the lubricating oil be highly refined, as partially refined and mildly refined oils will respond to the treatment of my invention.

In order to provide lubricating oils having improved properties, such as stability toward deterioration and the like, in accordance with my invention, the copper mercaptides, derived from terpenes, will be added to the lubricating oils in the proportion to provide concentrations of copper of from 50 P. P. M. to about 1000 P. P. M. and, in some cases, in concentrations as high as 2000 P. P. M. or more. When the copper mercaptides of my invention are employed in such amounts, the stability of the oils containing them will be improved. In general, I prefer not to employ the copper mercaptides, derived from terpenes, in proportions such as to provide copper in concentrations substantially above 1000 P. P. M., since the optimum results are obtained with concentrations of 1000 P. P. M. of copper and below and hence no additional benefits are obtained by employing concentrations materially above 1000 P. P. M. When the copper mercaptide, derived from a terpene, is incorporated in the oil in such proportions as to provide from 50 to about 200 P. P. M. of copper, it is generally essential to have present in the oil at least 0.1% of sulfur, in the form of oil-soluble sulfur compounds. When the concentration of copper is increased above 200 P. P. M., such amount of sulfur is not necessary and, when the proportion of copper approaches 500 P. P. M. and above, no sulfur may be necessary. However, it will usually be desired to have present in the oil, from about 0.1% to about 0.5% of sulfur, since such sulfur is effective to materially increase the stabilizing effect of the copper mercaptides, derived from terpenes. Usually, the optimum results will be obtained when the concentration of copper in the oil is within the range of from about 250 P. P. M. to about 1000 P. P. M. and I preferably employ the copper mercaptides, derived from terpenes, in such proportions as to produce copper concentrations in such range. However, it should be noted that all oil-soluble copper compounds are not equally effective on a copper basis. The optimum concentration depends upon the nature of the copper mercaptide, the nature of the lubricating oil treated therewith, and the degree of stabilization desired and must be determined experimentally for each copper mercaptide and each oil.

While copper compounds, which have been proposed heretofore for addition to lubricating oils, will actually accelerate corrosion of sensitive bearing metals by the oils, when employed in proportions substantially in excess of 500 P. P. M. of copper, I have found that the copper mercaptides of my invention are extremely effective to inhibit corrosion of sensitive bearing metals by the oils, even when they are employed in the oils in concentrations such as to provide 1000 P. P. M. or more of copper.

In general, the copper mercaptides, derived from terpenes, which are to be employed in accordance with my invention, are solid at ordinary temperatures. They may be added to the lubricating oil in the proportion finally desired in the oil However, some of them are soluble in hydrocarbon oils, such as lubricating oils, petroleum ether, benzene and other liquid hydrocarbons in such proportions as to provide concentrated solutions containing 10,000 P. P. M. or more of copper. For example, the copper mercaptide, derived from menthene, is soluble in SAE #10 oil, to the extent of at least 4.25% by weight and since it contains about 25.5% copper, it will provide at least 10,000 P. P. M. of copper in the oil. The copper mercaptides, derived from camphene and beta-pinene, are soluble in the same oil to the extent of at least 5% by weight. The preferred copper mercaptides, those derived from alpha-pinene, are soluble in the same oil to the extent of at least

34% by weight. Such concentrated solutions are particularly valuable commercial compositions, since they provide a simple and economical means for incorporating the copper mercaptides into a lubricating oil in the proportions desired for stabilizing such oil. Such concentrated solutions will have other uses in industry, such as, in plant sprays, insecticides and the like.

The copper mercaptides, derived from dipentene and terpinolene, are materially less soluble in oils. These mercaptides will, generally, be added directly to the lubricating oil in such proportions as to provide a saturated solution therein, in order to provide the concentration of copper desired for stabilizing the oil.

