Patented Dec. 3, 1940

2,223,793

UNITED STATES PATENT OFFICE

2,223,793

LUBRICATING COMPOSITION

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No Drawing. Application November 14, 1938, Serial No. 240,341

8 Claims. (Cl. 252—48)

The present invention relates to improved lubricating compositions and a method for producing the same.

As is well-known, the recent trend in modern machinery design has been toward more powerful and flexible machinery and toward increasing the efficiency by decreasing the effective area of contact of bearing and gear surfaces. The extent to which these trends may be carried is, however, sharply limited by the problems of lubrication thereby created. Certain types of bearings and gears, for instance, have recently come into wide use in which the operating pressures per unit area of working surface are so high that ordinary mineral oil lubricants will not provide adequate lubrication for satisfactory operation.

The main lubrication difficulty created by the newer machinery design is the difficulty in maintaining a film of lubricant between the lubricated metal parts. Under the high pressures per unit area of working surface employed, the thin film of lubricant between the metal surfaces is apt to rupture and thus allow metal to metal contact. This results in wear or scuffing, and under extreme conditions even to actual welding of the bearing metals.

It has been found that the addition of certain dopes or modifiers to ordinary lubricants increases the film strength and hence their ability to withstand greater working pressure without rupturing. Compounds capable of imparting this property to lubricants are commonly referred to as "extreme pressure dopes" or "E. P. dopes," and lubricating compositions containing them as "E. P. lubricants."

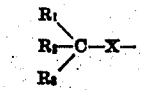
Although numerous compounds are capable of imparting E. P. characteristics to lubricants, nearly all of the known compounds have certain more or less objectionable characteristics. The main disadvantage often found in many of the E. P. compounds in use is the tendency to corrode the bearing surfaces and to create a sludge in the lubricant during use. Other disadvantages often found are the tendency to separate from the lubricant in cold weather and to raise the cloud and pour points of the lubricant.

Several E. P. compounds used are mixtures of two or more ingredients such as lead soaps, active sulfur, inactive sulfur, saponifiable vegetable oil, etc. Most of these, although showing high film strength on laboratory tests tend to form sludge or corrode the metal, especially alloy bearing metals, when used under severe conditions.

In general, it has been found that halogen (particularly chlorine) compounds tend to impart E. P. characteristics to lubricants. Although certain organic chlorine compounds are used to some extent, many of these compounds tend to break down during severe use, especially in the presence of moisture and thus cause corrosion of the metal parts. Another class of compounds found to impart E. P. characteristics to lubricants is the neutral organic esters of inorganic polybasic acids, especially phosphoric and thiophosphoric acids. These esters likewise tend to hydrolyze somewhat in the presence of moisture to form acid compounds which cause corrosion. The majority of these compounds furthermore must be used in appreciable quantities in order to impart the desired E. P. characteristics and in such quantities that they tend to promote channelling of the lubricant.

An object of the present invention is to provide new and superior E. P. lubricant compositions. Another object of the invention is to provide a class of E. P. compounds which, when added to lubricants, causes no substantial change in the other physical properties of the lubricant, such as the viscosity index, odor, pour point, channelling tendency, etc. Still another object of the invention is to provide a new class of E. P. compounds possessing the desirable properties of the chlorine compounds and of the organic esters of phosphoric and thiophosphoric acid hitherto used, but without their disadvantages. Still another important object of the invention is to provide a new class of E. P. compounds, which, when added to lubricants, impart extreme pressure characteristics but do not hydrolyze, corrode the metal parts or form sludge upon use, even in the presence of water and under severe conditions.

According to the present invention, common lubricants are made capable of affording lubrication under extreme pressure conditions without increasing the sludging or corrosion tendency of the lubricant by dissolving therein a small quantity of a suitable tertiary alcohol ester of a halide of phosphorus containing two halogen atoms attached to the phosphorus atom. The tertiary alcohol groups of the compounds of the present invention have the general structure



wherein R_1, R_2 and R_3 represent the same or different lipophile groups, and X represents oxygen or sulfur. As an example of the most suitable lipophile groups which may be attached to the tertiary carbon atom may be mentioned phenyl, toluenyl, xylenyl, diphenyl, chlorophenyl, p-tertiary octyl phenyl, p-isopropyl phenyl, orthophenyl phenyl, metaphenyl phenyl, alpha naphthyl, beta naphthyl, cyclohexyl phenyl, cyclopentyl phenyl, methoxyphenyl phenyl, phenoxypropyl phenyl, meta oxybenzyl phenyl, and the like.

