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SYNTHETIC LUBRICANT

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7 Claims. (Cl. 252-44)

Our invention relates to a method of synthesizing lubricants and more particularly to improved materials for addition to lubricants to increase their resistance to oxidation and formation of corrosive compounds during use.

This is a continuation-in-part of our co-pending application, Serial No. 218,630, filed July 11, 1938, now Patent No. 2,236,960, issued April 1, 1941.

It is well known that in order to obtain lubricants which are preeminently satisfactory from the standpoint of oxidation in use, it is necessary to refine the oil thoroughly and then to add an inhibitor of oxidation. The thorough refining may consist of more and heavier acid treatments or solvent treating so as to remove a considerable part of the oil and leave only the most stable portion. Such drastic refining is necessary in order to obtain stability with respect to sludge formation, but the oil is then subject to easy oxidation to form soluble acids and other corrosive materials. This can be prevented by the addition to the refined oil of small amounts of materials which either prevent the formation of these corrosive products or by some action render them inert.

Many of these additive materials are effective when added to poorly refined or even wholly unrefined lubricants. The addends may thus be substituted in whole or in part for the usual refining processes.

In the prior art of applying these principles to the manufacture of lubricants, many diverse types of materials have been suggested to be added to obtain improvement in various characteristics. It has been found that the addition of various metal-bearing organic compounds frequently improves film strength, oxidation resistance, non-corrosiveness, and other characteristics. In particular, tin in various combinations has been found to inhibit the development during use of corrosive materials. Lead compounds, particularly in combination with sulfur in some form (e. g. sulfurized oils) are used to improve film strength, especially in soap-thickened oils, such as greases and the like. Lead compounds do not in general, however, improve the oxidation and corrosive characteristics of a lubricant, and it is usually considered that lubricants containing lead compounds are unsuited for crankcase lubricants. They are usually employed in transmissions, differentials, and the like where temperatures are relatively low and no easily corroded metals are present.

One object of our invention is to provide improved inhibitors of oxidation and corrosion for addition to lubricants.

Another object of our invention is to provide oil-soluble organo-metallic compounds which contain relatively high percentages of metal.

A further object of our invention is to provide materials which are effective in extremely small amounts.

A still further object of our invention is to provide film-strength improving organo-metallic compounds suitable for use in lubricants and especially in crankcase lubricants.

Another object of our invention is to provide the possibility of including in one and the same addition agent factors for improving film strength, increasing resistance to the formation of oil-soluble (acidic) and oil-insoluble (sludge) oxidation products and decreasing corrosiveness developed during use.

Other and further objects of our invention will appear from the following description.

Briefly, our addition agents for accomplishing the above purposes are organo-metallic compounds containing more than one metallic atom per molecule but containing no metal-to-metal bonds, and in which the only carbon atoms attached to the metallic atoms are nuclear carbon atoms of an aromatic or heterocyclic ring system. None of the valences of the metallic atoms present in the molecule may be combined with the valences of another metal atom. More specifically, this application discloses the use of organic mercury compounds so constituted.

Since it is the metallic atom or atoms in the molecule and not the particular organic radicals present which are responsible for the desirable functions, it is apparent that the more metal atoms present in the molecule, the better. Organo-metallic compounds containing more than one metal atom per molecule are not extremely common, and most of those known have the plurality of metal atoms combined with each other in chains, for example, hexamethyl distannane, $(\text{CH}_3)_3\text{Sn}.\text{Sn}(\text{CH}_3)_3$. The bonds between the metal atoms in compounds of this type, however, are extremely weak as compared, for example, with the carbon-metal bond. As a result the compounds are relatively unstable chemically, tending to decompose and react readily.

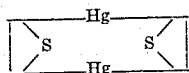
While the elements of group IV of the periodic table of the elements and a very few others, and in particular tin and lead, have to a very limited extent the ability to combine with themselves, no element possesses this characteristic to the extent which carbon does. Carbon is par excellence, the element which forms chains, clusters, and rings united by stable bonds. Furthermore, while the metal-metal bonds are weak, the carbon-metal bonds are quite strong, which provides greater stability. Hence, according to our invention, we use organo-metallic compounds containing two or more atoms of metal which may be the same or different and in which there are no metal-metal bonds, and in which the only carbon atoms attached to the

metallic atoms are nuclear carbon atoms of an aromatic or heterocyclic ring systems.

