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COPPER COMPOUNDS OF MERCAPTANS DERIVED FROM CAMPHENE

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This invention relates to new and valuable copper compounds and more particularly to the copper compounds of mercaptans derived from camphene.

It has recently been found that the addition of certain copper containing compounds to lubricating oils used in internal combustion engines imparts thereto desirable properties more particularly with regard to the stability of the oil. The copper containing ionogenic compounds which have been previously suggested for use in lubricating oils have certain disadvantages in that they do not effectively inhibit and often tend to cause bearing corrosion where the usual types of alloy bearings are employed in the engines. These copper containing compounds have also been found to have strong tinctorial properties and impart to the oils unnatural colors in the green, blue and purple range which are undesirable.

It is an object of this invention to produce new copper containing non-ionogenic organic compounds from the relatively inexpensive and readily available terpenes which show good solubility in organic compounds and lubricating oils and which impart to lubricating oils valuable non-sludging, non-lacquering and non-corrosive properties and which will not give to such oils unnatural and undesirable colors. It is a further object of the invention to provide new and valuable lubricating oil treating compounds comprising the copper compounds of mercaptans derived from camphene.

We have found that the copper compounds of mercaptans derived from camphene which may be prepared by reacting upon mercaptans derived from camphene with copper or copper salts show good solubility in lubricating oils and because of their high copper content are useful in decreasing the sludge formation and lacquering properties of the oil and in decreasing bearing corrosion in those cases where the oils tend to corrode alloy bearings. These copper compounds of mercaptans derived from camphene, furthermore, do not have the strong tinctorial properties of the previously suggested compounds but instead color organic solvents and oils when dissolved therein in light yellow to red and brown shades, depending upon their purity, which are not objectionable. These new copper containing compounds are made by a simple and economical process directly from camphene, which is a relatively inexpensive and readily available intermediate.

The compounds of the present invention may be prepared by reacting camphene with sulfur at

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temperatures of from 75 to 200° C., treating the resulting camphene-sulfur complex with hydrogen in the presence of a hydrogenation catalyst, that is active in the presence of sulfur, to form the mercaptan, reacting the mercaptan derived from camphene with a copper salt, preferably under conditions which maintain the copper salt in a cuprous state, and isolating the copper compound of the mercaptan (copper mercaptide), or extracting it from the reaction mass with a solvent such as organic solvents or lubricating oil. The sulfurization and hydrogenation may be carried out simultaneously in the presence or in the absence of an organic solvent. The formation of the copper compound may be effected directly in the organic solvent solution of the mercaptan or after isolation of the mercaptan, all as more particularly described in copending application Ser. No. 440,253, filed of even date herewith. A mercaptan derived from camphene may also be formed from camphene by the addition of hydrogen sulfide in the presence of sulfuric acid, phosphoric acid or other catalyst as more particularly described in U. S. P. 2,076,875. The mercaptans may be reacted with the copper salt or with the metal itself in the presence of air, although the exclusion of air from such reaction is preferred. Because cupric salts tend to oxidize the mercaptan to the disulfide the copperization of the mercaptan is preferably carried out with cuprous salts in the presence of a reducing agent or under conditions whereby the copper is maintained in the cuprous state. A preferred method for producing the copper salt is by adding an organic solvent solution of the mercaptan derived from camphene to an ammoniacal solution of a cuprous salt, such as cuprous chloride or cuprous acetate, in which there has been dissolved a reducing agent such as sodium hydrosulfite. This particular reducing agent not only maintains the copper in the cuprous state but it also tends to reduce any disulfide that might be formed in the reaction to the mercaptan whereby the yield of the copper mercaptide derived from the camphene is materially increased.

The new copper mercaptides derived from camphene may be dissolved directly in lubricating oil by stirring with or without heating or they may be dissolved in an organic solvent for use as a stock solution in treating lubricating oils. The copper salt of mercaptans derived from camphene are soluble in mineral oils, and hydrocarbon solvents such as benzene, hexane, paraffin oil, etc., as well as in organic solvents such as ether, alcohol, dioxan, etc.

The following examples are given to illustrate the invention. The parts used are by weight.

