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## BETA-HYDROPERFLUOROALKYL COMPOUNDS OF PHOSPHORUS

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This invention relates to beta-hydroperfluoroalkyl compounds of phosphorus and more particularly to beta-hydroperfluoroalkyl phosphinic acids and beta-hydroperfluoroalkyl phosphonic acids and their salts and to the process for preparing such acids.

Fires, involving petroleum hydrocarbons, aromatic hydrocarbons and other materials which are at the same time insoluble in water and less dense than water, have always posed a very serious problem. Due to their insolubility and lesser density, these materials float on water. Therefore, the usual system of fire fighting, involving a stream of water ejected from a hose or similar conduit, has been of little use with these materials since the fire is not smothered. In fact, more harm than good often has been the result since the burning liquids often spread on the water and cover a wider area than originally was the case.

Several methods are now used in attempts to overcome this problem. Two methods based on water involve a fog created by a special nozzle or a foam created by adding certain materials to water and dispensed with special equipment. While both of these methods of fire fighting have enjoyed success in certain situations, their usefulness is limited. It is necessary, in both cases, to approach the immediate vicinity of the source of the fire to apply the extinguishing agent because the fog or foam cannot be projected over a long distance as can a stream of water. This necessary approach creates a hazard to the fire fighting personnel. The area that can be covered by these methods is also limited so that large scale fires are not readily brought under control.

The other methods are based on nonaqueous systems. Three classes of extinguishing agents are used: gases, liquids and solids. The gases, carbon dioxide or certain brominated methanes such as bromotrifluoromethane, are limited to relatively small fire situations. Again, to be effective, these materials must be released at the source of the fire and must cover the entire fire. Like the fog and foam, they cannot be projected into a fire from a safe distance. Being gases under pressure, these materials must be stored and transported in heavy steel cylinders.

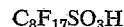
The liquids, e.g. carbon tetrachloride or chlorobromomethane, must be transported to the scene of a fire. They are also limited to small fires because of the volumes of materials required. They can be projected over some distance but most of the liquid extinguishing agents have fallen into disfavor because of the toxic nature of the materials or of their decomposition products.

The third class, solids, is composed of materials such as sodium bicarbonate. The solids, in the form of a very fine powder, are projected by means of a compressed gas into the fire. Since both the solid material and the compressed gas must be transported, the system is limited. The solids cannot be projected over too great a distance. Also, they must blanket the entire fire to be effective.

It is apparent from the foregoing discussion that fire extinguishing agents are needed which will be effective against fires involving hydrocarbons and similar materials, which do not have to be stored and transported in large volume to the scene of the fire, which can be projected over a sufficient distance so that the fire fighters need not approach the fire themselves, and which need not blanket the entire fire simultaneously to be effective.

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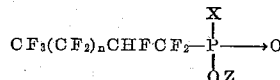
An obvious solution would be to provide a material which can be added to water so that the water will meet the requirements cited above. Although a great deal of research has been conducted on the search for materials to provide this obvious solution, the search has been completely unsuccessful. It has been theorized that a surface active agent, which would convert water to a mixture that would mix with and wet hydrocarbons, was necessary. Hydrocarbon based surface active agents were completely unsuccessful, as were the somewhat more efficient surface active agents  $H[CF_2CF_2]_nPO(OH)_2$ . Even the very highly active and somewhat spectacular perfluoroalkyl surface active agents  $C_7F_{15}CO_2H$ ,



and  $C_7F_{15}CONH(CH_2)_3N(CH_3)_3I$  were not successful in solving this problem.

