UNITED STATES PATENT OFFICE

2,450,903

PHOSPHORUS ACID ESTERS OF PETROLEUM PHENOLS

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2 Claims. (Cl. 260—461)

This invention relates to new organic phosphorus compounds, useful as blending agents in
organic compositions, and more particularly to novel phosphate and phosphite esters which func-
tion as improved plasticizers.

Alkaryl phosphates and alkaryl phosphites have been prepared from simple alkyl phenols
for use in plasticizing and similar purposes, but
these esters have had restricted application due to
limitations in their solubility, stability, and wet-
ting power.

In the past, the alkyl phenols generally em-
ployed in preparing alkaryl esters were mainly
cresols, xlenols, etc., made available by tar acids
commercially known as cresylic acid or by al-
kylation such phenols to introduce a paraffinic side
group. Other hydroxyaromatic compounds pre-
dominantly aromatic in character, such as naph-
thols and phenyl phenols, have also been pro-
posed.

According to the present invention, esters of
acids of phosphorus, and particularly phosphate
esters, are prepared from phenolic compounds
having distinctive properties and compositions
which confer upon the esters new and beneficial
properties or attributes particularly for use as
plasticizers. The phenolic compounds which now
have been found to be adapted for this purpose,
are those recovered from petroleum fractions and
known as petroleum phenols. The petroleum
phenols for the purpose of this invention may be
characterized as containing a total of about 9
to 23 carbon atoms per molecule with about 3 to
17 of these carbon atoms present in saturated hy-
drocarbon groups showing a deficiency of hy-
drogen for paraffinic or straight chain alkyl
groups. This deficiency of hydrogen can be ascribed aptly to the presence of cycloalkaphilic
hydrocarbon groups. Thus, while the saturated
hydrocarbons substituents of petroleum phenols
may be considered as paraffinoid, they do not have
the paraffinicity of simple alkyl groups.

Petroleum phenols are recovered from crude pe-
troleum and mainly from cracked petroleum
napthas, distillates and heating oil stocks. In
general, a petroleum fraction such as a heating
oil stock is treated with a strong aqueous or al-
coholic caustic solution to extract petroleum
phenols in the form of alkali phenolate salts. The
alkali phenolate salts in alkaline solution are
washed with petroleum ether or naphtha to re-
move residual hydrocarbons. The solution of the
salts is then treated with carbon dioxide or a weak
mineral acid in sufficient quantity to liberate only
the phenols from the salts, any naphthenic acid
salts present being thus kept undissociated in the
solution. The liberated phenols are separated
from the solution and may then be further puri-
fied by distillation, preferably under reduced
pressure or by blowing with air. If desired, the
phenols may be still further purified by redistil-
lution under vacuum. The boiling range of the
phenols finally recovered is generally higher than
the boiling range of the petroleum fraction from
which they are obtained. With sufficient puri-
fication and redistillation, the phenolic com-
ounds can be substantially freed from hydro-
carbons and other impurities such as naphthenic
acids.

Although it is difficult to isolate pure compo-
ents from the petroleum phenols, compounds in
close cut fractions of the petroleum phenols, and
particularly those of higher molecular weight
forming a major proportion of the components
cannot be identified with simple alkyl phenols
having corresponding molecular weights. To a
large degree, the petroleum phenols are indicated
to include polycyclic molecules which may be de-
scribed as polymethylene phenols and in the high-
er petroleum phenols such paraffinoil groups pre-
dominate over the aromatic groups. From ana-
lytical data including hydrogen and carbon
analyses, acetylation and saponification deter-
minations, iodine absorption, molecular weight
determinations by the freezing point method,
bolling point, etc., can be derived information
regarding the composition and structure of the
petroleum phenols. As a rule, the petroleum
phenols contain only a trace of cresols, if any,
and have a minimum formula weight of about
121.3, which is evidence of the fact that they
predominantly correspond in molecular weight
to higher homologues of ethyl phenol.

Comparative data is shown in the following
table on the calculated composition of butyl
phenol and the observed composition of a lower
petroleum phenol cut boiling in the range of 105°
to 125° C. at 5 mm. Hg absolute pressure and cor-
responding approximately to the simple butyl phenol in molecular weight:

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Calculated Composition of C₆H₅CH₂OH</th>
<th>Observed Composition of the Petroleum Phenol Cut</th>
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<tbody>
<tr>
<td></td>
<td>161.11</td>
<td>184</td>
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</table>

Based on the analysis in Table 1, the average empirical formula of the petroleum phenol cut is represented by C₆H₅(CH₂)₃CH₂OH. As will be shown later, the phosphate esters formed from this petroleum phenol cut have outstanding differences over the esters of the simple phenol.

