252-46.7

Phosphorus sulfide reacted with halogenated oxygen containing organic cpds.

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LUBRICANT

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

A number of additives for lubricating oils have been proposed heretofore which act to inhibit the formation of sludge and acid in the oil, and to prevent other forms of deterioration of the oil which adversely affect an internal combustion engine or other device which the oil is adapted to lubricate. For the most part, such oils are not required to lubricate surfaces operating under high pressures and in the preparation of such additives, no thought is usually given to this aspect of the lubricating properties of the oil.

It has also been proposed heretofore to provide additives for lubricating oils and greases which are adapted primarily to lubricate surfaces operating under high pressures, such materials are referred to as "E. P." (extreme pressure) lubricants, because they are adapted for use at very high pressures. Many uses to which the E. P. lubricants are adapted do not involve high temperature operation or other conditions which tend to deteriorate the oil. Therefore, in the manufacture of the E. P. lubricants, little attention has been paid to the effects of sludge or acid formation, and other manifestations of oil deterioration.

Recent developments in the field of mechanics have required lubricants which have E. P. properties, and also which resist deterioration because of the conditions of operation.

It is an object of the invention to provide a new composition suitable for use as a lubricant and also as an agent for addition to lubricating oils and greases to improve their E. P. characteristics, and also inhibit the formation of sludge and acid and other manifestations of deterioration under operating conditions.

Various other objects and advantages of the invention will be apparent as it is disclosed more fully hereinafter.

According to the present invention, it has been found that halogenated oxygen-containing organic compounds may be reacted with a phosphorus sulfide under appropriate conditions to obtain high yields of a reaction product which have improved properties with respect to the inhibition of acid and sludge formation, and also imparts these properties to lubricating oils and greases to which the reaction product is added, and which reaction product further has high E. P. properties and imparts the same to lubricating oils and greases.

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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. materials are not used normally as additives in oils for high temperature uses, such as in an internal combustion engine because high pressures are not encountered. Also under these conditions many of these lubricants are excessively corrosive. Under conditions under which such E. P. lubricants are normally used, corrosion is not a problem. Thus materials which are good E. P. additives ordinarily are not good inhibitors for sludge and acid formations in oils.

It is recognized that many sulfur-containing additives have been proposed as acid and sludge inhibitors. However, the additives which ordinarily inhibit sludge and acid formation do not impart E. P. properties to oils and greases.

In view of this state of the art, it is surprising to have discovered a material which imparts E. P. properties to oils and greases, and yet at the same time inhibits formation of sludge as well as acid, and minimizes corrosion, lacquer deposition and other difficulties which are usually inherent in high temperature operations.

The new additives can be used, for example, in gear boxes which operate at relatively high temperatures. In addition, the provision of a single additive for both purposes, even though both functions are not manifest simultaneously, is a marked advantage in marketing and for the users who need have on hand only a single universal additive.

The halogenated oxygen-containing organic compounds that may be used in accordance with my invention may be any of a wide variety of compounds. Preferably these materials should have a sufficiently high molecular weight to have a boiling point of at least 300° F. There is no upper limit to the molecular weight, except that high polymers are not preferred, and a halogenated oxygen-containing organic compound should be such that reaction product with a phosphorus sulfide is soluble in oil; and, in general, the halogenated oxygen-containing organic compound itself is oil soluble.

Included are various acids, both aliphatic and aromatic, such as chlorobenzoic acid, di-chlorobenzoic acid, chloronaphthenic acid, di-chlorodihydroxystearic acid, mono- and di-chloropalmitic acid and mono- and di-chlorostearic acid. Other examples include esters, such as methyldichlorostearate, chlorobutylpropionate, chloromethyl-

phthalate, chlorinated glycerides of fatty acids, such as vegetable oils, and similar esters.

Especially suitable are halogenated oxygen-containing waxes of the ester type, such as chlorinated degras, chlorinated sperm oil and 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 material is a product 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. This product 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. The waxes can be chlorinated to contain any extent of chlorine, for example from 5 to 30% or upwards.

