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LUBRICANT

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This invention relates to lubricants and additives for lubricating oils and greases.

Additives for lubricating oils are known in the art which act to inhibit the formation of sludge and acid in oil, to prevent the deposition of lacquer or varnish on the moving parts, and to prevent other forms of deterioration of the oil which have an undesirable effect on the device being lubricated, such as an internal combustion engine. The oils containing such additives, as a general rule, are not required to lubricate surfaces operating under high pressures and in preparing this type of additive, it is not common to consider this aspect of the lubricating properties of the oil.

Additives for lubricating oils and greases have also been proposed heretofore which are especially adapted to lubricate surfaces operated under high pressures, such as gear surfaces. These materials are referred to as "E. P." (extreme pressure) lubricants because they are adapted for use at unusually high pressures. Most uses for which the E. P. lubricants are designed do not involve high temperature operations or other conditions which result in deterioration of the oil. Therefore, in the manufacture of the E. P. lubricants, little attention is usually paid to the effects of sludge, acid or lacquer formation and other results attributable to oil deterioration.

The invention contemplates additives which have, or impart, E. P. properties and which also inhibit deterioration. Because of adverse conditions of operation, such additives can be used, for example, in gear boxes which operate at relatively high temperatures. The provision of such additives for a plurality of purposes is desirable even though more than one function is not manifest at any one time. Such an additive, which is of a universal matter, can be stocked by the user for a plurality of purposes, thus avoiding the purchase and use of a number of different additives for special purposes.

It is a principal object of the invention thereof to provide a new composition suitable for use as a lubricant and also as an additive for lubricating oils and greases to improve their E. P. properties and also to inhibit the formation of sludge, acid, lacquer and other results attributable to the deterioration of the oil under operating conditions.

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

In accordance with the present invention it has been found that a halogenated oxygen-containing organic compound may be reacted with phosphorus sulfide and the reaction product then converted into a heavy metal compound thereof. The resulting product has been found to be obtainable in good yields and to have improved properties with respect to the inhibition of acid and sludge formation and particularly the inhibition of lacquer formation, and also imparts these properties to lubricating oils and greases to which the product is added. Furthermore, the product and lubricating oils and greases contain the same high E. P. properties.

It is recognized that it has been proposed heretofore to use a wide variety of halogenated compounds as so-called E. P. additives. Such E. P. lubricants are not used normally as additives in oils for high temperature operation, such as in an internal combustion engine, because high pressures are not encountered. In addition, under these conditions of operation, many of these E. P. lubricants are excessively corrosive. The latter property is not of much concern because under conditions in which such E. P. lubricants are normally used, corrosion is not a problem. Thus, the halogenated materials which heretofore have been suggested as having good E. P. properties ordinarily are not good inhibitors for sludge and acid formation in oils.

It is also recognized that many sulfur-containing additives have been proposed and that metal compounds thereof have been suggested as acid, sludge, and lacquer inhibitors. However, the additives which are used for these purposes ordinarily do not impart E. P. properties to oils and greases and are not used for this purpose because apparatus operating under conditions normally conducive to sludge, acid, and lacquer formation does not operate at high pressures.

In view of this state of the art, it is unexpected that a material could impart E. P. properties to oils and greases and yet the same material function to inhibit the formation of sludge, acid, lacquer, corrosion, and other difficulties which are inherent in high temperature operations.

The halogenated oxygen-containing organic compounds that may be used in accordance with the invention may be any of a wide variety of compounds falling in this class. Preferably, these materials should have a sufficiently high molecular weight to have a boiling point of at least about 300° F. There is no upper limit to the molecular weight of the compound except that high polymers are not preferred, and the halogenated-oxygen-containing organic compound should be one which results in a reaction product with phosphorus sulfide that is soluble in the oil or grease which is to be used. In general, most of the halogenated oxygen-containing organic compounds themselves are oil soluble.

As illustrative of the compounds falling in this class, reference may be made to halogenated oxygen-containing acids, both aliphatic and aromatic, such as chlorobenzoic acid, di-chlorobenzoic acid, chloronaphthenic acid, mono- and di-chloropalmitic acid, mono- and di-chlorostearic acid and di-chloro dihydroxy stearic acid.

