

UNITED STATES PATENT OFFICE

2,188,943

LUBRICANT AND METHOD OF PRODUCING
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Serial No. 56,451

11 Claims. (Cl. 87-9)

The present trend in automobile design toward rapid acceleration and the use of hypoid gears has increased the unit loading on rear axles. In many cases the unit pressures encountered are sufficiently great to rupture the lubricating film when that film has been produced from ordinary mineral oil. Numerous other new mechanical power transmission devices, such as free-wheeling devices and the like, also develop pressures of these magnitudes. Lubricants having special lubricating properties designed for use under these conditions are referred to as extreme pressure lubricants. This invention is specifically directed to novel extreme pressure lubricants.

For lubrication of automobile gears and the like, prior to the advent of extremely high pressures per unit area of bearing, use was made of oils which were residual or overhead petroleum hydrocarbons of high viscosity of the general nature of cylinder stocks. Upon the increase of pressures as referred to above, it was found that mineral hydrocarbon lubricants alone were not capable of maintaining film and/or lubrication under the conditions encountered, and resort was had to extreme pressure lubricants consisting of the usual mineral hydrocarbon oils together with a characterizing ingredient which imparted extreme pressure lubricating properties to the lubricant. Characterizing extreme pressure ingredients commonly used have included free sulfur, chemically bound sulfur, chlorinated organic hydrocarbons, and the like. Such materials have the common disadvantage of corroding the metallic surface intended to be lubricated. Metallic soaps such as metal oleates, naphthenates, sulphonates, and the like, have also been used, but have been found to give only moderate aid in extreme pressure lubrication.

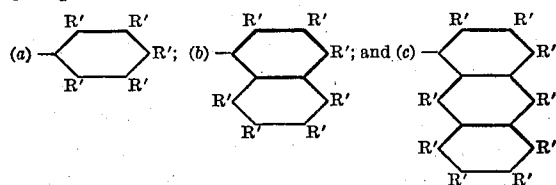
It is an object of this invention to provide an extreme pressure lubricant, together with a base for use in compounding same, which lubricant has superior properties, such as load carrying capacity, stability, maintenance of extreme pressure lubricating properties under sustained conditions of high loading, and non-corrosive properties. It is an object of this invention to prepare novel and valuable ingredients and to combine them with hydrocarbon lubricant oils to produce lubricants having high load bearing capabilities, to prepare such ingredients which have good characteristics of stability, which are less corrosive, and which impart a greater influence when present in much smaller amounts than are required with ordinary extreme pressure ingredients. Further objects are the provision of

methods of preparing lubricants containing these novel characterizing ingredients, lubrication of mechanisms involving extreme unit pressures, and other advantages as hereinafter appear.

This invention is based upon the discovery that novel lubricants having exceptional ability to lubricate effectively under conditions of extreme pressure loading may be produced by incorporating with a hydrocarbon lubricant oil a small proportion of a compound having the general formula



where R is an aryl radical, selected from the group consisting of radicals of the general types



In these general types R' may be any radical selected from the group consisting of hydrogen, hydroxy, aryl, alkyl, alkaryl, arakyl, halogen, nitro, or amino. The aryl compounds generally preferred for the purposes of this invention are those corresponding to the above general formula where R is selected from the groups (a) and (b) as defined above and where the R's are preferably hydrogen or alkyl. Where R' is alkyl, one or more of such alkyl substituents may be an alkyl of high molecular weight, such as, for example, an alkyl corresponding to a crystalline petroleum wax. The thiophosphites preferred for the purposes of this invention are the triaryltrithiophosphites. As examples of compounds of the preferred class suitable for the purposes of this invention, there may be given triphenyl trithiophosphite, the tritolyl trithiophosphites, and the trinaphthyl trithiophosphites.

Other compounds of this general type, generally suitable for the same purposes, particularly where in any given compound all three R's are the same, may be produced with radicals selected from the following group: Meta-hydroxy-phenylene, para-hydroxy-phenylene, tolyl, xylyl, xenyl (or biphenyl), methyl-xenyl, ethyl-xenyl, anisyl, ortho-phenetyl, chlor-phenylene (o,m,p), brom-phenylene (o,m,p), nitro-phenylene (o,m,p), amino-phenylene (o,m,p), methyl-naphthylene, phenyl-naphthylene, chlor-

naphthylenes, brom-naphthylenes, nitro-naphthylenes, amino-naphthylenes, corresponding anthryls, and the hydrogenated or cyclo forms of the above, usually designated as saturated closed ring compounds as, for example, cyclohexyl, methyl cyclohexyl, phenyl cyclohexyl, benzyl cyclohexyl, halogen, nitro and amino cyclohexyls and the like.

The preferred compounds with which this invention is concerned may be generally described as the reaction products resulting from the reaction of a compound of the nature a thiophenol, or substituted or condensed thiophenol, with phosphorus trichloride. The preferred proportions are three molecular amounts of the thiophenol substance to one molecular amount of the phosphorus trichloride.

