United States Patent Office 3,093,669 Patented June 11, 1963

3,093,669

REACTION PRODUCTS OF MOLYBDENUM PENTACHLORIDE AND DIALKYLPHOSPHITES

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No Drawing. Original application Dec. 19, 1960, Ser. No. 76,471. Divided and this application Sept. 7, 1961, Ser. No. 138,217

4 Claims. (Cl. 260—429)

This invention relates to novel organo-molybdenum derivatives and more particularly to oil-soluble reaction products of molybdenum pentachloride and hydrocarbyl substituted phosphites, which products impart resistance to oxidative deterioration when incorporated in lubricating oil compositions.

This application is a division of my co-pending application Serial Number 76,471, filed December 19, 1960.

Within recent years it has become common practice to impart improved properties to lubricants through the use of various types of additives or addition agents. Lubricating oils employed in internal combustion engines such as automotive and diesel engines require the use of one or more addition agents to improve their serviceability under certain adverse operating conditions. Among the more important additives employed are the type which function to prevent the formation and accumulation of sludge and varnish-like coatings on pistons and cylinder walls of the engine. Such additives which have the property of maintaining clean engines are referred to as "detergent-type" lubricant additives. The more effective addition agents which have been developed for compounding with lubricants are many sulfur-containing organic compounds such as, by way of example, sulfurized terpenes, sulfurized hydrocarbon oils, vegetable oils or animal oils, organic polysulfides, particularly polyalkyl polysulfides, metal salts of organo-substituted thioacids of phosphorus, metal salts of the reaction product of a phosphorus sulfide and a hydrocarbon such as, for example, polybutenes and other polyolefins, and combinations of the foregoing.

Corrosion inhibitors also play an important part in the formulation of efficient lubricants. Such corrosion inhibitors should effectively inhibit the corrosion of metal alloys of the type used in engine bearings and other engine parts. Recent increased use of silver and similar metals in the construction of improved internal combustion engines has created new problems in the use of sulfur-containing additives in lubricants for such engines; the primary problem created being the corrosion of such silver parts of the engine by the sulfur-containing additives. While such corrosion can be eliminated by avoiding the use of sulfur-containing additives in lubricants for such engines, this solution of the problem is accompanied by the loss of the highly desired beneficial effects of the additives of this type.

An object of the present invention is to provide novel oil-soluble organo-molybdenum compounds and a method of preparing the same. Another object is to provide novel oil-soluble organo-molybdenum compounds having particular utility as lubricant additives. A particular object is to provide novel oil-soluble reaction products of molybdenum pentachloride and hydrocarbyl substituted phosphites which have anti-oxidative properties in addition to having substantial metal corrosion inhibiting properties when added to mineral lubricating oils. A further object is to provide a composition which will inhibit the corrosion of silver and similar metals by sulfur and/or organic sulfur-containing compounds. Still another object is to provide a method of inhibiting the corrosion of engine parts in contact with lubricant compositions which contain sulfur and/or organic sulfur-containing compounds which are normally corrosive to metals. Other objects and advantages of the present invention will become apparent from the ensuing description thereof.

It has been discovered that certain novel oil-soluble reaction products of molybdenum pentachloride and hydrocarbyl substituted phosphites have anti-oxidant and/or anti-corrosion properties. Such products are extremely useful as additives for lubricants which are normally corrosive to metals with which such lubricants are in contact. Thus, in accordance with the present invention, the oil-soluble reaction products of molybdenum pentachloride are prepared by reacting molybdenum pentachloride with a hydrocarbyl substituted phosphite having the general formula $(RO)_2$—P—OH wherein R is a hydrocarbyl radical containing at least four carbon atoms. The reactants being employed in the molar ratio of about one mole of molybdenum pentachloride to about three moles of the hydrocarbyl substituted phosphite, preferably with a slight excess of the phosphite reactant. The reaction is carried out at atmospheric pressure and at temperatures of from 20° C. to about 140° C. Depending upon the temperatures employed, the reaction time may vary from about two hours to about 16 hours.

