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3,188,340

**POLYFLUORO ALKANAMIDOALKYL
PHOSPHATES**

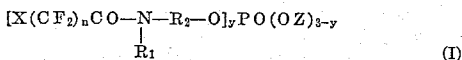
Alan K. Mackenzie, Redding, Conn., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware
No Drawing. Filed Dec. 3, 1961, Ser. No. 158,121
3 Claims. (Cl. 260-461)

This invention relates to novel processes for rendering solid materials oil-repellent and to the novel oil-repellency agents for use in such processes. By solid materials hereinabove I mean water-insoluble materials customarily employed in the manufacture of articles of utility, for instance textile fabric, textile yarns, leather, paper, plastic sheeting, wood, ceramic clays, as well as manufactured articles prepared therefrom such as articles of apparel, wall paper, paper bags, cardboard boxes, porous earthenware, etc. By oil-repellency, for the purpose of definiteness, I shall refer hereinafter to the quality of repelling, under the standard tests herein discussed, a light mineral oil such as a commercial liquid hydrocarbon or a vegetable oil such as peanut oil. But as a general proposition the materials treated according to this invention are found to possess repellency to oils, greases and fats generally, regardless of their origin (as for instance, mineral, vegetable or animal kingdom) or their consistency.

Heretofore, oil-repellency generally has been attained by high-cost processes or materials, and the end results have not been fully satisfactory. Oil-resistant glassine-type paper is costly to manufacture, and it is readily penetrated by water and water-vapor. Oil-repellency gained by coating paper or cardboard requires a separate operation and the protective surface film is easily broken when the paper is creased or folded, whereby the oil-repellency is lost.

It is a primary object of this invention to impart oil-repellency to water-insoluble solid materials by treatment with an aqueous bath of oil-repellency agents. A further object is to provide certain novel compounds which are useful for the foregoing purposes. Other objects and achievements of this invention will become apparent as the description proceeds.

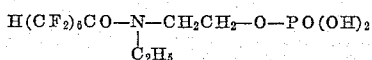
Now, according to this invention the foregoing principal objects are accomplished by treating water-insoluble materials with aqueous solutions of polyfluoro-alkanamido-alkyl phosphates and removing the excess water from the treated material. The polyfluoro-alkanamido-alkyl phosphates contemplated in this invention are novel compounds and may be defined by the formula



wherein X designates H or F, n is an integer from 6 to 12, R₁ is hydrogen or C₁ to C₄ alkyl, R₂ is a C₂ to C₁₂ alkylene bridging group, y is a number average value from 1 to 2.5, and Z is a water-solubilizing cationic ion, for instance, hydrogen, an alkali-metal, ammonium or substituted ammonium.

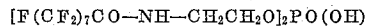
As further specific illustrations of the compounds employed by me according to this invention may be named the following compounds, which are formulated, for convenience, in free acid form but are preferably used in the

(2) Bis[2 - (pentadecafluoro - octanamido)ethyl] phosphate:

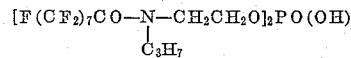


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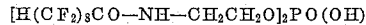
(2) Bis[2 - (pentadecafluoro - octanamido)ethyl] phosphate:



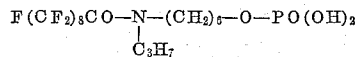
(3) Bis[2 - (N - propyl-pentadecafluoro-octanamido)ethyl] phosphate:



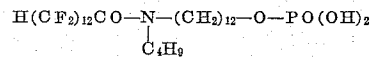
(4) Bis[2 - (9H - hexadecafluoro - nonanamido)ethyl] phosphate:



(5) 6 - (N - propyl - heptadecafluoro-nonanamido)hexyl phosphate:



(6) 12 - (N - butyl - 13H-tetracosafuoro-tridecanamido)-dodecyl phosphate:



The above compounds can be prepared by reacting the corresponding polyfluoro-alkanamido alkanols with phosphorus oxychloride or with phosphorus pentoxide, essentially as described in U.S. Patent 2,597,702. As in that patent, the products may be isolated as free acid (M=H) and then converted, by neutralization with the appropriate base, into an alkali-metal (say, sodium or potassium), ammonium or substituted ammonium salt. As convenient bases for obtaining substituted ammonium salts may be used commonly available, water-soluble, primary, secondary or tertiary amines such as methylamine, diethylamine, monoethanolamine, diethanolamine, morpholine, triethanolamine and bis(3-hydroxypropyl)-amine.

