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NAPHTHENYL ESTERS OF PHOSPHOROUS ACIDS

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This invention relates to naphthenyl esters of acids of phosphorus, some of which are new chemical compounds, the methods of preparing the same, and particularly to the use of such esters in lubricating oils to provide lubricants having improved properties.

Aliphatic and aromatic esters of ortho-phosphoric acids are known. Such esters have been employed as plasticizers in molding and coating compositions, particularly in those containing cellulose ethers and esters. They have also been proposed for use as textile lubricants and as assistants for extreme pressure lubricants and for many other purposes. Such prior known phosphates, particularly the higher aliphatic phosphates, have the disadvantage that, under certain conditions, they tend to exude from the compositions containing them.

The advantages of a high pressure lubricant become apparent when the present trend in design of automotive and other machine parts, and the increased strength of metal parts, due to the use of alloy steels, is considered. The pressures ordinarily found in well lubricated journal bearings do not exceed 2,000 lbs./sq. in. and for conditions such as this, a film of heavy oil can be expected to remain between the rubbing surfaces. When gears are considered, where the contact between surfaces is of very small width, the bearing pressures often reach values as high as 25,000 lbs./sq. in. Under such extreme pressure, it is unlikely that any oil or grease can be obtained which will be viscous enough to prevent metallic contact. The result of the lack of a lubricating film between the rubbing surfaces results in scoring and scuffing of the gears.

Failure to maintain lubricant films on idle bearing surfaces is now well recognized as the cause of 70 to 80% of the wear occurring on cylinder walls of automotive and other internal combustion engines. When an engine is stopped, the oil film on the vertical surfaces soon drains off and, when the machine is again started, an appreciable time elapses before the circulation provides oil for the formation of new lubricant films. An assistant which, when added to the motor oil, will prevent the separation of the oil film from the metal should prevent a large part of the wear now occurring.

Recently new bearing metals have been proposed for use in automobiles such as those composed of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys supported upon steel backings. These new alloys have many advantages over the older type, but are in general subject to destructive agencies of a corrosive nature. The more highly refined oils, particularly those obtained by solvent refining, appear to be particularly corrosive toward such new alloys.

Various agents have been added to oils to improve their properties. Among such agents which have been used are sulfur, sulfur-containing compounds, metal soaps, halogen compounds and the like. Some of these agents, such as the sulfur and halogen compounds, greatly improve the lubricating properties of the oils, whereas others, such as the metal soaps, have been of little value for this purpose. Some of such agents are corrosive or give rise to corrosive products, and are therefore objectionable. Many of such agents tend to increase or accelerate sludge formation in the oils to an objectionable extent, and are objectionable for this reason.

It is an object of the present invention to provide new materials for addition to lubricating oils for improving their properties. A further object is to provide improved lubricating oils. A still further object is to provide a method for preparing improved lubricants. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above objects may be accomplished in accordance with my invention, which comprises incorporating in lubricating oils, particularly petroleum lubricating oils, naphthenyl esters of the acids of phosphorus and mixtures of such esters, some of which esters are new chemical compounds. I preferably employ the naphthenyl esters of phosphorous acids; in other words, the naphthenyl phosphites and naphthenyl thiophosphites. These esters may, in general, be prepared by any of the methods well known to the art.

By the term "naphthenyl alcohols" as employed herein and in the claims, I mean the alcohols which are obtainable by the carboxylic reduction of naphthenic acids and their esters. These alcohols contain at least six carbon atoms and may contain as many as twenty or more car-

bon atoms. These naphthenyl alcohols contain the hydroxy group in a side chain as distinguished from the cycloaliphatic alcohols in which the hydroxyl group is attached to a carbon of the cyclic nucleus. A naphthenyl radical as employed hereinafter and in the claims will be understood to mean a radical derivable from such naphthenyl alcohols. The naphthenyl esters of my invention are those obtainable by esterifying such naphthenyl alcohols.

