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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of Triaryl Phosphates

We, GEIGY (U.K.) LIMITED, a British Company, whose Registered Office address is Simonsway, Manchester 22, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the production of esters of aromatic organic compounds, and in particular to the production of phosphates esters of alkylated phenols.

Mixtures of triaryl phosphates have established value as plasticisers for vinyl chloride polymers. These mixtures of triaryl phosphates have hitherto been prepared by phosphorylating commercially available, pre-formed alkylated phenols, for instance mixtures comprising cresols or xylenols obtained by coal tar distillation. We have now found that plasticisers having improved properties, in particular rendering thermoplastic polymers into which they are incorporated outstandingly stable to light, can be produced by phosphorylating, instead of the pre-formed alkylated phenols, an alkylated phenol product produced in a preliminary alkylation step from phenol.

The present invention therefore provides, in a process for the production of improved triaryl phosphate plasticisers by phosphorylat-

ing alkylated phenols, the improvement which consists in phosphorylating an alkylated phenol product containing free phenol, produced by contacting phenol with an alkylating agent containing from two to sixteen carbon atoms per molecule, the proportion of alkylating agent being within the range of from 5% to 65% by weight based on the weight of the phenol with which it is contacted.

According to the present invention, a process of producing phosphate esters comprises contacting phenol with an alkylating agent containing from two to sixteen carbon atoms per molecule, and contacting the alkylated phenol product which contains unreacted phenol with a phosphorylating agent to produce a mixture of two or more triaryl phosphate esters, the proportion of alkylating agent being within the range of from 5% to 65% by weight based on the weight of the phenol with which it is contacted. The present invention also comprises phosphate esters when produced by this process. The invention also provides polymeric or other organic compositions comprising phosphate esters produced by this process.

The phenol starting material is advantageously phenol derived from the decomposition of cumene hydroperoxide, or from the sulphonation of benzene. Preferably, the

[Price 25p]

SPECIFICATION AMENDED - SEE ATTACHED SLIP

75p

See Pg 16

phenol is in a form free or substantially free from alkylated phenols.

The alkylating agent may be chosen from any appropriate class of organic compound conventionally used in the alkylation of phenols by the Friedel-Crafts reaction and may be, for example, an alkyl halide, an alkanol or an olefin. If an alkyl halide is used, the alkyl group is preferably a straight- or branched-chain alkyl group containing from two to six carbon atoms or a cycloalkyl group containing from six to twelve carbon atoms, the halogen being chlorine or bromine. If an alkanol is used, this may be a primary, secondary or tertiary alkanol containing from two to six carbon atoms per molecule, particularly isopropanol, tertiary butyl or tertiary amyl alcohol or cyclohexanol.

The preferred alkylating agent is, however, an olefin containing from two to sixteen carbon atoms per molecule. The olefin may be straight- or branched-chain or cyclic, but is preferably a mono-ene and particularly a mono-ene containing from three to eight carbon atoms, propylene, isobutylene and diisobutylene being especially preferred. Examples of olefins which may be used as alkylating agent in the process include the following:—

ethylene, propylene, butene-1, butene-2, isobutylene, pentene-1, 2-methylbutene-1, hexene-1, cyclohexene, heptene-1, 2-methylpentene-1 (propylene dimer), octene-1, cyclo-octene, nonene-1, decene-1, cyclodecene, undecene-1, dodecene-1, cyclododecene, tetradecene and hexadecene.

The olefin may be a single olefin or a mixture of two or more thereof. Examples of mixtures which are particularly suitable for use as alkylating agents because of their ready availability include caprylene (a mixture of isomeric octenes), propylene trimer (a mixture of isomeric nonenes), propylene tetramer (a mixture of isomeric dodecenes), diisobutylene (a mixture of 2, 4, 4-trimethylpentene-1 and 2, 4, 4-trimethylpentene-2), triisobutylene (a mixture of dodecenes consisting predominantly of 2, 4, 4, 6, 6-pentamethylheptene-1), and tetra-isobutylene (a mixture of hexadecenes consisting predominantly of 2, 4, 4, 6, 6, 8, 8-heptamethylnonene-1).

If an olefin is used as alkylating agent, then in general the alkyl group introduced into the phenol molecule is an alkyl group containing same number of carbon atoms as are present in the olefin molecule. However, if the olefin used is diisobutylene, triisobutylene or tetra-isobutylene, in a proportion significantly below the proportion equimolar to the phenol with which the olefin is reacted, then the alkylated phenol product contains at least some of a tertiary alkylated phenol having a tertiarybutyl substituent in the phenolic nucleus, presumably from disproportionation of the cor-

responding higher tertiary-alkylated phenol with unreacted phenol.

The alkylation of the phenol may be carried out in a conventional Friedel-Crafts manner. Preferably, therefore, the alkylation is effected in the absence of a substantial amount of water. The alkylation is preferably carried out at a temperature in the range of from 15° to 250° C., a reaction temperature in the range of from 40° to 175° C. being particularly preferred, the choice of the reaction temperature employed depending on the nature of the reactants. The alkylation may be carried out at atmospheric pressure or at an elevated pressure; for example, if ethylene is used as alkylating agent, the reaction may conveniently be conducted at a superatmospheric pressure of up to 200 atmospheres.

The alkylation of the phenol is conveniently effected in the presence of an alkylation catalyst, which is preferably a Lewis acid or a Bronsted acid. Examples of Lewis acids which may be used include aluminium chloride, ferric chloride, stannic chloride, zinc chloride, boron trifluoride and complexes thereof, and titanium tetrachloride. Examples of Bronsted acids which may be used include sulphuric acid, orthophosphoric acid, *p*-toluene sulphonic acid, perchloric acid, sulphonated polystyrene resins or other acid forms of ion-exchange resins and acid-treated montmorillonite and other activated clays and earths. The proportion of catalyst present is preferably in the range of from 0.001% to 10% by weight, and especially from 0.05% to 5% by weight, based on the weight of the phenol present in the reaction mixture.

The alkylation is preferably carried out in the presence of gaseous hydrogen halide, particularly if a Lewis acid is used as alkylation catalyst. For instance, if the catalyst is aluminium chloride, the alkylation is preferably effected in the presence of hydrogen chloride which may be added to the reaction mixture or may be formed by decomposition of some of the aluminium chloride catalyst.

The proportion of alkylating agent to that of the phenol with which it is contacted in accordance with the invention is within the range of from 5% to 65% by weight of the alkylating agent based on the weight of the phenol or phenol mixture. If this proportion is substantially below 5%, the amount of unreacted phenol in the alkylation product, after phosphorylation, is found to be sufficient to cause the formation of relatively large quantities of the solid triphenyl phosphate in the phosphate ester product, and the presence of this solid material is unacceptable if the ester is to be used as a plasticiser or other purpose where a homogeneous ester or ester mixture is required. If the proportion of alkylating agent to phenol is substantially above 65%, the resulting phosphate ester pro-

duced is found to have too high a viscosity and boiling range to enable it to be readily purified or used as a plasticiser for vinyl chloride polymers or co-polymers, and the ester may have the further disadvantage of being completely compatible with the polymeric material.

Preferred proportions of alkylating agent to phenol are within the range of from 7% to 50% by weight of alkylating agent based on the weight of the phenol, a proportion within the range of from 10% to 40% by weight being especially preferred, as the phosphate esters produced from these proportions have especially good plasticising properties when incorporated into polyvinyl chloride. In particular, the phosphate esters produced from these proportions render polyvinyl chloride into which they are incorporated as plasticisers outstandingly stable to light.