The new products are viscous liquids of varying oil solubility depending upon the amount and nature of hydrocarbon substitution in the structure and nature of the base oil. They have particular value as anti-oxidants for lubricating oil lubricants, as bearing corrosion inhibitors and, because they are non-corrosive to silver in lubricant compositions, have a wide range of applicability. In general, it is desirable that the hydrocarbyl substituted phosphite reactant contain at least four carbon atoms, preferably 8 to 18 carbon atoms, in the hydrocarbyl substituent in order to provide adequate oil solubility in the final reaction product. The products then can be handled in the form of mineral oil concentrates which facilitate handling in the formulation of commercial lubricating oils and greases. The level of use in the finished lubricant, however, is usually quite small. For use as an oxidation inhibitor in a hydrocarbon oil susceptible to oxidative deterioration the concentration of the additive should be at least 0.2% by weight. Amounts above 0.5% give satisfactory results, but since such results may be obtained with lesser amounts, it is usually not economical to employ more than 0.5%.

In commercial formulations, the hydrocarbyl substituted phosphite-molybdenum pentachloride reaction products will ordinarily be used, as is customary in conjunction with other compatible lubricating oil additives, for example, pour depressants, viscosity index improvers, anti-rust agents, anti-foam agents and the like. The base may comprise any hydrocarbon oil subject to oxidative deterioration. For most applications, the oil will comprise a mineral form fraction of the usual viscous lubricating oil range.

More specifically the novel oil-soluble organo-molybdenum products of the present invention are the reaction products of molybdenum pentachloride and di-aliphatic phosphites having the general formula $(RO)_2$—P—OH wherein R is a straight or branched chain aliphatic radical having at least four, preferably 8–18 carbon atoms. Examples of suitable di-aliphatic phosphite reactants are: di-butyl phosphite, di-pentyl phosphite, di-cyclopentyl phosphite, di-hexyl phosphite, di-cyclohexyl phosphite, di-heptyl phosphite, di-octyl phosphite, di-nonyl phosphite, di-decyl phosphite, di-dodecyl phosphite, di-hexadecyl phosphite, and di-octadecyl phosphite.

The invention will be further illustrated by specific example wherein di-(2-ethylhexyl) phosphite is shown by

way of example as representative of the class of di-hydrocarbyl substituted phosphites which are suitable for purposes of the present invention. In the example, the additive was evaluated by means of the Modified Stirring Sand Corrosion Test (MSSCT) and the modified EMD silver bearing corrosion test.

The MSSCT test was run as follows: A copper-lead test specimen is lightly abraded with steel wool, washed with naphtha, dried and weighed to the nearest milligram. The cleaned copper-lead test specimen is suspended in a glass beaker, cleaned with a hot tri-sodium phosphate solution, rinsed with water, acetone and dried, and 300 grams of the oil to be tested, and 50 grams of a 30–35 mesh sand charged to the beaker. The beaker is then placed in a bath or heating block and heated to a temperature of 330° F. (±2° F.) while the contents are stirred by means of a stirrer rotating at 1300 r.p.m. The contents of the beaker are maintained at this temperature for forty-eight hours, after which the copper-lead test specimen is removed, rinsed with naphtha, dried and weighed. The test specimen is then replaced in the beaker and the test continued for another twenty-four hours (seventy-two hours total). At the conclusion of this time, the test specimen is removed from the beaker, rinsed with naphtha, dried and weighed.