Oil-soluble sulfur compounds which may be used in conjunction with the copper mercaptides, derived from terpenes, in accordance with my invention, include mercaptans, sulfides, disulfides, polysulfides, thioethers, thiophenols, thiocarbamates, xanthates, thio acids, dithio acids, sulphones, thioamides, and mixtures thereof. Specific examples of some of these types include dibenzyl disulfide, dipinane disulfide, dicyclohexyl disulfide, dibenzyl sulfide, dioctyl sulfide, dibutyl sulfone, pinane mercaptan, pentadecane-thiol-8, triphenyl phosphine sulfide, 1,2-bis (benzylthio) ethane, dithio-bisdiamyl formate, and dithiobis (dibutyl thio formamide). Most lubricating oils contain an appreciable quantity of dissolved naturally occurring sulfur compounds. It has been found that, these naturally occurring sulfur compounds are also effective when employed in conjunction with the copper mercaptides, derived from terpenes, in accordance with my invention. Preferably, I add the copper mercaptides, derived from terpenes, to such oils, in such proportion as will produce the optimum results with the amount of sulfur naturally present in the oil, rather than adding other sulfur compounds to the oil. Accordingly, I include the natural sulfur content of the oil when speaking of my preferred concentrations of sulfur. By an oil-soluble sulfur compound, I mean a compound that is sufficiently soluble in the lubricating oil to give a permanent solution at ordinary temperatures, containing at least 0.10% sulfur. It should be noted that sulfur compounds behave differently from elemental sulfur. The former enhance the stabilizing action of the copper mercaptides, derived from terpenes, while the later tends to detract from such stabilizing action. Accordingly, I specifically exclude elemental sulfur as a sulfur compound.

The products, obtained by sulfurizing unsaturated compounds, are particularly useful oil-soluble sulfur compounds when employed in accordance with my invention. It will be understood that an unsaturated compound is an organic compound which contains one or more sulfurizable carbon to carbon double bonds. These compounds include the sulfurized natural oils from vegetable, fish, and animal sources, as well as sulfurized synthetic unsaturated compounds. Sulfurized sperm, lard, corn and menhaden oils and sulfurized terpenes may be mentioned as examples of sulfurized natural oils. Examples of sulfurized synthetic unsaturated compounds include the products obtained by sulfurizing cetene, abietene, cyclohexene, dihydronaphthalene, menthene, dipentene, terpinene, terpinolene, oleyl alcohol, abietyl alcohol, methyl oleate and methyl abietate. Mixtures of sulfurized unsaturated compounds are equally suitable. The exact chemical structure of these sulfurized unsaturated compounds is not definitely known. It is known, however, that each double bond of such an unsaturated compound will ordinarily react with one, two, or three atoms of sulfur. I prefer to employ compounds which contain not more than one atom of sulfur for each double bond present. Sulfur, in excess of this quantity, tends to function as elemental sulfur in detracting from the stabilizing action of copper compounds and hence is undesirable.

A preferred class of sulfurized unsaturated sulfur compounds which may be employed in combination with the copper mercaptides, derived from terpenes, in accordance with my invention, is surfurized unsaturated dehydrated alcohols, prepared as described in the co-pending application of F. B. Downing and R. G. Clarkson, Serial No. 440,201, filed April 23, 1942.

It has been found that, when lubricating oils are employed in internal combustion engines, the properties of the lubricating oils are materially effected by the character of the fuel employed in the engine. It has been found that, when the motor fuel employed in an internal combustion engine contains tetra-ethyl lead, deterioration of the lubricating oil and corrosion of sensitive bearing metals are materially increased. On the other hand, it has been found that, when the lubricating oils of my invention are employed in internal combustion engines operating on motor oils containing tetra-ethyl lead, the effectiveness of the copper mercaptides, derived from terpenes, in stabilizing the lubricating oils, is very materially increased. It has been found that, the copper mercaptides, derived from terpenes, are still very effective to inhibit corrosion of sensitive bearing metals when the motor fuel contains substantial amounts of tetra-ethyl lead.

The most satisfactory method of determining the stability of a lubricant in an internal combustion engine is by actual use of the lubricant in the engine. I employ the following engine test, which correlates well with results obtained in the field. Six-cylinder 1940 and 1941 model Chevrolet engines (in some cases fitted with one copper-lead bearing) are operated on a block mounting at a speed of 3150 R. P. M. (equivalent to a road speed of 60 miles per hour) against a load of 35 brake horse power (equivalent to that obtained in road operation) applied by means of a dynamometer. The oil in the sump is maintained at 280° F. and the cooling jacket liquid at 200° F. The test is run for 66⅔ hours (corresponding to road operation for 4000 miles), except in cases where the oil deterioration is so extensive that such lengthy operation is impractical. The degree of deterioration of the oil in this test corresponds directly to that obtained in equal periods of heavy-duty service and is indicative of that observed in longer periods of less severe service.

