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POLYFLUORALKYLPHOSPHONIC ACIDS, PHOSPHINIC ACIDS AND THEIR SULPHUR ANALOGUES

by

Walter Blochl

EDITED TRANSLATION

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POLYFLUORALKYLPHOSPHONIC ACIDS, PHOSPHINIC ACIDS AND THEIR SULPHUR ANALOGUES

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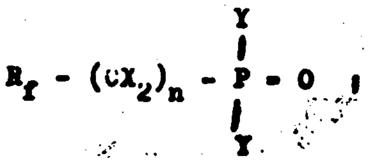
Patent No. 1443533

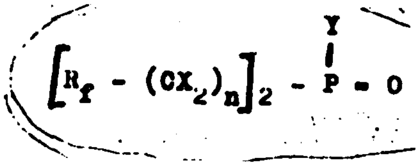
Walter Blochl

Procedure for producing polyfluoroalkylphosphonic-, -thiophosphonic-, -phosphinic- and -thiophosphinic acids and their derivatives and their use as surface-active substances, as lubricants and lubricant additives and for oil- and dirt-repellent impregnation of textiles, paper, leather, varnish and wood.

The present invention describes the production of polyfluoroalkylphosphonic- and -phosphinic acids, -thiophosphonic- and -thiophosphinic acids which do not contain fluorine in the α- and β-positions to phosphorus, and also their derivatives and their use for oil- and dirt-repellent impregnation of textiles, paper, leather, varnish, and wood. Likewise the use of these compounds as surface-tension-lowering substances and as lubricants and lubricant additives will be described. They possess new properties and thereby differ more from the previously known, comparable nonfluorinated compounds. In this case we are talking primarily about alkylphosphonic acids and -phosphinic acids whose alkyl chain carries a perfluoroalkyl remainder with at least six perfluorinated carbon atoms, whereby there can be no fluorine in α- and β-postions to the phosphorus. These fluoroalkylphosphonic acids are chemically and thermally more stable than pure perfluoroalkylphosphorus compounds, and have the general formula



$$R_f - (CX_2)_n - \overset{\displaystyle Y}{\underset{\displaystyle Y}{P}} = O ,$$



$$\left[R_f - (CX_2)_n\right]_2 - \overset{\displaystyle Y}{P} = O$$

whereby R_f is a perfluoroalkyl remainder with more than 5 carbon atoms which, however, can have a chlorine or hydrogen atom in the ω-position, but preferably is a perfluoroalkyl remainder with 8-20 carbon atoms.

X can be hydrogen or an aliphatic alkyl remainder, Y designates alkoxy-, aralkoxy-, aroxy- or amine remainder, halogen, -SH, or -OH.

n is larger than 1, preferably 2 or 3.

The oxygen can be totally or partially replaced by sulfur. The derivatives of the free acids and their salts bring about a great reduction in the surface tension in ionizing solvents such as water or alcohol. The solutions foam even with very small concentrations. Above all, the phosphonic acid salts are excellent wetting and emulsifying agents.

The esters and amides of the acids are very good wetting agents for waxes in quantities from 0.1 to 0.01 $^0/_0$. They faciltate the uniform application of varnish, metal, and plastic and inhibit the melting out of individual components. The waxed surfaces are not as easily soiled and the appearance of water spots is prevented. The esters of the corresponding thio-acids are excellent lubricating oils for metals. Even small additions of about 2 $^0/_0$ to normal lubricating oils raises their lubricating effect at high bearing pressures and reduces wear. The oils are protected from oxidation.

Of special significance are the acid derivatives which carry polymerizing ester- or amide groups. Thus the acid amides which can be derived from ethylenimine are outstanding substances for impregnating textiles, paper, leather and wood. The glycidyl esters are likewise suited for this. With diluted solutions of these two classes of compounds textiles, leather, paper and other materials can be easily impregnated and given excellent resistance to washing. Very dilute aqueous solutions or emulsions of the amide, or solutions of glycidyl ester in trichloroethylene are particularly suitable. By short-term heating to 120° C the impregnation on the substrate can be hardened. Textiles or paper which have been thus impregnated repel oil, gasoline, heptane and dirt. Water is also repelled well. At the same time the materials acquire a flame-resistant behavior. The production of these compounds is possible using the given methods.