As illustrative of the halogenated oxygen-containing organic esters, there may be mentioned methyl di-chlorostearate, chlorinated alkyl esters of benzoic acid, such as chloromethyl benzoate, chlorinated esters of monoatomic alcohols of fatty acids, such as chlorobutyl propionate, and chlorinated glyceride of fatty acids, such as chlorinated vegetable oils.

Especially suitable are halogenated oxygen-containing waxes of the ester type, such as chlorinated degras, chlorinated sperm oil, chlorinated hydrogenated waxes. One commercially available hydrogenated sperm oil has an iodine value of 6–7, a melting point of 50–52° C., a free fatty acid content (as oleic) of 1.0–2.0%, a saponification value of 135–138, and about 36% of unsaponifiables. Another commercially available product is made by treating hydrogenated sperm oil to remove a portion of the glycerides therefrom. This product will be referred to hereinafter as refined hydrogenated sperm oil. It has an iodine value of 6.0, a melting point of 48–50° C., a free fatty acid content (as oleic) of 0.4%, a saponification value of 125, and 45% of unsaponifiables.

Additional examples of halogenated oxygen-containing organic materials include chlorinated alcohols and phenols, ketones, aldehydes, and other compounds.

Any of the above compounds may be used in admixture with each other or in admixture with other compounds in which the halogenated oxygen-containing organic compound is a predominant ingredient thereof. Preferably such a compound or mixture should be saturated because the compounds with too high an iodine value tend to polymerize under the reaction conditions.

Halogenated oxygen-containing organic compounds have been referred to generally as a class and compounds of any halogen may be used. Chlorinated compounds are the most economic and competitive and since they give satisfactory results the respective chlorinated compounds have been listed as illustrative.

Of the phosphorus sulfides available, phosphorus pentasulfide is relatively inexpensive and readily available commercially. Inasmuch as desirable results are obtained with it, the invention is described using phosphorus pentasulfide as illustrative.

The heavy metal compounds, as these are defined herein, include any metal other than the alkali metals and alkaline earth metals. Examples of these metals are arsenic, lead, copper, iron, zinc, tin, antimony, and bismuth. These are readily available and relatively inexpensive and, therefore, would probably comprise the metals that are used in the commercial adaptation of the invention.

The product of the invention is preferably made in two stages or reaction steps. In the first step, the halogenated oxygen-containing organic compound is reacted with the phosphorus sulfide. This reaction product is then converted into the desired corresponding metal compound thereof.

In carrying out the reaction between the halogenated oxygen-containing organic compound and the phosphorus sulfide, the reaction conditions should be adjusted and the proportions of the material should be selected so as to obtain a reaction product having a substantial amount of sulfur.

In the preferred embodiment, a temperature is employed which is high enough to replace a major portion of the oxygen of the organic compound with sulfur. The observed facts appear to indicate a reaction in which at least a part of the sulfur of the sulfide replaces oxygen of the halogenated oxygen-containing organic compound and at least part of the displaced oxygen combines with the phosphorus to form a phosphorous and oxygen-containing residue.

The temperature which should be used varies somewhat depending primarily upon the molecular weight of the halogenated oxygen-containing organic compound and the rate that it is desired to have reaction effected. In view of these variables it is impossible to assign a precise numerical temperature that is optimum for all of the compounds, but in general the temperature should be above about 270° F., preferably in the range of 290 to 310° F. Temperatures in excess of 350 to 400° F. are not essential and there is no point in using a higher temperature than that which causes the reaction to proceed smoothly in the desired length of time.

The amount of phosphorus sulfide to be used in the first step of making the product, preferably should be at least about equivalent to the theoretical amount that would be required to replace all of the oxygen in the halogenated oxygen-containing organic compound with sulfur. The amount of the sulfide will vary with the molecular weight and the amount of oxygen in the compound so that the precise amount involves simple chemical calculations. A slight excess over the theoretical amount of the sulfide, for instance, about 10% or more, may be of assistance in forcing the reaction to completion.