Other methods of synthesis are also available and are summarized at the end of this specification.

The requisite initial polyfluoro-alkanamido alkanols themselves may be prepared by converting the corresponding polyfluoroalkanoic acids to the acid chlorides, which are then reacted with amino alkanols. Details of the preparation of a representative member of this group of compounds is given in Example 1 below.

The treatment of textile fibers or other water-insoluble materials with polyfluoro-alkanamido-alkyl phosphates according to this invention may be achieved by any of the ordinary procedures, for instance padding, spraying or brushing, using aqueous solutions of said agents, and the quantity thereof put into the aqueous bath will usually be calculated to deposit on the fiber a weight of the agent equal to from 0.05% to 3% by weight of the fiber. In padding procedures, the amount of moisture left on the fiber after squeezing will, of course, be taken into account.

The preparation of the requisite aqueous solutions may be facilitated by first dissolving the phosphate agent in an organic solvent, such as acetone, methanol, or ethanol, followed by dilution with water, or a solution of the free acid phosphate in an organic solvent may be diluted with an aqueous amino or ammonia solution.

According to a preferred procedure, however, textile fiber (or other materials) treated with the mentioned phosphates is further treated (in optional sequence) with a water-soluble linear polymer containing cationic nitrogen whereby to endow said material with the power of exhausting the phosphate from the aqueous bath. The treatment then assumes the aspect of an exhaust bath procedure, and the quantity of phosphate put into the bath is essentially the entire quantity that it is desired to deposit on the fiber (or other materials).

Further details on this aspect of my invention are given in my copending application Serial No. 53,884 (filed Sep-

tember 6, 1960), now U.S. Patent No. 3,112,241, but for the sake of completeness, the essential features thereof are repeated here.

As examples of commercially available cationic polymeric materials suitable for use in this invention may be mentioned:

(a) The polymers or copolymers of quaternary derivatives or acid salts of esters of a dialkylamino alcohol and acrylic acid or methacrylic acid. Specific dialkylamino alcohols suitable for forming these esters include 2-(dimethylamino)ethanol, 2-(diethylamino)ethanol, 2-(dipropylamino)ethanol, 2-(N-methyl-N-cyclohexylamino)ethanol, 3-(diethylamino)propanol and 4-(diethylamino)butanol. The esters are prepared according to the method set forth in U.S. Patent 2,138,763, then quaternized, for example, in an aqueous solution of dimethyl sulfate, and the resulting quaternary ammonium salt is polymerized, or two or more of them are copolymerized, by known procedure. The esters may also be converted to acid salts with acids such as acetic, formic or hydrochloric, and polymerized or copolymerized by known procedure. (See for instance U.S. Patent 2,138,762.)

Preferred cationic compounds of this group are the polymers derived from the dimethyl sulfate quaternization product or from the acetic acid addition salt of 2-(dimethylamino)ethyl methacrylate and 2-(diethylamino)ethyl methacrylate.

(b) Water-soluble urea resins possessing cationic N-atoms, for instance one prepared from urea, formaldehyde, tetraethylene-pentamine, and hydrochloric acid as described by Suen, in "Polymer Processes," edited by Schioldknecht (Interscience, 1956), page 343.

(c) Melamine-formaldehyde resins possessing cationic N-atoms, for instance the acid colloid prepared from formaldehyde, melamine, and hydrochloric acid as described by Suen, loc. cit., at pages 315, 344.

(d) The quaternized or acid salts or polymerized ethylenimine, for instance those having a molecular weight of 30,000 to 40,000.

(e) Cationically modified nitrogen-containing starches, certain representatives of which appear in commerce.

The above agents themselves may be applied to the desired solid materials by ordinary procedures, for instance by padding, exhaustion, spraying or brushing, using aqueous solutions of the agents.