The preferred embodiment of this invention contemplates an extreme pressure lubricant comprising a small proportion of a triaryl trithiophosphite, that is a compound of the general formula $(ArS)_3P$, with a hydrocarbon mineral oil. This new composition possesses distinct advantages as an extreme pressure lubricant capable of maintaining an oily lubricant film under high unit loading and preventing seizure of the metallic parts in contact under extreme pressures.

As an example of my new extreme pressure compounds, and their method of manufacture, I may describe the manufacture of triphenyl trithiophosphite, $(C_6H_5S)_3P$. This and other aryl trithiophosphites are easily prepared. For example, one molecular proportion of phosphorus trichloride is gradually added to three molecular proportions of thiophenol. Hydrochloric acid gas is evolved and is measured as it forms, since the formation of each molecular amount of product is accompanied by the evolution of three molecular amounts of HCl gas, and its measurement forms an easy means of control. The reaction proceeds without difficulty at ordinary temperatures, but I have found it best to finally heat the mixture to about 160° C. in order to insure complete reaction. The reaction mixture so produced is chiefly triphenyl trithiophosphite. The main impurities are dissolved HCl and a small amount of thiophenol. These may be removed by distilling until a temperature (in the liquid) of 150° C. is reached. The addition of a hydrocarbon solvent such as "Stoddard", (which has a boiling range of 300° F. to 400° F.), prior to the distillation, aids in the complete removal of impurities. The residual product solidifies at about 74° C. and if desired may be obtained in a very pure form by recrystallizing from a solvent such as ethyl alcohol. The crude product, however, may be used for the purposes of this invention without this further purification. The specific compound thus formed, triphenyl trithiophosphite, is a white crystalline product which is quite soluble in mineral oil. It does not darken the original color of the mineral oil and it has no tendency to separate from the oil or to form sludge under normal storage conditions. It is a stable substance of high boiling point. Similar compounds may be similarly prepared from any of the thiophenols or substituted or condensed thiophenols as outlined above, having similarly effective properties. The same is true for the preparation of the triaryltrithiophosphites in general.

As an example of the ability of extreme pressure lubricants containing these novel characterizing ingredients, the following tabular data is presented. In evaluating oils or lubricants of this type

use may be made of the Almen Pin Test Machine described by Mougey and Almen (Proc. A. P. I. 1931, page 77), where a pin is rotated in bearings so designed that increasing pressure may be applied to the lubricated surface. This machine is used widely in such comparative evaluations. In the following tabulation of results from the Almen Pin Test Machine, column 1 shows the pressure in pounds per square inch applied to the lubricated contact surface. The other columns show the torque in foot pounds transmitted through the pin at the given pressures with the respectively described lubricants, and also show the pressure at which lubrication failed, resulting in seizure of the surface of the bearing and pin.

Almen tests of samples

1	2	3	4	5	6
Weights	Original viscous mineral oil	Containing 1% $(C_6H_5S)_3P$	Containing 2% $(C_6H_5S)_3P$	Containing 5% $(C_6H_5S)_3P$	2% sample after 24 hrs. at 300° F.
1,000					
2,000	0.5	0.7	0.7	0.7	0.7
3,000	Seized	0.9	1.0	1.0	1.0
8,000		2.7	2.4	2.7	2.4
9,000		3.2	2.7	2.9	2.6
10,000		Seized	2.9	3.2	2.9
19,000			4.2	3.8	3.9
20,000			4.5	3.8	4.0
21,000			4.8	3.9	4.1
22,000			6.0	Seized	4.1
23,000			Seized		4.2
24,000					4.2
25,000					6.0
26,000					Seized

In the above described tests, the oil used in column 2 is a mineral hydrocarbon oil of cylinder stock type having the following characteristics:

Saybolt Universal viscosity at 210° F. 165"
 Color Lovibond 170-210
 Pour 20° F.

This is oil of the type commonly used in compounding extreme pressure lubricants, and in the absence of characterizing ingredients is frequently used alone, although the data show it to be quite ineffective for the purpose. This same oil was used in compounding the oils whose tests appear in columns 3 to 6, inclusive. In column 3, it was compounded with 1% of triphenyl trithiophosphite. In column 4, it was compounded with 2% of that ingredient, and in column 5 with 5%. In column 6, the oil of column 1 was compounded with 2% of triphenyl trithiophosphite, and in order to test the persistence of the characterizing ingredient upon exposure to heat, the sample was subjected to heat at 300° F. for 24 hours, afterward being cooled and tested with the results shown in column 6. Generally similar results may be obtained with the other compounds mentioned above and the general classes of compounds defined above. The novel extreme pressure lubricants herein disclosed are quite effective for the purposes intended and are stable under conditions of heating far in excess of those to which they are ordinarily subjected in actual use. Lubricating oils so prepared are not corrosive to the metals encountered in use, since they do not darken or corrode copper or steel when maintained in contact with them for 24 hours at 300° F.