Through the Michaelis-Arbusov reaction of phosphinic acid ester, preferably methyl ester, with a fluorohalogen alkane of the general formula:

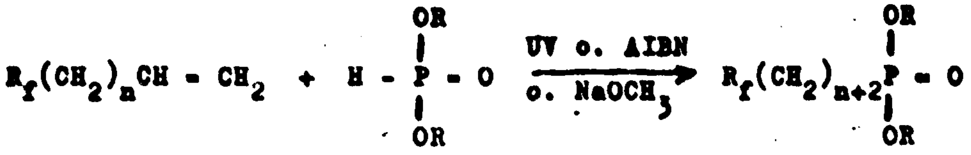
$$R_f - (CX_2) . Z$$

wherein R_f is a perfluoroalkyl remainder with more than five carbon atoms. In the ω-position this remainer can have a fluorine atom replaced by a chlorine- or hydrogen atom.

X is hydrogen or a small alkyl remainder with fewer than five carbon atoms. Z indicates a halogen, preferably chlorine or bromine.

Preferably the components are mixed in a molar ratio and heated to 120° C to 170° C in a nitrogen atmosphere. After several hours the reaction mixture can be separated by distillation. The yields contain up to 90 $^{0}/_{0}$ of the desired fluoroalkane phosphonic acid ester.

A second usable method for ester production is the addition of phosphorous acid ester to olefins which have a longer perfluoroalkyl chain but are not fluorinated.



$$R_f(CH_2)_nCH = CH_2 + H - \overset{OR}{\underset{OR}{P}} = O \xrightarrow[o.\ NaOCH_3]{UV\ o.\ AIBN} R_f(CH_2)_{n+2}\overset{OR}{\underset{OR}{P}} = O$$

n = 0 to 5

This reaction proceeds with a very high yield and produces pure products. In addition to UV-irradiation the addition can also be radically triggered wth azoisobutyric acid dinitrile at 60-70° C or with peroxide initiators such as tertiary butyl peroxide. Sodium alcoholate is also an exceptionally good catalyst for the reaction. When using the analogous thiophosphorous acid ester simple heating is sufficient.

A new and particularly simple procedure consists of the addition of perfluoroalkyl iodides to alkylenephosphonic acid derivatives. Here we are talking particularly about vinyl phosphonic acid and allylphosphonic acid and their derivatives. Vinylphosphonic acid chloride is a particularly well-suited starting material on which perfluoroalkyliodide can be added advantageously between 170° C and

400° C using UV-radiation or radical-forming catalysts, such as azoisobutyric acid dinitrile as well as by thermal stimulation. The obtained fluoroalkylphosphonic acid chlorides are easily saponified and yield valuable surface-active phosphonic acids which are de-iodized into acid salt solution using zinc dust. The phosphonic acids obtained in this manner easily add two moles of epichlorohydrin by ring separation. These esters can then be converted in as water-free a medium as possible into glycidyl esters using HCl-separation by epoxy ring formation with an HCl acceptor, such as amines or alkalis. These esters are excellent impregnating agents for textiles and excellent raw materials for varnish. If one replaces fluoroalkylphosphonic acid dichloride with equivalent ethylenimine-pyridine-ether solutions then the diamides with ethylenimine are formed which can be freed from iodine in an aqueous medium with sodium amalgam. Following extraction with tri [trichloroethylene] and subsequent distillation separation of the extracting agent the diamide is recovered which is partially soluble in water and which also has an excellent oleophobic impregnating effect on all cellulose substrates and on wool substrates.

Example 1.