The tertiary alcohol groups, such as any of the above, are linked through oxygen or sulfur, as the case may be, directly to the phosphorus atom, which, in turn, is attached to two halogen atoms. Thus, for example, the compounds of the present invention have the structures

$$\text{ester}-P=Hal_2$$

in the case of phosphorous compounds, and

$$\text{Ester}-\overset{\overset{O}{\|}}{P}=Hal_2$$

in the case of phosphoric compounds wherein, in both cases, Hal represents an atom of halogen, and ester represents an alcohol residue of the above-described class.

These compounds, particularly the phosphorous compounds, are exceptionally well suited as E. P. compounds, since they effectively raise the film strength of lubricants; they are not corrosive or sludging; they have a suitable solubility in lubricants; they are effective in small concentrations and do not appreciably alter the other physical properties of the lubricant; they are easy to prepare, inexpensive, easily handled and do not possess an objectionable odor; they are stable to heat and do not volatilize from the lubricant.

The following typical example clearly demonstrates the effectiveness of the present type of E. P. compounds in increasing the film strength of ordinary lubricants. Three samples of a lubricating oil which had a viscosity of 80 seconds (S. U. at 210° F.) were prepared. The first sample was left undoped and to the second and third were added .05% and 1.5% by weight of triphenyl methoxy phosphorus dichloride, respectively. Tests were conducted on the Timken tester to determine the film strength of the samples with the following results:

Sample	Timken	
	O. K. value	Lbs./in.² failure
1	2,700	5,714
2	8,575	11,430
3	34,280	37,110

As can be seen, the addition of only .5% of the E. P. compound greatly enhanced the load carrying capacity of the hydrocarbon oil, while the addition of 1.5% rendered the oil suitable for use under the most severe conditions of extreme pressure.

While I do not desire my invention to be limited by the soundness or accuracy of any theories advanced to explain the advantageous results obtained, I believe that the excellent ability of the present E. P. compounds to impart E. P. characteristics to ordinary lubricants is due to the presence of the the very strong polar group, i. e., the phosphorus-halogen linkage in combination with the very voluminous lipophillic group of strong negative character.

It will be noticed that the lipophillic ester groups of the present invention are much more voluminous than the ester groups of other esters of phosphorus, such as triphenyl phosphate, tricresyl phosphate, etc., hitherto used. As a consequence, it is to be expected that the present compounds will be effective in much lower concentrations, and this is indeed the case.

The phosphorus-halogen linkage contained in the present compounds, it is seen, combines the effective polar groups of both the neutral esters of phosphorus and the chlorine compounds hitherto found to possess valuable E. P. characteristics. While organic esters of phosphorus containing one or two halogen atoms attached to the phosphorus atom have long been known, it was hitherto believed impossible to utilize these compounds as E. P. compounds due to the fact that most compounds of this structure readily hydrolyze to give halogen acid and an acid ester of phosphorus. Thus, for example, all of the halogen-containing esters of phosphorus of the general structures

$$O=P(OR)(Hal)_2,\quad O=P(OR)_2Hal,\quad P(OR)Hal_2 \text{ and } P(OR)_2Hal$$

wherein R represents an aromatic or alkyl group are readily hydrolyzed under mild conditions, most of them, in fact, being hydrolyzed almost completely by simply contacting with cold water. I have found, however, that if the lipophillic ester group attached to the phosphorus atom through oxygen or sulfur is a suitable tertiary alcohol group, very stable compounds are formed which are exceptionally resistant to hydrolysis. The extraordinary resistance of the present compounds to hydrolysis will be appreciated when compared with other comparatively stable compounds such as the chlorine compounds and esters of phosphorus, commonly used in E. P. lubricants. Thus, for example, the ordinary chlorine compounds commonly used and the common organic esters of phosphoric acid such as tributyl phosphate, triphenyl phosphate, tricresyl phosphate, triphenyl phosphite, etc., very slowly hydrolyze in the presence of water, especially if hot, and are readily hydrolyzed in a short time by heating with dilute alkali. The present compounds, on the other hand, show no hydrolysis with either hot or cold water and can even in most cases be boiled with concentrated aqueous caustic soda without any noticeable hydrolysis. As a consequence of the stability and resistance of the present compounds against hydrolysis, these compounds may be used in lubricants even in the presence of moisture without fear of corrosion or sludging.