It is an object of this invention to provide new and improved surface active agents. Another object is to provide substances which can be added to water to render it effective for extinguishing fires, particularly fires involving hydrocarbons and similar materials. A further object is to provide aqueous solutions which can be projected over fairly long distances for extinguishing hydrocarbon and like fires and which are effective for that purpose without simultaneously blanketing the entire fire. A still further object is to provide substances which can be stored and transported in small volume and added to water at the scene of a fire. Other objects are to provide new phosphorus acids and their salts and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accord with this invention which comprises compounds of the formula



wherein  $n$  is an integer of from 2 to 5,  $X$  represents a member of the group consisting of  $H$  and  $OZ$ , and  $Z$  is a member of the group consisting of  $H$ ,  $Na$ , and  $K$ ; and aqueous solutions of from about 0.1% to about 1% by weight of such compounds which are valuable fire extinguishing compositions, particularly for fires involving hydrocarbons and like materials.

It has been found that the compounds of the above formula are new and improved surface active agents and are useful as chemically stable organic acids and salts. The free acids are strong acids resembling mineral acids, and their salts resemble typical salts of strong acids. The acids and the salts are soluble in water and in hydrocarbons, halogenated hydrocarbons, and many other organic solvents. Most particularly, aqueous solutions of such acids are very effective to extinguish fires involving hydrocarbons, such as gasoline and other petroleum products, benzene, and like materials which are lighter than and immiscible with water, when such aqueous solutions are sprayed on such fires from an ordinary hose nozzle or any other suitable means. The ability of aqueous solutions to extinguish fires of such character appears to be unique with the acids of this invention.

In light of the fact that aqueous solutions of other surface active agents, including the best prior perfluoroalkyl surface active agents, would not extinguish fires involving hydrocarbons or similar materials, it was completely unexpected that aqueous solutions of the compounds of this invention in the free acid form would extinguish such fires. Aqueous solutions of these acids wet and mix with hydrocarbons, as do aqueous solutions of some of the prior perfluoroalkyl surface active agents, but the solutions of the acids of this invention are the only ones known that act as fire extinguishing agents when

applied to a hydrocarbon fire as an ordinary stream of water. The concentration of material necessary to produce the effect may vary somewhat with the length of the polyfluoroalkyl chain, decreasing somewhat with increase in the chain length. A concentration of from about 0.1% to about 1% by weight of an acid of this invention is sufficient to produce the desired effect. Usually, it is preferred to employ a concentration of from about 0.5% to about 1% by weight of the acid based on the water.

The acids of this invention find ready application in situations where large volumes of hydrocarbons or similar materials are stored, where water itself is readily available at every location but where the other special extinguishing agents described previously are ineffective or where storage and/or transport of such other materials is uneconomical or inconvenient. Such situations would include oil refineries, chemical plants using or manufacturing large volumes of benzene, alkyl benzenes, styrene or similar materials, or on certain ships such as tankers which transport petroleum or other flammable chemical materials.

The equipment necessary to add the subject acids to a water stream will be readily apparent to those skilled in the art, and is reasonably inexpensive and not space consuming. It can easily be installed in the pumper truck of a fire control system or in the fire control system of a ship. Storage of the acids of this invention poses no problem since only about one pound of acid per 1000 pounds of water is necessary. Since the acids are very dense, the storage volume is low; a quart of the acid weighs about four to five pounds.

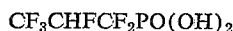
The reason why the subject acids produce this desired effect while other perfluoroalkyl surface active agents do not is not understood.

Besides the unique property described above, the acids and salts of this invention are excellent surface active agents for many liquids. Given in the table below is a comparison of some of the preferred compounds wherein  $n$  is 4, with several other surface active agents containing perfluoroalkyl groups of similar size. For comparison, the surface tension of water at 25° C. is 72 dynes/cm.

