

PATENT SPECIFICATION

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(54) BENZENE PHOSPHONOUS ACID COMPOUNDS, THEIR PRODUCTION AND USE AS STABILIZERS FOR ORGANIC MATERIALS

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle/Switzerland, a Body Corporate organised according to the laws of Switzerland, 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 a method of stabilizing organic materials using, as stabilizers, benzene phosphonous acid compounds in which two, three or four benzene nuclei are bound together and which contain one, two or three phosphorus atoms. These compounds are free acids, their salts with inorganic cations, their esters, thioesters or amides. Some of these compounds are novel, and the invention also relates to these novel compounds and to the manufacture thereof.

The invention provides a benzene phosphonous acid compound of the formula (I)



wherein m is 1 or 2,



is an unsubstituted or substituted diphenyl or terphenyl radical,
 Q is the direct linkage or an unsubstituted or substituted phenylene radical, X_1 is a radical of the formula (II)



and X_2 is a hydrogen atom or a radical of the formula (IIa)

[Price 25p]

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wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or an unsubstituted hydrocarbon radical,
Y is an oxygen or sulfur atom or a radical of the formula (III)



and Z is any one of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; or an inorganic salt, preferably a metal salt, of such a compound wherein at least one -P(OH)_2 group is present in the molecule; provided that when

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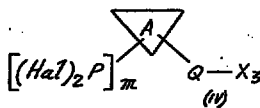
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is an unsubstituted diphenyl radical and m is 1 and the group -Q-X_2 is a hydrogen atom, then X_1 is other than a -P(OH)_2 radical substituted in a 4-position on the diphenyl radical.

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Such a compound can be prepared by a process of the present invention which includes reacting a compound of the formula

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wherein m,

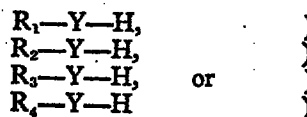


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and Q are as defined above, Hal is a halogen atom and X_2 is a hydrogen atom or a radical of the formula

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with a compound of the formula (VI)



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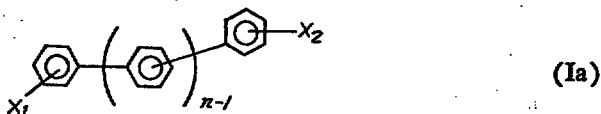
wherein R_1 , R_2 , R_3 and R_4 are as defined above, or with a mixture of two or more compounds of the formula (VI), the molar proportion of compound of the formula (VI), or mixture of compounds of the formulae (VI):compound of the formula (IV) being x:1, wherein x is the number of Hal atoms in the compound of the formula (IV).

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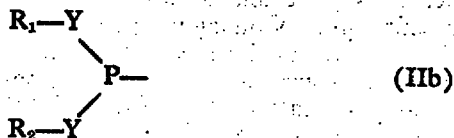
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In particular, the present invention provides a compound within the formula (I) and of the formula (Ia)

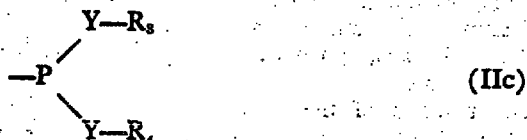
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wherein n is 1 or 2, X_1 is a radical of the formula



and X_2 is a hydrogen atom or a radical of the formula

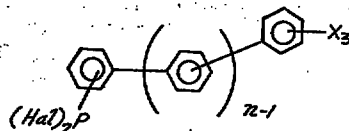


wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or a hydrocarbon radical, which hydrocarbon radical contains not more than 16 carbon atoms and is an aliphatic, alicyclic and/or aromatic radical, Y is an oxygen or sulfur atom or a radical of the formula

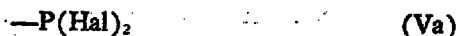


wherein Z is any one of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; an inorganic salt, preferably a metal salt, of such a compound wherein at least one $-P(OH)_2$ group is present in the molecule; provided that when n is 1, and X_2 is a hydrogen atom, then X_1 is other than a $-P(OH)_2$ radical substituted in a 4-position on the diphenyl radical.

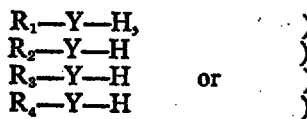
Such a compound can be prepared by a process within the present invention which includes reacting a compound of the formula (IVa)



wherein n is 1 or 2, Hal is a chlorine or bromine atom, and X_3 is a hydrogen atom or a radical of the formula



wherein Hal is a chlorine or bromine atom with a compound of the formula (VIa)



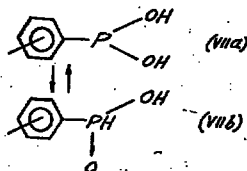
wherein R_1 , R_2 , R_3 and R_4 are as defined above for the formula (Ia), or with a mixture of two or more compounds of the formulae (VIa), the molar proportion of compound of the formula (VIa), or mixture of compounds of the formulae (VIa): compound of the formula (IVa) being x:1, wherein x is the number of Hal atoms in the compound of the formula (IVa).