The petroleum phenols used in preparing the phosphate and phosphite esters may be segregated into close cut fractions by distillation, in which greater vacuum is used to avoid decomposition as the distillation temperature rises. The distillation, for example, may begin at 94° C. under a pressure of 4 mm. Hg absolute and proceed to a temperature of 190° C. under an absolute pressure of 3 mm. Hg, the overhead being collected in approximately 10% cuts. The distillation ranges under the specified reduced pressures and the average empirical formula of each cut, as determined by analyses for carbon and hydrogen, are as follows:

<table>
<thead>
<tr>
<th>Cut</th>
<th>Temperature °C. and Pressure</th>
<th>Per Cent Cut</th>
<th>Average Formula Based on Analysis for C and H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94°4 mm. Hg</td>
<td>10.3</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>2</td>
<td>99°4 mm. Hg</td>
<td>10.3</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>3</td>
<td>102°4 mm. Hg</td>
<td>10.0</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>4</td>
<td>107°4 mm. Hg</td>
<td>10.3</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>5</td>
<td>110°4 mm. Hg</td>
<td>10.3</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>6</td>
<td>110°5 mm. Hg</td>
<td>10.3</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>7</td>
<td>125°4 mm. Hg</td>
<td>10.4</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>8</td>
<td>130°5 mm. Hg</td>
<td>10.4</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>9</td>
<td>147°5 mm. Hg</td>
<td>10.4</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
<tr>
<td>10</td>
<td>160°5 mm. Hg</td>
<td>6.0</td>
<td>C₆H₅(CH₂)₃CH₂OH</td>
</tr>
</tbody>
</table>

From the average empirical formulae of the petroleum phenols, as shown in Table 2, can be recognized that the constituent groups in the phenol nucleus have a definite deficiency of hydrogen as compared with simple alkyl phenols which necessarily have the following general formula:

C₆H₅(CH₂)₃OH

In contrast to this, the lower petroleum phenols, except for the lowest boiling fractions difficult to free from hydrocarbons, have the following general formula:

C₆H₅(CH₂)₃·CH₂OH

Petroleum phenols vary somewhat according to their source and in many instances the hydrogen deficiency is greater than shown in the components illustrated where 2 is less than 1, or even a negative quantity, the total quantity 2n + x being smaller than the average molecular weight increases. For instance, in the cut having the average formula:

C₆H₅(CH₂)₃·CH₂OH

the value of 2n + x is 7.5, which makes

x = (7.5 - 2.33)

which is equal to 0.9, and in

C₆H₄·CH₂OH

x is equal to negative 0.7.

This deficiency of hydrogen becomes progressively greater as the molecular weight of the phenols is greater and varies somewhat with the petroleum fraction source. With this deficiency of hydrogen there is also an occurrence of additional non-phenolic oxygen which can be more accurately determined in the higher petroleum phenols. The di- and poly cyclic rings in the petroleum phenols are regarded as being analogous to the higher molecular weight petroleum hydrocarbons which are built up of fused rings having one or more carbon atoms shared in common.

The low petroleum phenols have been observed to boil without substantial decomposition in the range of about 75° C. to 150° C. under a pressure of 1 to 8 mm. Hg absolute pressure. The higher petroleum phenols, which are generally extracted from petroleum heating oil fractions boiling above 150° C., are characterized by compounds boiling in the range of 150° C. to about 360° C. under about 1 to 6 mm. Hg absolute pressure. Although the high phenols which have more than about 10 carbon atoms per molecule, tend to darken in color, they are very valuable for producing phosphate and phosphite esters which serve very well as addition agents in hydrocarbon products such as lubricants, heavy fuels, hydrocarbon resins, etc., on account of the high miscibility of these esters with such materials.

Further, considering the higher petroleum phenols having more than 10 carbon atoms per molecule, i.e., where x indicates about 5 to 17 carbon atoms, and possibly more, per molecule in the constituent group, the average empirical formula may be represented by:

C₆H₅(CH₂)₃·OH

wherein x lies in the range of about —1 to —5, and y indicates an average of 0 to +1 non-phenolic oxygen atoms in the molecule. This same average empirical formula applies, in general, to all petroleum phenols when x is an algebraic quantity ranging from below —1 to —5.