The alkylated phenol product by contacting phenol with the alkylating agent is a mixture of unreacted phenol with one or more phenols alkylated with alkyl groups each preferably having the same number of carbon atoms as contained in the molecule of the alkylating agent.

The process of the invention may conveniently be carried out by reacting substantially the whole of the product resulting from the alkylation of the phenol with the alkylating agent with the phosphorylating agent to produce the alkylated phenol phosphate ester or esters. The alkylated phenol product from the alkylation stage may, for instance, be used as starting material in the phosphorylation stage, if desired with the addition of further phenol or with the addition of further alkylated phenol which has already been prepared by the alkylation process. Alternatively, the alkylated phenol product may be recovered from the alkylation reaction and, if desired after purification, used as starting material in the phosphorylation stage.

The product of the phenol alkylation may, for instance, be freed from part or all of any alkylation catalyst present: part or all of the catalyst may advantageously be removed if it would interfere with the course of the subsequent phosphorylation reaction, and replaced with another Lewis acid in order, for example to prevent catalyst deactivation or contamination or to provide a more effective catalyst for the phosphorylation reaction. Furthermore, part of the unreacted phenol may be removed from the alkylated phenol product resulting from the alkylation and the unreacted phenol thus separated off may be recycled to the alkylation stage with or without the addition of a further quantity of phenol to provide a continuous process. However, if it is desired to use the same catalyst for both the alkylation and phosphorylation stages, a particularly preferred catalyst is aluminium chloride.

The phosphorylation of the alkylated phenol

product, produced by the reaction of the phenol with the alkylating agent, may be carried out under a wide range of conventional phosphorylation reaction conditions. If the reaction is effected in the presence of a Lewis acid catalyst, this may be different from, but is preferably the same as, the catalyst used in the alkylation stage. The preferred phosphorylation catalyst is, however, aluminium chloride. The proportion of catalyst present is preferably in the range of from 0.001% to 5% by weight, and especially from 0.05% to 1% by weight based on the weight of the phenol present in the alkylated phenol product reacted with the phosphorylating agent. The preferred phosphorylating agent is phosphorus oxychloride, but phosphorus oxybromide or phosphoric acid may also be employed.

The phosphorylation is preferably carried out at a temperature in the range of from 15° to 250° C., a reaction temperature in the range of from 100° to 225° C. being particularly preferred in order to obviate the use of larger proportions of phosphorylating agent with respect to the alkylated phenol product which may be necessary to secure good yields of the desired phosphate ester when operating the reaction at lower temperatures.

The proportion of the phosphorylating agent to that of the alkylated phenol product may be varied within a wide range, depending on the nature of the reactants and the reaction conditions, but is preferably within the range of from 1 to 5 moles, and particularly within the range of from 2.5 to 3.5 moles, of alkylated phenol product per mole of phosphorylating agent.

The alkylated phenol phosphates produced in accordance with the present invention are valuable in a wide variety of uses. For instance, they find application as plasticisers or other additives to vinyl chloride polymers and co-polymers, polyolefins, cellulose esters, or other synthetic polymers; in the formulation of hydraulic or other functional fluids; as ignition control or other additives for fuels; and as extreme pressure additives or other additives to lubricants. Furthermore, the phosphate esters produced in accordance with the present invention have satisfactory toxicological properties as compared with phosphate esters produced by processes already in commercial use.

It is an advantage of the process of the present invention that, by controlling the addition of the alkylating agent to the phenol, the proportion of alkyl groups in the alkylated phenol product thus obtained can be adjusted to provide, after the subsequent phosphorylation stage has been carried out, a phosphate ester product which is especially suited to any particular desired application. For instance, it is well known that if a phosphate ester is to have optimal usefulness as a plasticiser for

vinyl chloride polymers or co-polymers, the proportion of alkyl groups present in the plasticiser ester or ester mixture has to be within certain limits, which may depend on the nature of the composition plasticised. The present invention provides a process which is particularly suited to the production of such esters or ester mixtures, in that the degree of alkylation required is readily achieved by controlling the addition of the alkylating agent to the phenol.

The present invention also provides compositions of organic materials to which phosphate esters are conventionally added to improve the physical properties of the said materials comprising a functionally effective proportion of a phosphate ester produced by a process of the invention. The composition may, for example, comprise synthetic polymer, for instance vinyl chloride polymers and co-polymers, polyolefins or cellulose esters and a plasticising proportion of the ester. The organic material may also be, for example, a hydraulic fluid or other functional fluid and a proportion of a phosphate ester of the invention sufficient to render the hydraulic fluid or other functional fluid fire-resistant; a liquid hydrocarbon fuel and a proportion of a phosphate ester of the invention sufficient to provide an ignition control additive; or a lubricant, especially a synthetic lubricant based on complex organic esters, and a proportion of a phosphate ester of the invention sufficient to provide an extreme pressure additive. The present invention also provides a process of producing compositions of organic materials comprising a functionally effective proportion of a phosphate ester produced by a process of the invention, which comprises admixing the organic material with the phosphate ester or esters. The following Examples further illustrate the present invention. Parts by weight shown therein bear the same relation to parts by volume as do kilograms to litres. Parts and percentages are expressed by weight unless otherwise stated.

EXAMPLE 1.

940 parts of phenol were placed in a reactor and fitted with a stirrer, gas inlet tube, thermometer and reflux condenser. After heating the reactor at 50° C., 44.5 parts of anhydrous aluminium chloride were added. Isobutylene was then passed in, while stirring the reaction mixture vigorously, until 71 parts of isobutylene had been absorbed. During the addition of the isobutylene, the temperature of the reactor contents was maintained at 50° C. by external cooling.

The reaction product, comprising 81.2% phenol and 18.8% *p*-tertiarybutyl-phenol, was cooled to 15° C. and 537.0 parts of phosphorus oxychloride were added over 45 minutes while maintaining the reaction mixture at 50° C. The resulting mixture was gradually heated to 150° C. over 4 hours and was then

maintained at 150° C. for a further period of 4 hours.

To the resulting product, after cooling, were added 1500 parts by volume of toluene and the mixture was washed with a mixture of 100 parts by volume of concentrated hydrochloric acid and 2000 parts by volume of water for 30 minutes at 60° C. and then with a mixture of 50 parts by volume of concentrated hydrochloric acid and 2000 parts by volume of water for 10 minutes at 60° C. This acid washing was then followed by a five-fold washing with 2,000 parts by volume of water for 10 minutes at 60° C. The toluene present was then distilled off and the product subjected to fractional distillation.

The fraction distilling over at boiling range 218° to 256° C. at 0.7 millimetre of mercury pressure, amounting to 998 parts, was collected. The fraction was washed, firstly, with a mixture of 30 parts of 46% sodium hydroxide solution and 1335 parts of water for 3 hours at 40° C. and, secondly, with a mixture of 15 parts of 46% sodium hydroxide solution and 1335 parts of water for 1 hour at 40° C. This alkali wash was then followed by washing twice with 2000 parts of water for 30 minutes at 40° C. to remove any sodium hydroxide present. The resulting product was dried by heating at 95° to 100° C. at 12 to 15 millimetres of mercury pressure.