The compounds of the formula (IV) used as starting materials in processes within the present invention can be produced from unsubstituted or substituted aromatic hydrocarbons, which contain 2, 3 or 4 benzene nuclei, bound together by a single bond. Examples of such hydrocarbons are diphenyl, o-, m- and p- terphenyl, m- quaterphenyl, p- quaterphenyl, 1,2,4-triphenyl-benzene and 1,3,5-triphenyl-benzene. From these hydrocarbons the compounds of formula (IV) can be produced by reaction with a phosphorus trihalide, preferably with phosphorus trichloride. This reaction can be performed at very high temperatures in the gaseous phase. To avoid side-reactions it is, in general, advantageous to work under milder conditions, using

catalysts. Friedel-Crafts-Catalysts are suitable, especially water-free aluminium chloride. It is preferable to work with a surplus of phosphorus trichloride at its boiling temperature. Working up the reaction mixture, the aluminium chloride complex with the dichlorophosphine is first decomposed, for instance with phosphorus oxychloride or with pyridine. In principle these methods of manufacture are known. These and other analogous procedures for the production of compounds of formula (IV) are collectively described by K. Sasse in "Handbuch von Houben-Weyl, Methoden der organischen Chemie, 4th edition (1963), Vol. XII/1, organische Phosphorverbindungen", part 1, pages 302—318.

Examples of compounds of the formula (VI) are water, hydrogen sulfide, ammonia, alcohols, phenols, mercaptans, thiophenols and organic primary and secondary amines.

The reaction of the starting materials of formulae (IV) and (VI) normally proceeds easily; to avoid side-reactions, it is often necessary to smooth the vehement reaction by cooling externally. When the reaction is carried out using water, as the compound of the formula (VI) it is preferred to use it in excess, to cool, and to add the halophosphine of formula (IV) slowly, so that the temperature does not rise too high as a result of the exothermic reaction. When carrying out the hydrolysis in this way, the product obtained is a colourless, powdery compound, containing radicals of the following structure:



Such a derivative of benzene phosphonous acid has acid properties and, by reacting it with an inorganic base or with a salt containing an inorganic cation, it is converted to its corresponding salt. Examples of such inorganic reagents are calcium hydroxide, zinc oxide, sodium carbonate, potassium hydrogen carbonate, aluminium acetate, barium chloride, nickel acetate and zinc chloride. The hydrolysis of a halophosphine of formula (IV) and the conversion of the hydrolysis product which contains radicals of the above formulae (VIIa) or (VIIb) into a salt thereof, may also be performed in a one step process. For this purpose, as described above, an excess of the water used for the hydrolysis can be mixed, in advance, with the desired inorganic reagent, and the halophosphine of formula (IV) then slowly added to this mixture with stirring. If, instead of water, other compounds of formula (VI) are to be used for the reaction, water vapour is carefully excluded. In general, phenols react smoothly if heated for instance to 100—150°C, whereby the hydrogen halide splits off.

Hydrogen halide acceptors, such as pyridine or trialkylamines can be added to remove the hydrogen halide split off.

This method is preferred if alcohols are used as reactants. If the compounds of formula (IV) are reacted with organic amines or with ammonia, the amine or ammonia is used in excess, which excess serves as a binding agent for the hydrogen halide split off.

The reactions described above are analogous to processes which are, in principle, known. A collective summary has been published in the aforementioned book by K. Sasse (compare p. 318 ff.).

Any of the benzene nuclei in a di- or terphenyl radical of



or in a phenylene radical of Q [in the formulae (I) and (IV)] may be substituted by, for example, an alkyl or cycloalkyl group.

Examples of the alkyl and cycloalkyl groups are methyl, ethyl, propyl, butyl, isobutyl, amyl, 2,2-dimethylpropyl, octyl, dodecyl, isopropyl, tert.-butyl, 2,6,8-trimethyl-4-nonyl, 2-ethyl-hexyl, 2,4,6,8-tetramethyl-nonyl and cyclododecyl. In a preferred compound of the formula (I) or (Ia), the diphenyl or terphenyl radical of

and the phenylene radical of Q are both unsubstituted; alternatively they may be substituted by one or more halogen atoms, especially chlorine or bromine or by one or more alkoxy radicals such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, hexyloxy, dodecyloxy and 2-ethylhexyloxy.

The hydrocarbon radical of any of R_1 , R_2 , R_3 , R_4 [in the formulae (II) and (VI)] and



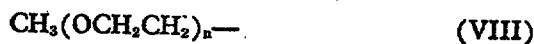
[in the formula (III)] may be an alkyl or cycloalkyl group, examples of which are given above.

The abovementioned hydrocarbon radicals of any of R_1 , R_2 , R_3 , R_4 and



may, for example, alternatively, be an aryl radical.