As demonstrated in the following examples, phosphate and phosphite esters have been prepared from petroleum phenol cuts similar to those illustrated in Table 2.

**Example 1: Preparation of phosphate esters**

A 272 gram fraction of petroleum phenols having a boiling range of 80° C. to 105° C. at 6 mm. Hg absolute pressure was reacted with 102 grams of phosphorus oxychloride used in the proportion of one-third mol per mol of phenol. The mixture was gradually heated in the presence of 2 grams of magnesium powder as catalyst from 100° C. up to 180° C. In the course of about three hours, during which time hydrogen chloride was evolved. The reaction may be represented by the general equation:

3R·CH₂OH + POCl₃ → (R·CH₂O)₃PO + 3HCl

where R represents saturated hydrocarbon substituted having a carbon to hydrogen atomic ratio of about 3:2.75. The reaction product was dissolved in toluene, then washed with dilute hydrochloric acid, followed by dilute alcohol, and finally water. After the washing steps, the toluene solvent was evaporated off and the residual product was distilled under reduced pressure. In the distillation, a fraction was collected at 230° C. to 255° C. under an absolute pressure of 1.5
mm. Hg, and this fraction on analysis showed a molecular weight corresponding to that of tri-(propyl phenyl) phosphite, \((\text{C}_3\text{H}_7\text{H}_5\text{O})_3\text{PO}\). The yield was 51% based on the phosphorus oxychloride employed, and the product was a pale yellow liquid having a viscosity of 430 Saybolt seconds at 100° F. as compared to 132 seconds for tricyclic phosphite.

**Example 2: Preparation of phosphite esters**

A 300 gram fraction of petroleum phenols having a boiling range of 105° C. to 130° C. under an absolute pressure of 6 mm. Hg was reacted with 103 grams of phosphorus oxychloride in the absence of any catalyst. The reaction and isolation of the product was carried out as described in Example 1. A 33% yield of phosphite ester having a boiling range of 265° C. to 265° C. under an absolute pressure of 1.5 mm. Hg was obtained.

**Example 3: Preparation of phosphite esters**

A petroleum phenol fraction boiling from 75° C. under absolute pressure of 6 mm. Hg to 110° C. under an absolute pressure of 1.5 mm. Hg was reacted with phosphorus oxychloride by the method described in Example 2. The product which distilled in the range of 215° C. to 305° C. under an absolute pressure of 2.5 mm. Hg had the average empirical formula

\[(\text{C}_3\text{H}_7\text{H}_5\text{O})_3\text{PO},\]

**Example 4: Preparation of phosphite esters**

A 183 gram fraction of petroleum phenols boiling from 75° C. under absolute pressure of 6 mm. Hg to 110° C. under an absolute pressure of 1.5 mm. Hg was reacted with 50.7 grams of phosphorus trichloride by heating up to 190° C. in the course of about 9 hours. The reaction may be represented by the general equation:

\[3\text{R-}\text{OH} + 3\text{PCl}_3 \rightarrow (\text{R-}\text{O})_3\text{P}-3\text{HCl},\]

where \(\text{R}\) represents hydrocarbon substituent groups, e.g., a polymethylene group, and \(\text{Ar}\) represents a cyclic nucleus, e.g., a phenyl group. A 70% yield of phosphite esters was obtained. The product distilled at 220° C. to 275° C. under an absolute pressure of 2.5 mm. Hg.

The temperature of reaction, of course, is controlled to suit the particular reactants, their relative proportions, and specific catalytic activity, if a catalyst is used. Usually, a temperature below 200° C. is convenient for effecting the esterification or condensation at a suitable rate without excessive formation of objectionable by-products. The use of phosphorus pentachloride in place of phosphorus oxychloride permits reaction to proceed readily at temperatures as low as 0° C.

The procedures disclosed in the foregoing examples may be modified by use of various diluent media for the reaction, and the use of other known methods of purification. Pyridine, pyridine with benzol, and similar alkaline solutions may be employed as the solvent when chlorides and oxychlorides of phosphorus are used. Higher boiling solvents such as alkyl halides are useful for chlorides employed, and higher reactivities. The esterification of the petroleum phenols with the phosphorus acids may also be carried out with admixed simple phenols or halogenated phenols to obtain desirable products of modified solubility and viscosity. For example, phenol, itself, or cresol may be admixed with the petroleum phenols prior to the esterification or be used to complete the esterification, about one or two mols of the simple phenol may be employed for each mol of petroleum phenols.

