

UNITED STATES PATENT OFFICE

2,494,332

EXTREME PRESSURE LUBRICANTS

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3 Claims. (Cl. 252—46.7)

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The present invention relates to extreme pressure lubricants and more particularly to additives which may be combined with various lubricating oils, greases, and the like, to impart extreme pressure properties thereto, and to methods of preparing such additives.

In the lubrication of modern machinery it is frequently necessary to provide lubricants having higher load bearing capacities than are provided by ordinary mineral oil products. Under conditions of extreme pressure it has been found necessary to provide certain additive compositions for lubricating oils and greases which are effective to prevent metal to metal contact between parts being lubricated under conditions where the unusual pressures encountered would cause failure of ordinary lubricating films.

Various compounds, usually including materials such as sulfur, chlorine, phosphorus, and the like, have been included in extreme pressure lubricants and are usually compounded in such a way that they are relatively inactive at ordinary temperatures. These materials become active, however, when conditions arise, such as the application of extreme pressure between moving parts, etc., which result in elevated temperatures. For example, when the normal lubricating oil film begins to break between two metallic parts, such, for example, as opposed gear elements operating under heavy load, high friction results which, of course, causes an increase in temperature at the point or area of contact. This causes a chemical reaction between the extreme pressure material and the metal parts involved to deposit on the latter a very thin but highly protective film of metal sulfide, metal chloride, or metal phosphide, etc.

The use of halogens, especially chlorine, and/or sulfur, and/or phosphorus compositions in oils and greases for the purposes referred to above is well known in the art. It is also known that certain organic compounds including some or all of these materials are effective extreme pressure additives for lubricants. In general, the prior art compositions used for imparting extreme pressure properties to lubricating compositions fall into two classes. One class includes certain sulfur-chlorine organic extreme pressure compositions which have been found to be quite effective for carrying moderate loads at high

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speeds. These compositions may substitute or add phosphorus also. Such lubricants give good test results on the SAE extreme pressure testing machine and are quite satisfactory for the lubricating of passenger cars and light trucks. When tested on the Timken lubricant and wear test machine, however, the prior art compositions of the high speed type carry relatively poor loads and are found to be inadequate for proper lubrication in heavy truck operations under conditions where low speed and high torque prevail.

Another class of compounds, commonly used in the prior art, includes other sulfur-phosphorus products and may also include chlorine in some cases. Some of these are quite satisfactory for heavy truck duty, frequently being capable of carrying high loads on the Timken machine. These prior art compounds, however, are somewhat less satisfactory for high speed operation, for example, in the lubrication of passenger automobiles, and they are found to give low test results on the SAE machine.

The present invention is based upon the discovery that certain organic ester derivatives which include phosphorus and halogens, and preferably also contain sulfur, are effective extreme pressure agents at both high and low speeds. According to this invention, halogenated esters of cyclic carboxylic acids or substituted cyclic carboxylic acids are reacted with an alkali salt of an alkyl, alkenyl, aryl or aralkyl thiophosphoric or thiophosphorous acid to yield materials which contain all three of the desirable constituents, halogen, sulfur, and phosphorus. The relative chemical activities of these ingredients, in the compositions of this invention, appear to be well adjusted to meet the lubrication needs of widely different operating conditions. The cyclic or substituted cyclic carboxylic acids in the esters may include saturated and unsaturated alicyclic rings and substituted benzenoid rings. Some of these types are described below under Example I.

More specifically, the invention comprises the halogenation, for example, chlorination of rosin esters, hydrogenated rosin, methylated rosin, or partly hydrogenated and/or methylated rosin derivatives and/or mixtures thereof. This may be carried out by introducing gaseous chlorine, or liquid bromine, into the rosin derivative at a suitable temperature, within the range, for example,

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of 70° to 250° F. The hydrogenated material is then reacted with a suitable salt, for example, an alkali metal salt such as the sodium salt of an alkoxy thio acid of phosphorus. The products are prepared by halogenating the rosin or rosin derivative first and then reacting to form the ester. The alkoxy group on the thio acid preferably is a short chain, branched, or linear, having 1 to about 8 carbon atoms. Isopropyl, butyl, isobutyl, isoamyl groups, and the like are satisfactory. Materials so prepared have been found very useful in the preparation of general purpose lubricants having excellent and unexpected extreme pressure properties under extremely different and difficult lubricating conditions.