The abovementioned hydrocarbon radicals may be substituted. Examples of the aryl and substituted alkyl radicals are phenyl, 2-, 3- or 4-methylphenyl, dimethylphenyl (mixtures of isomers), p-tert.butylphenyl, 2-methoxyphenyl, 3-chlorophenyl and dichlorophenyl (mixtures of isomers), 2-methoxyethyl, 2-methoxypropyl, 2-phenoxyethyl, 2-(2'-phenoxyethoxy)-ethoxy, 2-cresoxyethyl, benzyl, 4-chlorobenzyl, 2,4-dichlorobenzyl, 2-chlorethyl and substituents of formula



wherein n is from 2 to 12 inclusive.

Examples of the heterocyclic ring formed by combination of the radical Z together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 or R_4 is attached to the same N-atom [formula (III)], are the heterocyclic radicals pyrrolidino, piperidino, hexamethylenimino and morpholino.

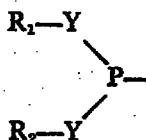
The present invention also provides a method of stabilizing an organic material against the action of heat, light or oxygen which includes treating the material with, as a stabilizer, one or more compounds of the formula



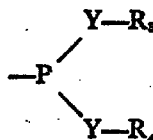
wherein m is 1 or 2,



is an unsubstituted or substituted diphenyl or terphenyl radical, Q is the direct linkage or an unsubstituted or substituted phenylene radical, X_1 is a radical of the formula



and X_2 is a hydrogen atom or a radical of the formula

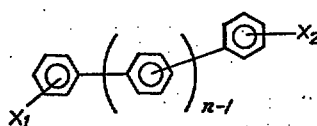


wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or an unsubstituted or a substituted hydrocarbon radical,
 Y is an oxygen or sulfur atom or a radical of the formula

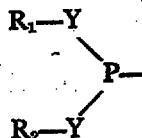


and Z is any one of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; or an inorganic salt, preferably a metal salt, of such a compound wherein at least one ---P(OH)_2 group is present in the molecule.

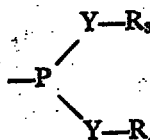
In particular, the invention also provides a method of stabilizing an organic material against the action of heat, light or oxygen which includes treating the material with, as a stabilizer, one or more compounds of the formula



where n is 1 or 2, X_1 is a radical of the formula



and X_2 is a hydrogen atom or a radical of the formula



wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or a hydrocarbon radical, which hydrocarbon radical contains not more than 16 carbon atoms and is an aliphatic, alicyclic and/or aromatic radical, Y is an oxygen or sulfur atom or a radical of the formula



wherein Z is any one of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; or an inorganic salt, preferably a metal salt, of such a compound wherein at least one ---P(OH)_2 group is present in the molecule.

By this method the above compounds can either be incorporated in the material sensitive to light, oxygen or heat, or applied to its surface to form a protective film. By their stabilizing effect they protect these sensitive substances from degradation. They have a wide range of application in the processing of plastics; for example, they can be employed as stabilizers for cellulose acetate, cellulose propionate, cellulose acetobutyrate, polyethylene, polypropylene, polyvinyl chloride, polyvinyl chloride-acetate, polyamides, polystyrene, ethyl cellulose, cellulose nitrate, polyvinyl alcohol, silicone rubber, melamine-formaldehyde and ureaformaldehyde resins, allyl casting resins, polymethylmethacrylate, polyesters and polyacrylonitrile.

The stabilizers of the present invention can also be used to protect natural products such as rubber, cellulose, wool and silk from degradation.

The materials to be protected may be present in the form of sheet or film, panels, tubing, rods, tapes, coatings, fibres, granules, powders or other solid forms, or as

solutions, emulsions or dispersions. The stabilizers can be incorporated in, or applied to these materials by known methods. One of the best methods of application consists of intimately mixing the stabilizer and the plastic material, e.g. polypropylene granules, in a kneading or other suitable machine and extrusion moulding the mixture. This technique ensures homogeneous blending, which is important for effective protection. Extrusion moulding is employed to produce a variety of products, including films, tubing and filaments. The latter can be converted into woven fabrics.

If polypropylene, for instance, is to be processed as woven fabric the stabilizer is normally mixed with it prior to extrusion as filament yarn. However, these stabilizers can be applied with equally good effect to textile yarns and fabrics, for example from an aqueous bath containing the stabilizing compound in superfine dispersion. Textiles of polyester and cellulose acetate fibres are suitable for this exhaust method of application.

The plastics need not necessarily be polymerized when the new compounds are added. The latter can be blended with the monomers or prepolymers prior to the condensation or other polymerization reaction yielding the final polymer.

Besides their use for the stabilization of, for example, clear films or other plastics materials, the stabilizers of the present invention are suitable for application in or on opaque, semi-opaque or translucent materials having a surface which is subject to degradation by light, oxygen or heat. Examples of such materials are foamed plastics, opaque film and sheeting, opaque papers, transparent and opaque pigmented plastics, fluorescent pigments and automobile and furniture polishes, creams, lotions and similar products, which latter group of products may be opaque, clear or translucent.