By an acid of phosphorus as employed herein and in the claims, I intend to include the various phosphoric and phosphorous acids such as the ortho, meta, pyro and hypo acids together with the corresponding thio acids in which one or more of the oxygens are replaced by sulphur atoms. Among the esterifying derivatives of acids of phosphorus, the following are the most common:

Phosphorus oxychloride, $POCl_3$
Phosphorus pentoxide, P_2O_5
Phosphorus pentachloride, PCl_5
Phosphorus trichloride, PCl_3
Phosphorus pentasulfide, P_2S_5
Phosphorus sulphochloride, $PSCl_3$
Phosphorus trisulphide, P_4S_6 and
Phosphorus trisulpho tetrabromide, $P_2S_3Br_4$.

The process of making naphthenyl esters of ortho-phosphoric acid may be carried out by placing one or more of the naphthenyl alcohols alone or dissolved in a suitable solvent, such as benzene, toluene, chloroform and the like, in a vessel connected with a reflux condenser. The material in the vessel is warmed to the desired temperature, preferably 30° to 100° C., under reduced pressure and phosphorus oxychloride is then gradually admitted in liquid or vapor form. The reaction is carried to completion under reduced pressure in the heated vessel and the hydrogen chloride formed is continuously removed. The resulting phosphates may be purified by distillation under reduced pressure. The resulting product comprises the mono-, di-, or tri-naphthenyl phosphate, depending upon the proportion of alcohol employed. When more than one molecular proportion of the alcohol is employed and the alcohol comprises a mixture of naphthenyl alcohols, the resulting product is a mixture of phosphates which apparently contains a substantial proportion of mixed phosphates each of which contains two or more different naphthenyl radicals.

The esters of orthophosphoric acid may also be obtained by heating the naphthenyl alcohol on a water bath and then adding phosphorus pentachloride thereto, slowly. The product may be washed with water and dried in vacuo.

The esters of ortho phosphoric acid may also be obtained by dissolving a mixture of the alcohols in ether or other suitable solvent, such as pyridine or other tertiary base, and then heating with phosphorus pentoxide under a reflux condenser. When ether is used as the solvent, the ester separates on cooling. When pyridine and like compounds are used, the solvent is removed by distillation, the product washed with water and dried by heating under reduced pressure.

The esters may also be prepared by first reacting the alcohols with sodium to obtain the corresponding alkoxides and then reacting the alkoxides with phosphorus oxychloride or the like.

An alternative procedure comprises first preparing the naphthenyl iodides or other halides and then reacting the halide with the silver salt of pyrophosphoric, metaphosphoric, orthophosphoric or other acid of phosphorus to obtain the neutral or acid esters, depending upon the proportions employed.

If it is desired to obtain pure mixed esters of ortho phosphoric acid, it will be desirable to react one molecular proportion of phosphorus oxychloride with one or two molecular proportions of the naphthenyl alcohol. The resulting product is principally the chloride of the mono- or di-naphthenyl phosphates. After removal of the hydrogen chloride, a second alcohol or mixture of alcohols, different from the first, an alkali metal phenolate or a free phenol in the presence of a tertiary base is added, preferably in excess. By this method, the pure mixed neutral or acid esters are obtained.

Catalysts such as copper powder or a metallic chloride may be added to the reaction liquid in order to facilitate the splitting off of the hydrogen chloride. Also, the degree of reduced pressure employed may vary within wide limits depending upon the desire of the operator and the materials being treated.

The esters of the other acids of phosphorus may be prepared in similar manner to the methods disclosed above by substituting the proper esterifying derivative for the phosphorus oxychloride and the like, disclosed above. For example, when phosphorus trichloride is employed, the phosphites will be produced. When phosphorus sulphochloride is employed, the resulting products will be the monothio ortho-phosphates. When phosphorus pentasulfide is employed, the dithio ortho-phosphates result. When phosphorus trisulpho tetra bromide is employed, the corresponding trithio pyro-phosphates will be produced. The meta-phosphates may be obtained by treating the neutral ortho-phosphates with concentrated sulphuric acid.