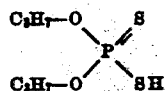
An example of the operation of the process of this invention is described below:

Example I

A commercial mixture of methyl esters of rosin having the general approximate formula, $C_{15}H_{25}COOCH_3$, was chlorinated by passing gaseous chlorine through the ester at a temperature of 150° to 160° F. to a final chlorine content of 19.96%. The rosin esters used are more fully described below. The esters are in the form of a viscous pale yellow liquid which appears to contain about 84% of a mixture of the methyl esters of several isomeric forms of abietic acid. The ester material is a proprietary product of the Hercules Powder Company sold under the trade name "Abalyn." It is classified as a methyl abietate having an acid number of about 5, a saponification number of about 18 to 50, the sample tested having a number of 25, and a boiling point of about 360° to 365° C.

An alkoxy thiophosphoric acid, specifically diisopropyl dithiophosphoric acid, was prepared as follows:

480 grams of 99% isopropyl alcohol were placed in a glass flask equipped with a stirrer and reflux condenser. 444 grams of phosphorus pentasulfide (P_2S_5) were added in about ten equal portions over a period of 15 minutes. The temperature rose spontaneously to about 120° F., and heat was then applied, and refluxing began at 130° F. As the reaction proceeded, the temperature was raised to 210° F. and held at this point for two hours, at which time no refluxing could be observed, indicating substantially complete conversion of the alcohol to the dithiophosphoric acid. The product was then cooled and filtered, and was found to contain 14.76% phosphorus and 28.56% sulfur, corresponding approximately to the following formula:



(Theoretical P=14.5%, S=29.9%)

Thereafter 60 grams diisopropyl dithiophosphoric acid prepared as above, were mixed with 540 grams of isopropyl alcohol (91%) as a solvent and 11 grams NaOH dissolved in 33 grams of water. The mixture was stirred and heated to reflux (178° F.) to promote reaction and then cooled to 120° F. Thereafter 540 grams of chlorinated ester prepared as above were added and heating was continued with refluxing for four hours. The alcohol and water were then stripped off under vacuum and the remaining product was filtered. Obviously other aliphatic alcohols may be used in lieu of isopropyl, those of 2 to about 10 carbon atoms being preferred.

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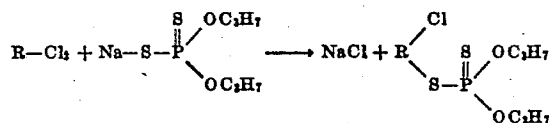
The quantity of dithiophosphate was selected in this case so as to react with approximately one-seventh of the chlorinated esters, and the final product therefore consisted of about 6 mols of chlorinated ester to one mol of the thiophosphate condensation product.

It will be understood, of course, that the proportions of thiophosphate and chlorinated esters may be varied over a wide range. Thus mol ratio of thiophosphate to chlorinated esters may vary from about 1:50 to about 2:1, the latter case representing complete reaction between the sodium salt and all the chlorine in the particular dichloro esters here used. When a higher proportion of chlorine is added to the original esters, even higher mol ratios of thiophosphate to chloro ester may be used.