Benzene phosphonous acid esters and their stabilizing effect are known from the literature. Comparing these compounds, for instance with those described in the Belgian Patent 724 802, the stabilizers of the present invention have essential advantages. They are less fugitive, have less inclination for migration and are more soluble in many materials to be protected. Moreover the connection of at least two benzene nuclei in the stabilizers of the present invention has the effect that they absorb ultra violet rays. They therefore give protection against heat or oxygen, and also against decomposition by sunlight. Comparable phosphorus compounds do not appear to have such a combined protective effect. In spite of this so-called polyvalent effect it is in many cases advantageous to mix the new stabilizers with other types of light absorbers or stabilizers.

Those mixtures of agents often display a synergistic effect and protect the treated materials to a particularly high degree against ultra violet light, heat and oxidative degradation at the same time. As explained above the stabilizers of the present invention can be used for various organic materials.

The suitability of a stabilizer within the present invention for the protection of a certain organic material depends upon the kind and number of the substituents in the stabilizing compound. The following relations between the chemical constitution of the stabilizing compound and plastics materials which are to be protected, have, for instance, been observed:—

For the protection of polypropylene, stabilizers which are especially suitable contain one or several aliphatic or cycloaliphatic radicals which contain at least 6, and preferably 8 to 20 carbon atoms.

For the protection of polyvinylchloride, stabilizers which are especially suitable contain a radical of R_1 , R_2 , R_3 or R_4 which is an aryl radical, which radical may be substituted by one or more C_{1-6} alkyl radicals or chlorine atoms.

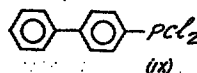
For the protection of polyesters and of polyamides stabilizers which are especially suitable contain several ether groups as substituents in one or more of the radicals R_1 , R_2 , R_3 or R_4 .

The present invention also provides organic materials which contain the above-mentioned stabilizers. As exemplified above, the incorporation of the stabilizers into the materials to be protected can be effected at any stage of processing by known methods, and the amount of added stabilizer may vary within wide limits, for instance between 0.01 and 5%, preferably between 0.05 to 1%, by weight based on the weight of material to be protected.

In the following examples F means melting point; Kp boiling point; λ wavelength, λ max the wavelength of maximum light absorption in nanometer units; parts and per centages are by weight and temperatures in degrees Centigrade.

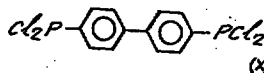
Examples of the production of the intermediate products of formula (IV)

- a). In the absence of moisture a solution of 46.2 parts of diphenyl, 165 parts of phosphorus trichloride, and 44.8 parts of AlCl_3 is heated under reflux during the course of 3 hours; 53.5 parts of phosphorus oxychloride are subsequently added and the mixture is stirred for a further 15 minutes. After cooling to 0° the AlCl_3 - POCl_3 complex, precipitated in the form of granules, is filtered off, is washed thoroughly with chlorobenzene, and the filtrate is evaporated in a vacuum. As residue 65 parts (85% of theory) of 4-diphenyl-dichlorophosphine of formula



are obtained in the form of a red, light oil of a pungent smell.

- b). Working up is effected as described under a), but in place of 44.8 parts of AlCl_3 , 106 parts are used, and in place of 53.5 parts of phosphorus oxychloride, 122.6 parts are used. Thus, 85.2 parts of 4,4'-diphenyl-bis-(dichlorophosphine) of formula



are obtained in the form of a red, light oil of a pungent smell.

- c). In the absence of moisture a solution of 34.5 parts of p-terphenyl, 330 parts of phosphorus trichloride, and 52 parts of aluminium chloride are heated under reflux during the course of 5 hours; 61.3 parts of phosphorus oxychloride are subsequently added and the mixture is stirred for a further 15 minutes, is cooled to 0° , the resulting Al-complex is filtered off, is washed with phosphorus trichloride, and the filtrate is evaporated in a vacuum.

As residue 29 parts of 4,4'' - (p - terphenyl) - bis - (dichlorophosphine) of formula



are obtained in the form of light yellow crystals.

Examples of the end-products of formula (I)

These are listed in the following Table 1 where the melting points of crystalline compounds are indicated in column F. These compounds melt at a temperature considerably higher than room temperature. The other indicated compounds are specified in column F as 'oil'. λ_{max} means the maximum of light absorption which is expressed by nanometer (nm) units. The constitution formulae indicated in table 1 are confirmed by elemental analyses.

TABLE 1

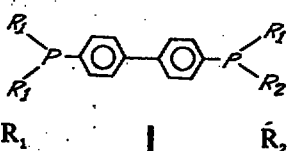
Example No.	Constitution of the compounds of general formula		F	λ max. (nm)
	R_1	R_2		
1	$-\text{O}-\text{C}_4\text{H}_9$	$R_1 = R_2$	oil	252
2	$-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$	$R_1 = R_2$	oil	250
3	$-\text{O}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$	$R_1 = R_2$	oil	253
4	$-\text{O}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$	$-\text{O}-\text{C}_4\text{H}_9$	oil	254
5	$-\text{O}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$	$-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$	oil	253
6	$-\text{S}-\text{C}_{12}\text{H}_{25}$	$R_1 = R_2$	42–43°	270
7	$-\text{S}-\text{C}_6\text{H}_4+$ *	$R_1 = R_2$ *	110–111°	255
8	$-\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_4$	$R_1 = R_2$	168–169°	263
				