The quantity of cationic agent added may vary from 0.05% to 10% on the weight of the material being treated, while that of the phosphate, as already mentioned, may be from 0.05% to 3%. The optimum amount will depend upon such factors as the nature of the material, and in the case of paper pulp on the nature of the pulp, the particular cationic material selected, the composition of the phosphate, and the degree of oil-repellency desired. As a rule, a given combination of agents in specified amounts produces a greater effect on unbleached kraft pulp than on bleached kraft or bleached sulfite pulp. Of the phosphates, the ammonium or substituted ammonium salts are more effective than the free phosphoric acid, and the ω -F compounds ($X=F$) are more effective than the corresponding ω -H compounds ($X=H$). Also, the bis-polyfluoro-alkanamido-alkyl phosphates are more potent than the mono compounds.

The order of treatment of the solid material with the polyfluoro-alkanamido-alkyl phosphate and polymeric cationic N-containing material is immaterial, provided care is taken to eliminate or minimize contact between the two agents except when either of them is in contact with the solid material being treated. This means that the cationic agent may be applied first and then after a little time to permit complete exhaustion of the agent onto the material being treated, the fibers of a pulp for example, the polyfluoro-alkanamido-alkyl phosphate may be applied. Or the reverse sequence may be followed, with a time interval to allow for exhaustion of

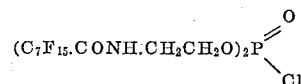
the phosphate compound onto the fiber. Or again, the two agents may be fed simultaneously through separate pipes into the vessel or pipe containing the pulp, provided vigorous agitation (or turbulent flow in the case of a pipe) is applied to insure rapid contact of each agent with the pulp, thus minimizing time of contact between the two agents when not in contact with the pulp. When a pulp is to be diluted in a fan pump or head box, however, the phosphate and cationic N-containing treating agents may be added separately to the stream of water with which the dilution is effected.

Without limiting this invention, the following examples are given to illustrate the preferred mode of operation. Parts mentioned are by weight.

Example 1.—Preparation of the polyfluoro-alkanamido-alkyl phosphates

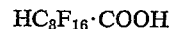
A mixture of 82.8 parts of perfluorooctanoic acid ($C_7F_{15}\cdot COOH$) and 47 parts of benzotrichloride is heated under nitrogen at 120° C. for about 18 hours. Fractional distillation of the reaction mass yields perfluorooctanoyl chloride, having a boiling range of 133° to 134.5° C. at atmospheric pressure. To 44.9 parts of this chloride is added 15.3 parts of ethanolamine, with gradual raising of the temperature to 75° to 80° C. The mass is cooled to room temperature, washed with 10% aqueous hydrochloric acid and with water, dried by azeotropic with benzene, and recrystallized twice from benzene. The resultant N-(2-hydroxyethyl)perfluorooctanamide, $C_7F_{15}\cdot CONH\cdot CH_2CH_2OH$, melts at 62° to 65° C. and has an infrared spectrum corresponding to the N-hydroxy-alkylamide structure.

To a dry benzene-ethyl ether solution of 9 parts of the above N-(2-hydroxyethyl)perfluorooctanamide is added a dry benzene solution of 1.53 parts of phosphorus oxychloride and 1.58 parts of pyridine, with agitation at 5° to 10° C. The mixture is heated to distill off ethyl ether, and is then held at reflux temperature for one hour. The product is bis(perfluorooctanamido-ethyl) phosphochloridate, which may be represented by the formula



To the reaction mass containing the above intermediate are now added 1.1 parts of water and 0.8 part of pyridine, and refluxing is continued for another hour. The mass is then cooled to room temperature, and allowed to settle into layers. The upper, benzene-water layer, is decanted off, and the lower layer is washed four times with 10 parts of water, then mixed with 80 parts of benzene, and dehydrated by azeotropic distillation. Anhydrous ammonia is now bubbled through the hot benzene solution to saturation, and the mass is cooled to room temperature. The solid product is filtered off and dried. It constitutes a mixture of ammonium mono- and bis[2-(pentadecafluoro-octanamido)ethyl] phosphate, containing 75% by weight of the bis-ester as determined by fluorine analysis.

When the same procedure is repeated except for starting with 9H-hexadecafluoro-nonanoic acid,



a mixture of ammonium mono- and bis[2-(9H-hexadecafluoro-nonamido)ethyl] phosphate is obtained, falling within Formula I above and having an average γ -value of 1.76, based upon fluorine analysis.