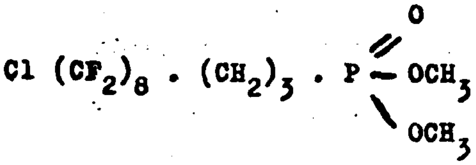
7 g 1-iodoperfluorodecane are mixed with 1.2 g of

vinylphosphonic acid dichloride and irradiated for 20 hours with a 500-W mercury-vapor lamp in a glass ampoule in a protective gas atmosphere excluding oxygen. During this time it is shaken continuously. The light violet fluid is dissolved in 15 cm^3 of tetrahydrofuran and added by drops to 0.9 g of ethylimine and 1.6 g pyridine in 10 cm^3 of ether with cooling and stirring. After drawing off the pyridine hydrochloride the solvent is evaporated. The remaining oil is taken up in 400 cm^3 of acetone and a cotton cloth, a piece of suede leather, and a piece of filter paper are impregnated with it. The piece of suede was exposed to room-temperature air for one day. All pieces show a strong wash-stability and water- and oil-repellent character. Gasoline beads up on it. The pieces are not easily soiled and are then very easily cleaned. If one ignites the cotton or paper over a flame the flame stops burning as soon as the unburned pieces are held out of the flame. The charred edges do not have an afterglow.

Example 2.

24 g of 1-iodo-8-chloroperfluorooctane are mixed with 6 g of allylphosphonic acid dimethyl ether and 50 cm^3 of diisopropyl ether and after the addition of 0.5 g of azoisobutyric acid dinitrile the mixture is heated under a nitrogen atmosphere to 70° C for five

hours. Then the same quantity of AIBN is once again added and the mixture heated for 8 hours. The solvent is distilled off and the reaction mixture is shaken for 4 hours with 100 cm^3 of 10-$^0/_0$ aqueous sodium bisulfite solution. Then 100 cm^3 of trichloroethylene is added, shaken and the heavy phase is drawn off. The extracting agent is distilled off. From the residue under a vacuum at Kp = 125° C and 1 mm Hg, 16.2 g of pure fluoroalkylphosphonic acid residue are recovered, the elementary analysis of which confirms the following formula.



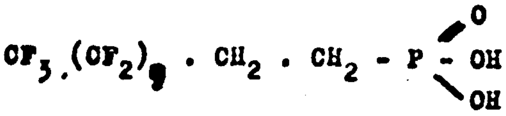
$$\mathrm{Cl\,(CF_2)_8 \,.\, (CH_2)_3 \,.\, P(=O)(OCH_3)(OCH_3)}$$

The yield is 65 $^0/_0$ of the theory for iodine alkane. This oily substance is an excellent incombustible lubricant for bearings and its density is so great that is does not form oil specks on water.

Example 3.

8 g of 1-iodo-perfluorodecane are placed with 1.5 g of vinylphosphonic acid chloride in a pyrex Carius tube and heated to 220° C for 5 hours. Following cooling the Carius tube is opened and the content trickled into 20 cm^3 of hot water and this mixture is treated with 10 cm^3 of concentrated HCl and stirred with zinc dust

for 1 hour. It is then decanted from the zinc and shaken briefly with 25 cm³ of concentrated sulfuric acid. The heavier nonaqueous layer is separated in mild heat and in fact consists of fluoroalkyl phosphonic acid with the formula:



$$CF_3.(CF_2)_9 \cdot CH_2 \cdot CH_2 - P\begin{matrix} \nearrow O \\ - OH \\ \searrow OH \end{matrix}$$

