

UNITED STATES PATENT OFFICE

2,643,261

PHOSPHORUS-CONTAINING LUBRICATING
OIL ADDITIVES

Alfred H. Matuszak, Jersey City, and Charles A. Weisel, Somerville, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application October 1, 1948,
Serial No. 52,394

3 Claims. (Cl. 260—399)

1

The present invention relates to phosphorus-containing lubricating oil additives and also lubricants containing such additives which have exceptional properties which are highly useful in lubricating oil compositions and the like. The invention pertains more particularly to certain combined esters involving phosphorus, a mono-basic acid radical, and a polyhydric alcohol radical.

It has been suggested in the prior art that certain organic derivatives of acids of phosphorus, for example, the organic phosphates and phosphites such as tricresyl phosphates, tributyl phosphites, and the like, have certain useful properties in lubricating oils.

It is also known in the prior art that esters of certain polyhydroxy alcohols have some utility as rust inhibiting compounds, and the present invention is based upon the discovery that unexpected desirable properties may be obtained by combining organic-phosphorus radicals with such ester radicals. Some of the properties so obtained are extreme pressure load-carrying properties, rust, and other corrosion inhibiting properties, and the like. By combining these materials into a single molecule, the properties obtained are materially superior to those which can be obtained by a physical combination of the ingredients. The new types of esters have desirable properties in themselves but the invention contemplates also their combination with oils such as mineral lubricating oil, synthetic oils, coating compositions, rust inhibiting slushing oils, and the like.

The esters which characterize the present invention may be prepared by reacting pentaerythritol, dipentaerythritol, polypentaerythritol, and the like, with a mono-basic acid and a phosphorus-containing acidic compound. The ester of the polyhydric alcohol and mono-basic acid is preferably prepared first either as a mono-ester or as a polyester. This ester is then subsequently treated with a phosphorus-containing acidic compound to produce the phosphate ester product disclosed herein. The mono-basic acid is preferably an aliphatic acid which may be saturated or unsaturated and is preferably of a chain length of 6 to 24 carbon atoms. Although a long chain acid having a single unsaturated bond such as oleic acid and its immediate homologs is preferred, other acids or mixtures of acids such as tall-oil acids or those acid mixtures derived from naturally occurring products may be employed without affecting appreciably the desired properties of the phosphate ester. The phosphorus-containing acidic compound may be

2

POCl_3 , PCl_5 , PSCl_3 , and the like, or mixtures of any two or more of these.

The method of preparing esters and the probable formulas of such esters are set forth in greater detail below. The esters are found to be effective oiliness agents, anti-wear agents, extreme pressure additives, rust and other corrosion inhibitors, and they may have other desirable properties. They appear to be useful in preventing the sticking of piston rings in internal combustion engines and they also have some utility as pour point depressors, film strengtheners, viscosity index improvers, and detergents. The lighter compounds, i. e., those of lower molecular weight, may be used as ingredients of penetrating fluids, varnish removers, and the like. These materials are useful also as sludge dispersers in internal combustion engine oils. For the above purposes, the proportions may vary but in general the combined esters of the present invention may be blended into base oils in concentrations as low as 0.01% by weight to as high as 10% by weight or more. In some cases, it is desirable to market concentrates in mineral oil, for example, and in such cases the concentrations of the combined esters may be considerably higher, for example, 50% or more by weight, depending upon the solubility of the phosphorus-containing esters.

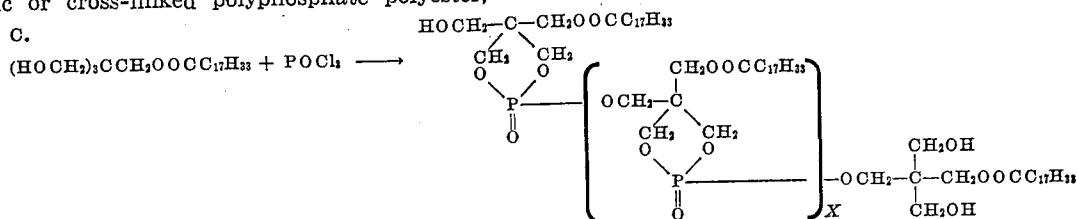
Although these materials are particularly useful for blending into mineral base lubricating oils, they may also be blended into petrolatums, lubricating greases, coating or slushing compounds, and into analogous oils and compositions based on synthetic lubricants such as the esters of dibasic acids, polyalcohol derivatives, and the like.

Since these materials involve the esterification of polyhydric compounds which may have several hydroxyl groups, the polyester compounds may be either monomeric or polymeric in nature. The invention contemplates also the use of mixtures of monomers or polymers or both. Also for some purposes a mono-hydric alcohol may be employed to form a part of the ester linkages of the phosphorus-containing reagent. As previously suggested, the mono-basic acid is normally a monocarboxylic acid such as oleic, stearic, lauric, one of their homologs, a mixture of their homologs such as might be derived by the oxidation of petroleum products, or a mixture of acids obtained from naturally occurring products.