9	$-\text{O}-\text{C}_4\text{H}_9$	$R_1 = R_2$	oil	260
10	$-\text{O}-\text{C}_8\text{H}_{17}(\text{iso})$	$R_1 = R_2$	oil	259
11	$-\text{O}-\text{C}_{13}\text{H}_{27}$	$R_1 = R_2$	oil	259
12	$-\text{O}-\text{C}_6\text{H}_3(\text{X})+$ *	$R_1 = R_2$ *	94–96°	273
13	$-\text{O}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$	$R_1 = R_2$	oil	265
14	$-\text{O}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$	$-\text{O}-\text{C}_8\text{H}_{17}$	oil	268
15	$-\text{S}-\text{C}_{12}\text{H}_{25}$	$R_1 = R_2$	54–56°	300
16	$-\text{S}-\text{C}_6\text{H}_4+$ *	$R_1 = R_2$ *	184–186°	250
17	$-\text{N}(\text{C}_4\text{H}_9)_2$	$R_1 = R_2$	oil	261

TABLE I (Continued)

Example No.	Constitution of the compounds of general formula		F	λ max. (nm)
18			oil	271
19			oil	262
20	*		oil	264
21			oil	264
22		$R_1 = R_2$	oil	292
23	*	$R_1 = R_2$ *	199-199.5°	298
24		$R_1 = R_2$	oil	292
25			oil	292
26		$R_1 = R_2$	63-65°	308
27	*	$R_1 = R_2$ *	187-189°	310
28		$R_1 = R_2$	oil	296

* The symbols + signify the tertiary butyl radical.

Examples of the production of end-products of formula (I)

The Examples are numbered in the same way as the corresponding compounds of the above Table 1.

Example 7.

In the absence of moisture a solution of 43.5 parts of 4-diphenyl-dichlorophosphine [Example a), formula (IX)] in 100 parts of toluene is added at 0-5° to 56.8 parts of 4-tert.butyl thiophenol and 35 parts of triethylamine in 200 parts of toluene; the mixture is allowed to react over night at 40°, the precipitated triethyl ammonium chloride is filtered off, the filtrate is evaporated in a vacuum, and the oily residue is purified by crystallization from methanol-ether. Constitution formula and characteriza-

tion of this compound and the compounds of the production Examples cited below are indicated in the above Table 1.

Example 9.

In the absence of moisture a solution of 28.35 parts of 4,4'-diphenyl-bis-(dichlorophosphine) [Example b), formula (X)] in 100 parts of chlorobenzene is added at 0—5° to 23.6 parts of n-butanol and 32 parts of triethylamine in 300 parts of chlorobenzene; the mixture is allowed to react over night at 40°, the precipitated salt is filtered off, the filtrate is evaporated in a vacuum, and a light yellow oil is obtained.

Example 13.

A solution of 47.5 parts of 4,4'-diphenyl-bis-(dichlorophosphine) in 100 parts of toluene is added at 0—5° to 117.5 parts of 4-nonylphenol and 55 parts of triethylamine in 400 parts of toluene; the mixture is allowed to react overnight at 50—60°, the precipitated triethyl ammonium chloride is filtered off, the filtrate is evaporated in a vacuum, and thus, a yellow viscous residue is obtained.

The same compound is also obtained by mixing the starting materials without triethylamine and without toluene and gradually heating to 140—160°, while passing carbon dioxide through the mixture until the evolution of hydrogen chloride ceases.

Example 15.

A solution of 20.0 parts of 4,4'-diphenyl-bis-(dichlorophosphine) in 100 parts of toluene is added at 0—5° to 45.4 parts of dodecyl mercaptan and 22.8 parts of triethylamine in 200 parts of toluene; the mixture is then allowed to react overnight at 40°, the precipitated triethyl ammonium chloride is filtered off, the filtrate is evaporated in a vacuum, and the residue is crystallized from ether.

Example 27.

A solution of 31.0 parts of 4,4'' - (p - terphenyl) - bis - (dichlorophosphine), Example c), formula (XI), is added at 0—5° to 48.1 parts of 4-tert.butyl thiophenol and 30.1 parts of triethylamine in 300 parts of toluene; the mixture is allowed to react overnight at 40°, the precipitated triethyl ammonium chloride is filtered off, the filtrate is evaporated in a vacuum, and the residue is crystallized from benzene-methanol.

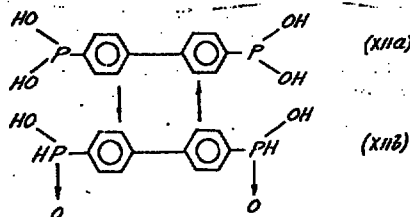
In place of 30.1 parts of triethylamine, 24 parts of anhydrous pyridine may also be used as acid-binding agent.