TABLE  
Surface Tensions In Water

Conc., Wt. percent.....	0.001	0.005	0.01	0.05	0.1	0.5	1.0
Agent	Surface Tension, dynes/cm., 25° C.						
$\text{CF}_3(\text{CF}_2)_4\text{CHF}(\text{CF}_2)_2\text{P}(\text{O})(\text{OH})_2$	62	55	43	21	18	16	15
$\text{CF}_3(\text{CF}_2)_4\text{CHF}(\text{CF}_2)_2\text{PH}(\text{O})(\text{ONa})$			33	25	21	18.6	18.0
$\text{CF}_3(\text{CF}_2)_4\text{CHF}(\text{CF}_2)_2\text{PH}(\text{O})(\text{OH})$							15.0
$\text{H}(\text{CF}_2\text{CF}_2)_4\text{P}(\text{O})(\text{OH})_2$	67	59	55	45	40	27	22
$\text{C}_7\text{F}_{15}\text{CO}_2\text{H}$			65	50	40	16	16
$\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$					41		
$\text{CF}_3\text{CHF}(\text{CF}_2)_2\text{PO}(\text{OH})_2$							39

The data, from which the table was derived, indicate that all of these agents had reached their ultimate lowering of surface tension at 1.0% concentration. The advantage of all of these agents, except



over hydrocarbon containing agents is apparent since agents containing hydrocarbon groups reach their ultimate lowering of surface tensions of water solutions at 28–30 dynes/cm. The compound  $\text{CF}_3\text{CHF}(\text{CF}_2)_2\text{PO}(\text{OH})_2$  illustrates the properties of compounds similar to the subject compounds but outside the range of this invention. This latter compound compares very unfavorably with the compounds of this invention. Aqueous solutions of  $\text{CF}_3\text{CHF}(\text{CF}_2)_2\text{PO}(\text{OH})_2$  have no fire extinguishing properties for hydrocarbon fires.

It is apparent from the table that

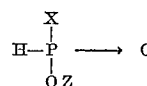


is more efficient than the other types of fluorinated surface active agents in lowering aqueous surface tensions and that the similar agent  $\text{CF}_3(\text{CF}_2)_4\text{CHF}(\text{CF}_2)_2\text{PH}(\text{O})(\text{ONa})$ , while less efficient than the previous example, is nevertheless more efficient than the other types. Thus, the acids and salts of this invention are unexpectedly found to be more efficient than any other known type of fluorinated, anionic surface active agent.

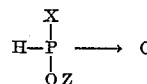
The acids of this invention are also effective in reducing the surface tension of hydrocarbons and chlorinated hydrocarbons. Thus, a 0.043 wt. percent solution of  $\text{CF}_3(\text{CF}_2)_4\text{CHF}(\text{CF}_2)_2\text{P}(\text{O})(\text{OH})_2$  in benzene lowered the surface tension by seven dynes/cm. In comparison,  $\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$  at 0.1% concentration in benzene, lowered the surface tension only 5–6 dynes/cm. A 0.08 wt. percent solution of  $\text{CF}_3(\text{CF}_2)_4\text{CHF}(\text{CF}_2)_2\text{P}(\text{O})(\text{OH})_2$  in 1,1,2-trifluoro-1,2,2-trichloroethane ( $\text{CF}_2\text{Cl}-\text{CFCl}_2$ ) lowered the surface tension by 2.5 dynes/cm. Considering that the initial surface tension was 17.6 dynes/cm., any lowering is remarkable.

The acids and salts of this invention can be applied to many of the uses known for perfluoroalkyl surface active agents. These uses include evaporation inhibition for gasoline, improving the surface protection, flow, spreading penetration and atomization or sprayability of petroleum hydrocarbons, and for wax emulsions. They can be used as surface active agents for strongly corrosive or highly oxidizing media such as pickling baths, electroplating baths and in such strong acids as 98% sulfuric acid, nitric-hydrofluoric acid mixtures or red fuming nitric acid. They can be used as emulsifying agents for fluorocarbon-oil and fluorocarbon-water systems and for systems containing the chlorofluorocarbon propellants used in "aerosol" applications. These acids and salts are also useful as emulsifying agents for polymerizations, particularly those involving fluorinated olefins.