Esters of thio acids of phosphorus may be produced by treating the naphthenyl thio alcohols with an esterifying derivative of phosphorus. The resulting compounds will generally have the naphthenyl radical attached to the phosphorus through a sulphur atom. These esters may be called thio esters of the acids of phosphorus to distinguish them from the esters of the thio-acids in which the naphthenyl radical is attached to the phosphorus through an oxygen atom.

When the neutral esters are treated with alkali, the alkali metal salt of the dinaphthenyl ester is obtained. These salts may be prepared by boiling one part by weight of the neutral phosphate with 8 parts by weight of sodium hydroxide dissolved in 192 parts by weight of water for two hours. These salts are soluble or dispersible in water. The sodium salts of the mixed dinaphthenyl phosphates can be employed to emulsify a mineral oil in a large amount of water to obtain an emulsion which can be diluted indefinitely with water.

The neutral naphthenyl esters can also be hydrolyzed by cooking with an acid such as hydrochloric acid to yield mixtures of the mononaphthenyl and dinaphthenyl phosphates.

While the sodium salts of the acid esters of my invention are soluble in water, the salts obtained with organic bases, such as triethanolamine or methyl glucamine, are even more soluble. These various salts also form a part of my invention.

In order more clearly to illustrate my invention and the preferred modes of preparing my new compounds, the following examples are given:

Example 1

A mixture of naphthenyl alcohols boiling between 101 and 141° C. at 19 mm. was obtained by hydrogenation of a mixture of ethyl naphthenates. This mixture of naphthenyl alcohols had an average molecular weight of 160 as calculated from analytical determinations of the saponification number of the ethyl naphthenates from which they were obtained. 25 parts by weight of this mixture was mixed with 100 parts of benzene. 8 parts by weight of phosphorous oxychloride was then added slowly. The mixture was placed in a glass vessel attached to a reflux condenser and heated at the reflux temperature under a slight vacuum for 20 hours. The slight vacuum served to assist in the removal of the hydrogen chloride which was formed. The benzene solution was then washed with warm water until neutral and the benzene evaporated. The mixture was then steam distilled until no more oily liquids came over. The solution in the steam distillation flask was then extracted with benzene and the layers separated. The benzene layer was then evaporated on a steam bath leaving dinaphthenyl phosphate. The last traces of benzene were removed by heating under reduced pressure. The product was a light yellow viscous liquid, soluble in aromatic hydrocarbons and insoluble in water. Determination of the phosphorus content indicated that the product was the expected dinaphthenyl phosphates.

Example 2

A mixture of naphthenyl alcohols, having a boiling point between 101 and 141° C. at 19 mm., having an indicated molecular weight of 169, as calculated from analytical determinations of hydroxyl number, was obtained. 100 parts by weight of this mixture was mixed with 200 parts of benzene and 32 parts of phosphorus oxychloride was then added slowly. The mixture was placed in a glass vessel attached to a reflux condenser and allowed to stand at room temperature for 3 hours under a slight vacuum. The mixture was then heated in a steam bath over night under a slight vacuum. The reaction mixture was then poured into an excess of dilute sodium carbonate solution and the mixture steam distilled until there was no further detectable distillation of oily materials. The residue in the steam distillation flask was then extracted with benzene and thoroughly washed with water. The benzene solution was dried by distillation of the benzene, the last traces of the benzene being removed under reduced pressure. The product was a light yellow viscous liquid, soluble in aromatic hydrocarbons and insoluble in water. Determination of the phosphorus content indicated the product to be dinaphthenyl phosphates.