The following ratings are employed to determine the stability of the oil and its effect on the engine. Samples of the oil used are removed from the crankcase at intervals and analyzed for total sludge (naphtha insolubles) and asphaltenes (chloroform solubles) by the method described in J. Ind. Eng. Chem., anal. ed. 6, 419 (1934) and for viscosity rise and neutralization number by the well-known A. S. T. M. methods. On the basis of these analyses, the condition of the oils is rated as excellent, good, fair, poor or bad. At the end of the run, the engine is disassembled, inspected and rated as to cleanliness. In the system of cleanliness rating employed, a

clean engine would score 100 points. Points are deducted from this score based on the quantity and quality of sludge and other deposits in various parts of the engine. An engine with a score of about 50 points by this system would be so badly fouled as to be in imminent danger of mechanical failure due to impaired lubricant circulation caused by the presence of large amounts of sludge or other deposits or due to seizure of valve mechanisms or other moving parts. The copper-lead bearing is weighed before and at the end of the test to determine the loss in weight of sensitive bearing metals. The engine scores are more accurate and reproducible for relatively clean engines with scores of 90–100 than for dirty engines with scores of 50–70 because it is difficult to determine the exact degree of dirtiness of a very dirty engine. Conversely, low bearing corrosions of the order of 0.10 to 0.20 gram per bearing are more accurate and reproducible than high bearing corrosions of the order of 0.5 to 1.0 gram per bearing.

The following oils, each obtained from a different refiner and selected as being typical of the types employed in ignition-engine lubrication, were used in the tests.

Percent S	Oil	Type	SAE grade	Viscosity index
0.24	A	Solvent extracted Mid-Continent base	20	92
0.06	B	Solvent extracted Pennsylvania base	10	107
0.23	C	Solvent extracted Pennsylvania base	20	107

The tests in Table I demonstrate the effective action of the oil-soluble copper mercaptides, derived from terpenes, in improving oil condition and engine cleanliness and retarding bearing corrosion in an engine operating on a motor fuel containing 1 cc. of tetra-ethyl lead per gallon of motor fuel. The corrosion of copper-lead bearings is given as the weight in grams lost by the bearing during the engine test. This figure also includes the weight loss due to wear.

The amount of sulfur, naturally present in the oils used, was determined by the burner test. In this test, a sample of oil is blended with 3 parts by weight of naphtha. The mixture is burned, and the combustion products are absorbed by a sodium carbonate solution. On addition of a barium chloride solution to the sodium carbonate solution, barium sulfate precipitates. From the quantity of barium sulfate obtained (corrected for traces of sulfur in the naphtha and reagents), the percent sulfur present in the oil is calculated.

oils. They also have the advantage, over other types of copper compounds which have been proposed heretofore, of being very effective to inhibit corrosion of sensitive bearing metals, even when employed in concentrations such as to provide 1000 P. P. M. or more of copper. They also have the advantage of having a high copper content and a lack of undesirable color properties. Most oil-soluble copper compounds are characterized by green, blue, or purple colors and have high tinctorial properties so that their use in lubricating oil imparts to the oil, a distinct unnatural and undesirable colorization. The copper mercaptides from terpenes on the other hand, are light yellow in color when pure and, when crude, may be red or brown in color but they have low tinctorial properties and their addition to lubricating oils does not impart undesirable colorization to the oils. They are made from cheap and readily available materials, and their method of manufacture is economical so that they can be provided in large quantities at low cost. Most of them have high solubility in lubricating oils, so that they can readily be incorporated in the oils in the proportions usually desired.

While the stabilizing action of copper mercaptides, derived from terpenes, in lubricants for internal combustion engines is most striking in so-called heavy-duty service, a similar effect is also obtained in less severe service. Internal combustion engines in which these additives may be employed with beneficial results include engines designed for use in passenger automobiles, trucks, tanks, buses, tractors, aircraft and stationary and semi-stationary power plants. Furthermore, the beneficial action of these additives is not limited to any particular type or kind of oil. Excellent results can be obtained in mildly refined as well as in highly refined oils and in paraffinic base oils as well as in naphthenic and asphaltic base oils. The copper mercaptides, derived from terpenes, may also be employed in conjunction with other additives such as pour point depressants, viscosity index improvers, thickeners, detergents and the like.