Thus, it can be observed that the esters of lower petroleum phenols and phosphorus acids both approximate in the range of 200° C. to 300° C. at 1.5 to 2.5 mm. mercury absolute pressure and have average empirical formulae represented by \((\text{R-}\text{C}_6\text{H}_5\text{O})_3\text{PO} = \text{R}\) and \((\text{R-}\text{C}_6\text{H}_5\text{O})_3\text{PO} = \text{R}\), wherein \(\text{R}\) representing saturated hydrocarbon substituents of carbo-cyclic groups linked to phosphorus through oxygen atoms, contains carbon and hydrogen in an average atomic ratio which is less than \(n:2n+1\), \(n\) being the number of the saturated substituent carbon atoms. The minimum of this atomic ratio of carbon to hydrogen in the saturated hydro-carbon substituent groups, \(\text{R}\) is about 0.44, but usually it is higher, ranging up to about 0.55, or more.

The petroleum phenol and phosphate esters, thus prepared, have physical properties decidedly different from those of the simple phenol phosphate and phosphate esters having similar molecular weights. This is plainly demonstrated by a comparison between tri(para-tertiary butyl-phenyl) phosphate and the phosphate esters of petroleum phenols having approximately the same molecular weights.

<table>
<thead>
<tr>
<th>Physical State</th>
<th>Appearance</th>
<th>Color</th>
<th>Melting Point</th>
<th>Solubility</th>
<th>Phosphite Esters of Petroleum Phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>White</td>
<td>None (clear)</td>
<td>101-109° C.</td>
<td>Insoluble above a 4% Concentration.</td>
<td>Viscous Liquid</td>
</tr>
</tbody>
</table>

1 Calculated content is 6.36% for \((\text{C}_3\text{H}_7\text{H}_5\text{O})_3\text{PO} = \text{O}\).
2 At room temperature (22 to 25° C.) in paraffinic petroleum oil having a viscosity of 315 Saybolt seconds at 100° F.

The very good oil solubility of this petroleum phenol phosphate at low temperatures is representative and has proved to be a valuable property, in the utilization of these esters. The phosphate esters of the petroleum phenols dissolve in both aromatic and paraffinic naphthas very readily, even without application of heat, are soluble in all proportions. This is an important advantages over the known esters of simple alkyl phenols and phosphoric acid, which do not dissolve without heating, because the heating tends to cause decomposition and discoloration.

It is to be noted that the petroleum phenol phosphate esters under normal conditions exist as a viscous liquid, whereas, the simple phenol phosphate ester is a solid and this solid is miscible with the same oil solvent, only above the melting point of the solid. The combination of excellent solubility in organic solvents, clear transparency and light color makes the esters of lower petroleum phenols very valuable as plasticizers or gelatinizers of various cellulose derivatives including cellulose acetate, nitrocellulose, and cellulose ethers. In this respect, it is important to note that the petroleum phenol phosphates are soluble in cellulose acetate to a practical degree, even though this cellulose derivative has been one of the most difficult to provide with a soluble plasticizer. The phosphates of petroleum phenols are compatible with benzyl cellulose in substantially all proportions.

A comparison of viscosities of petroleum phenol
phosphate and phosphite esters produced according to methods in the foregoing examples with the viscosity of triorthocresyl phosphate is given in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Viscosity in Saybolt Universal Seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 100° F.</td>
</tr>
<tr>
<td>Tri-orthocresyl phosphate</td>
<td>132</td>
</tr>
<tr>
<td>Phosphate esters of petroleum phenols</td>
<td>400 to 522</td>
</tr>
<tr>
<td>Phosphite esters of petroleum phenols</td>
<td>387</td>
</tr>
</tbody>
</table>

The exceedingly higher viscosities of the petroleum phenol esters is quite significant with regard to their complex structure and their properties.

Very favorable results were obtained in using phosphates of petroleum phenols having a molecular weight corresponding to that of propylphenol as a plasticizer and according to the following formula:

<table>
<thead>
<tr>
<th></th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>9</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>1</td>
</tr>
<tr>
<td>Acetone</td>
<td>31</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>31</td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>14</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>14</td>
</tr>
</tbody>
</table>

Compositions of such formulae were tested with the same technique which had been used in testing other known plasticizers such as triresyl phosphate. Films of these compositions 0.003 inch in thickness were cast. On drying, the composition containing 10% of the plasticizer formed a clear film. This denotes, that the petroleum phenol phosphate plasticizers are compatible with cellulose acetate in as high as a 10% concentration.