Example 3

A mixture of the ethyl esters of naphthenic acids was prepared and such esters were reduced by sodium reduction. This produced a mixture of naphthenyl alcohols boiling between 130 and 160° C. at 1 mm. and having an average molecular weight of 274 as calculated from an analytical determination of the hydroxyl number. Thirty-seven and five-tenths parts by weight of this mixture was mixed with 100 parts of toluene. Seven parts by weight of phosphorus oxychloride was added slowly. The mixture was placed in a glass vessel attached to a reflux condenser and heated gently on a steam bath under slight vacuum to remove liberated hydrogen chloride. After heating for 24 hours, 3.5 parts of phosphorus oxychloride was added, in order to have present sufficient phosphorus oxychloride so that only the dinaphthenyl phosphate would be formed. The mixture was heated under slight vacuum in the steam bath for three additional hours. Benzene was added to the reaction mixture and the benzene solution washed thoroughly with dilute sodium carbonate solution. Very stable emulsions were formed, which were broken with difficulty by heating with sodium chloride solution. The emulsions formed again when water was added. Dilute hydrochloric acid was then added to decompose the sodium salt and the solution washed thoroughly with water. The benzene layer was separated and the benzene was removed under vacuum on the steam bath. The product was a light yellow colored very viscous liquid, soluble in aromatic hydrocarbons and insoluble in water. Determination of the phosphorus content indicated the product to be dinaphthenyl ortho-phosphates. This material was added to an oil in 2% concentration and the resulting lubricant witthstood a load of about 28,000 lbs./sq. in., when tested on the Almen machine.

While the phosphates will to some extent reduce the tendency of lubricating oils to corrode alloy bearing metals such as cadmium-silver, copper-lead and caymium-nickel alloys, I have found that the naphthenyl phosphites and naphthenyl thiophosphites are particularly effective for retarding corrosion of such bearing alloys by lubricating oils. The following additional examples illustrate this desirable property:

Example 4

A solution of 41 gms. naphthenyl alcohols, having an average molecular weight of 274, and 12 gms. pyridine was prepared in 250 cc. benzene. To this was added, slowly and with vigorous agitation, a solution of 6.9 gms. phosphorus trichloride in 50 cc. benzene. The reaction mixture was agitated 1 hour at 25° C. and subsequently heated 1 hour on a steam bath. After chilling, the solution was filtered to remove the solid pyridine hydrochloride, shaken for 30 minutes with 20 gms. sodium carbonate monohydrate to complete the removal of chlorine-containing compounds, filtered, and the solvent removed under reduced pressure. A clear liquid residue was obtained, weighing 40 gms., which upon analysis yielded the following data: phosphorus (found), 3.45%; phosphorus (calculated), 3.65%; N_D^{25}, 1.4965.

The effect of this material on the film strength of an SAE 30 oil was determined on the Almen machine with the following results:

	Load supported
Oil alone	3,000 lbs./sq. in.
Oil+1% naphthenyl phosphite	24,000 lbs./sq. in.

The effect of this material on inhibiting the corrosion of a copper-lead alloy bearing and a cadmium-silver alloy bearing was determined on an SAE 30 oil as follows:

Fifty grams of oil containing 0.5% by weight of the naphthenyl phosphite were placed in 125 cc. Erlenmeyer flasks each equipped with a 1 mm. capillary inlet tube through which moist air was passing at the rate of 2 to 3 bubbles per second. Strips cut from the bearings were suspended in the flasks in a position such that half of the surface of each strip was immersed in the oil and half exposed to the vapors. The flasks and contents were placed in an oil bath at 170° C. for 50 hours. A control test was run simultaneously.

At the end of the test, the bearing strips were removed, washed with chloroform and acetone, and weighed. The data obtained are as follows:

	Mg. loss per 10 gms. for	
	Copper-lead alloy	Cadmium-silver alloy
Oil alone	100	102
Oil+0.5% naphthenyl phosphite	5	0

Example 5

A solution of 23 gms. naphthenyl mercaptans, having an average molecular weight of 180, and 10 gms. pyridine was prepared in 100 cc. benzene. To this was added, slowly and with vigorous agitation, a solution of 5.5 gms. phosphorus trichloride in 50 cc. benzene. The reaction mixture was agitated 1 hour at 25° C. and subsequently heated 1 hour on a steam bath. After chilling, the solution was filtered to remove the solid pyridine hydrochloride, shaken for 30 minutes with sodium bicarbonate to complete the removal of chlorine-containing compounds, filtered, and the solvent removed under reduced pressure. A clear liquid residue was obtained weighing 21 gms. Upon analysis this yielded the following data: phosphorus (found), 5.28%; phosphorus (calculated), 5.45%; sulfur (found), 15.49%; sulfur (calculated), 16.9%; N_D^{25}, 1,5269.