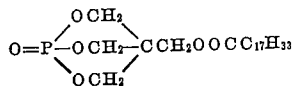
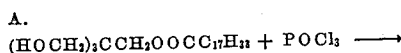
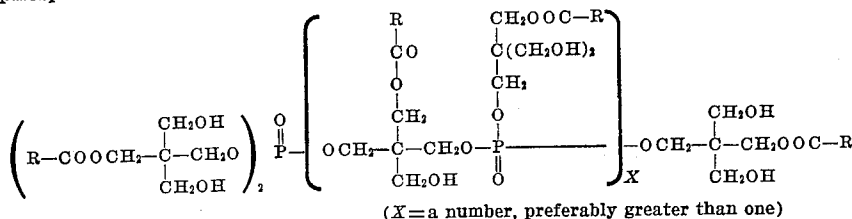
Pentaerythritol is a typical example of a polyhydric alcohol whose ester may be reacted with a phosphorus-containing acidic compound to produce a combined ester of the type under con-

3

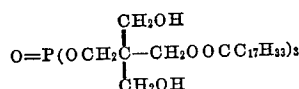
sideration. As mentioned previously, the monobasic acid ester may first be prepared, after which the ester may be reacted with a phosphorus-containing compound. For example, pentaerythritol mono-oleate may be reacted with POCl_3 to yield a mixed phosphate ester of pentaerythritol mono-oleate. The same reaction may be carried out with PCl_3 or PSCl_3 . In the case of those reactions where hydrochloric acid is released in the reaction, it is desirable to remove the HCl and this may be done conveniently by employing a neutralizing agent such, for example, as pyridine. The following equations illustrate, respectively, monomeric phosphate polyesters, a polymeric or cross-linked polyphosphate polyester,



and a phosphate polyester prepared from pentaerythritol mono-oleate and POCl_3 and a monohydric alcohol ROH which is indicated in Equation C reacted with the phosphorus atom.

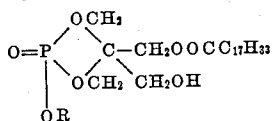
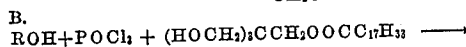
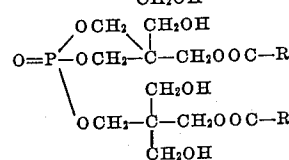
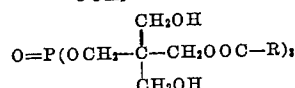
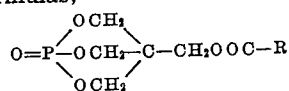


and/or



By the above reaction a monophosphate polyester compound may be obtained.

In general, several types of monophosphate polyesters can be prepared, having the following general formulas;



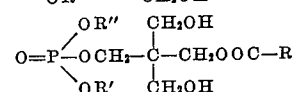
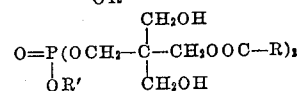
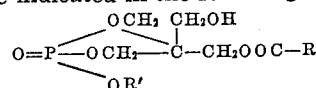
Alcohol Treated Monomer

$\text{R} = \text{C}_1 - \text{C}_{30}$ hydrocarbon radical

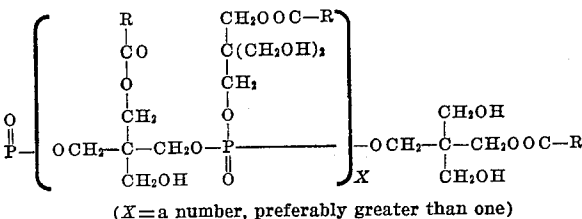
4

By this formula there is obtained a monophosphate mixed polyester.

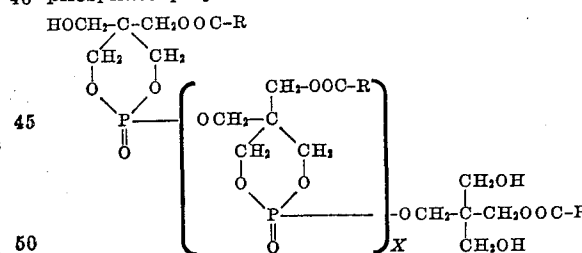
General types of monophosphate mixed polyesters are indicated in the following formulas:



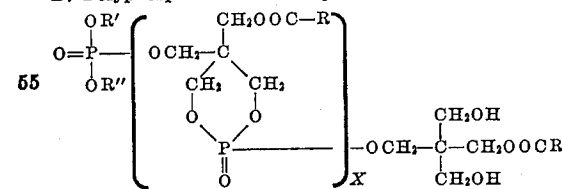
By this formula a polyphosphate polyester may be obtained. Analogous non-cyclic products also may be prepared. An example is indicated in the next formula.