After the initial reaction between the halogenated oxygen-containing organic compound and the sulfide, a residue comprising phosphorus and oxygen will settle out as a sludge together with any other insoluble materials and the reaction product may be decanted or may be separated by filtering or centrifuging.

The separated reaction product is then converted into the corresponding heavy metal compound as described heretofore. The metal, preferably, is in the form of the oxide or hydroxide.

The amount of the metal compound to be employed will depend somewhat on the molecular weight of the metal compound and the initial reaction product. Generally the amount will vary from 1 to 15% depending upon these factors. The amount of the metal compound will also depend on whether the reaction product is to be completely or partially reacted with the metal compound. If desired, the amount of the metal compound may be such as only to react with a part of the initial reaction product so as to form a mixture of the initial reaction product and the metal compound thereof. Such a mixture is advantageous under some circumstances since it embodies the properties of both ingredients. The initial reaction product can also be treated with a plurality of the above metals and the plurality of metals may include one of the heavier metals with a minor proportion of an alkali or alkaline earth metal. In cases of certain of the heavier metals, the oxides or hydroxides of which may not be reactive, the initially reacted product may be converted into an alkali metal compound thereof and this may be reacted with a salt of the heavier metal to replace the alkali metal to form the desired heavier metal compound. If desired, only a part of the alkali or alkaline earth metal may be replaced and in this way a mixture of two metals may be formed.

In making the metal compounds the initial reaction product, preferably after it has been separated from the residue, is heated to a temperature of about 180° to 350° F., preferably 300° F., and the metal compound added.

The reaction is continued until the desired amount of the metal compound is incorporated, which may be from 1 to 8 hours. The reaction mixture is then settled or centrifuged and the metal compound is separated from any unreacted metal oxide or other insoluble materials.

The amount of the above described metal compound to be added to oils or greases depends upon the characteristics of the oil or grease and the intended use thereof. Generally, the amount will be within the range of 0.5 to 15%, but under some circumstances much smaller amounts show a noticeable improvement. Inasmuch as the metal compound itself is a lubricant, there is no upper limit to the amount that may be used. It is uneconomical, however, to add more than is necessary to impart the desired properties to the oil.

The following specific example is included merely as illustrative of the invention, but without limiting the scope of the invention as otherwise described and defined herein:

Example I

(A) Chlorinated refined hydrogenated sperm oil containing 30% chlorine is reacted with 20% of phosphorus pentasulfide at a temperature of 300° F. After the reaction is complete, which requires about 1 hour, the material was permitted to stand, during which time a by-product residue settles and the reaction product was decanted.

(B) The above reaction product was reacted with 5% arsenic trioxide by heating at a temperature of 300° F. for about 1 hour. The mixture was filtered to separate the metal compound from any impurities.

In order to evaluate the metal compound as an inhibitor in a lubricating oil, and also to determine its capacity for imparting E. P. properties, it was added in an amount of 9% to an oil comprising 60% Pennsylvania Bright Stock and 40% No. 300 Red Oil. This was compared with the same oil, not containing an additive, with the same oil containing 9% of the same chlorinated refined hydrogenated sperm oil, and with the same oil containing 9% of the initial reaction product.

The inhibiting characteristics of the three

samples were tested in an ethyl motor operation under procedure IV in which the operating conditions are as follows:

Speed	1200 R. P. M.
Jacket temperature	212° F.
Sump temperature	300° F.
Air fuel ratio	15:1
Compression ratio	7:1
Catalyst	0.1% Fe_2O_3 as Neodex iron naphthenate

The results of this test are as follows:

Additive	None	Example A	Example B	Refined Hydrogenated Sperm Oil Chlorinated
Amount ..... percent	None	9	9	9
Length of run .. hours	10	20	20	20
Sludge	4.5	2.5	0.8	20
Acid Number	4.5	1.5	1.5	2.0
Viscosity Increase	385	241	174	2,000
Skirt Number	3.0	3.0	0.0	4.0
Demerit Rating	15.8	4.7	2.0	23

In the above test it was necessary to discontinue the operation of the engine at the end of 20 hours with the oil containing chlorinated refined hydrogenated sperm oil since the viscosity of this oil increased such that the engine could not be further lubricated. With the additive of the invention made in accordance with the invention, the run could be continued for a much longer time. The metal compound of the invention is much superior from the standpoint of corrosion as compared with clorinated refined hydrogenated sperm oil, and is also superior to the reaction product thereof with phosphorus pentasulfide.