The effect of this material on the film strength of an SAE 30 oil was determined on the Almen machine with the following results:

	Load supported
Oil alone	3,000 lbs./sq. in.
Oil+1% naphthenyl trithiophosphite	24,000 lbs./sq. in.

The effect of this material on inhibiting the corrosion of bearings lined with a silver-cadmium alloy and with a cooper-lead alloy was determined on an SAE 30 oil as follows:

Fifty grams of oil containing 0.5% by weight of the naphthenyl trithiophosphite were placed in 125 cc. Erlenmeyer flasks each equipped with a 1 mm. capillary inlet tube through which moist air was passing at the rate of 2 to 3 bubbles per second. Strips cut from a silver-cadmium alloy bearing and a copper-lead alloy bearing were suspended in the flasks in such a fashion that half the surface of each strip was immersed in the oil and half exposed to the vapors. The flasks and contents were placed in an oil bath at 170° C. for 50 hours. A control test was run simultaneously. At the end of the test, the bearing strips were removed, washed with chloroform and acetone, and weighed. The data obtained are as follows:

	Mg. loss per 10 grams for	
	Copper-lead alloy	Silver-cadmium alloy
Oil alone	85.5	244.1
Oil+0.5% naphthenyl trithiophosphite	4.9	0

I have found that the naphthenyl phosphites and the naphthenyl thiophosphites have a further advantage over the prior art compounds in that they have greatly improved sludging characteristics over similar compounds proposed in the prior art. They do not tend to cause the oil to form sludge or accelerate the formation of sludge in the oil to the extent that similar compounds heretofore proposed do. When the corrosion tests disclosed in Examples 4 and 5 were run, the tendency of the treated oils to form sludge was also tested. The results of such tests are given in the following table:

Compound	Concentration percent by wt.	Length of test	Temperature of test	Mg. sludge per 10 gms. oil
		Hrs.	*° C.*	
Naphthenyl phosphite	0.5	50	170	17.5
Naphthenyl trithiophosphite	0.5	50	170	4.6
Triphenyl phosphite (commercial grade)	0.5	50	170	23.1

The sludge values were determined by diluting 10 gms. of the oil to a volume of 100 cc. with a highly refined petroleum naphtha, allowing the solution to stand at 0° C. for one hour, filtering the solution on a weighed Gooch crucible, and weighing the collected sludge.

From the above tests, it will be apparent that the oil containing the phosphites and thiophosphites of my invention had much less tendency toward the formation of sludge than triphenyl phosphite, which is a representative of similar types of compounds which have been proposed for addition to lubricating oils.

The preferred esters of the acids of phosphorus of my invention are derived from naphthenyl alcohols obtained by hydrogenation or sodium reduction of derivatives of naphthenic acids from petroleum, and particularly the esters of the phosphorous acids. However, I intend to include within the scope of my invention the mixed esters such as dinaphthenyl ethyl ortho-phosphate, dinaphthenyl cresyl ortho-phosphate, dinaphthenyl 9, 10-octadecenyl ortho-phosphate, dinaphthenyl dodecyl ortho-phosphate, acid naphthenyl dodecyl ortho-phosphate, acid naphthenyl ethyl ortho-phosphate, acid naphthenyl cresyl ortho-phosphate, acid naphthenyl tetradecyl ortho-phosphate, acid naphthenyl 9, 10-octadecenyl ortho-phosphate, acid naphthenyl phenyl ortho-phosphate and similar compounds. These mixed phosphates may be obtained by esterifying a mixture comprising at least one molecular proportion of the naphthenyl alcohols and one molecular proportion of a different alcohol or a phenol. They may also be obtained by first esterifying the naphthenyl alcohols and then reacting with the other alcohol or phenol. Alternatively the other alcohol or phenol may be first esterified and then reacted with the naphthenyl alcohols.