This product, even in very minute concentrations, reduces the surface tension of water and other polar solvents and is an excellent emulsifier for highly fluorinated liquids and resins. Convert the phosphonic acid obtained in this manner into a diisopropylether solution by drop by drop addition of a double molar quantity of epichlorohydrin while stirring for two hours in the recycle and then separate with a suspension of finely divided sodium hydroxide in polyglycol, in a quantity equal to the molar quantity of the epichlorohydrin, stirring for three hours, and then boil off the hydrogen chloride in the recycle. It is then treated with 80 cm³ of trichloroethylene and washed twice by shaking, each time with 30 cm³ of water. The solvents are evaporated from this solution. From the remaining glycidyl ester - preliminary condensate mixture 5 g are emulsified using an ultraturrax [Tr. note: This term could not be found in available sources.] in 50 cm³ of warm 0.2-$^{0}/_{0}$ aqueous solution of phosphonic acid produced according to this example which has been neutralized to a pH of 8 with sodium hydroxide;

simultaneously 0.5 g of polyvinyl alcohol is added as a stabilizer. This suspension can be kept for a long time and can be diluted further with water. Using a suspension diluted to 1 °/₀ content of impregnating agent a piece of cotton is impregnated, squeezed, dried, and heated by ironing. Then the material is washed out well with water until it is free of emulsifier. After drying oil, water, gasoline, and benzene are repelled by this material. Compared to an untreated sample this impregnated fabric also displays flame resistance.

Example 4.

3 g of glycidyl ester reaction mixture from **Example** 3 is mixed vigorously with 50 cm³ of a 20-°/₀ solution of Epikote® 834 in methylisobutylketone. To this solution add the same quantity of 9-°/₀ solution of Versamid® 125 in metaylisobutylketone. The pot life of varnish produced in this manner is about two hours. Two degreased iron plates are dipped into this varnish. One is dried at 25° C for 30 hours, the other is dried at 150° C for 10 minutes. On both samples, on which the varnish has now hardened, water, oil, heptane and toluol bead up. A comparison plate with the same varnish without the addition of the fluorophosphonic acid derivative does not show this property. Varnished surfaces soiled with oil vapor and dust are

comparably easier to clean if they contain fluorophosphonic acid compounds as an additive. In contrast to normal epoxy resin varnish, the surface of synthetic resin varnish modified with fluoroalkylphosphonic acid derivatives does not become dull even after prolonged contact with solvents which would otherwise cause it to swell.

Example 5.

3 g of glycidyl ester reaction mixture from Example 3 are dissolved in 30 cm^3 of trichloroethylene in the ratio 1:1 and mixed well with 0.15 g of diethylene triamine (NH_2-C_2H_4-NH-C_2H_4-NH_2). This solution is then thinly sprayed onto an incompletely hardened layer of epoxy resin varnish and left to harden for 24 hours. This coating protects the varnish from the swelling effect of solvents.

A cellulose regenerative film immersed in this solution diluted to 1:10, after drying for 24 hours becomes water-, oil-, and glue repellent and antiadhesive. A polyethylene sheet or plate treated in the same manner shows a considerably lesser permeability to water vapor, oxygen, solvents, odors and flavors than an untreated test piece.

Example 6.

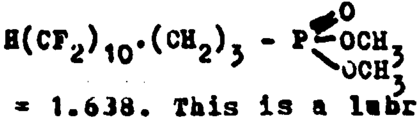
A polyester textile fabric is immersed briefly in the diluted solution prepared in Example 5 and dried. After 24 hours the test piece is water- and oil repellent and hydrocarbons also bead up on it.

Example 7.

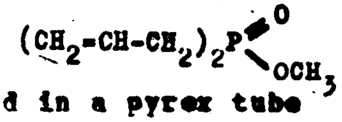
15 g of vinylphosphonic acid dichloride together with 60 g of perfluorooctyl iodide is injected as a mixture, at a rate of 0.4 g/m, up into a pyrex glass tube 2 meters long with a 6-mm inner diameter which is wound into a vertical spiral. This glass spiral is heated to 300° C. At the lower outlet of the reaction tube the vapors are fed under no pressure into 100 cm^3 of 10-$^0/_0$ aqueous solution of ammonia. After throughput of the total quantity this solution is neutralized with concentrated hydrochloric acid, zinc dust is added and it is stirred for four hours at 40° C. It is then decanted from the zinc and 100 cm^3 of concentrated sulfuric acid are added whereby the mixture is allowed to heat up to 60° C. The aqueous sulfuric acid solution is separated and the phosphonic acid which is insoluble in the sulfuric acid is easily crystallized out. One obtains 55.2 g of