The beta-hydroperfluoroalkyl acids of phosphorus and their salts of this invention are readily prepared by reacting a perfluoroolefin of the structure  $\text{CF}_3(\text{CF}_2)_n\text{CF}=\text{CF}_2$  with a phosphorus compound of the structure



in the presence of a free-radical initiator at a temperature of from about 50° C. to about 200° C. The perfluoroolefins are readily obtained by the pyrolysis of perfluorinated acids of the formula  $\text{CF}_3(\text{CF}_2)_n\text{CF}_2\text{CF}_2\text{CO}_2\text{H}$  or their sodium salts, which acids are well known and commercially available. The phosphorus compounds of the formula



include hypophosphorous acid,  $\text{H}_3\text{PO}_2$ , phosphorous acid,  $\text{H}_3\text{PO}_3$ , alkali hypophosphites such as sodium hypophosphite,  $\text{NaH}_2\text{PO}_2$ , alkali phosphites such as  $\text{Na}_2\text{HPO}_3$ , and the lower alkyl, aryl, and halo aryl esters of hypophos-

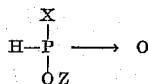
phorous acid and phosphorous acid, represented by methyl hypophosphite,  $\text{H}_3\text{P}(\text{O})(\text{OCH}_3)$ , and dimethyl phosphite,  $\text{HP}(\text{O})(\text{OCH}_3)_2$ .

The free radical initiators which are employed in the process constitute a well known class of materials conventionally employed in reactions of the character involved. Such initiators, which are suitable for the present process, include the acyl peroxides such as benzoyl peroxide and acetyl peroxide, alkyl peroxides such as di-tert-butyl peroxide, alkyl azo compounds such as azo-bis-alpha-isobutyronitrile, and alkyl metal compounds such as tetraethyllead. The preferred initiator, from the standpoint of ease of handling, safety and freedom from toxicity, is the alkyl peroxide di-tert-butyl peroxide.

The reaction temperatures employed will be those which are well known to the art for use with the various classes of initiators. The acyl peroxides and alkyl azo

compounds usually require temperatures of from 50° C. to about 100° C. The preferred reaction temperature for the preferred di-tert-butyl peroxide will be from about 115° C. to about 175° C.

When the phosphorus compound,



is such that Z is an alkyl or aryl group, the resulting product will be an ester. The esters are readily converted to the acids by treatment with a mineral acid, such as hydrochloric acid, preferably by refluxing the mixture of the ester and the mineral acid for a short time. The alkali metal salts also readily convert to the free acids by treatment with a mineral acid, such as hydrochloric acid. Also, the free acids of this invention can be readily converted to the salts by treatment with a hydroxide, oxide, carbonate, or bicarbonate of the metal. The esters are also saponified by strong bases. The alkyl esters, in common with most alkyl esters of strong acids, decompose at elevated temperatures, although they can be distilled at reduced pressures. The esters are water insoluble but are soluble in hydrocarbons, halogenated hydrocarbons, and many other organic solvents.

In order to more clearly illustrate this invention, preferred modes of carrying them into effect and the advantageous results to be obtained thereby, the following examples are given in which the amounts and proportions are by weight except where specifically indicated otherwise.

#### EXAMPLE 1

##### Dimethyl Beta-Hydroperfluoroheptylphosphonate

A silver lined 400 ml. shaker tube was charged with 150 g. (0.43 mole) of perfluoroheptene-1, 47.0 g. (0.43 mole) of dimethyl phosphite and 3.1 g. (0.02 mole) of di-tert-butyl peroxide. The mixture was heated for one and one-half hours at 127° C.-176° C. while shaking. The product weighed 185 g. Distillation gave 104 g. (70% recovery) of unreacted perfluoroheptene-1, B.P. 82° C. The residue, remaining after removing excess dimethyl phosphite, weighed 41.0 g. (20% conversion, 65% yield).