The phosphate ester produced was an almost colourless oily liquid consisting of a mixture of triphenyl phosphate, tri-*p*-tertiarybutyl-phenyl phosphate and mixed phosphates derived from both phenol and *p*-tertiarybutyl-phenol in various proportions, and had an acid value of less than 0.1. (In all the Examples in this Specification, acid values are expressed as milligrams hydroxyl per gram).

EXAMPLE 2.

The procedure described in Example 1 was carried out except that the passage of isobutylene into the heated reactor was continued until 176 parts had been absorbed, the proportions of reactants and the reaction and recovery conditions being otherwise essentially the same.

The reaction product from the alkylation of the phenol with the isobutylene consisted of 55.7% phenol and 42.3% *p*-tertiarybutyl-phenol. The phosphate ester produced was an almost colourless oily liquid, having boiling range 196° to 258° C. at 10.3 millimetres of mercury pressure, amounting to 1131 parts and having acid value 0.2. The ester product consisted essentially of triphenyl phosphate, tri-*p*-tertiarybutyl-phenyl phosphate and mixed phosphates derived from both phenol and *p*-tertiarybutyl-phenol in various proportions.

EXAMPLE 3.

The procedure described in Example 1 was carried out except that propylene was used as

alkylating agent instead of isobutylene, the propylene being passed into the heated reactor containing the phenol and aluminium chloride until 168 parts had been absorbed. The proportions of reactants and the reaction and recovery conditions were otherwise essentially the same.

The reaction product from the alkylation of the phenol with the propylene consisted of unreacted and isopropylated phenol. The phosphate ester produced was an almost colourless oily liquid having boiling range 185° to 210° C. at to 1.5 millimetres of mercury pressure, amounting to 1100 parts and having acid value 0.19. The ester product consisted of triphenyl phosphate, tri-isopropyl-phenyl phosphate and mixed phosphates derived from both phenol and isopropyl phenol in various proportions.

In order to demonstrate the superior properties of the phosphate esters produced by the procedures described in Examples 1 to 3 over phosphate esters produced by similarly phosphorylating commercially available pre-formed alkyl phenols instead of the alkylated phenol produced as a first stage in those Examples, the following comparative Examples A to D are given followed by a description of the comparative tests made on the seven phosphate ester products in plasticising vinyl chloride film.

COMPARATIVE EXAMPLE A

The phosphorylation of Example 1 was carried out using 1080 parts commercially available cresol, obtained from coal tar distillation and consisting of:—

<i>o</i> -cresol	0.8%
<i>p</i> -cresol	33.9%
<i>m</i> -cresol	54.5%
2, 4-xyleneol	9.2%
2, 6-xyleneol	1.5%

for the alkylated phenol there used, the proportions of reactant and the reaction and recovery conditions being otherwise essentially the same.

The phosphate ester produced was a yellow, oily liquid having acid value less than 0.1, amounting to 1054 parts and having boiling range 202° to 210° C. at 0.7 millimetre of mercury pressure.

COMPARATIVE EXAMPLE B.

The procedure described in Comparative Example A was carried out except that the cresol starting material used had been subjected to purification by treatment with sulphuric acid and distillation of the product before reaction. The proportions of reactants and the reaction and recovery conditions were otherwise essentially the same.

The phosphate ester produced was an oily liquid having acid value 0.1, and was paler yellow in colour than the product of Comparative Example A.

COMPARATIVE EXAMPLE C.

The procedure described in Comparative

Example A was carried out except that the reactants used in the phosphorylation were 1145 parts of commercially available xyleneol produced by the distillation of coal tar and consisting of:—

2, 3-xyleneol	4.0%
2, 4-xyleneol	19.2%
2, 5-xyleneol	15.4%
2, 6-xyleneol	0.5%
3, 4-xyleneol	6.8%
3, 5-xyleneol	18.3%
<i>o</i> -cresol	0.6%
<i>m</i> -cresol	13.2%
<i>p</i> -cresol	12.1%
unknown	9.9%

42.5 parts of anhydrous aluminium chloride and 512.0 parts of phosphorus oxychloride, the reaction and recovery conditions being otherwise essentially the same.

The phosphate ester produced, consisting of a mixture of triaryl phosphates derived from xyleneols and cresols, amounted to 1212 parts having boiling range 207° to 237° C. at 0.3 millimetre of mercury pressure and acid value 0.4.

COMPARATIVE EXAMPLE D

The procedure described in Comparative Example C was carried out except that the xyleneol used in the phosphorylation had been purified by treatment with sulphuric acid and distillation of the product, the proportions of reactants and the reaction and recovery conditions being otherwise essentially the same.

The phosphate ester produced, consisting of a mixture of triaryl phosphates derived from xyleneols and cresols amounted to 1126 parts having boiling range 198° to 225° C. at 0.2 millimetre of mercury pressure and having acid value 0.1.

Samples of each of the seven phosphate esters produced by Examples 1 to 3 and Comparative Examples A to D were formulated into polyvinyl film in a conventional manner, the composition in each case being

65 parts "Breon 111" polyvinyl chloride

35 parts phosphate ester under test

3 parts "Ferroclore 1820" stabiliser

(Breon and Ferroclore are Trade Marks)

The film samples were then tested for stability to heat and light.

The heat stability tests were conducted in an oven heated at 180° C. The results showed that the polyvinyl chloride containing the phosphate esters of the present invention had the same good stability to heat as did the samples containing the phosphate esters made by the conventional procedures described in Comparative Examples A to D.

The light stability tests were carried out by the exposing pressed samples of the same polyvinyl chloride formulations used in the heat stability tests, having a thickness of 0.05 inch, to a "Xenotest" lamp. Even after 600 hours exposure, the film samples containing, as plasticisers, the phosphate esters pro-

duced by the procedures of Examples 1 to 3 showed no significant detectable change in colour, whereas the film samples containing the plasticiser phosphate esters produced by the procedures of Comparative Examples A to D exhibited marked yellowing.

EXAMPLE 4

282 parts of phenol and 13.3 parts of anhydrous aluminium chloride were placed in a reactor and the temperature of the reactor contents was raised to 120° C. Propylene was then passed into the mixture over a period of 1½ hours, after which time the uptake of propylene was 42 parts (equivalent to 1 mole per 3 moles of phenol). The reaction mixture was then cooled to 15° C. and 161.4 parts of phosphorus oxychloride, representing 5% excess over the equimolar proportion of phenol, were added over 30 minutes while maintaining the reactor at 15° C. The reaction mixture was then heated to 150° C. over 4 hours and then maintained at the same temperature for a further period of 4 hours, during which hydrogen chloride gas was evolved.

To the resulting product, after cooling, were added 250 parts of toluene and the mixture was washed with aqueous hydrochloric acid at 60° C. and then with water. The toluene and any traces of water were then removed by distillation at 0.2 millimetre of mercury pressure.

The fraction distilling off at boiling range 190° to 238° C. was collected and washed with aqueous sodium hydroxide solution and with water at 40° C. Traces of water were removed by distillation at 12 to 15 millimetres of mercury pressure. The phosphate ester produced, consisting of triphenyl phosphate and isopropylated phenyl phosphates, was treated with activated carbon and finally filtered.

In this way, 290.4 parts of the purified product were obtained, representing a yield of 78.5% based on the amount of propylene

passed into the reactor. The product had an acid value of 0.07.

EXAMPLE 5.

The procedure described in Example 4 was carried out using 63 parts of propylene, which were passed into the reactor at 120° C. for 2.75 hours, the proportions and reaction and recovery conditions being otherwise essentially the same.