In the modified EMD test a silver strip 2 cm. x 5.5 cm. with a small hole at one end for suspension is lightly abraded with No. 0 steel wool, wiped free of any adhering steel wool, washed with carbon tetrachloride, air-dried and then weighed to 0.1 milligram. Three hundred cc. of the oil to be tested is placed in a 500 cc. lipless glass beaker and the oil is heated to a temperature of 300° F. (±2° F.) and the silver test strip suspended in the oil so that the strip is completely immersed therein. The oil in the beaker is stirred by means of a glass stirrer operating at 300 r.p.m. At the end of twenty-four hours, the silver strip is removed and while still hot rinsed thoroughly with carbon tetrachloride and air-dried. The appearance of the strip is then visually noted and given ratings according to the following scale:

(1)—Bright
(2)—Stained
(3)—Grey-black
(4)—Black, smooth
(5)—Black, flake

After the visual inspection the silver strip is immersed in a 10% potassium cyanide solution at room temperature until the silver surface assumes its original bright or silver appearance. The silver strip is then washed successively with distilled water and acetone, air-dried and weighed. A weight loss of 20 mg. or less is considered passing.

Example I

A charge of 91 grams (0.33 mole) of molybdenum pentachloride and 100 ml. of benzene was placed in a glass reaction vessel equipped with a reflux condenser, thermometer, a dropping funnel and a stirrer. Thereafter, 306 grams (1.0 mole) of di-(2-ethylhexyl) phosphite in 200 ml. of benzene was added dropwise with stirring at room temperature over a period of 2.5 hours. At the end of the addition of the di-(2-ethylhexyl) phosphite the temperature of the resulting reaction mixture had risen to 35° C. Thereafter, the resulting mixture was stirred and heated under refluxing conditions for a period of one hour. At the end of the heating period the reflux condenser was removed from the reaction vessel and a porous glass gas dispersion tube was inserted into the reaction medium. Thereafter nitrogen was passed through the reaction mixture, with continued heating and stirring, to remove the benzene and hydrogen chloride formed by the reaction, until no more odor of benzene and hydrogen chloride was noted at which time the reaction temperature was 130° C. After cooling, a deep purple liquid reaction product was obtained which analyzed 8.2% molybdenum, 9.67% chlorine, and 5.31% phosphorus.

The product was tested at the 0.5% concentration level in solvent extracted SAE 40 grade Mid-Continent oil containing about 2.8% of a detergent of the barium neutralized phosphorus sulfide-polybutene reaction product type. The oil gave a bright EMD silver strip and MSSCT weight losses of 234.1 mg. at 48 hours and 315.2 mg. at 72 hours, whereas, the same oil without the product of this example gave a MSSCT loss of 870.4 mg. at 48 hours.

In the preparation of the novel oil-soluble organo-molybdenum products of the present invention it is advisable to use an inert solvent or diluent for the reactants. Inert solvents which have been found suitable for use are those having boiling points within the range of from about 75° C. to about 115° C. such as, for example, benzene and toluene.

The hydrocarbyl substituted phosphites which are used as reactants in the preparation of the oil-soluble organo-molybdenum products of this invention are readily available from the reaction of phosphorus trichloride with one or more of the appropriate alcohols. This reaction is well known and in the case of alcohols generally requires a molar ratio of reactants of 3:1 (alcohol:phosphorus trichloride). The alcohols may be pure materials or mixtures containing varying chain lengths depending upon their origin. Inasmuch as the alcohols, used in the preparation of the substituted phosphites may be mixtures, it will be apparent that the di-hydrocarbyl substituted phosphites will contain hydrocarbyl substituents of varying chain lengths. Consequently R in the general formula $(RO)_2$—P—OH may be the same or different. It is only essential that R contain at least four carbon atoms so as to impart oil solubility to the final organo-molybdenum product of the invention.