Owing to their greater molecular weight, viscosity, and complexity, the petroleum phenol ester plasticizers are able to impart exceedingly better flexibility, tenacity, and durability to cellulose derivatives used in films, lacquers, or molding compositions than simpler compound hitherto recommended as plasticizers. Their desirable high stability, as shown by their marked resistance to water, alkalis, and acids, and low solubility may also be credited to their relatively high molecular weights and complexity. Another generally useful property of these improved esters is their high wetting power for increasing spreading of compositions and for dispersing added ingredients, such as fillers, pigments, and driers. A valuable property belonging particularly to the phosphate esters is their oxidation inhibiting action.

Although the petroleum phenol phosphates and phosphites have been shown to be especially useful as plasticizers with cellulose derivatives, their valuable properties make them also useful in various other compositions, as in various other resins and plastics, in lubricating compositions, greases, fuels, insecticides, dust collecting agents, cable oils, insulating oils and compounds, textile oils, process oils, finishes, adhesives, polishes, and inks. They are sufficiently non-flammable and water resistant to be used as fireproofing and water-proofing agents.

The present application is a continuation in part of co-pending application Serial No. 248,901, filed December 31, 1938, now abandoned.

In using the liquid phosphorus acid esters of petroleum phenols as plasticizers for organic solids which are normally too hard or brittle or for any other reason normally require plasticizing, the amount of these esters to be used will normally range from about 1% to 30% and generally from about 5% to 15% by weight on the basis of the substance being plasticized, i. e. not including any volatile solvent.

As the higher petroleum phenols tend to be somewhat darker than the lower ones, the phosphate or phosphite esters of the higher petroleum phenols are most advantageously used for plasticizing either substances which inherently have a substantial amount of a color ranging from red through brown to black, as for instance high melting point normally brittle asphalt, cracking oil tar, etc. or for normally light colored or colorless substances such as clear yellow or pale natural red or even colorless synthetic plastics such as cellulose acetates and the like with which has been blended a pigment or soluble dye or other insoluble fillers with which it would not be objectionable to use a minor proportion of plasticizer having a tendency to impart a reddish brown coloration to the plastized composition.

To illustrate the invention as applied particularly to the preparation of a phosphate ester of the higher petroleum phenols, the following additional example is given.

Example 5: Tripetroleum phenolphosphates of higher phenols

The petroleum phenols used in this experiment boiled at 145° to 185° C. under 1 mm. pressure. They had an acetyl No. of 210.5 which means that the phenols contained on the average, side chains of about 11.5 carbon atoms. In converting the above phenols into a tri-ester, the following procedure was used.

A 3-way flask equipped with a stirrer, a return condenser and a dropping funnel, was charged with 50 cc. absolute alcohol. To this was then gradually added 3.45 gms. (=0.15 mole) of metallic sodium. When all the sodium had dissolved, 40 gms. (=0.15 mole) of the above described petroleum phenols and 200 cc. of toluene were added as solvent. The mixture was then refluxed. The alcohol which collected in the water trap was then removed from time to time.

When all the alcohol had been removed, the reaction mixture was cooled and the dropping funnel was charged with 7.5 gms. (=0.05 mole) of phosphorus oxychloride, and 7.5 cc. of toluene. The latter was then added to the reaction mixture drop by drop with rapid stirring. When all the chloride had been added, the mixture was refluxed for 1 hour.

After cooling, the reaction mixture was poured into water, acidified with hydrochloric acid and extracted with ether. The extract was washed, and dried, and the solvents were finally removed under reduced pressure at 100° C.

The tri-ester was obtained as a viscous dark red oil.

This invention is not intended to be limited by any of the specific examples which have been given merely for the sake of illustration, but only by the appended claims in which it is intended to cover all novelty inherent in the invention as well as all modifications coming within the scope and spirit of the invention.

What is claimed is:

1. Liquid phosphoric acid esters of petroleum phenols having at least 11 carbon atoms and boi-
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ing above 150° C. at 6 mm. pressure, said esters being soluble in hydrocarbon oils at room temperature in all proportions.

2. Liquid phosphorus esters of petroleum phenols having at least 11 carbon atoms and boiling above 150° C. at 6 mm. absolute pressure, said esters being soluble in hydrocarbon oils at room temperature in all proportions and said esters boiling about 300° C., at 2 mm. absolute pressure.

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

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<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
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