Example

547 parts of camphene (having a distilling range of 157.3° C. to 160.1° C. with 80% distilling between 158.0° C. and 159.1° C., a refractive index of N_{20}^{D} 1.4950 a freezing point of 37.9° C. and a specific gravity of 0.8366) and 249 parts of sulfur are heated in a steel autoclave, provided with agitation, at 150° C. for 10 hours under autogenous pressure. The condensation mixture is cooled to room temperature, and 40 parts of reduced nickel catalyst are added. The mixture then is hydrogenated at 150° C. and under a pressure of 600–700 lbs. per sq. in. until hydrogen absorption is complete as shown by absence of further pressure drops. After cooling, the crude product is filtered to remove the catalyst, and fractionally distilled at 25 mm. mercury pressure to obtain an essentially pure mercaptan with a boiling range of 115–118° C., a melting point of 44.5° C. and a sulfur content of 18.37%, and a higher boiling derivative having a boiling range of 122–123.5° C., which is liquid at ordinary temperatures and contains 18.85% of sulfur.

In a reaction vessel in which the air has been displaced with nitrogen, 13.4 parts of cuprous chloride are dissolved in 203 parts of 8.7% aqueous ammonia solution. Any blue color from cupric salts present in the cuprous chloride is removed by slowly adding a small quantity of a reducing agent such as sodium hydrosulfite. 20.8 parts of crude mercaptan, as obtained above prior to distillation, dissolved in 36 parts of ether (or kerosene) are added to the solution and the mixture is agitated for two hours under a nitrogen atmosphere. A reflux condenser or external cooling is preferably employed as the heat of reaction is often sufficient to vaporize a portion of the ether. The ether layer (upper) is decanted from the aqueous layer (lower) and filtered to remove traces of insoluble material. The ether fraction is then evaporated under vacuum at room temperature, giving a dark red resinous residue which on trituration with 80 parts of dry acetone yields a bright yellow ether soluble acetone insoluble powder which melts at 138° C. and has a sulfur content of 14.14% and a copper content of 26.22%.

The copper mercaptide of the distilled fraction of the mercaptan derived from camphene as described boiling at 115–118° C. at 25 mm. pressure when prepared according to the procedure outlined in paragraph two of this example, melts at 186.0° C. and has a sulfur content of 13.62% and a copper content of 26.20%.

The copper mercaptide of the distilled fraction of the mercaptan derived from camphene as described boiling at 122–123.5° C. at 25 mm. pressure when prepared according to the procedure outlined in paragraph two of this example, melts at 221° C. and has a sulfur content of 13.74 and a copper content of 26.20%.

It is of course understood that when the starting material contains a different ratio of isomers or impurities which form the copper mercaptides the resulting copper compounds may differ in their melting range from that given in the specific example.

As illustrated in the above example the copper mercaptides derived from camphene may be produced from the isolated mercaptans or they may be produced from the crude mercaptans, for in the copperization step any unreacted material or impurities which do not form the copper compounds are eliminated by the acetone extraction or by the use of similar solvents which do not dissolve the copper mercaptide. The acetone wash may of course be omitted if the mercaptan which is employed is relatively pure or the acetone may be substituted by other solvents.

The ether employed as the solvent for the mercaptan in the preparation of the copper compounds may be omitted or it may be substituted by other organic solvents such as benzene, ligroin, kerosene, petroleum ether or lubricating oils. The use of the solvent in this reaction is preferred for it facilitates working up of the final product.

This invention contemplates the preparation of new copper mercaptides of camphene irrespective of the process employed for the preparation of the mercaptan derived from the camphene, for it will be obvious that the mercaptan derived from the camphene may be produced by other processes than those mentioned above such as by the use of hydrogen sulfide or by replacing a halogen in the camphene molecule by the —SH group.

I claim:

1. The copper compound of a mercaptan derived from camphene obtained by reacting a cuprous salt with a mercaptan derived from camphene by reacting camphene with sulfur to form a camphene-sulfur complex and hydrogenating the camphene-sulfur complex with hydrogen in the presence of a catalyst.

2. Copper compounds of mercaptans derived from camphene obtained by reacting camphene with sulfur to form a camphene-sulfur complex, hydrogenating the camphene-sulfur complex with hydrogen in the presence of a catalyst to form the mercaptans and then reacting the resulting mercaptans with cuprous chloride in aqueous ammonia solution in the presence of a reducing agent under conditions whereby the copper is maintained in the cuprous state.

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