Additional examples include chlorinated alcohols and phenols, chlorinated ketones, aldehydes, ethers, 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 the predominate ingredient thereof.

Preferably, the compound or mixture should not be too unsaturated, since compounds with too high an iodine value tend to polymerize.

The halogenated oxygen-containing organic compounds have been referred to heretofore as the generic class and insofar as is known any of the compounds of any of the halogens may be used. However, only chlorinated compounds would be 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 and since particularly desirable results are obtained with it, it is described as illustrative.

In carrying out the reaction between the halogenated oxygen-containing organic compound and the phosphorus sulfide, the proportions should be selected and the temperature conditions adjusted so as to obtain a reaction product having a substantial amount of sulfur. In the preferred embodiment, a temperature is employed such that sulfur will replace a major portion of the oxygen of the organic compound. The reaction indicated by the observed facts appears to be one in which at least a part of the sulfur of the sulfide replaces oxygen of the halogenated oxygen-containing organic compound and at least a part of the displaced oxygen combines with the phosphorus to form a phosphorus and oxygen containing residue.

The temperature to be used may vary somewhat, depending upon the molecular weight of the halogenated oxygen-containing organic compound and the rate of the reaction desired. In view of the variables involved, it is difficult to assign a temperature in numerical terms that is optimum for all of the compounds, but in general the temperature should be above about 270° F., preferably in the range of 285 to 325° F., for example around 300° F. Temperatures in excess of 350 to 400° F. are not required and there is no point in using a higher temperature than that which will cause the reaction to proceed smoothly.

The amount of the phosphorus sulfide to be used in making the reaction product in accordance with the preferred embodiment should be at least about equivalent to the theoretical amount required to replace 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 but no difficulty is involved in making simple, chemical calculations. In the case of methyl-di-chlorostearate, for example, the amount of phosphorus pentasulfide would be 24%. In general, the range will be from 15 to 35%. A small excess over the theoretical amount of the sulfide, for example 5 to 15%, may be of assistance in forcing the reaction to completion.

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

The amount of the reaction product to be added to an oil or grease varies, but is usually within the general range of 0.5% to 15%. Even smaller amounts give a noticeable improvement. There is no upper limit as the reaction product itself is a lubricant.

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

Example I

300 parts of di-chlorostearic acid is reacted with 110 parts of phosphorus pentasulfide at a temperature of 300° F. After the reaction is complete, which requires about one hour, the material was permitted to stand during which time a by-product residue settles and the reaction product was decanted. The material may be used as a lubricant as such, or may be added to a lubricating oil in an amount such that the reaction product present is from 0.1 to 15%, preferably about 2 to 6%.

In order to evaluate the reaction product as an inhibitor in a lubricating oil, it was added to an S. A. E. 30 lubricating oil in an amount of 1% and was tested along with the same oil not containing an additive in an ethyl motor operation under procedure II, in which the operating conditions are as follows:

Type of motor	Ethyl motor series 30
Engine speed	1200 R. P. M.
Sump temperature	300° F.
Jacket temperature	212° F.
Compression ratio	7:1
Air-fuel ratio	15:1

The results are as follows:

Oil used	S. A. E. 30	S. A. E. 30
Additive	None	Example I.
Amount of Additive	do	1%.
Length of Run	20 hours	20 hours.
Sludge	5.0	0.4.
Acid Number	2.5	1.68.
Viscosity Increase	357	80.
Piston Rating	8.0	4.0.
Demerit Rating	19.0	6.8.

The same oil containing 1% of the additive was evaluated for E. P. properties under the Cornell test and was found to withstand 4000 pounds as compared with 800 pounds for the oil without the additive.

Example II

Methyl di-chlorostearate is reacted with 33% of phosphorus pentasulfide at a temperature of 300° F. After the reaction is complete, which requires about 1 to 2 hours, the material was permitted to stand during which time a by-product residue settles and the reaction product was decanted. The material may be used as a lubricant as such, or may be added to a lubricating oil in an amount such that the reaction product present is from 0.1 to 15%, preferably about 2 to 6%.