this acid. The ammonium salt of the triethylamine of this phosphonic acid can be added in quantities of 0.01 to 0.1 $^{0}/_{0}$ to commercial hard waxes for floor care. Hard waxes modified in this manner do not water-spot in contrast to normal waxes.

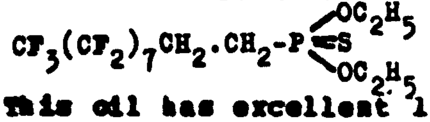
Example 8.

As described in Example 7, a mixture of 65 g of 8-hydrogen-1-iodoperfluorodecane with 15 g of allylphosphonic acid dimethyl ester is forced into a Hastelloy C tube one meter in length with a 3-mm inside diameter, with a speed of 3 cm³/min, under a pressure of 300 atm. Using an oil bath the tube was kept at about 270° C. At the other end of the tube the liquid is cooled and using a pressure retaining valve the pressure is reduced from 300 atm to normal pressure and dissolved in 100 cm³ of methanol. After throughput of the total quantity the mixture is shaken vigorously with sodium amalgam. After addition of water the heavier ester layer is separated. 67 g of  $H(CF_2)_{10}\cdot(CH_2)_3-P(=O)(OCH_3)(OCH_3)$ were recovered; Kp = 137° C; density (25° C) = 1.638. This is a lubricating and hydraulic oil with high density so that it does not float on water. It does not corrode metals and does not soften elastomers.

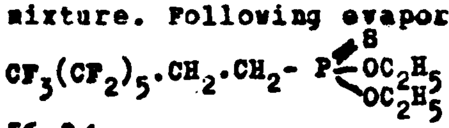
Example 9.

For preparing a bistluoroalkylphosphinic acid methyl ester 1.9 g of diallylphosphinic acid methyl ester  $(CH_2=CH-CH_2)_2P(=O)OCH_3$ and 19 g of 1-iodoperfluorohexadecane are melted in a pyrex tube excluding oxygen. This tube is heated and shaken for an hour at 260° C in an oil bath. It is then cooled and the reaction mixture dissolved in 100 cm^3 of trichloroethylene and shaken vigorously for 10 hours with an aqueous $NaHSO_3$ solution. Then this solution is washed with water. This solution is excellent for caring for varnish; it does not attack the varnish and has an oil- and soil-repellent effect.

Example 10.

To a mixture of 6 g of monothiophosphorous acid-0,0-diethyl ester and 18 g of 1,1,2-trihydroperfluorodecane(1) gradually add 1.5 cm^3 of a concentrated alcohol sodium ethylate solution. After heating for five hours at 90° C and subsequent distillation 13 g of  $CF_3(CF_2)_7CH_2.CH_2-P(=S)(OC_2H_5)_2$ will be obtained; Kp = 123° C at 1 mm Hg. This oil has excellent lubricating properties.

Example 11.

Dissolve 6 g of monothiophosphorous acid-0,0-diethyl ester in 100 cm³ of benzene and treat it while stirring and cooling, with an absolute alcohol sodium ethylate solution which was made from 0.87 g of Na. Heat to 50° C and at this temperature add by drops 19 g of 1-iodo-1,1,2,2-tetrahydroperfluorooctane in 50 cm³ of benzene. After stirring for four hours at this temperature, cool and filter the mixture. Following evaporation of the solvent 11 g of  $CF_3(CF_2)_5 \cdot CH_2 \cdot CH_2 - P(=S)(OC_2H_5)_2$ remain; Kp = 102° C at 1 mm Hg. The yield is 56-°/o.

Claim 1.