The present E. P. compounds may be dissolved in any of the common lubricants such as mineral oils, vegetable oils and the like to increase their film strength. Mineral oil, for example, may be only slightly refined or highly refined with sulfuric acid and/or by treatment with any of the solvents commonly used for that purpose. Since refining treatments in general decrease the film strength of the oil, especially refining by solvent extraction, the present E .P. compounds may be most advantageously used in highly refined oils. For example, very highly refined mineral oils having low film strength may be greatly improved by the addition thereto of

only about 0.1% of the present E. P. compounds, These compounds may, of course, be used in oils of various viscosities, synthetic mineral oils, mixtures of mineral oils containing pour point depressors, waxes, etc., grease bases, cutting and pouring oils, etc.

The present E. P. compounds may be used in any proportion from traces up to their limit of solubility. While, in general, concentrations in the order of 0.5% are sufficient to raise the breakdown pressure of common mineral oil lubricants about 5,000 to 7,000 pounds per square inch (as measured by the Timken tester) much higher film strengths may be obtained by employing larger quantities.

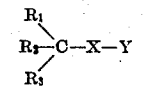
The solubility of the present E. P. compounds in mineral oils varies considerably with the nature and size of the lipophile groups, increasing, in general, as the number of carbon atoms in the aromatic groups increases. The compounds of the present invention, especially the lower members, such as tritoluenyl methoxy phosphorous dichloride, tri-p-tertiary butyl phenyl methoxy phosphorous dichloride, etc., have the advantage of not being too soluble in the usual mineral lubricants. It is, therefore, practical to saturate the mineral lubricant with these compounds. This is of advantage since with such lubricant compositions, adsorption of the E. P. compound on the bearing surface is enhanced.

The present compounds may be easily prepared, in general, with very good yields according to well-known methods. One suitable method, for example, is to add the alcohol to half its weight of the desired halide of phosphorus at about 0° C., allow to stand for a short time and then heat to about 100° C. to complete the reaction. The product may be recovered pure from the reaction mixture by washing with water, dissolving in a solvent such as chloroform, and reprecipitating by adding a diluent such as acetone.

Although throughout the present description I have frequently referred to the problem of lubrication under conditions of extreme pressure, and have chosen to refer to my new lubricating composition in the customary manner as extreme pressure or E. P. lubricants, it is to be understood that the lubricant compositions of the present invention may also be used to advantage for lubrication under moderate or even very mild conditions, such as, for example, in the lubrication of the bearings, etc., in internal combustion engines, in ordinary gear transmissions, reduction gear assemblies, cable greases, cup greases and the like. In such cases, where the lubricant is designed to be used under conditions involving only moderate working pressures only very small quantities such as, for example, 0.05% to 0.15% of the present E. P. compounds need be used. It should be understood, however, that unlike the more common hitherto used E. P. compounds, the use of more of the present E. P. compounds in the lubricant than is essential for the purpose for which it is to be used is not detrimental to the lubricant.

I claim as my invention:

1. A lubricant comprising a mineral lubricating oil and an amount sufficient to impart extreme pressure properties of a compound having the structure

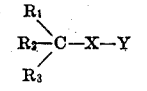


wherein R_1, R_2 and R_3 represent aryl radicals, X is an element selected from the group consisting of oxygen and sulfur, and Y is a phosphorous halide radical containing two halide atoms attached to the phosphorus.

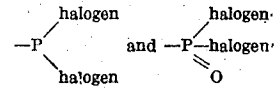
2. The lubricant of claim 1 wherein the phosphorus is trivalent.

3. The lubricant of claim 1 wherein the halogen is chlorine.

4. A lubricant comprising a mineral lubricating oil and an amount sufficient to impart extreme pressure properties of a compound having the structure



wherein R_1, R_2 and R_3 represent aryl radicals, X is an element selected from the group consisting of oxygen and sulfur and Y is a radical selected from the group consisting of



5. A lubricant comprising a mineral lubricating oil and an amount sufficient to impart extreme pressure properties of an ester combining aryl tritertiary carbinol with a halide of phosphorus, said ester containing two halogen atoms attached to the phosphorus.

6. A lubricant comprising a mineral lubricating oil and an amount sufficient to impart extreme pressure properties of a mono ester combining butyl phenyl tritertiary carbinol with phosphorus trichloride, said ester containing two atoms of chlorine attached to the phosphorus.

7. A lubricant comprising a mineral lubricating oil and an amount sufficient to impart extreme pressure properties of a mono ester combining phenyl tritertiary carbinol with phosphorus trichloride, said ester containing two atoms of chlorine attached to the phosphorus.

8. A lubricant comprising a mineral lubricating oil and an amount sufficient to impart extreme pressure properties of a mono ester combining butyl phenyl tritertiary thiocarbinol with phosphorus trichloride, said ester containing two atoms of chlorine attached to the phosphorus.

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