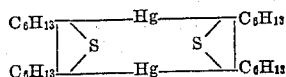
It is to be understood that in practicing our invention, oil-soluble organo-metallic compounds of the type described are to be selected. Some of the examples described below have only limited solubility in hydrocarbon oils. It is to be remembered, however, that because of the high content of metal in our compounds, extremely small amounts are often effective. Thus we may use as little as 0.001 per cent of some of these compounds and it will be seen that a fairly insoluble material may dissolve to a sufficient extent to be satisfactory for our purpose. In general, 0.001 per cent or more of our addition agent is used, and we may add one, two, or even five per cent or more.

Furthermore, it is well known that different types of oils have different capabilities of dissolving a given material. For some purposes, therefore, we prefer paraffinic, and for other purposes asphaltic, naphthenic, or mixed base lubricants. Another method of obtaining a satisfactory mixture of addition agent with the hydrocarbon oil is the use of a mutual solvent to bring the addend into solution. Alternatively peptizing agents may be added to maintain the organo-metallic compound in permanent suspension.

Many of the more difficultly soluble materials are rendered more soluble by the introduction of alkyl groups, particularly those containing four or more carbon atoms. The isoamyl, octyl, lauryl, and octyl, lauryl, and octadecyl radicals and radicals from paraffin wax greatly increase the solubility of organic compounds in oil. One or more of such groups may be introduced as required, for example, dimercury-2,2',5,5'-dithienylene,



melts above 330° C. and is insoluble in most organic solvents, but the tetrahexyl derivative,



is much more soluble.

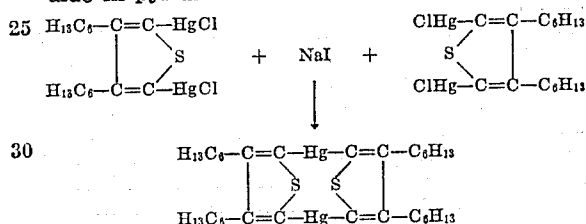
The tetrahexyl derivative shown above may be prepared by the following illustrative method in which 2,5 dichloromercuri thiophene is used as a starting material.

The 2,5 dichloromercuri thiophene may be prepared by reacting 10 parts of thiophene in 100 parts of solvent with 1,000 parts of cold saturated solution of mercuric chloride and 200 parts of a 33 1/3 per cent solution of crystallized sodium acetate. The desired product will be in the precipitate which may be collected over a period of several days. The resultant mixed mono- and di-mercurated thiophene may be separated by dissolving the mono-mercurated thiophene with hot alcohol in which solvent the di product is not soluble. See Volhard, Annalen 1891, 267, 176; Steinkopf and Bauermerster, Annalen 1914, 403, 59; Finze, Gazzetta 1915, 45 ii 280; Steinkopf, Annalen, 1921, 424, 23; textbook of Inorganic Chemistry, Volume XI, part I, Goddard and Goddard, edited by J. Newton Friend—publishers, Chas. Griffin and Company, London, page 97.

The 2,5 dichloromercuri thiophene may be alkylated direct, or the thiophene may be al-

kylated prior to reaction to form the mercuri halide. The alkylated thiophenes are prepared according to methods perfectly similar to those used in the production of the corresponding alkylated benzene hydrocarbons from benzene; thus from iodthiophene and an alkyl iodide by means of sodium; from thiophene, alkyl halides, and aluminum chloride, etc. See Richter's "Organic Chemistry," Volume III, Heterocyclic Compounds (1923), P. Blakistons and Sons, page 22. Using 84 parts of thiophene and 240 parts of hexyl chloride with thirty parts of aluminum chloride all refluxed in a suitable organic solvent such as carbon disulfide, petroleum ether, etc., yields the 3-4 dihexylthiophene. Using this compound in the mercuric chloride reaction disclosed above instead of thiophene would yield 3-4 dihexyl 2,5 dichloromercuri thiophene.

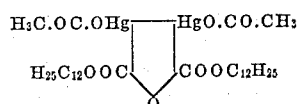
Two molecules of the 3-4 dihexyl 2,5 dichloromercuri thiophene may be condensed to form the di-mercury tetrahexyldithienyl. To 10 parts of dihexyl dichloromercuri thiophene in 1,000 parts of pyridine, add 7.5 parts of sodium iodide in pyridine solution.



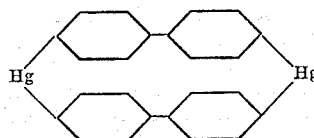
See textbook of Inorganic Chemistry, Goddard and Goddard, Volume XI, part I (1928), Charles Griffin, page 84.