The reaction product was evaluated by adding it to an S. A. E. 30 lubricating oil in an amount of 1% and was tested along with the same oil not containing an additive in an ethyl motor operation under procedure II, as described in connection with Example I.

The results are as follows:

Oil used	S. A. E. 30	S. A. E. 30
Additive	None	Example II.
Amount of Additive	do	1%.
Length of Run	20 hours	20 hours.
Sludge	5.0	0.2.
Acid Number	2.5	0.56.
Viscosity Increase	357	32.
Piston Rating	8.0	0.0.
Demerit Rating	19.0	1.0.

The excellence of the reaction product of this example in inhibiting the formation of sludge, acid, lacquer, and increase in viscosity is readily apparent from the above data. In particular, there is a decrease in the acid formation which is entirely unexpected in view of the halogen in the starting material.

The same oil containing 1% of the additive of Example II was tested for E. P. properties by the Cornell test and was rated 4000 pounds as compared with 800 pounds for the blank oil.

Example III

Chlorinated refined hydrogenated sperm oil containing 30% chlorine was reacted with 20% phosphorus pentasulfide at a temperature of 300° F. The reaction was permitted to proceed for one hour, following which the reaction product was separated from a sludge.

In order to evaluate the reaction product as an additive, both with reference to its properties in inhibiting the deterioration of an oil and for improving 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 any additive, and with the same oil containing 9% of the same chlorinated refined hydrogenated sperm oil.

The inhibition 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 are as follows:

Additive	None	Example III	Chlorinated Refined Hydrogenated Sperm Oil
Amount of Additive..per cent	None	9	9
Length of Run.....hours	10	20	20
Sludge	4.5	2.5	20.0
Acid Number	4.5	1.5	2.0
Viscosity Increase	385	241	2,000
Skirt Number	3.0	3.0	4.0
Demerit Rating	15.8	4.7	23

In the above run, it was necessary to discontinue the engine operation at the end of 20 hours with the oil containing the chlorinated refined hydrogenated sperm oil as the viscosity of the oil increased to a point where the engine could not be lubricated further. With the additive made in accordance with Example III, however, the run could be continued much longer. It will be seen that the chlorinated refined hydrogenated sperm oil per se is not satisfactory as an additive for lubricating oil to be used in an internal combustion engine because of the high sludge formation, and viscosity increase. Furthermore the corrosion of the oil containing chlorinated refined hydrogenated sperm oil is about 6 times as bad as the oil containing the additive of the invention. After the reaction of chlorinated refined hydrogenated sperm oil with phosphorus pentasulfide, in accordance with the invention, it has desirable properties as an additive and the corrosion is within acceptable limits.

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

Additive	None	Example III	Chlorinated Refined Hydrogenated Sperm Oil
Amount of Additive..per cent	None	9	9
Maximum pounds tested	15	50	35

From the above it will be seen that while chlorinated refined hydrogenated sperm oil improves the E. P. properties of the oil somewhat, the reaction product in accordance with the invention has superior E. P. properties.

This application is a continuation-in-part of application Serial No. 482,491, filed April 9, 1943, now Patent No. 2,419,153, dated April 15, 1947, which is a continuation-in-part of application Serial No. 297,178, filed September 28, 1939, now Patent No. 2,361,957, dated February 8, 1944.

It will be obvious to one skilled in the art that a variety of materials are within the halogenated oxygen-containing organic compound defined generically herein and illustrated by the several examples, and that different procedures may be adopted in making the new composition. All such variations as fall within the scope of the following claims are intended to be included within the invention.

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, 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, 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.

3. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, 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.

4. As a lubricant and as an addition agent for lubricating oils and greases to inhibit their deterioration and improve their E. P. properties, 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.

5. 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 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.

6. 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 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.

7. 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 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.

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 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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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,242,260	Prutton	May 20, 1941
2,252,984	Rutherford	Aug. 19, 1941
2,307,183	Zimmer	Jan. 5, 1943
2,352,818	Whittier	July 4, 1944
2,355,240	Reiff	Aug. 8, 1944