#### EXAMPLE 2

##### Beta-Hydroperfluoroheptylphosphonic Acid

The residue from Example 1 was heated under reflux for several hours with concentrated hydrochloric acid. Evaporation of the volatile liquid left 26.0 g. of beta-hydroperfluoroheptylphosphonic acid,



as a dark heavy oil, completely soluble in absolute alcohol or water.

*Analysis.*—Calculated for  $\text{C}_7\text{F}_{14}\text{H}_3\text{O}_3\text{P}$ : P, 7.16%; milliequivalents of hydrogen ion/g. 4.63. Found: P, 7.8%; milliequivalents of hydrogen ion/g. 4.5.

Titration with standardized alkali gave  $\text{pK}_{\text{a}1}=2.8$  for the first acid group and  $\text{pK}_{\text{a}2}=5.0$  for the second acid group.

#### SURFACE TENSIONS OF AQUEOUS SOLUTIONS

The surface tensions of aqueous solutions of the acid were measured at 25° C. using a Du Nouy tensiometer. The solutions were allowed to stand for two hours after preparation before measurements were made. The results are shown below.

#### SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF $\text{CF}_3(\text{CF}_2)_4\text{CHFCF}_2\text{P}(\text{O})(\text{OH})_2$

Conc., wt. percent.....	1.0	0.5	0.25	0.125	0.0625	0.0315	0.015	0.008	0.004	0.002
dynes/cm., 25° C.....	15.1	15.0	17.0	18.0	19.0	27.9	36.2	47.5	53.2	58.3

#### SURFACE TENSIONS OF NONAQUEOUS SOLUTIONS

A benzene solution of  $\text{CF}_3(\text{CF}_2)_4\text{CHFCF}_2\text{P}(\text{O})(\text{OH})_2$  (0.043 wt. percent) was found to have a surface tension 7 dynes/cm. lower than benzene itself at 25° C.

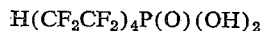
With a benzene solution of omega-hydroperfluoro-octylphosphonic acid,  $\text{H}(\text{CF}_2\text{CF}_2)_4\text{P}(\text{O})(\text{OH})_2$ , of concentration similar to the above solution, measurements indicated no change in the surface tension.

Kerosene, containing 0.1 wt. percent



exhibits a surface tension of 6 to 8 dynes/cm. lower than kerosene itself, at 25° C.

When a 0.1 wt. percent solution of



in kerosene was prepared, the surface tension was unchanged.

A 0.082 wt. percent solution of



in 1,1,2-trifluoro-1,2,2-trichloroethane,  $\text{CF}_2\text{Cl}-\text{CFCl}_2$ , at 25° C., exhibits a surface tension of 15.3 dynes/cm. 1,1,2-trifluoro-1,2,2-trichloroethane itself exhibits a surface tension of 17.6 dynes/cm. at 25° C.

A solution of  $\text{H}(\text{CF}_2\text{CF}_2)_4\text{P}(\text{O})(\text{OH})_2$  in 1,1,2-trifluoro-1,2,2-trichloroethane exhibits the same surface tension as the solvent itself. This  $\omega$ -hydro-compound does not dissolve to any apparent extent in the trifluorotrichloroethane.

Perfluorooctanoic acid,  $\text{C}_8\text{F}_{17}\text{COOH}$ , has no effect on the surface tension of 1,1,2-trichloro-1,2,2-trifluoroethane at any concentration up to and including the saturated solution.

#### EXAMPLE 3

##### Diethyl Beta-Hydroperfluoroheptylphosphonate

A mixture of 200 g. (0.57 mole) of perfluoroheptene-1, 80.0 g. (0.57 mole) of diethyl phosphite and 4.4 g. of di-tert-butyl peroxide was heated in a silver lined shaker tube at 160° C.-170° C. for two hours. The clear, tan product weighed 269 g. Distillation gave 100 g. of recovered perfluoroheptene-1, 19.0 g. of a mixture of the olefin and diethyl phosphite, and 37.0 g. of recovered diethyl phosphite. The product,



distilled at 76° C. at 4.0 mm. Hg pressure to 83° C. at 2.0 mm. pressure with some decomposition,  $n_D^{25}$  1.3816 to 1.3466, 42.1 g. A residue, composed of 43.5 g. of  $\text{CF}_3(\text{CF}_2)_4\text{CHFCF}_2\text{P}(\text{O})(\text{OH})_2$ , was also obtained.