The product had boiling range 175° to 206° C. at 1 millimetre of mercury pressure, 336.7 parts being obtained representing a yield of 87%. The ester obtained, which consisted of a mixture of triphenyl phosphate and isopropylated-phenyl phosphates, had an acid value of 0.08.

EXAMPLE 6.

The procedure described in Example 4 was carried out using 84 parts of propylene passed into the reactor over 3½ hours, the proportions and reaction and recovery conditions being otherwise essentially the same.

336 parts of the purified phosphate ester product were obtained, representing a yield of 79.6% and consisting of a mixture of triphenyl phosphate and isopropylated-phenyl phosphates. The product had an acid value of 0.01.

EXAMPLES 7 TO 9.

The procedure described in Example 4 was carried out, except that the quantities of isobutylene shown in Table 1 were passed into the mixture of phenol and aluminium chloride have instead of the propylene there used during the stated periods, the proportions and reaction and recovery conditions being otherwise essentially the same.

The boiling ranges and amounts of the purified phosphate esters obtained, in each case consisting essentially of a mixture of triphenyl phosphate, tri-*p*-tertiarybutyl-phenyl phosphate and mixed phosphates containing both phenol and *p*-tertiarybutyl-phenol in various proportions are shown in Table 1.

TABLE 1

Example	7	8	9
Parts isobutylene introduced:	33.7	42.1	50.5
Passed in for (minutes):	25	35	50
Boiling Range:	185° to 218°C. (0.1 millimetre)	200° to 235°C. (0.6 millimetre)	216° to 252°C. (1 millimetre)
Parts ester obtained:	257.8	292.5	332.8

EXAMPLES 10 TO 13

The procedure described in Example 4 was carried out, except that isobutylene was passed into the mixture of phenol and aluminium chloride instead of the propylene there used, the temperature of the reactor contents being maintained at 50°C. during the alkylation instead of at 120°C. The proportions and reaction and recovery conditions were otherwise essentially the same.

The boiling ranges and properties of the purified phosphate esters thus produced, in each case consisting essentially of a mixture of triphenyl phosphate and tertiarybutylated-phenyl phosphates, were essentially the same as those in Examples 7 to 9.

EXAMPLES 14 TO 16.

The procedure described in Example 4 was carried out except that di-isobutylene (a mixture consisting of 75% 2, 4, 4-trimethylpentene-1 and 25% 2, 4, 4-trimethylpentene-2) was used as alkylating agent instead of the propylene there used, the quantities of di-isobutylene introduced into the mixture of phenol and aluminium chloride being shown in Table 2 and the proportions and reaction and recovery conditions being otherwise essentially the same.

The purified phosphate esters thus produced, in each case comprised triphenyl phosphate, tri-*p*-tertiarybutyl-phenyl phosphate and mixed phosphates containing both phenol and *p*-tertiarybutyl-phenol in various proportions.

TABLE 2

Example	14	15	16
Parts di-isobutylene introduced:	33.6	42.0	50.4
Parts ester obtained:	297.6	353.5	330.0

The analysis of the hydrolysate from the phosphate ester did not reveal the presence of any octylated phenol which might have been expected from the use of an octene as alkylating agent, indicating complete disproportionation to the tertiarybutyl analogue.

As a comparison with Examples 14 to 16 of the invention, the same procedure was attempted in two separate runs except that the amounts of di-isobutylene introduced into the mixture of phenol and aluminium chloride in the reactor were 6.8 parts and 8.4 parts, representing proportions of alkylating agent based on the weight of phenol in the reactor of approximately 2.4% and 3.0% (compared with the equivalent figures of 12.0%, 15.0%, and 18.0% respectively for the proportions used in Examples 14, 15 and 16), and which are thus not embodiments of the present invention.

On reaching the step of removing toluene and traces of water from the phosphorylated product, solid triphenyl phosphate precipitated out, so that a homogeneous ester product could not be produced.

EXAMPLE 17.

This Example illustrates the use of phosphate esters produced by the process of the present invention as plasticisers for cellulose triacetate film.

A solution of cellulose triacetate in a solvent mixture comprising 90 parts by volume methylene chloride and 10 parts by volume methanol was prepared by dissolving 50 parts cellulose

triacetate (acetyl content 62.5%, expressed as acetic acid) in 350 parts of the solvent mixture. To this was added 10 parts of plasticiser and the container was rotated on a tumbler for 24 hours to mix the components thoroughly. The solution was allowed to stand until all air bubbles were released and then cast on a strip of aluminium foil using a doctor blade adjusted to give a film thickness of 0.5 millimetre when dry. The films, when dry, were removed from the aluminium foil and stored at a constant temperature of 23°C. and 50% relative humidity for seven days before testing.

A range of phosphate esters prepared from phenol alkylated with isobutylene or propylene as described in Examples 1, 2 and 3 were used as plasticisers as shown in Table 3, triphenyl phosphate being also included to give comparative data. In all cases dry, clean, flexible films were obtained which showed no change on storage for two months at 23°C. and 50% relative humidity.

Tensile strength determinations were carried out on portions of these films at 23°C. and 50% relative humidity using 3 inch long dumbbell-shaped specimens cut from the film using a sharp knife-edged punch. Testing was carried out at a rate of extension of 0.25 inch per minute, the tensile strength being calculated from the maximum load recorded and the initial area of cross-section. Eleven specimens were tested from each film and the value quoted in Table 3 for the

respective compositions is the arithmetic mean of these results. The plasticiser content in each case was 20% expressed by weight based on the weight of the cellulose triacetate.

TABLE 3

	Tensile strength (Kg/mm ²)
Triphenyl phosphate	5.45
Alkylated phenol phosphate as prepared in Example 1	6.24
Alkylated phenol phosphate as prepared in Example 2	6.29
Alkylated phenol phosphate as prepared in Example 3	6.50

10 The results demonstrate the improved plasticising properties of the phosphate esters produced by the process of the present invention as compared with triphenyl phosphate, which is the conventional cellulose triacetate plasticiser.

EXAMPLE 18.

15 The following Example illustrates the use of the esters of the present invention in hydraulic fluid compositions.

20 Phosphate esters produced by the processes described in Examples 2 and 3 were found to possess properties rendering them valuable base-stocks in formulating industrial fire-resistant hydraulic fluids; in particular the esters have been found to have high flash points, fire points and autogeneous ignition temperatures.

Other desirable requisites for hydraulic

fluids which the esters possess include superior viscosity/temperature properties, low pour points and little tendency to crystallise at low temperatures.

These properties are shown in Table 4. Viscosity determinations, pour points, flash points and fire points were carried out by the methods described in "Institute of Petroleum Standards for Petroleum and its Products," Part 1; autogeneous ignition temperatures and Viscosity Indices by methods described in "Book of ASTM Standards," Part 17. A.S.T.M. slopes were obtained from tables prepared from A.S.T.M. Viscosity-temperature charts. Low temperature storage tests consisted of maintaining samples of the fluids, in sealed glass tubes, for seven days at each of a series of gradually decreasing temperatures.

TABLE 4

	Phosphate ester prepared by Example 2	Phosphate ester prepared by Example 3
Viscosity at 210°F (centistokes)	4.91	3.77
Viscosity at 100°F (centistokes)	36.84	22.76
Viscosity Index (210° to 100°F.)	35.4	26.4
A.S.T.M. Slope (210° to 100°F.)	0.829	0.837
Flash point (°F.)	475	460
Fire point (°F.)	605	590
Autogeneous ignition temp. (°F.)	1130	1177
Pour point (°F.)	-10	-25
Low temperature storage	No cloud or crystals at temperatures down to -32°C.	