A more general formula for the cyclic polyphosphate polyester is the following:



D. Polyphosphate Mixed Polyesters



It will be noted that several of the compounds shown above contain free or unesterified hydroxyl groups. The number of such unesterified hydroxyl groups in any of the above polyester compounds may be varied, or if desired, the polyester may be completely esterified by properly regulating the ratio of the reactants. It will be understood, therefore, that the formation of many polyesters not shown in the above formulas is possible and that the polyesters coming within the scope of the invention are not limited by these formulas. The reactions indicated may be caused to proceed at various rates by changing the reaction temperature which is normally kept between 0 and 150° C., the exact operating tem-

perature being dependent to a large degree upon the reactivity of the phosphorus containing reactant or reactants. These polyester products are readily synthesized and in some cases may be prepared without the use of the catalysts, but it may be desirable to use a catalyst such as sulfuric acid, toluene sulfonic acid, or the like, in the alcohol-carboxylic acid esterification process. Generally no catalyst is required in preparing the phosphate esters. Instead of using POCl_3 , PCl_3 may be used, in which case polyesters will be produced which contain phosphite and monobasic acid ester linkages.

As previously described in connection with Formulas B and C above, the polymeric or cross-linked as well as the mono-hydric alcohol treated polyester compounds may also be formed in reactions involving the phosphorus-containing sulfides. The invention is not limited to the compounds named, since many equivalent substances will suggest themselves to those skilled in the art. Various modifications and combinations of the several reagents are possible.

The invention will be more fully understood by reference to the following examples:

EXAMPLE 1

A mixed phosphate of a C_8 oxo alcohol (prepared by combining an olefin with carbon monoxide and hydrogenating) and pentaerythritol mono-oleate was prepared as follows: To a constantly stirred mixture containing 135 parts by weight of pentaerythritol mono-oleate, 350 parts of benzene, 130 parts of C_8 oxo alcohol and 127 parts of pyridine there were added drop by drop 77 parts of phosphorus oxychloride (POCl_3).

The temperature was maintained below 10°C . while the POCl_3 was being added. After addition was completed, the mixture was permitted to warm to room temperature after which it was refluxed for 3 hours. The mixture thereafter was thoroughly washed with water and the solvent benzene was stripped therefrom at 150°C . at a reduced pressure of 10 mm. This yielded in addition to the solvent 20 parts of the C_8 oxo alcohol. The higher boiling residue, which amounted to 260 parts by weight, consisted of the mixed phosphate ester.

The mixed ester prepared as just described was evaluated for its rust inhibiting properties by employing it in various concentrations in a standard phenol extracted Mid-Continent lubricating oil of about 120 S. U. S. viscosity at 210°F . The test compositions so prepared were used as a crankcase oil in a standard single cylinder Wisconsin engine. After running the engine for eight hours with each of the test oils, the cylinder was removed from the engine and stored without any further treatment in a Tenney humidity cabinet in which the temperature was caused to vary between 72° and 90°F . and the relative humidity between 94 and 53% during each 24 hour cycle. Such conditions highly favor rusting and simulate a typical summer day in Cuba.

After five days' storage under the warm humid conditions just described, the amount of rust which developed was determined and recorded in terms of percent of the total cylinder barrel area rusted. The base oil alone and the base oil with 1% by weight of pentaerythritol mono-oleate without any other inhibitor were evaluated for comparative properties along with the base oil containing, respectively, 0.25%, 0.5%, and 1% by weight of the ester. The results of these tests are tabulated as follows:

Table I

Oil	Wisconsin Engine Rust Tests—Blend	Percent Cylinder Barrel Area Rusted After 5 Days
A.....	1 wt. percent Ester in Base Oil.....	2
B.....	0.5 wt. percent Ester in Base Oil.....	9
C.....	0.25 wt. percent Ester in Base Oil.....	11
D.....	1 wt. percent Pentaerythritol Mono-Oleate in Base Oil.....	10
E.....	Base Oil (no added rust inhibitor).....	35

These data show very clearly that the mixed phosphate ester composition prepared as described above greatly inhibits cylinder barrel rusting when employed as an additive in a crankcase lubricating oil. In addition, this pentaerythritol mono-oleate C_8 oxo alcohol phosphate appears to be a more effective rust inhibitor than the pentaerythritol mono-oleate from which it is derived. Pentaerythritol mono-oleate itself has been considered a very effective inhibitor and the substantial superiority of the mixed ester prepared as above is noteworthy.