The diethyl ester was redistilled, B.P. 105° C.-113° C. at 10.0 mm. pressure.

*Analysis.*—Calculated for  $\text{C}_{11}\text{F}_{14}\text{H}_3\text{O}_3\text{P}$ : C, 27.05%;

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F, 54.5%; P, 6.35%. Found: C, 29.3%; F, 50.4%; P, 5.9%.

## EXAMPLE 4

*Sodium Beta-Hydroperfluoroheptylphosphinate*

A mixture of 70.0 g. (0.20 mole) of perfluoroheptene-1, 21.2 g. (0.20 mole) of sodium hypophosphite monohydrate, 0.20 g. of di-tert-butyl peroxide and 78 g. of tert-butyl alcohol was heated for three hours at 115° C.-140° C. The product weighed 145.0 g.

A portion of the product (10.0 g.) was evaporated to dryness giving 4.51 g. of soft, white solid, containing mostly sodium beta-hydroperfluoroheptylphosphinate,



and small amounts of sodium hypophosphite and tert-butyl alcohol. The infrared spectrum showed an adsorption band at  $4.2\mu$  due to the P—H bond and a shoulder at  $7.84\mu$  to  $8.06\mu$  due to the P→O bond. The expected, strong C—F adsorptions were also present.

*Analysis.*—Calculated for  $\text{C}_7\text{F}_{14}\text{H}_2\text{PO}_2\text{Na}$ : P, 6.82%. Found: P, 6.8%.

The surface tension of aqueous solutions of the product are given below.

## SURFACE TENSIONS, AQUEOUS SOLUTIONS OF



Conc., wt. per- cent.....	1.0	0.5	0.25	0.125	0.063	0.0315	0.016
dynes/cm., 25° C.	18.4	18.6	17.3	20.3	23.4	27.1	30.6

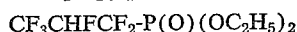
When a 1% solution of the salt was converted to the free beta-hydroperfluoroheptylphosphinic acid by addition of hydrochloric acid, the surface tension decreased from 18.4 dynes/cm. to 15.8 dynes/cm., indicating the greater surface activity of the free acid.

## EXAMPLE 5

*Diethyl Beta-Hydroperfluoropropylphosphonate*

A mixture of 150.0 g. (1.0 mole) of perfluoropropene, 138 g. (1.0 mole) of diethyl phosphite and 6.0 g. of di-tert-butyl peroxide was heated at 153° C.-170° C. for two hours. The liquid product weighed 234 g.

Distillation of the product gave 44.0 g. of diethyl phosphite, 34.0 g. of intermediate cuts, and 89.2 g. of diethyl beta-hydroperfluoropropylphosphonate,



B.P. 87° C. at 10 mm. pressure,  $n_D^{25}$  1.3606.

*Analysis.*—Calculated for  $\text{C}_7\text{H}_{11}\text{F}_6\text{O}_3\text{P}$ : C, 29.1%; F, 39.6%; H, 3.8%; P, 10.75%. Found: C, 29.4%; F, 37.6%; H, 4.0%; P, 11.3%.

## EXAMPLE 6

*Beta-Hydroperfluoropropyl Phosphonic Acid*

The ester,  $\text{CF}_3\text{CHFCF}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ , from Example 5 was hydrolyzed to the free acid by reflux with concentrated hydrochloric acid. The product was isolated in the same manner as described in Example 2.