EXAMPLE 19.

The following Example illustrates the use of the esters of the present invention as extreme-pressure additives for lubricating oils.

Phosphate esters produced by the processes described in Examples 1 and 3, when added in small quantities to lubricating oils (which can be naturally occurring or synthetic), have been shown to provide increased load-carrying and anti-wear properties. In other words they are useful as mild extreme-pressure/anti-wear activities.

The well-known Shell 4-Ball Lubricant Testing Apparatus was used to measure the Mean Hertz Load and Incipient Seizure Load of a paraffin oil (Shell Talpa 20) (viscosity 88 centistokes at 100°F.) with and without the addition of the phosphates of the invention. This apparatus consists essentially of a half-inch diameter steel ball which is rotated at a speed of 1,420 revolutions per minute in contact with three similar balls held stationary

in a test cup, by means of a clamping ring and nut, and immersed in the oil under test. A lever system exerts a known, variable force (applied load) between the stationary balls and the rotating ball. During the test small circular scars are worn on each of the fixed balls and the size of the scars gives an indication of the anti-wear and load carrying properties of the lubricant.

The Mean Hertz Load is obtained from a series of test runs carried out at twenty different specified loadings and is the average of these loads corrected for the difference between the actual diameters of the wear scars formed and the Hertz diameter which is the area of contact between the balls under static load. The Incipient Seizure Load is the applied load at which the oil film first breaks down, with a rapid increase in friction and wear resulting. The oil film can subsequently re-form at this stage.

TABLE 5

Additive Used	Concentration	Mean Hertz Load (Kg)	Incipient Seizure Load (Kg)
None	—	19.6	45—48
Phosphate prepared by Example 1	2% w/w	27.2	60—63
Phosphate prepared by Example 3	2% w/w	23.6	55—57

The results obtained from tests carried out on the alkylated phenol phosphates prepared by Examples 1 and 3 are shown in Table 5. These clearly indicate the beneficial effect of adding the phosphate esters to the oil.

EXAMPLE 20.

The following Example illustrates the use of the esters of the present invention as plasticisers in tiles made of vinyl polymers or copolymers which are fixed to the surface to be tiled with bituminous adhesives.

It is already well known that if vinyl tiles containing certain types of plasticiser are affixed with bituminous adhesives, the plasticiser may diffuse out of the polymer, and cause the adhesive to soften and flow out between the tiles. If the softened adhesive reaches the decorative surfaces of the tiles, they may be spoiled by being stained with the softened adhesive. Accordingly tests have been devised to measure the ability of a plasticiser not to migrate into bituminous adhesive, for instance the "asphalt leaching test." In this test, paper strips, coated on one side with bitumen, immersed in the plasticiser and the colour change of the plasticiser is determined after immersion of the bitumen-coated paper for one hour.

This test was carried out upon a sample of a phosphate ester prepared in accordance with Example 3 except that sulphuric acid-activated fullers' earth was used as catalyst in the alkylation stage instead of the aluminium chloride there used. The initial colour, as measured on the Lovibond comparator, was 0.5 yellow, 0.0 red, and the final colour was 1.2 yellow, 0.1 red. As a comparison, the same test was carried out on a sample of phosphate ester produced as described in Comparative Example C; the initial colour of this trixylenyl phosphate was 0.57 yellow, 0.0 red and the final colour was 6.0 yellow, 1.0 red.

This comparison illustrates, therefore, the slight colour change of 0.7 yellow, 0.1 red produced by the phosphate ester of the present

invention, as against the very marked colour change of 5.5 yellow 1.0 red produced by a typical phosphate ester of the prior art, and signifies that the phosphate ester of the invention would have especial and unexpectedly great value as a plasticiser for vinyl polymer tiles to be fixed with a bituminous adhesive.

EXAMPLE 21.

940 parts of phenol were placed in a reactor fitted with stirrer, gas inlet tube, thermometer and reflux condenser. The phenol was melted and 75 parts of "Fulmont 237" activated montmorillonite (The Fullers' Earth Union Ltd., Redhill, Surrey—Fulmont is a Trade Mark) were added. The reactor was now heated to 105° to 110° C. and propylene was passed in, while stirring the mixture vigorously until 240 parts of propylene had been absorbed. During the addition of the propylene the temperature of the reactor was maintained at 105° to 110° C. The reaction mixture was allowed to cool and the montmorillonite was removed by filtration. The reaction product was found by gas/liquid chromatographic analysis to have the following percentage composition:—

phenol	41.7
mono-isopropylphenols	44.3
di-isopropylphenols	10.9
tri-isopropylphenols	1.6
ethers	1.3
unknown	0.2

By repeating this procedure, except that the amount of the montmorillonite was reduced to 18.8 parts, the proportion of the other reactants remaining unchanged, an isopropylated phenol product having a substantially identical percentage composition was obtained.

44.5 parts of anhydrous aluminium chloride were added, followed by the addition of 537 parts of phosphorus oxychloride over a period of 45 minutes while maintaining the reaction mixture at 50° C. The recovery procedure described in Example 1 was then followed. The fraction distilling over the boiling range 200—220° C. at 0.5 millimetre of mercury

pressure, amounting to 1158 parts, was collected. This fraction was washed and dried as described in Example 1.

- 5 The phosphate ester produced was an almost colourless oil consisting of a mixture of triphenyl phosphate, and mixed phosphates derived from both phenol and isopropylated phenols in various proportions, and had an acid value of 0.1.

10 EXAMPLES 22 TO 27.

- The phosphate ester produced by the procedure described in Example 21 was subjected to a standard testing to determine its liquid physical properties and to evaluate its plasticising properties (Example 22). A sample of the ester, and of the two other phosphate esters (Examples 23 and 24) produced by the procedure of Example 21, except that the amounts

of propylene used in the alkylation stage had the values given in Table 6 instead of the 240 parts in the procedure of Example 21, and of three other phosphates (Examples 25 to 27) produced by the procedures described in Examples 7, 8 and 14 respectively, were each formulated into polyvinyl film in a conventional manner, the composition in each case being

- 65 parts polyvinyl chloride ("Breon III")
35 parts phosphate ester under test
4 parts white lead paste
1 part calcium stearate

The results of the determination of liquid physical properties and evaluation of plasticising properties are shown in Table 6. These results illustrate the value of the phosphate esters of the present invention as plasticisers of polyvinyl chloride.