Example 2.—Treatment of paper pulp

Four parts of dry, unbleached kraft pulp are agitated vigorously in a vessel containing 300 parts of water, and 4 parts of an aqueous 0.5% solution of the polymer of dimethyl sulfate-quaternized 2-(diethylaminoethyl) methacrylate are added. (This provides 0.5% of the polymer on the dry weight of the pulp.) Agitation is con-

tinued for five minutes (or longer), and then is added 1 part of a 0.4% water solution of a mixture of mono- and bis[2-(pentadecafluoro-octanamido)ethyl] phosphate, ammonium salt, having a y -value of about 1.75, as prepared in Example 1. (This quantity calculates to 0.1% on the weight of the dry pulp.) After additional stirring for five minutes or more, the slurry of pulp is conveyed to the screen of a paper making machine, and a sheet of paper is formed and is subsequently dried on a rotary drier in the usual way.

When the above process is repeated, except for employing 2 or more parts of the 0.4% solution of the mixed ammonium (polyfluorooctanamido)ethyl phosphate, paper having 0.2% or more of the agent on the fiber is obtained.

Paper thus prepared may be evaluated for its oil-repellency rating by the "Nujol"- n -heptane test described more fully in my said copending application Serial No. 53,884, new U.S. Patent No. 3,112,241, under the heading "A. Testing of surface-treated, sheet material" (also in U.S. Patent 2,958,613), except that the swatches of fabric there mentioned are replaced here by sheets of the paper to be evaluated.

When thus tested, three papers prepared according to the above example and having respectively 0.1%, 0.2% and 0.3% of the agent on the fiber were found to possess the following ratings:

(P=amount of polyfluoro-alkanamido-alkyl phosphate in the paper, expressed as a percentage on the weight of the dry pulp.)

| P, percent | Oil-repellency rating |
|------------|-----------------------|
| 0.1 | 50 |
| 0.2 | 90 |
| 0.3 | 100+ |

It will be noted that with as little as 0.1% of the phosphate in combination with 0.5% of the polymeric quaternary derivative a definite oil-repellency is imparted to the paper, and with 0.2% and 0.3% of the phosphate a high order of oil-repellency is achieved.

Example 3.—Treatment of paper pulp

Using the same paper pulp, the same cationic polymer and the same procedure and proportions as in Example 2, except using as polyfluoro agent a mixture of ammonium mono- and bis[2-(9H-hexadecafluoro-nonanamido)ethyl] phosphate having a y -value of 1.76, as obtained at the end of Example 1, and oil-repellent paper of the same high qualities as in Example 1 is obtained.

Samples of paper prepared according to this example and in which the phosphate deposit was 0.3% and 0.4%, respectively, based on the weight of the fiber, were evaluated for oil-repellency rating according to Test B of my aforesaid copending application. This test measures the resistance of the paper to penetration by peanut oil by noting the time that it takes for a drop of said oil to pass from the upper surface of a horizontally supported sheet to its undersurface. The results were as follows:

(P has same meaning as in Example 2, but refers to the phosphate agent employed in Example 3.)

| P, percent | Time in seconds | Oil-repellency Rating |
|------------|-----------------|-----------------------|
| 0.0 | Less than 10 | 0 |
| 0.3 | 420 | 0 to 50 |
| 0.4 | More than 1,800 | 70 |

It will be noted that a definite oil-repellency is imparted to paper made in the procedure of this example, particularly when the amount of the polyfluoroalkanamido-alkyl phosphate was 0.4% on the weight of the fiber.

Example 4.—Treatment of fabrics

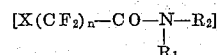
100 parts of various fabrics such as cotton poplin, cotton sateen, wool, nylon, acrylic fiber and polyester fiber

are dipped into an aqueous bath containing 1000 or more parts of water and 1 part by weight of the acetic acid salt of a polymer obtained from 2-(diethylamino)ethyl methacrylate. The fabric is agitated in the bath for 5 minutes or more, removed, squeezed, and reimmersed in a bath containing 1000 parts or more of water and 1 part of ammonium bis[2-(9H-hexadecafluoro-nonanamido)ethyl] phosphate. The fabric is again agitated in the bath for 5 minutes or more, removed, squeezed, and air-dried. The fabrics are found to have an oil-repellency rating of at least 70 as measured by the above referred to heptane-Nujol test.