The amount of these novel ingredients which may be added to mineral hydrocarbon oils to produce extreme pressure lubricants will vary from about 1 to about 5%, although it is pre-

ferred to use about 2% to produce lubricants of desired properties.

In the claims, the term "extreme pressure lubricating composition" means either (and includes all) the finished lubricant as actually used, the characterizing extreme pressure lubricant itself, or any intermediate extreme pressure lubricant base, admixture or dilution containing the active ingredient.

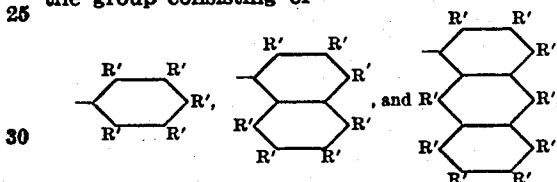
I claim:

1. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small proportion of a triarylthiophosphite.

2. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small proportion, sufficient to act as a characterizing extreme pressure ingredient, of a compound of the general formula

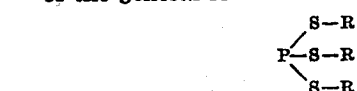


where at least one R is a radical selected from the group consisting of

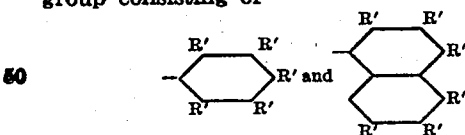


and where the R's are radicals selected from the group which consists of hydrogen, hydroxy, alkyl, aryl, aralkyl, alkaryl, alkoxy, halogen, nitro, and amino.

3. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small amount, sufficient to act as a characterizing extreme pressure ingredient, of a compound of the general formula

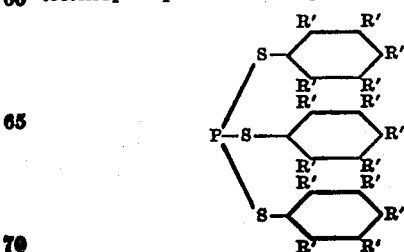


where the R's are radicals selected from the group consisting of



and where the R's are selected from the group which consists of hydrogen and alkyl.

4. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small amount, sufficient to act as a characterizing extreme pressure ingredient, of a triarylthiophosphite of the general formula

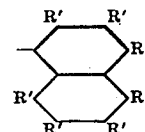


where the R's are radicals selected from the group which consists of hydrogen and alkyl.

5. An extreme pressure lubricating composition, consisting of a hydrocarbon lubricant and a small amount, sufficient to act as a characterizing extreme pressure ingredient of a triarylthiophosphite of the general formula



where each of the said R's is a radical of the general type



and where the R's are radicals selected from the group consisting of hydrogen and alkyl.

6. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small amount of a compound selected from the group consisting of triphenyltrithiophosphites, tritolyltrithiophosphites, and trinaphthyltrithiophosphites, sufficient to increase the load bearing capacity thereof.

7. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and small amount of a triarylthiophosphite wherein the aryl radicals are selected from the group consisting of phenyl, tolyl, naphthyl, meta-hydroxy-phenylene, para-hydroxy-phenylene, tolyl, xylyl, xenyl (or biphenyl), methyl-xenyl, ethyl-xenyl, anisyl, ortho-phenetyl, chlor-phenylene (o,m,p), brom-phenylene (o,m,p), nitro-phenylene (o,m,p), amino-phenylene (o,m,p), methyl-naphthylene, phenyl-naphthylene, chlor-naphthylenes, brom-naphthylenes, nitro-naphthylenes, amino-naphthylenes.

8. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small amount, but not in excess of 5%, of a triarylthiophosphite.

9. An extreme pressure lubricating composition consisting of a hydrocarbon lubricant and a small amount, but not in excess of 5%, of a compound selected from the group consisting of triphenyl trithiophosphites, tritolyl trithiophosphites, and trinaphthyl trithiophosphites, sufficient to increase the load bearing capacity thereof.

10. The method of lubricating relatively moving bearing surfaces engaged under extreme pressure which comprises maintaining between said surfaces a hydrocarbon lubricant film and at the same time chemically acting upon said engaged surfaces with a minor proportion of a triarylthiophosphite contained within the lubricant film.

11. A lubricating composition comprising a hydrocarbon lubricant and in admixture therewith a minor proportion of a triaryl trithiophosphite in which at least one aryl radical has at least one relatively long alkyl substituent of the general character corresponding to paraffin wax.

WILLIAM L. EVERS.

CERTIFICATE OF CORRECTION.

Patent No. 2,188,943.

February 6, 1940.

WILLIAM L. EVERS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 1, for the word "automobile" read --automotive--; line 32-33, for "materails" read --materials--; same page, second column, line 33, for "R's" read --R's--; page 3, first column, lines 33 and 54, and second column, lines 1 and 21, claims 2, 3, 4, and 5 respectively, for "R's" read --R's--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of June, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.