TABLE 6

Example	22	23	24	25	26	27
Alkylating agent	propylene	propylene	propylene	iso-butylene	iso-butylene	di-iso-butylene
Parts Agent	240	105	340	33.7	42.1	33.6
Parts Phenol	940	940	940	282	282	282
Viscosity (centistokes at 25°C.)	77.6	42.8	155.4	54.3	62.7	43.5
Density (gm./ml. at 25°C.)	1.144	1.181	1.119	1.178	1.170	1.188
Refractive Index at 25°C.	1.5481	1.5553	1.5423	1.5564	1.5551	1.5562
Hazen number	75	100	200	75	50	60
I.R.H.D. (hardness)	88	81	94.8	88.7	90.5	87.8
T _g (°C.)	+10	+6	+13	+12.5	+14.6	+9
Clash & Berg (°C.)	+3	0	+5	+7.5	+8.5	+6
Volatility	0.91	2.0	0.8	1.38	1.09	—
Compound	1.3	3.8	2.4	5.73	1.08	1.2
Volume resistivity (ohm.cm.)	$\times 10^{13}$	$\times 10^{12}$	$\times 10^{13}$	$\times 10^{13}$	$\times 10^{14}$	$\times 10^{13}$

Example	22	23	24	25	26	27
Extractions (%)						
Water	+0.06	0.17	+0.32	+0.05	0	0.4
Soap	11.4	13.3	8.5	10.1	9.0	11.8
Detergent	7.4	13.5	5.6	10.3	9.0	12.5
Mineral Oil	12.5	14.0	9.3	10.1	8.0	10.6
Olive Oil	12.6	14.0	8.9	10.8	8.6	10.5
Petrol	14.9	15.0	16.6	17.4	18.0	18.2

The T_g figure given is the temperature in degrees Centigrade at which the material has a modulus of rigidity of 1000 kilograms per square centimetre; it is a low-temperature stiffness figure.

The I.R.H.D. figure is the International Rubber Hardness Degrees.

The volatility is given as the percentage weight loss from a $15 \times 1 \times 0.1$ centimetre specimen in 96 hours at 82.5°C . in a forced draught air oven. The extractions are given as percentage weight loss from a thin sheet ($3 \times 3 \times 0.007$ inch) immersed under the following conditions.

Petrol	75% iso-octane; 25% toluene; 1 hour at 23°C .
Mineral Oil	Oil to specification D.E.F. 2001; 24 hours at 60°C .
Olive Oil	B.P. quality; 24 hours at 60°C .
1% Soap	1% solution of soap flakes in distilled water; 24 hours at 60°C .
1% detergent	1% solution of triethanolamine lauryl sulphate in distilled water; 24 hours at 60°C .
Distilled water	24 hours at 60°C .

EXAMPLE 28

940 parts of phenol and 94 parts of "Fulmont 237" activated montmorillonite were placed in a reactor, which was then heated to 150°C . and 325 parts of capryl alcohol were added from below the surface of the reactor contents over a period of 4 hours: water distilling from the reaction mixture was collected in a trap. The reaction mass was stirred at 150°C . for a further period of 1 hour after all the capryl alcohol had been added and the resulting mixture was then allowed to cool below 80°C . 250 parts of benzene were added and the mixture was heated until all the water remaining in the

reaction mass was removed as the benzene/water azeotrope. The excess benzene was removed by distillation, and the montmorillonite present was removed by filtration after the phenol mixture had been allowed to cool.

44.5 parts of anhydrous aluminium chloride were added, followed by 524 parts of phosphorus oxychloride, added over a period of 45 minutes while maintaining the reaction mixture at 50°C . The recovery procedure described in Example 1 was then followed.

The ester product, consisting of triphenyl phosphate and mixed phosphates derived from both phenol and capryl phenols, was a pale yellow oil boiling over the range 172°

to 275° C. at 0.1 millimetre of mercury pressure. It had acid value 0.2 and amounted to 1120 parts.

EXAMPLE 29

- 5 The phosphate ester produced by the procedure described in Example 28 was subjected

to a standard testing procedure, as described in Examples 22 to 27, to determine its liquid physical properties and to evaluate its plasticising properties.

The results are shown in Table 7. These results illustrate the value of the phosphate ester in plasticising polyvinyl chloride.

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TABLE 7

Viscosity:	58.4 centistokes at 25°C.
Density:	1.135 grams per millilitre at 25°C.
Refractive index:	1.5409 at 25°C.
Hazen Colour:	50
I.R.H.D. (hardness)	83.5
T _g (°C.):	+4.5
Clash & Berg (°C.):	-3.5
Volatility (%):	0.8
Compound Volume Resistivity (ohm.cm.):	1.4×10^{12}
Extractions (%)	
Water:	+0.05
Soap:	9.6
Detergent:	6.2
Mineral Oil:	12.1
Olive Oil:	12.9
Petrol:	16.3

The significance of the properties measured is as described in Examples 22 to 27.

EXAMPLE 30

- 15 940 parts of phenol were placed in a reactor fitted with stirrer, dropping funnel, thermometer and reflux condenser. 10 parts of concentrated sulphuric acid were added and the reactor was heated to 100° C. 280 parts of caprylene were added dropwise over a period of 1 hour and the reaction mass was then maintained at 100° to 105° C. for a further 4 hours. The excess sulphuric acid was neutralised by stirring the reaction mixture with 11 parts of solid sodium carbonate at 100° to 105° C. for 2 hours and the solid was removed

by filtration after cooling. To the filtrate, which was 1124 parts of a mixture of phenol and capryl phenols, was added 41 parts of anhydrous aluminium chloride, followed by 495 parts of phosphorus oxychloride added over a period of 45 minutes while maintaining the reaction mixture at 50° C. The recovery procedure described in Example 1 was then followed.

The ester product, consisting of triphenyl phosphate and mixed phosphates derived from both phenol and capryl phenols, was a pale yellow oil boiling over the range 168° to

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280° C. at 0.2 millimetre of mercury pressure. It had acid value of 0.2 and amounted to 1092 parts.

EXAMPLE 31

- 5 376 parts of phenol were placed in a reactor fitted with stirrer, dropping funnel, thermometer and reflux condenser. 0.06 part of perchloric acid (specific gravity 1.70) was added and the mixture heated to 45° C. 109
- 10 parts of cyclohexene were added dropwise over a period of 1 hour maintaining the reaction temperature at 45° C. The mixture was stirred at 45° C. for a further 1 hour, and then un-
- 15 reacted cyclohexene (amounting to 17 parts) was removed by distillation at 12 millimetres of mercury pressure.
- 17 parts of anhydrous aluminium chloride were added, followed by 215 parts of phosphorus oxychloride, added over a period of
- 20 45 minutes while maintaining the reaction mixture at 50° C. The resulting mixture was gradually heated to 150° C. over 4 hours and was then maintained at 150° C. for a
- 25 further period of 4 hours.
- To the resulting product, after cooling, were
- added 600 parts by volume of toluene and the
- mixture was washed with a mixture of 40
- 30 parts by volume of concentrated hydrochloric acid and 800 parts by volume of water for 30 minutes at 60° C. and then with a mixture
- of 20 parts by volume of concentrated hydro-
- 35 chloric acid and 800 parts by volume of water for 10 minutes at 60° C. This acid washing was then followed by a five-fold washing with
- 800 parts by volume of water for 10 minutes
- 40 at 60° C. The toluene present was then removed by distillation and the product subjected to fractional distillation.
- The fraction distilling over at boiling range
- 40 182° to 250° C. at 0.1 millimetre of mercury pressure, amounting to 388 parts, was collected. The fraction was washed, firstly, with a mixture
- of 12 parts 46% sodium hydroxide solution and 530 parts of water for 3 hours at
- 45 40° C. and, secondly, with a mixture of 6 parts of 46% sodium hydroxide solution and 530 parts of water for 1 hour at 40° C. This alkali wash was then followed by washing
- twice with 800 parts of water for 30
- 50 minutes at 40° C. to remove any sodium hydroxide present. The resulting product was dried by heating at 95° to 100° C. at 12 to 15 millimetres of mercury pressure.
- The phosphate ester produced was a pale
- 55 yellow, oily liquid consisting of a mixture of triphenyl phosphate and mixed phosphates derived from both phenol and cyclohexyl phenols, and had an acid value of less than 0.1.
- WHAT WE CLAIM IS:—
- 60 1. A process of producing phosphate esters which comprises contacting phenol with an alkylating agent containing from two to sixteen carbon atoms per molecule, and contacting the alkylated phenol product which
- 65 contains unreacted phenol with a phosphory-

lating agent to produce a mixture of two or more triaryl phosphate esters, the proportion of alkylating agent being within the range of from 5% to 65% by weight based on the weight of the phenol with which it is

2. A process as claimed in Claim 1, wherein the phenol starting material is phenol derived from the decomposition of cumene hydroperoxide, or from the sulphonation of benzene, and is in a form free or substantially free from alkylated phenols.