I do not know the exact mechanism by which the copper mercaptides, derived from terpenes, function as lubricant stabilizers. They appear to function primarily, if not entirely, through protection of the oil from the deleterious effects of oxidation during use in the engine. The concentrations employed are insufficient to produce any worthwhile detergency or lubricity in the oil, and the copper mercaptides, derived from terpenes, appear to function as antioxidants rather than as detergents or film strength improvers. Furthermore, the lubricating oil compositions dis-

Table I

Oil	Additive	P. p. m. Cu in oil	Per cent S in oil	Hours tested	Oil condition rating	Engine cleanliness rating	Cu-Pb corrosion
A	None (avg. 4 runs)	0	0.24	66⅔	Bad	55.0	1.05
A	Cuprous mercaptide from alpha-pinene	120	0.25	66⅔	Good	86.0	0.81
A	do	800	0.28	66⅔	Excellent	90.5	0.20
B	None	0	0.06	33⅓	Bad	63.0	1.20
B	Cuprous mercaptide from alpha-pinene	120	0.07	33⅓	Bad	65.0	0.45
B	do	250	0.07	66⅔	Fair	74.0	0.62
B	do	500	0.08	66⅔	Excellent	89.5	0.07
B	do	1,000	0.12	66⅔	Excellent	93.0	0.17
B	do						
C	None	0	0.23	50	Poor	56.0	0.38
C	Cuprous mercaptide from alpha-pinene	250	0.24	66⅔	Good	86.0	0.18
C	do	500	0.26	66⅔	Good	90.0	0.23

From the above tests it will be apparent that the copper mercaptides, derived from terpenes, are extremely effective stabilizers for lubricating closed are free-flowing liquid lubricants suitable for crankcase use and are not greases.

While I have disclosed the preferred embodi-

ments of my invention, it will be understood that such specific embodiments are given for illustrative purposes only and that various modifications may be made therein without departing from the spirit or scope of my invention. For example, I have disclosed generally, the use of copper mercaptides, derived from terpenes. It will be apparent that mixtures of any two or more oil-soluble copper mercaptides of my invention may be employed, if desired. Accordingly, I intend to cover my invention broadly as in the appended claims.

I claim:

1. A hydrocarbon oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide at least 50 P. P. M. of copper.

2. A hydrocarbon oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide at least 250 P. P. M. of copper.

3. A hydrocarbon oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide a saturated solution containing at least 50 P. P. M. of copper.

4. A hydrocarbon oil having incorporated therein an oil-soluble copper mercaptide, derived from a pinene by the introduction of an —SH group into the pinene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide at least 50 P. P. M. of copper.

5. A hydrocarbon oil having incorporated therein an oil-soluble copper mercaptide, derived from a pinene by the introduction of an —SH group into the pinene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide a saturated solution containing at least 50 P. P. M. of copper.

6. A hydrocarbon oil having incorporated therein an oil-soluble cuprous mercaptide, derived from alpha-pinene by the introduction of an —SH group into the pinene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide at least 50 P. P. M. of copper.

7. A hydrocarbon oil having incorporated therein an oil-soluble cuprous mercaptide, derived from alpha-pinene by the introduction of an —SH group into the pinene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide a saturated solution containing at least 50 P. P. M. of copper.

8. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide at least 50 P. P. M. of copper.

9. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide at least 50 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

10. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide from 50 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

11. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper mercaptide, derived from a pinene by the introduction of an —SH group into the pinene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide from 50 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

12. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper-treated hydrogenated sulfurized terpene, wherein the copper is chemically combined with the hydrogenated sulfurized terpene, in an amount sufficient to provide from 50 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

13. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper-treated hydrogenated sulfurized pinene, wherein the copper is chemically combined with the hydrogenated sulfurized pinene, in an amount sufficient to provide from 50 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

14. A hydrocarbon lubricating oil having incorporated therein copper-treated hydrogenated sulfurized alpha-pinene, wherein the copper is chemically combined with the hydrogenated sulfurized alpha-pinene, in an amount sufficient to provide from 50 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

15. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper mercaptide, derived from a terpene by the introduction of an —SH group into the terpene and replacement of the hydrogen of such —SH group by copper, in an amount sufficient to provide from about 250 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

16. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper-treated hydrogenated sulfurized terpene, wherein the copper is chemically combined with the hydrogenated sulfurized terpene, in an amount sufficient to provide from about 250 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

17. A hydrocarbon lubricating oil having incorporated therein an oil-soluble copper-treated hydrogenated sulfurized pinene, wherein the copper

is chemically combined with the hydrogenated sulfurized pinene, in an amount sufficient to provide from about 250 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

18. A hydrocarbon lubricating oil having incorporated therein copper-treated hydrogenated sulfurized alpha-pinene, wherein the copper is chemically combined with the hydrogenated sulfurized alpha-pinene, in an amount sufficient to provide from about 250 to about 1000 P. P. M. of copper, and a small proportion, sufficient to impart substantial oil-stabilizing properties to the copper, of sulfur in the form of oil-soluble organic sulfur compounds.

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