In Examples 4, 5, 14, 18, 19, 20, 21, and 25 of Table 1 there are mentioned esters of phosphonous acids which contain in the same molecule radicals derived from different alcohols, phenols or mercaptans. The production thereof is effected in a manner analogous to that described in the above production Examples by reacting the chlorophosphines with a mixture of the corresponding compounds of formula (VI). Thus, mixtures of esters are always obtained; aside from the main constituents which are of the formulae given in Examples 4, 5, 14, 18, 19, 20, 21, and 25 these mixtures also contain other esters, wherein the equivalent ratio of the radicals is shifted.

The following Examples relate to end-products which are obtained by hydrolysis of 4,4'-diphenyl-bis-(dichlorophosphine) of formula (X), partly as free phosphonous acids, and partly in the form of the salts with inorganic cations.

Example 29.

80 Parts of 4,4'-diphenyl-bis-(dichlorophosphine) of formula (X) produced as described in Example b), are diluted with 20 parts of chlorobenzene and slowly added to 300 parts of water while stirring well, and the temperature is kept at 0—5° by external cooling. The reaction is completed at 20° after 18 hours. The thin colourless precipitate is filtered off and is dried at 90° in a vacuum. The crude product obtained is appropriate for use as a stabilizer. It consists mainly of the compound of formula



and impurities which probably consist of anhydrides of the acid of formula (XII). Other impurities contain chlorine, since a small number of the chlorine atoms in the starting product of formula (X) escape from the hydrolysis reaction by coating with the insoluble precipitate.

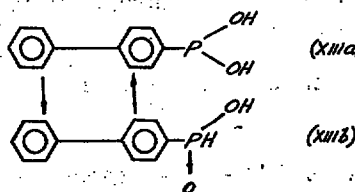
Example 30.

The process described in Example 29 may be simplified by not effecting isolation or purification of the intermediate product of formula (X) (precipitation of the aluminium chloride by phosphorus oxychloride).

46.2 Parts of diphenyl, 106 parts of aluminium chloride, and 165 parts of phosphorus trichloride are heated under reflux during the course of 2 hours; the excess of phosphorus trichloride is subsequently removed by distillation and the viscous residue is taken up in 40 parts of chlorobenzene. Hydrolysis is then effected with 300 parts of water as described in Example 29. The fine colourless powder obtained contains 16.7% of phosphorus, 1.1% of chlorine, and 3.8% of aluminium.

Example 31.

The 4-diphenyl-dichlorophosphine of formula (IX) described in Example a) is hydrolyzed in accordance with methods described in Example 29; after the working up a colourless fine powder is obtained which mainly consists of the compound of the following formula



Example 32.

26 Parts of the compound obtained in accordance with Example 29 are mixed by stirring with a solution of 21 parts of barium chloride in 100 parts of water and boiled under reflux during the course of 3 hours. After cooling to 5° the colourless precipitate is filtered, is washed with water and is dried at 90° in a vacuum. The resulting barium salt contains 18.9% of barium.

In an analogous manner the light green nickel salt (content of nickel is 6%) is obtained from 25 parts of nickel acetate and the colourless zinc salt (content of zinc is 4.1%) from 27 parts of chloride of zinc.

Example 33.

Proceeding in a manner analogous to that described in Example 30 the resulting colourless powder is suspended in 400 parts of water while stirring; calcium oxide is gradually added in an amount such that after stirring at 80° for a longer period the pH value does not sink below 5°; the mixture is cooled to 5° and the precipitate is filtered. The resulting colourless salt contains 4.1% of calcium, 6.3% of aluminium, and 3.3% of chlorine.

Examples of the use of end-products of formula (I)

A. Stabilization against oxidative degradation

A few of the compounds cited in the above Examples are tested to determine their effect as stabilizers against oxygen as follows: 0.1% of a compound of formula (I) are homogeneously incorporated in polypropylene which contains 0.2% of 4,4'-methylene-bis-(2,6-di-tert.butylphenol) as antioxidant. After displacing the air, the plastics material, in the form of thin small plates is then kept under oxygen in a closed system. It is then heated to 190°, whereby an excess pressure of about 20 mm Hg is developed. The oxidation of the plastics material results in a decrease of pressure. The rate of this decrease of pressure is small if the effectiveness of the stabilizer or the mixture of the stabilizers is high. The test results are summarized in the following Table 2. The figures signify the time expressed in minutes which passes until the excess pressure decreases to zero.

TABLE 2

Incorporated phosphorus compounds of formula (I)	
Example No.	Minutes
—	119
29	179
30	193
31	200
32 (Ba — salt)	229
32 (Ni — salt)	207
32 (Zn — salt)	290
33	195

A further series of tests were conducted as described above, except that all samples of polypropylene (including the control sample) had, incorporated therein, as stabilizer, 0.07% of 4,4'-methylene-bis-(2,6-di-tert.butylphenol) and 0.13% of dilaurylthiodipropionate in addition to the compound of the formula (I). The samples were compared as described above. The results are summarized in the following Table 3.