It will be understood that the details of the above examples may be varied widely without departing from the spirit of this invention.

Thus, although the polyfluoro-alkanamido-alkyl phosphates are listed singly in the table hereinabove and may indeed be employed as single, distinct compounds, they may also be used as mixtures of the mono-, bis- and triesters prepared with a single polyfluoro-alkanamido-alkyl alkanol. The bis-polyfluoro-alkanamido-alkyl phosphates are more effective than the mono-compounds, and where mixtures are unavoidable, it is preferred to use such mixtures wherein the bis-polyfluoro-alkanamido-alkyl compounds predominate (i.e. y has an average value greater than 1.5). Fully alkylated phosphates (i.e. $y=3$) do not impart oil-repellency, but where a mixture is readily available they constitute an inert, harmless diluent for the active mono- and bis-compounds. Therefore, mixtures of polyfluoro-alkanamido-alkyl phosphates having a y value greater than 2, say up to $y=2.5$, are usable. Altogether, compounds having a y -value of 2 are preferred, but mixtures having an average y -value between 1.0 and 2.5 can be used.

An alternative method of forming the novel compounds of this invention is to subject to chlorine oxidation the corresponding bis-(or mixture of mono and bis)-(polyfluoro-alkanamido-alkyl) phosphonates, following the procedures described by E. N. Walsh in J.A.C.S., vol. 81, page 3023, for analogous non-fluorinated compounds. These procedures are expressed schematically by the following series of equations, wherein G represents the radical



as defined in Formula I hereinabove, R represents the alkyl radical of any conveniently available dialkyl phosphonate, and the reactions for producing a bis compound are used to typify the production of both bis, mono and mixtures of these compounds. (R may be, for instance, methyl, ethyl or phenyl.)

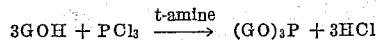
Step 1.—Formation of the phosphonate.

Method A: Ester-interchange with an available dialkyl phosphonate:

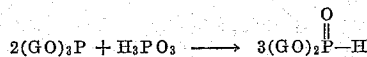


Method B: Direct reaction with PCl_3 :

(a) Preparation of phosphite—



(b) Conversion into phosphonate—



(The initial compound GOH used in these two methods may be prepared as in the first paragraph of Example 1.)

Step 2.—Oxidation of phosphonate to phosphochloride:

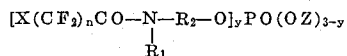


Step 3.—Hydrolysis: This is effected by the aid of water and pyridine as in Example 1.

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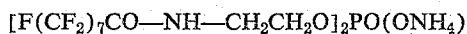
I claim as my invention:

1. A compound of the formula



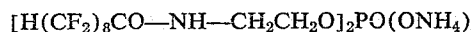
wherein X is an atom of the group consisting of hydrogen and fluorine, R₁ is a member of the group consisting of hydrogen and lower alkyl, R₂ is a C₂ to C₁₂ alkylene bridging group, n is an integer from 6 to 12, y is a number of an average value from 1.5 to 2.5, and Z is a water-solubilizing cation selected from the class consisting of sodium, potassium, ammonium, lower alkyl ammonium, lower hydroxyalkyl ammonium, and morpholinium.

2. A compound having the formula



8

3. A compound having the formula



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| | 3,094,547 | 6/63 | Heine | ----- | 260-461 |
| 15 | 3,096,207 | 7/63 | Cohen | ----- | 260-461 |

CHARLES B. PARKER, *Primary Examiner*.RICHARD D. NEVIUS, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,188,340

June 8, 1965

Alan K. Mackenzie

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 45, for "acomplished" read -- accomplished --; line 65, for "(2) Bis[2-(pentadecafluoro-octanamido)ethyl]phos-" read -- form of a salt as above indicated. --; column 2, line 67, for "qauntity" read -- quantity --; column 5, line 19, for "new" read -- now --; line 69, for "paper" read -- papers --.

Signed and sealed this 28th day of September 1965.

REAL)

test:

RNEST W. SWIDER
testing Officer

EDWARD J. BRENNER
Commissioner of Patents