3. A process as claimed in Claim 1 or Claim 2 wherein the alkylating agent is an alkyl halide, an alkanol or an olefin.

4. A process as claimed in Claim 3 wherein the alkylating agent is an alkyl halide, the alkyl group being a straight- or branched-chain alkyl group containing from two to six carbon atoms or a cycloalkyl group containing from six to twelve carbon atoms, and the halogen being chlorine or bromine, or wherein the alkylating agent is a primary, secondary or tertiary alkanol containing from two to six carbon atoms per molecule.

5. A process as claimed in Claim 3 wherein the alkylating agent is a straight- or branched-chain or cyclic olefin containing from two to sixteen carbon atoms per molecule.

6. A process as claimed in Claim 5 wherein the alkylating agent is propylene, isobutylene or di-isobutylene.

7. A process as claimed in Claim 5 wherein the alkylating agent is ethylene, butene-1, butene-2, pentene-1, 2-methylbutene-1, hexene-1, cyclohexene, heptene-1, 2-methylpentene-1 (propylene dimer), octene-1, cyclooctene, nonene-1, decene-1, cyclodecene, undecene-1, dodecene-1, cyclododecene, tetradecene, hexadecene, caprylene, propylene trimer, propylene tetramer, tri-isobutylene, or tetra-isobutylene.

8. A process as claimed in any of the preceding Claims wherein the alkylation is effected in the absence of a substantial amount of water.

9. A process as claimed in any of the preceding Claims wherein the alkylation is carried out at a temperature in the range of from 15° to 250° C.

10. A process as claimed in Claim 9 wherein the alkylation is carried out at a temperature in the range of from 40° to 175° C.

11. A process as claimed in any of the preceding Claims wherein alkylation is effected in the presence of a Lewis acid or a Bronsted acid as alkylation catalyst.

12. A process as claimed in Claim 11 wherein the alkylation catalyst is aluminium chloride or an acid-treated montmorillonite.

13. A process as claimed in Claim 11 wherein the alkylation catalyst is ferric chloride, stannic chloride, zinc chloride, boron trifluoride or a complex thereof, titanium tetrachloride, sulphuric acid, orthophosphoric

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280° C. at 0.2 millimetre of mercury pressure. It had acid value of 0.2 and amounted to 1092 parts.

EXAMPLE 31

5 376 parts of phenol were placed in a reactor fitted with stirrer, dropping funnel, thermometer and reflux condenser. 0.06 part of perchloric acid (specific gravity 1.70) was added and the mixture heated to 45° C. 109
10 parts of cyclohexene were added dropwise over a period of 1 hour maintaining the reaction temperature at 45° C. The mixture was stirred at 45° C. for a further 1 hour, and then unreacted cyclohexene (amounting to 17 parts)
15 was removed by distillation at 12 millimetres of mercury pressure.

17 parts of anhydrous aluminium chloride were added, followed by 215 parts of phosphorus oxychloride, added over a period of
20 45 minutes while maintaining the reaction mixture at 50° C. The resulting mixture was gradually heated to 150° C. over 4 hours and was then maintained at 150° C. for a further period of 4 hours.

25 To the resulting product, after cooling, were added 600 parts by volume of toluene and the mixture was washed with a mixture of 40 parts by volume of concentrated hydrochloric acid and 800 parts by volume of water for
30 30 minutes at 60° C. and then with a mixture of 20 parts by volume of concentrated hydrochloric acid and 800 parts by volume of water for 10 minutes at 60° C. This acid washing was then followed by a five-fold washing with
35 800 parts by volume of water for 10 minutes at 60° C. The toluene present was then removed by distillation and the product subjected to fractional distillation.

40 The fraction distilling over at boiling range 182° to 250° C. at 0.1 millimetre of mercury pressure, amounting to 388 parts, was collected. The fraction was washed, firstly, with a mixture of 12 parts 46% sodium hydroxide solution and 530 parts of water for 3 hours at
45 40° C. and, secondly, with a mixture of 6 parts of 46% sodium hydroxide solution and 530 parts of water for 1 hour at 40° C. This alkali wash was then followed by washing twice with 800 parts of water for 30
50 minutes at 40° C. to remove any sodium hydroxide present. The resulting product was dried by heating at 95° to 100° C. at 12 to 15 millimetres of mercury pressure.

55 The phosphate ester produced was a pale yellow, oily liquid consisting of a mixture of triphenyl phosphate and mixed phosphates derived from both phenol and cyclohexyl phenols, and had an acid value of less than 0.1.

WHAT WE CLAIM IS:—

60 1. A process of producing phosphate esters which comprises contacting phenol with an alkylating agent containing from two to sixteen carbon atoms per molecule, and contacting the alkylated phenol product which
65 contains unreacted phenol with a phosphory-

lating agent to produce a mixture of two or more triaryl phosphate esters, the proportion of alkylating agent being within the range of from 5% to 65% by weight based on the weight of the phenol with which it is
70 contacted.

2. A process as claimed in Claim 1, wherein the phenol starting material is phenol derived from the decomposition of cumene hydroperoxide, or from the sulphonation of benzene,
75 and is in a form free or substantially free from alkylated phenols.

3. A process as claimed in Claim 1 or Claim 2 wherein the alkylating agent is an alkyl halide, an alkanol or an olefin.
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4. A process as claimed in Claim 3 wherein the alkylating agent is an alkyl halide, the alkyl group being a straight- or branched-chain alkyl group containing from two to six carbon atoms or a cycloalkyl group containing
85 from six to twelve carbon atoms, and the halogen being chlorine or bromine, or wherein the alkylating agent is a primary, secondary or tertiary alkanol containing from two to six carbon atoms per molecule.
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5. A process as claimed in Claim 3 wherein the alkylating agent is a straight- or branched-chain or cyclic olefin containing from two to sixteen carbon atoms per molecule.

6. A process as claimed in Claim 5 wherein the alkylating agent is propylene, isobutylene or di-isobutylene.
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7. A process as claimed in Claim 5 wherein the alkylating agent is ethylene, butene-1, butene-2, pentene-1, 2-methylbutene-1,
100 hexene-1, cyclohexene, heptene-1, 2-methylpentene-1 (propylene dimer), octene-1, cyclooctene, nonene-1, decene-1, cyclododecene, undecene-1, dodecene-1, cyclododecene, tetradecene, hexadecene, caprylene, propylene trimer, propylene tetramer, tri-isobutylene, or tetra-isobutylene.
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8. A process as claimed in any of the preceding Claims wherein the alkylation is effected in the absence of a substantial amount
110 of water.

9. A process as claimed in any of the preceding Claims wherein the alkylation is carried out at a temperature in the range of from 15° to 250° C.
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10. A process as claimed in Claim 9 wherein the alkylation is carried out at a temperature in the range of from 40° to 175° C.