The surface tensions of 0.1% by weight aqueous solutions of  $\text{CF}_3\text{CHFCF}_2\text{P}(\text{O})(\text{OH})_2$  at 25° C. was found to be 39 dynes/cm.

## EXAMPLE 7

*Fire Extinguishing Experiments*

A water solution containing 0.5 wt. percent of



was prepared. The surface tension was found to be 15.7

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dynes/cm. When this aqueous solution was sprayed on gasoline contained in a small aluminum cup, the aqueous solution was visually observed to mix with and spread over the gasoline whose surface tension was 20–22 dynes/cm. When pure water is sprayed on gasoline in the same cup, it does not mix or spread on the gasoline but rather collects into droplets and sinks under the gasoline.

When gasoline in a small aluminum cup is ignited and an aqueous solution containing 0.5 wt. percent of



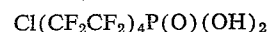
is sprayed onto the burning gasoline, the flames are extinguished in 1 to 2 seconds.

When 1% by weight of



is dissolved in water, the surface tension is about 15 dynes/cm. When this solution is sprayed onto gasoline burning in a small aluminum cup, the flames are extinguished in about 2 seconds.

When about a 1% by weight solution of



in water is sprayed onto gasoline burning in a small aluminum cup, the flames are not extinguished.

When a 1% by weight solution of



in water (having a surface tension of 39 dynes/cm.) is sprayed onto burning gasoline in a small aluminum cup, the flames are not extinguished.

When gasoline is ignited in a small aluminum cup and an aqueous solution containing 0.5% by weight of either perfluorooctanoic acid ( $\text{C}_7\text{F}_{15}\text{CO}_2\text{H}$ ) or perfluorooctanesulfonic acid ( $\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$ ), is sprayed onto the burning gasoline, the flames are not extinguished.

When 1% by weight of  $\text{H}(\text{CF}_2\text{CF}_2)_4\text{P}(\text{O})(\text{OH})_2$  is dissolved in water to produce the minimum surface tension available (22 dynes/cm.) and the resulting solution is sprayed onto gasoline burning in a small aluminum cup, the flames are not extinguished and sometimes flare up.

When a solution containing enough commercial soap to produce the minimum surface tension obtainable (28–30 dynes/cm.) or water itself is sprayed on gasoline burning in a small aluminum cup, the flames are not extinguished but almost invariably flare up.

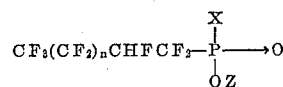
It will be understood that the preceding examples have been given for illustrative purposes solely and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be readily apparent to those skilled in the art that, subject to the limitations set forth in the general description, the materials, proportions, conditions and techniques employed may be widely varied without departing from the spirit or scope of this invention.

From the preceding description, it will be apparent that this invention provides new beta-hydroperfluoroalkyl phosphonic acids, beta-hydroperfluoroalkyl phosphinic acids, and salts of such acids, which have valuable new, beneficial properties, and more particularly are superior surface active agents and are particularly valuable for converting water to an effective fire extinguishing composition, especially for extinguishing hydrocarbon and like fires. Accordingly, this invention constitutes a valuable advance in and contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

I claim:

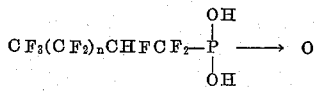
1. A compound of the formula



wherein  $n$  is an integer of from 2 to 5, X represents a

member of the group consisting of H and OZ, and Z is a member of the group consisting of H, Na and K.

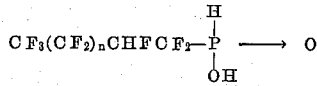
2. A compound of the formula



wherein  $n$  is an integer of from 2 to 5.

3. Beta-hydroperfluoroheptylphosphonic acid.

4. A compound of the formula



wherein  $n$  is an integer of from 2 to 5.

5. Beta-hydroperfluoroheptylphosphonic acid.

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