TABLE 3

Incorporated phosphorus compounds of formula (I)	
Example No.	Minutes
	48
3	96
5	61
6	102
9	78
10	84
12	105
13	165
14	81
15	105
18	102
19	177
20	98
21	96
26	89
27	60

B. Stabilization against brownish discolouration

On heating polypropylene in which 0.2% of the stabilizer 2,2'-methylen-bis-(4-methyl-6-tert.butylphenol) has been incorporated a brownish discolouration takes place at about 220°. This discoloration may be avoided if 0.1% of a compound of formula (I) is incorporated at the same time.

In the ageing of small plates of polypropylene in a furnace at 140° a strong brownish discolouration takes place after only one day if the plastics material only contains 0.2% of 2,2'-methylen-bis-(4-methyl-6-tert.butylphenol). If the plastics material contains, in addition, 0.1% of a compound given in the above Table 1 it remains colourless after 4 days at 140°.

WHAT WE CLAIM IS:—

1. A benzene phosphonous acid compound of the formula (I)



(I)

15

wherein m is 1 or 2,



15

TABLE 3

Incorporated phosphorus compounds of formula (I)	
Example No.	Minutes
—	48
3	96
5	61
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9	78
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WHAT WE CLAIM IS:—

1. A benzene phosphonous acid compound of the formula (I)



(I)

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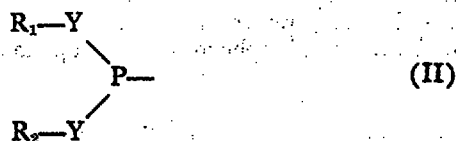
wherein m is 1 or 2,



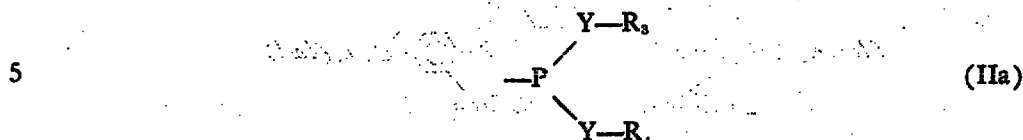
* C L M S *

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is an unsubstituted or substituted diphenyl or terphenyl radical, Q is the direct linkage, or an unsubstituted or substituted phenylene radical, X_1 is a radical of the formula (II)



and X_2 is a hydrogen atom or a radical of the formula (IIa)



wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or an unsubstituted or a substituted hydrocarbon radical, Y is an oxygen or sulfur atom, or a radical of the formula (III)

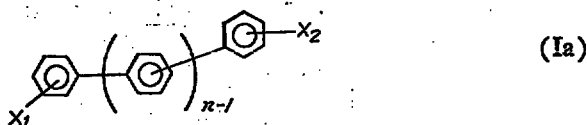


wherein Z is any of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; or an inorganic salt of such a compound wherein at least one $-P(OH)_2$ group is present in the molecule; provided that when



is an unsubstituted diphenyl radical and m is 1, and the group $-Q-X_2$ is a hydrogen atom, then X_1 is other than a $-P(OH)_2$ radical substituted in a 4-position on the diphenyl radical.

2. A compound according to claim 1 of the formula (Ia)



wherein n is 1 or 2, X_1 is a radical of the formula (IIb)



and X_2 is a hydrogen atom or a radical of the formula (IIc)



wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or a hydrocarbon radical, which radical contains not more than 16 carbon atoms and is an aliphatic,

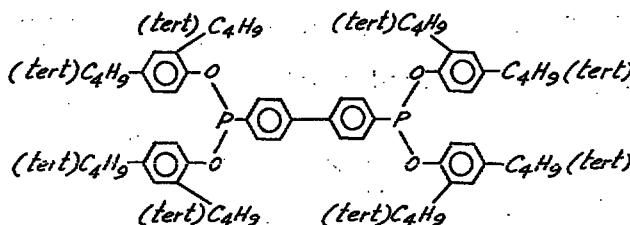


alicyclic and/or aromatic radical, and Y is as defined in claim 1; or an inorganic salt of such a compound wherein at least one $-\text{P}(\text{OH})_2$ group is present in the molecule; provided that when n is 1 and X_2 is a hydrogen atom, then X_1 is other than a $-\text{P}(\text{OH})_2$ radical substituted in a 4-position on the diphenyl radical.

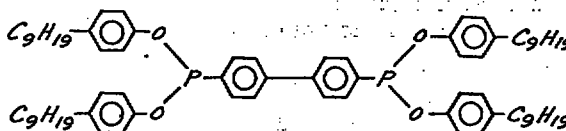
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3. A benzene phosphonous acid compound of the formula

5

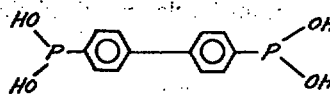


4. A benzene phosphonous acid compound of the formula



5. A benzene phosphonous acid compound of the formula

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6. Those compounds of the formulae (I) and (Ia), other than the compounds of the formulae given in claims 3, 4 and 5, which are specifically disclosed herein.