11. A process as claimed in any of the preceding Claims wherein alkylation is effected in the presence of a Lewis acid or a Bronsted acid as alkylation catalyst.
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12. A process as claimed in Claim 11 wherein the alkylation catalyst is aluminium chloride or an acid-treated montmorillonite.
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13. A process as claimed in Claim 11 wherein the alkylation catalyst is ferric chloride, stannic chloride, zinc chloride, boron trifluoride or a complex thereof, titanium tetrachloride, sulphuric acid, orthophosphoric
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* C L M S *

acid, *p*-toluene sulphonic acid or a sulphonated polystyrene resin or other acid form of an ion-exchange resin.

14. A process as claimed in any of Claims 11 to 13 wherein the proportion of catalyst present is in the range of from 0.001% to 10% by weight, based on the weight of the phenol present in the reaction mixture.

15. A process as claimed in Claim 14 wherein the proportion of catalyst present is in the range of from 0.05% to 5% by weight, based on the weight of the phenol present in the reaction mixture.

16. A process as claimed in any of the preceding Claims wherein the alkylation is carried out in the presence of gaseous hydrogen halide.

17. A process as claimed in any of the preceding Claims wherein the alkylated phenol product which is contacted with the phosphorylating agent is a mixture of unreacted phenol with one or more phenols alkylated with alkyl groups each having the same number of carbon atoms as contained in the molecule of the alkylating agent.

18. A process as claimed in Claim 17 wherein the alkylated phenol product used is substantially the whole of the product resulting from the alkylation of the phenol with the alkylating agent.

19. A process as claimed in Claim 17 wherein the alkylated phenol product which is contacted with the phosphorylating agent is substantially the whole of the product resulting from the alkylation of the phenol with the alkylating agent, part or all of any alkylation catalyst present having been removed.

20. A process as claimed in Claim 17 or Claim 18 wherein further phenol or further alkylated phenol already prepared by the alkylation process is added to the alkylated phenol product to be contacted with the phosphorylating agent.

21. A process as claimed in any of the preceding Claims wherein part of the unreacted phenol is removed from the alkylated phenol product resulting from the alkylation, the unreacted phenol thus separated off is recycled to the alkylation stage to provide a continuous process and a further quantity of phenol is added to the unreacted phenol separated from the alkylated phenol product for recycling to the alkylation stage.

22. A process as claimed in any of the preceding Claims wherein the phosphorylation of the alkylated phenol product is carried out in the presence of a Lewis acid as catalyst.

23. A process as claimed in Claim 22 wherein the catalyst is aluminium chloride.

24. A process as claimed in Claim 22 or Claim 23 wherein the proportion of phosphorylation catalyst present is in the range of from 0.001% to 5% by weight based on the weight of the phenol present in the alkylated

phenol product reacted with the phosphorylating agent.

25. A process as claimed in Claim 24 wherein the proportion of phosphorylation catalyst present is in the range of from 0.05% to 1% by weight based on the weight of the phenol present in the alkylated phenol product reacted with the phosphorylating agent.

26. A process as claimed in any of the preceding Claims wherein the phosphorylating agent is phosphorus oxychloride.

27. A process as claimed in any of the preceding Claims wherein the phosphorylation is carried out at a temperature in the range of from 15° to 250° C.

28. A process as claimed in Claim 27 wherein the phosphorylation is carried out at a temperature in the range of from 100° to 225° C.

29. A process as claimed in any of the preceding Claims wherein the proportion of the phosphorylating agent to that of the alkylated phenol product is within the range of from 1 to 5 moles of alkylated phenol product per mole of phosphorylating agent.

30. A process as claimed in Claim 29 wherein the proportion of the phosphorylating agent to that of the alkylated phenol product is within the range of from 2.5 to 3.5 moles of alkylated phenol product per mole of phosphorylating agent.

31. A process as claimed in any of the preceding Claims wherein the proportion of alkylating agent to phenol is within the range of from 7% to 50% by weight of alkylating agent based on the weight of the phenol.

32. A process as claimed in Claim 31 wherein the proportion of alkylating agent to phenol is within the range of from 10% to 40% by weight based on the weight of the phenol.

33. A process of producing a mixture of phosphate esters in accordance with Claim 1 and substantially as described in any of Examples 1 to 16.

34. A process of producing a mixture of phosphate ester or esters in accordance with Claim 1 and substantially as described in any of Examples 21, 28, 30 and 31.

35. A mixture of phosphate esters, when produced by a process claimed in any of Claims 1 to 30 and 33.

36. A mixture of phosphate esters, when produced by a process claimed in any of Claims 31, 32 and 34.

37. A composition comprising an organic material to which phosphate esters are conventionally added to improve the physical properties of the said materials and a functionally effective proportion of a mixture of phosphate esters claimed in Claim 35.

38. A composition claimed in Claim 37 wherein the organic material is a vinyl chloride polymer or co-polymer, a polyolefin or



a cellulose ester, the content of phosphate esters being present in a proportion sufficient to plasticise the organic material.

39. A composition claimed in Claim 37 wherein the organic material is a hydraulic fluid, the content of phosphate esters being present in a proportion sufficient to render the hydraulic fluid fire-resistant.

40. A composition claimed in Claim 37 wherein the organic material is a liquid hydrocarbon fuel, the content of phosphate esters being sufficient to provide an ignition control additive.

41. A composition claimed in Claim 37 wherein the organic material is a lubricant, the content of phosphate esters being sufficient to provide an extreme-pressure additive.

42. A composition in accordance with Claim 37 and substantially as described in any of Examples 17 to 20.

43. A composition comprising an organic material and a functionally effective proportion of a mixture of phosphate esters claimed in Claim 36.

44. A composition claimed in Claim 43 wherein the organic material is a vinyl chloride polymer or co-polymer, a polyolefin or a cellulose ester, the content of phosphate esters being present in a proportion sufficient to plasticise the organic material.

45. A composition claimed in Claim 43 wherein the organic material is a hydraulic fluid, the content of phosphate esters being present in a proportion sufficient to render the hydraulic fluid fire-resistant.

46. A composition claimed in Claim 43

wherein the organic material is a liquid hydrocarbon fuel, the content of phosphate esters being sufficient to provide an ignition control additive.

47. A composition claimed in Claim 43 wherein the organic material is a lubricant, the content of phosphate esters being sufficient to provide an extreme-pressure additive.

48. A composition in accordance with Claim 43 and substantially as described in any of Examples 22 to 27 and 29.

49. A process of producing a composition claimed in Claim 37 which comprises admixing the organic material with the mixture of phosphate esters.

50. A process of producing a composition claimed in Claim 37 and substantially as described in any of Examples 17 to 20.

51. A composition of an organic material and a mixture of phosphate esters when produced by a process claimed in Claim 49 or Claim 50.

52. A process of producing a composition claimed in Claim 43 which comprises admixing the organic material with the mixture of phosphate esters.

53. A process of producing a composition claimed in Claim 43 and substantially as described in any of Examples 22 to 27 and 29.

54. A composition of an organic material and a mixture of phosphate esters when produced by a process claimed in Claim 52 or 53.

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SPECIFICATION NO 1146173

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DONALD RICHARD RANDELL

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of CIBA-GEIGY AG., a Swiss Body Corporate, of Basle, Switzerland.

THE PATENT OFFICE

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