While the above-described reaction products can be suitably employed alone in combination with a base oil, they are usually used in combination with other lubricant addition agents which impart various desired characteristics to the base oil. Usually, these reaction products are used in conjunction with detergent-type additives, particularly those which contain sulfur or phosphorus and sulfur addition agents. This type is usually used in amounts of from about 0.002% to about 10%, and preferably from about 0.01% to about 5%. Among the phosphorus- and sulfur-containing addition agents are the neutralized reaction products with a phosphorus sulfide and a hydrocarbon, an alcohol, a ketone, an amine or an ester. Of the phosphorus sulfide reaction product additives, I prefer to employ the neutralized reaction products of a phosphorus sulfide, such as a phosphorus pentasulfide, and a hydrocarbon of the type described in U.S. 2,316,082, issued to C. M. Loane et al. April 6, 1943. As taught in this patent, the preferred hydrocarbon constituent of the reaction is a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefin hydrocarbons, such as propylene, butenes, amylenes or copolymers thereof. Such polymers may be obtained by the polymerization of mono-olefins of less than 6 carbon atoms in the presence of a catalyst, such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride, or other similar halide catalysts of the Friedel-Crafts type.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The phosphorus sulfide-hydrocarbon reaction product, when neutralized with a basic reagent containing a metal constituent, is characterized by the presence or retention of the metal constituent of the basic reagent.

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the acidic reaction product with a suitable basic compound, such as hydroxide, carbonate, oxide or sulfide of an alkaline earth metal or an alkali metal, such as for example, potassium

hydroxide, sodium hydroxide, sodium sulfide, calcium oxide, lime, barium hydroxide, barium oxide, etc. Other basic reagents can be used, such as for example, ammonia, or an alkyl or aryl-substituted ammonia, such as amines. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the acidic reaction product either as such or dissolved in a suitable solvent, such as naphtha with a solution of the basic reagent. As an alternative method, the reaction product can be treated with solid alkaline compounds; such as KOH, NaOH, Na_2CO_3, CaO, $Ba(OH)_2$, Na_2S, and the like, at an elevated temperature of from about 100° F. to about 600° F. Neutralized reaction products containing a heavy metal constituent, such as for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron and the like, can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocarbon reaction product which has been treated with the phosphorus sulfide-hydrocarbon reaction product, which has been treated with a basic reagent, such as above-described.

Other phosphorus sulfide reaction products which can be used are the reaction products of a phosphorus sulfide and a fatty acid ester of the type described in U.S. 2,399,243; the phosphorus sulfide-degras reaction products of U.S. 2,413,332; the reaction product of an alkylated phenol with the condensation product of P_2S_5 and turpentine of U.S. 2,409,877 and U.S. 2,409,878; the reaction product of a phosphorus sulfide and stearonitrile of U.S. 2,416,807, etc.

The above described molybdenum carbonyl compounds can be used in combination with lubricant base oils, such as hydrocarbon oils, synthetic hydrocarbon oils, such as those obtained by the polymerization of hydrocarbons, such as olefin polymers, for example, polybutenes, polypropylene and mixtures thereof, etc.; synthetic lubricating oils of the alkyleneoxide type, for example, the "Ucon oils," marketed by Carbide and Carbon Corporation, as well as other synthetic oils, such as the polycarboxylic acid ester-type oils, such as the esters of adipic acid, sebacic acid, maleic acid, azelaic acid, etc.

While this invention has been described in connection with the use of the herein-described additives and lubricant compositions, their use is not limited thereto; but the same can be used in products other than lubricating oils, such as for example, fuel oils, insulating oils, greases, non-drying animal and vegetable oils, waxes, asphalts, and any fuels for internal combustion engines, particularly where oxidation must be combatted.

Concentrates of a suitable oil base containing more than 10% of an oil-soluble reaction product of molybdenum pentachloride and a hydrocarbyl substituted phosphite alone or in combination with other additives can be used for blending with hydrocarbon oils or other oils in the proportions desired for the particular conditions of use to give a finished product containing at least 0.2% of the molybdenum carbonyl compound.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as come within the spirit of the appended claims.

I claim:

1. The reaction product of about 1 mole of molybdenum pentachloride and about 3 moles of a phosphite having the formula $HOP(OR)_2$ wherein R is a C_{4-18} hydrocarbyl radical of the group consisting of alkyl and cycloalkyl radicals.
2. The product of claim 1 wherein R is alkyl.
3. The product of claim 1 wherein R is octyl.
4. The product of claim 1 wherein R is 2-ethylhexyl.

References Cited in the file of this patent

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