The product thus obtained was a clear brown oily liquid, having the following analysis:

	Per cent
Phosphorus	14.3
Sulfur	25.6
Chlorine	14.19

It is believed that the condensation reaction proceeds according to the following equation:



where R represents a mixture of esters having the following approximate composition:

Approximate composition of commercial rosin esters

	Per cent
Methyl esters of abietic and neoabietic acid (contain 2 conjugated double bonds per mol)	23
Methyl ester of dihydroabietic acid (contains 1 double bond per mol)	22
Methyl ester of tetrahydroabietic acid (contains no double bonds)	22
Methyl ester of dehydroabietic acid (contains one benzenoid ring)	17
Unsaponifiable matter (pinenes, ethers, etc.)	16
	100

A blend of 10% by weight of the filtered product described above was prepared in SAE 90 grade mineral lubricating oil having the following characteristics:

Mineral oil components

	Stock A	Stock B
Percent used	50	50
Crude type	(1)	(1)
Refining method	(1)	(1)
Gravity, API	21.9	29.8
Flash	585	445
Vis/100	4909.4	375.1
Vis/210	204.3	58.0
VI	85	105
Con. Carbon	2.88	0.07
Sulfur	0.92	0.34

1 Mid-Continent.
2 Propane extracted.
3 Phenol extracted.

Tests on the Timken and SAE machines showed the product to have excellent extreme pressure properties and these properties were improved even further by the addition of a small

amount of tricresyl phosphate. The results of tests on the Timken and SAE machines are shown in the following:

Table I

Additives (In SAE 90 Oil)	Timken Machine			SAE Machine, Scale Lbs. Carried at 1000 R. P. M.
	OK Load (Lbs. on Lever)	Scar Width (in $\frac{1}{4}$ in.)	Unit Load (Lbs./Sq. In.)	
None (Mineral oil only).....	10	1.65	7,350	<20
10% Above Product.....	43	1.5	36,800	360
10% Above Product + Tricresyl Phosphate.....	63	2.05	42,500	365

It is to be understood that this invention is not limited to the particular esters, nor to the particular thiophosphoric acid referred to above, but may be applied to a great variety of esters and thiophosphoric acids. For example, it is shown in copending application Serial No. 9,617 filed February 19, 1948, by L. A. Mikeska and the present applicant, that dithiophosphoric acids derived from ditertiary octylphenol, ditertiary octyl phenol sulfide, and similar aryl and alkaryl hydroxy compounds can be used successfully in carrying out this reaction. It is also shown in the same application that esters of glycerin (for example, lard oil) and of monohydroxy alcohols (for example, sperm oil) are equally effective. It is therefore apparent that the essential limitations on the type of cyclic ester which may be used are as follows:

(1) It must react with halogens to form addition or substitution products capable of further reaction with an alkali salt. This includes both saturated and unsaturated rings except benzenoid rings, the latter being specifically excluded. It also includes alkyl and alkenyl (straight and branched chain) substituted rings whether benzenoid or not.

(2) The final condensation product must be relatively non-volatile at temperatures up to about 200° F.

(3) The final condensation product must be soluble in mineral oils to the extent of at least 1%. In general, this includes cyclic esters having molecular weights between about 150 and 2000.

Other halogens than chlorine, for example, bromine, may be employed to produce the halogenated esters. Likewise, in lieu of dithiophosphoric acids, the corresponding dithiophosphorous acids, or mixtures of these may be used. The proportions of reactive materials to be included in the additive composition per se should lie within the following limits:

Chlorine.....	Per cent About 5 to 50
Thiophosphate.....	About 1 to 25

Final product (additive)

P.....	Per cent 0.1-2.5
S.....	0.2-5
Cl.....	4-40

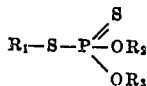
While the use of a 10% blend of the additive in mineral oil is suggested above, the proportions may vary from as little as 1.0% by weight based on the total composition, to as much as 20% or more, or the additive may be packaged and sold separately for combination by the ultimate user in suitable proportions and with various lubricating oils as will be understood by those skilled in the art. It will be understood further that lubricat-

ing compositions containing the extreme pressure additive described above may contain other materials such as oiliness agents, antioxidants,

corrosion inhibitors, viscosity index improvers, and the like.