A method for producing polyfluoroalkyl phosphonic acids and -phosphinic acids, as well as their sulfur analogs, which do not contain fluorine in the α- and β-position to phosphorus is distinguished by the fact that one adds fluoroiodoalkane thermally or radically to unsaturated polyfluoroalkylphosphonic acids and -phosphinic acids or that one adds phosphorous acid ester ionically or radically, using the method presented, to fluoroolefins which contain no fluorine on the double bond, or, using a known method, that one converts them with fluorohalogenalkanes which do not contain fluorine in the α- and β-position to the reactive halogen, according to Michaelis-Arbusov with trialkylphosphites.

Claim 2.

A method for oil-, dirt- and water-repellent impregnation which simultaneously has a flame retardant effect on textiles, paper, leather, and wood is distinguished by the fact that polymers or monomers of the fluoroalkylphosphonic-, thiophosphonic- and fluoroalkylphosphinic and thiophosphinic acid derivatives chemically anchored to the substrate are either applied or are produced in situ, and they do not have fluorine in the α- and β-position to phosphorus.

Claim 3.

Method for oil- and water-repellent-, as well as anti-adhesive coating of varnish and plastic surfaces and sheets for a simultaneous reduction of the permeability by easily penetrating organic substances and inorganic gases is characterized by the fact that one applies fluoroalkylphosphonic acid derivatives which interlace chemically with the substrate or which polymerize in situ, in the given case with the addition of a polymerization catalyst or hardener, or mixes them with varnish or the sheet composition prior to processing.

Claim 4.

Lubricating- and hydraulic oils which are heavier than water are characterized by the fact that based on fluoroalkyl phosphonic acid ester and -thiophosphonic acid ester which do not have fluorine in the α- and β-positions to phosphorus, they are used as a lubricant additive and as lubricating oil.

Claim 5.

A method according to Claim 1 is characterized by the fact that chlorofluoroiodoalkanes or fluoroiodoalkanes are heated together with unsaturated alkylphosphonic acids, -thiophosphonic acids, -phosphinic acids, and -thiophosphinic acids or their derivatives in the gas- or liquid mixture, advantageously at temperatures higher than 150° C, preferably between 200 and 350° C.

Claim 6.

A method according to Claims 1 and 5 is characterized by the fact that unsaturated phosphorus derivatives, preferably vinyl- and allylphosphonic- and -thiophosphonic acid chlorides are heated between 250° C and 350° C between 10 minutes and 10 seconds with fluoroiodoalkanes, preferably perfluoroalkyl iodide with 6-25 carbon atoms.

Claim 7.

A method according to Claim 1 is characterized by the fact that one adds fluoroiodoalkanes or chlorofluoroiodoalkanes to unsaturated alkylphosphonic- and -phosphinic acids or their derivatives such as chlorides, fluorides, esters, and amides in a mixture, diluted or undiluted, using radical-forming radiation, preferably with UV light.

Claim 8.

A method according to Claim 1 is characterized by the fact that one adds fluoroiodoalkanes or chlorofluoroiodoalkanes to unsaturated alkylphosphonic acids and -phosphinic acids or their derivatives using a radical-forming catalyst such as azoisobutyric acid nitrile, or benzoyl peroxide.

Claim 9.

A method according to Claim 1 is characterized by the fact that using a known method one brings to reaction halogenfluoroalkanes, which do not contain fluorine in the α- and β-position to the reactive halogen, with trialkylphosphites according to the Michaelis-Arbusov reaction.

Claim 10.

A method according to Claim 1 is characterized by the fact that in a known manner to fluoroolefins and halogenfluoroolefins which do not have fluorine in the double bond, one adds phosphorous acid derivatives, preferably the dialkylester, thermally through irradiation with UV light or catalytically.

Claim 11.

A method according to Claim 3 is characterized by the fact that one coats the surface of the substrate with the compound types described in Example 3, advantageously adding a catalyst, such as organic polyamines.

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