The neutral esters of my invention may be employed as plasticizers in molding and coating compositions, particularly those comprising cellulose ethers, such as the benzyl ethers, and cellulose esters, such as the nitrate and acetate. The acid phosphates and their alkali metal salts such as sodium and potassium and the ammonium and amine salts are useful as wetting agents, detergents, textile lubricants and the like. The acid phosphates are also useful as lubricant assistants for extreme pressure lubricants. For example, when 2% of dinaphthenyl phosphate, such as that obtained in accordance with Example 3, is added to a medium viscosity mineral oil, SAE-30, and dissolved therein by heating, the oil was able to maintain a lubricant film under

extreme high pressure which it would ordinarily not withstand, and had a much higher degree of "oiliness".

The method of testing my compounds was that devised by J. O. Almen (Oil and Gas Journal, 30, 109, 1931). This method consists of running a ¼" diameter drill rod between two halves of a split bushing which is maintained stationary. The load on the bushing is controllable and provision is made for measuring the torque developed by the friction of the lubricant film. A hydraulic system for increasing the loading on the bushing until the oil film breaks and the metal seizes is provided. The rubbing speed is about 50 feet per minute and the method of loading is gradual, one weight being added to the loading lever each ten seconds. Each weight added to the loading lever increases the pressure on the bushing by about 125 lbs. The machine provides for beam loadings up to 20 weights which corresponds to a pressure of 20,000 lbs./sq. in. on the full projected area of the drill rod. The bearing surface of the bushing is cut to a diameter 0.007 inch larger than the drill rod so that, before any wear occurs, the actual bearing surface is a line. As wear occurs, the bearing surface widens but seldom covers the bushing. After a test, the width of the bearing scar can be measured and an approximate value for the actual bearing pressure obtained. The values given in the preceding examples represent the calculated actual bearing pressures which were reached in the tests without failure of the film. These values represent film strength or film resistance.

When subjected to the above test, a good grade of paraffin oil will withstand a pressure of only 3 to 5,000 lbs./sq. in. When an oil containing sulfur is tested by the same method, such oil will show a film strength of about 20,000 lbs./sq. in. and will give a torque reading of over 4.0 lbs. ft. at this load.

This application is in part a continuation of my copending application Serial No. 11,809, filed March 19, 1935, for Esters of the acids of phosphorus. In such copending application, I have disclosed the phosphates both generically and specifically, and the phosphites and thiophosphites generally. Also, in such copending application, I have disclosed that these compounds are useful additions to lubricating oils for producing extreme pressure lubricants. The present application includes a description of the preparation of the phosphites and thiophosphites and the results of tests of lubricating oils containing such compounds.

While I have disclosed the preferred embodiments of my invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that many modifications may be made therein without departing from the spirit of my invention. Accordingly, the scope of my invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

I claim:

1. A naphthenyl ester of a phosphorous acid.

2. A naphthenyl ester of a thiophosphorous acid.

3. A trinaphthenyl phosphite.

4. A trinaphthenyl thiophosphite.

5. A trinaphthenyl trithiophosphite.

6. A mixture of naphthenyl esters of a phosphorous acid obtained by reacting an esterifying derivative of a phosphorous acid with at least one molecular proportion of a mixture of naphthenyl alcohols.

7. A mixture of naphthenyl esters of a phosphorous acid obtainable by reacting an esterifying derivative of a phosphorous acid with three molecular proportions of a mixture of naphthenyl alcohols.

8. A mixture of naphthenyl esters of a thiophosphorous acid obtainable by reacting an esterifying derivative of a phosphorous acid with at least one molecular proportion of a mixture of naphthenyl mercaptans.

9. A mixture of naphthenyl esters of a thiophosphorous acid obtainable by reacting an esterifying derivative of a phosphorous acid with three molecular proportions of a mixture of naphthenyl mercaptans.

10. A mixture of trinaphthenyl phosphites.

11. A mixture of trinaphthenyl trithiophosphites.

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