15

7. A process for preparing a benzene phosphonous acid compound of the formula (I), given and defined in claim 1, which includes reacting a compound of the formula (IV)

15



wherein m,



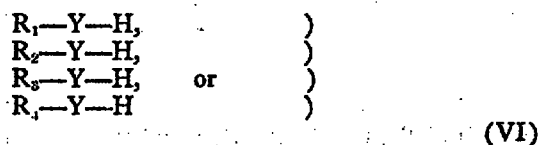
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and Q are as defined in claim 1, Hal is a halogen atom and X_3 is a hydrogen atom or a radical of the formula (V)

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wherein Hal is a halogen atom, with a compound of the formula (VI)



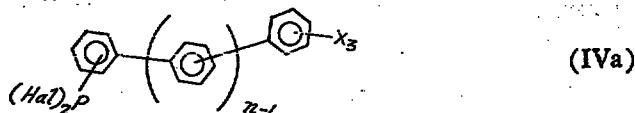
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wherein R_1 , R_2 , R_3 and R_4 are as defined in claim 1, or with a mixture of two or more compounds of the formulae (VI), the molar proportion of compound or compounds of formula (VI):compound of the formula (IV) being $x:1$, wherein x is the number of Hal atoms in the compound of the formula (IV); and optionally, when a $-\text{P}(\text{OH})_2$ radical is present in the product, reacting the resultant benzene phosphonous acid with an inorganic base, or with a salt containing an inorganic cation to produce the corresponding inorganic salt thereof.

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8. A process for producing a benzene phosphonous acid compound of the formula (Ia), given and defined in claim 2, which includes reacting a compound of the formula (IVa)

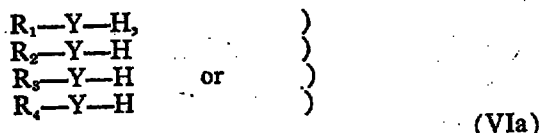


wherein n is 1 or 2, Hal is a chlorine or bromine atom, and X_3 is a hydrogen atom or a radical of the formula (Va)



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wherein Hal is a chlorine or bromine atom, with a compound of the formula (VIa)



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wherein R_1 , R_2 , R_3 and R_4 are as defined in claim 2, or with a mixture of two or more compounds of the formulae (VIa), the molar proportion of compound or compounds of the formula (VIa):compound of the formula (IVa) being $x:1$, wherein x is the number of Hal atoms in the compound of the formula (IVa); and optionally, when a $-\text{P}(\text{OH})_2$ radical is present in the product, reacting the resultant benzene phosphonous acid with an inorganic base or with a salt containing an inorganic cation to form the corresponding inorganic salt thereof.

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9. Processes for producing benzene phosphonous acid compounds of the formulae (I) and (Ia) or the inorganic salts thereof, substantially as herein described and exemplified.

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10. A method of stabilizing an organic material against the action of heat, light or oxygen which includes treating the material with, as a stabilizer, one or more compounds of the formula

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wherein m is 1 or 2,



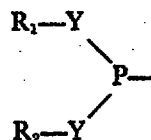
in atom

V)

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is an unsubstituted or substituted diphenyl or terphenyl radical, Q is the direct linkage or an unsubstituted or substituted phenylene radical, X_1 is a radical of the formula

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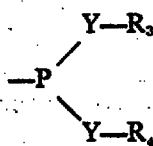


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VI)



and X_2 is a hydrogen atom or a radical of the formula

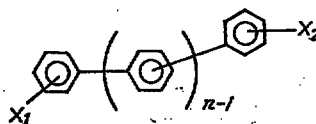


wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or an unsubstituted or a substituted hydrocarbon radical, Y is an oxygen or sulfur atom or a radical of the formula

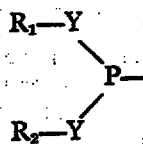


and Z is any one of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; or an inorganic salt of such a compound wherein at least $1-P(OH)_2$ group is present in the molecule.

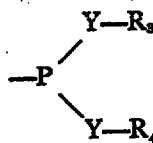
11. A method of stabilizing an organic material against the action of heat, light or oxygen which includes treating the material with, as a stabilizer, one or more compounds of the formula



wherein n is 1 or 2, X_1 is a radical of the formula



and X_2 is a hydrogen atom or a radical of the formula



wherein each of R_1 , R_2 , R_3 and R_4 is independently a hydrogen atom or a hydrocarbon radical, which hydrocarbon radical contains not more than 16 carbon atoms and is an aliphatic, alicyclic and/or aromatic radical, Y is an oxygen or sulphur atom or a radical of the formula



wherein Z is any of R_1 , R_2 , R_3 or R_4 , or forms, together with the N-atom to which it is attached and whichever of R_1 , R_2 , R_3 and R_4 is attached to the same N-atom, a heterocyclic ring; or an inorganic salt of such a compound wherein at least $1-P(OH)_2$ group is present in the molecule.

12. An organic material containing, as a stabilizer, against the action of heat, light or oxygen, one or more compounds of the formula given and defined in claim 10.

13. An organic material containing, as a stabilizer against the action of heat, light or oxygen, one or more compounds of the formula given and defined in claim 11.

14. An organic material according to claim 12 or claim 13 which contains a further stabilizer or co-stabilizer against the action of heat, light or oxygen.



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