The composition of this invention may be marketed as a concentrate, e. g. about 10% to 100% in a suitable solvent, which may be a lube oil of paraffinic, naphthenic, or other type, or other solvents such as xylene, kerosene, and the like. The use of 0.05 to 5.0% (on the basis of finished lubricant) of a separate phosphorus-containing composition such as tricresyl phosphate, tricresyl phosphite, and other organic derivatives of acids of phosphorus appears to augment the effectiveness of additives of the general type described above without increasing their corrosivity toward metals while at the same time improving the oiliness characteristics of the lubricant. For this reason the use of tricresyl phosphate, phosphite, and related materials, is recommended but is not essential inasmuch as the reaction product described above is a very effective extreme pressure agent in and of itself. The effectiveness of the agent appears to be due to the fact that it combines the load-carrying capacity of halogen, preferably chlorine, with those of sulfur and phosphorus. At the same time the composition appears to have good oiliness characteristics and to possess other properties which are desirable in lubricants of the extreme pressure type.

The composition of this invention is not to be confused with that described in U. S. Patent No. 2,347,592 to Cook and Thomas which describes hydrogenated abietyl alcohol esters of dithiophosphoric acid used as corrosion inhibitors. The present composition has the general formula

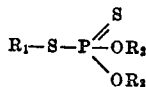


where R_1 is a rosin ester as described above, preferably halogenated, chlorine being the preferred halogen, the halogen content being preferably such as to provide 4 to 40%, preferably 5 to 20%, chlorine or other halogen in the product; R_2 and R_3 are similar or dissimilar alkyl hydrocarbon groups of straight or branched chain, preferably saturated and preferably of 2 to 10 carbon atoms.

The lubricating oil in which this additive may be used may vary considerably in type and viscosity. In general, petroleum base oils having a viscosity between 35 and 1000 S. S. U. at 210° F. are suitable.

What is claimed is:

1. A composition for use in lubricants and the like, consisting essentially of a material having the general formula



wherein R_1 is a halogenated rosin ester, and R_2

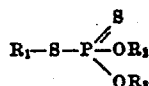
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and R₃ are aliphatic hydrocarbon groups of 2 to 10 carbon atoms each.

2. Composition as in claim 1 wherein R₁ is a chlorinated rosin ester.

3. Composition as in claim 1 wherein R₁ is chlorinated methyl abietate.

4. A lubricating composition consisting essentially of petroleum base oil of lubricating viscosity containing 1 to 20% by weight of a material having the general formula



wherein R₁ is a halogenated rosin ester, and R₂ and R₃ are aliphatic hydrocarbon groups of 2 to 10 carbon atoms each.

5. Composition as in claim 4 wherein R₁ is chlorinated methyl abietate.

6. Composition as in claim 4 wherein R₁ is chlorinated methyl abietate and R₂ and R₃ are isopropyl radicals.

7. The process of combining halogen, sulfur and phosphorus in a normally non-corrosive load carrying agent for lubricants which comprises halogenating an alkyl ester of rosin acids and reacting the halogenated product with an alkoxy dithiophosphoric acid salt of an alkali metal to

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obtain a condensation product of said halogenated ester and said thio salt.

8. The process which comprises chlorinating methylated rosin acids to a chlorine content of 5 to 50% by weight and thereafter reacting an alkoxy dithiophosphoric acid salt of an alkali metal with said chlorinated material to produce a condensation product containing active chlorine, sulfur and phosphorus.

9. The method of preparing an extreme pressure additive for mineral oil base lubricants which comprises chlorinating a commercial rosin ester consisting predominantly of methyl esters of abietic acids at a temperature of the range of about 70° to 250° F. to a chlorine content of the order of 5 to 50% by weight, neutralizing isopropyl di-thiophosphoric acid with sodium hydroxide, and condensing the isopropyl dithiophosphate and the chlorinated ester at a temperature of about 178° F.

ELMER B. CYPHERS.

REFERENCES CITED

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

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