The following are preferred examples of our addition agents which are given as illustrations and not as limitations:

1. 3,4-diacetoxymercurifurane-2,5-dicarboxylate dilauryl ester:

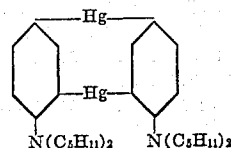


2. Dimercury bisdiphenyl,

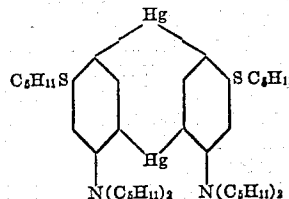


and particularly its alkylated homologues such as the tetraamyl derivative.

3. 4,6-dimercuri-bis-diamylaniline:



4. 4,6-dimercuri-bis-diamyl aniline-3-amylthioether:



It will be observed that all of the foregoing

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compounds typical of the class of compounds contemplated herein are characterized by the presence of more than one mercury atom, namely two such atoms, and that the only carbon atoms to which the mercury atoms are attached are nuclear carbon atoms of an aromatic or a heterocyclic ring system. It will be further observed that the mercury atoms in such compounds may also be attached to atoms of other non-metals, such as oxygen, in addition to being attached to said nuclear carbon atoms. It will be still further observed that the mercury atoms may be common to more than one heterocyclic ring system, such as, for example, in dimercury-2,2',5,5'-dithienylene above. And, it will be further observed that a metal-to-metal, or mercury-to-mercury, bond is absent in these compounds.

It may be desirable to include in one and the same blend based on a hydrocarbon oil, in addition to the addends here described, other addends for specific purposes. Thus we may add a pour point depressor such as a naphthalene-chlor wax condensation product and a viscosity index improver such as certain resins or polymerized hydrocarbons in addition to our organo-metallic compounds. Furthermore, other metallic compounds may be added to the blend without interfering with the action of our ingredients. Indeed, in some cases it is advantageous to combine with our organo-metallic compounds in a hydrocarbon oil blend such materials as calcium dichlorostearate, chromium oleate, tin octadecyl phthalate, aluminum stearate, and other metallic soaps.

Our addends are admirably adapted for use in lubricating oils of all types including those designed for use in automotive crankcases, Diesel oils, and any other oils of lubricating viscosity. Furthermore, our addends are advantageously blended in gasoline and other petroleum fuels either directly or after being blended first in a lubricating oil and then added to the fuel. Soap-thickened mineral oils of all types, ranging from those showing only a slight increase in viscosity over that of the mineral oil alone, to the semi-solid and solid greases containing fifty per cent or more of soap, are amenable to treatment according to our invention.

It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is therefore to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, we claim:

1. A lubricant comprising a major proportion of oil of lubricating viscosity and a minor proportion of an organo-mercury compound containing more than one metallic atom but no metal-to-metal bonds, and in which the only carbon atoms attached to the metallic atoms are nuclear carbon atoms of a ring system selected from the group consisting of aromatic and heterocyclic ring systems.

2. A lubricant comprising a major proportion of oil of lubricating viscosity and a minor proportion of an organo-mercury compound containing more than one mercury atom but no mercury-to-mercury bonds, and in which the only carbon atoms attached to the mercury atoms are nuclear carbon atoms of a ring system selected from the group consisting of aromatic and heterocyclic ring systems.

3. A lubricant comprising a major proportion of oil of lubricating viscosity and a minor proportion of an organo-mercury compound containing more than one mercury atom but no mercury-to-mercury bonds, in which the only carbon atoms attached to the mercury atoms are nuclear carbon atoms of a ring system selected from the group consisting of aromatic and heterocyclic ring systems, and in which the mercury atoms are common to more than one ring system of said group of ring systems.

4. A lubricant comprising a major proportion of oil of lubricating viscosity and a minor proportion of an organo-mercury compound containing more than one mercury atom in which all the valences of the mercury atoms are satisfied by nuclear carbon atoms of a ring system selected from the group consisting of aromatic and heterocyclic ring systems.

5. A lubricant comprising oil of lubricating viscosity and from 0.001 to 5 per cent of an organo-mercury compound containing more than one metallic atom but no metal-to-metal bonds, and in which the only carbon atoms attached to the metallic atoms are nuclear carbon atoms of a ring system selected from the group consisting of aromatic and heterocyclic ring systems.

6. A lubricant comprising a major proportion of oil of lubricating viscosity and a minor proportion of dimercury-2,2',5,5'-tetrahexyldithienylene.

7. A lubricant comprising a major proportion of oil of lubricating viscosity and a minor proportion of dimercury tetra-amyldisphenyl.

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