EXAMPLE 2

A blend of mineral lubricating oil of about 45 S. U. S. viscosity at 210°F . containing 2% by weight of the mixed phosphate ester of Example 1 was tested in a Shell Four Ball machine and also in an Almen machine to determine its anti-wear properties and film strength properties, respectively. The base oil was also tested and for comparative purposes the same oil containing 2% by weight of a standard commercial oiliness agent and one containing 2% of pentaerythritol mono-oleate were evaluated in the same manner. The results of these tests were as follows:

Table II

LOAD CARRYING PROPERTIES OF OILINESS AGENTS

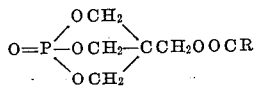
Oil	Blend	Shell 4-Ball Machine, 20 kg. Load—30 Min., Wear Spot Dia., mm.	Almen Machine, Weights Carried, Gradual Loading
A.....	2% Mixed Phosphate Ester (Example 1) in Base Mineral Oil.....	0.39	8
B.....	2% Commercial Oiliness Agent in Base Mineral Oil.....	0.52	4
C.....	2% Pentaerythritol Mono-Oleate in Base Mineral Oil.....	0.52	4
D.....	Base Mineral Oil.....	0.65	2-3

The foregoing data indicate that esters prepared according to the present invention possess superior properties in anti-wear and film strength to either the standard commercial oiliness agent or to the pentaerythritol mono-oleate ester from which the mixed ester was derived.

In general the invention includes the phosphorus containing esters (including thiophosphorus esters) of alcohols which are also partially esterified by a monobasic acid, especially a monobasic fatty acid having 6 to 30 carbon atoms, preferably 8 to 24 carbon atoms. The composition by itself, as well as an ingredient of lubricating oil is contemplated.

More specifically, the invention contemplates the mixed phosphate and/or phosphite esters of alcohol partially esterified with a monobasic acid, preferably an organic acid, especially a fatty acid of 6 to 30 carbon atoms. The somewhat narrower range of 8 to 24 carbon atoms in the fatty acid

chain is preferred for some purposes. The rust inhibiting composition may have the formula



where R is an alkyl group of 6 to 30 carbon atoms, but the invention comprehends various modified formulas, as indicated above, and also 10 comprehends their use in varying proportions, from as little as 0.01% to 50% by weight, based on the total composition, in lubricants such as lubricating oils, greases, etc. The higher percentages will be used, for example, in concen- 15 trates, the normal amounts to be employed in finished products being generally within the range of 0.01 to 10%, by weight, based on the total composition. For use in internal combustion en- 20 gines, the preferred range is from 0.1% to 5%, based on the weight of the finished lubricant.

The invention comprehends not only the mixed esters in the technical sense (e. g. esters of a polyhydric alcohol, partially esterified by an acidic derivative of phosphorus and partially esterified by an organic acid) but also mixtures of simple or mixed esters. Thus, in reacting a phosphorus containing reagent and an organic acid with alcohol, a rather complex mixture may be obtained. The various formulas given 30 above are probably somewhat idealized. When pentaerythritol monooleate is reacted with POCl_3 , for example, the product may or may not be properly described by a specific formula. However described, this product, and the varia- 35 tions mentioned above, are found useful for the purposes of this invention.

Thus a composition derived from a monohy- 40 dric alcohol, such as a C_8 oxo alcohol or equivalent, a polyhydric alcohol such as pentaerythritol

or its equivalent, a phosphorus-containing acid-ic material such as POCl_3 or the alternative compounds mentioned above, and a fatty acid such as oleic acid or the like is a highly desirable product, and is the essence of this invention, al- 5 though chemical formula is not susceptible of exact definition. Lubricants, preferably but not necessarily of mineral base, are improved by these products as previously described.

What is claimed is:

1. As a new composition of matter, a phos- phorus-containing ester prepared by reacting to- gether pentaerythritol mono-oleate and a C_1 to C_{30} monohydroxy aliphatic alcohol at tempera- 15 tures not above reflux with a phosphorus-con- taining material selected from the group which consists of POCl_3 , PCl_5 , and PSCl_3 , in the pres- ence of pyridine and a solvent, said ester being stripped of water and of said pyridine and sol- vent after reaction is substantially complete.

2. Composition according to claim 1 wherein the alcohol is a C_8 oxo alcohol.

3. Composition according to claim 1 wherein the phosphorus-containing material is POCl_3 .

ALFRED H. MATUSZAK.
CHARLES A. WEISEL.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,365,291	Pruett	Dec. 19, 1944
2,373,811	Cook	Apr. 17, 1945
2,407,279	Hull	Sept. 10, 1946
2,408,744	Engel	Oct. 8, 1946
2,413,353	Hunter	Dec. 31, 1946
2,422,630	Musselman et al.	June 17, 1947
2,426,691	Jenkins	Sept. 2, 1947
2,446,944	Morgan	Aug. 10, 1948