The same samples were tested by the Timken test at 800 R. P. M. to evaluate their E. P. properties. The results are as follows:

Additive	None	Example A	Example B	Refined Hydrogenated Sperm Oil Chlorinated
Amount ..... percent	None	9	9	9
Maximum pounds tested	15	50	60	35

From the above data it will be seen that the metal compounds of the invention are superior, both in their E. P. properties and their inhibition to deterioration of the oil.

This superiority in both these respects is independent of the chlorine content of the refined hydrogenated sperm oil. Similar tests carried out with chlorinated refined hydrogenated sperm oil containing 10% chlorine revealed results of the same order, namely, they demonstrate the superiority of the metal compound as imparting to the oil an improved resistance against corrosion of the bearings and higher E. P. properties.

The manner in which the invention would be applied to other halogenated oxygen-containing starting materials and other metals will be obvious from the above example in view of the disclosure heretofore, and for this reason further examples are not included.

It will be apparent to one skilled in the art that a variety of materials are included within the generic designations and that different procedures be included. All such variations as fall within the scope of the following claims are intended to be included in the invention.

This application is a continuation-in-part of our application Serial Number 482,491, filed April

9, 1943, now Patent No. 2,419,153, dated April 15, 1947.

We claim:

1. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, a heavy metal compound of the reaction product of a halogenated oxygen-containing organic compound reacted with an amount of a phosphorus sulfide at least about equivalent to the theoretical amount required to replace the oxygen in the halogenated oxygen-containing organic compound with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

2. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, a heavy metal compound of the reaction product of a chlorinated oxygen-containing organic compound reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated oxygen-containing organic compound with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

3. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, a heavy metal compound of the reaction product of a chlorinated fatty acid reacted with an amount of a phosphorus sulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated fatty acid with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

4. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, a heavy metal compound of the reaction product of a chlorinated ester of a fatty acid reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated fatty acid ester with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

5. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, a heavy metal compound of the reaction product of a chlorinated ester type wax reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated ester type wax with sulfur from the sulfide. reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

6. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, the arsenic compound of the reaction product of a chlorinated ester type wax reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated ester type wax with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

7. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, the arsenic compound of the reaction product of a chlorinated hydrogenated sperm oil reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated hydrogenated sperm oil with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

8. A lubricating composition comprising a mineral oil lubricant and an amount of an addition agent to inhibit the deterioration and improve the E. P. properties thereof, said addition agent being a heavy metal compound of the reaction product of a halogenated oxygen-containing organic compound reacted with an amount of a phosphorus sulfide at least about equivalent to the theoretical amount required to replace the oxygen in the halogenated oxygen-containing organic compound with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

9. A lubricating composition comprising a mineral oil lubricant and an amount of an addition agent to inhibit the deterioration and improve the E. P. properties thereof, said addition agent being a heavy metal compound of the reaction product of a chlorinated fatty acid reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated fatty acid with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

10. A lubricating composition comprising a mineral oil lubricant and an amount of an addition agent to inhibit the deterioration and improve the E. P. properties thereof, said addition agent being a heavy metal compound of the reaction product of a chlorinated ester of a fatty acid reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated fatty acid ester with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

11. A lubricating composition comprising a mineral oil lubricant and an amount of an addition agent to inhibit the deterioration and improve the E. P. properties thereof, said addition agent being a heavy metal compound of the reaction product of a chlorinated ester type wax reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated ester type wax with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

12. A lubricating composition comprising a mineral oil lubricant and an amount of an addition agent to inhibit the deterioration and im-

prove the E. P. properties thereof, said addition agent being the arsenic compound of the reaction product of a chlorinated ester type wax reacted with an amount of phosphorus pentasulfide at least about equivalent to the theoretical amount required to replace the oxygen in the chlorinated ester type wax with sulfur from the sulfide, reacted at a temperature above 270° F. to form a reaction product which is separable from a phosphorus and oxygen-containing by-product residue.

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