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3,112,241

PROCESS OF IMPARTING OIL-REPELLENCY TO SOLID MATERIALS, AND MATERIALS THUS PRODUCED

Alan Kenneth Mackenzie, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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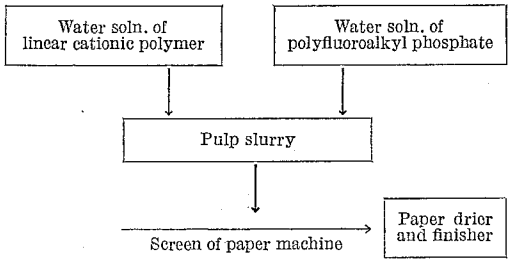
8 Claims. (Cl. 162—164)

This invention relates to novel processes for rendering solid materials oil-repellent and to the novel materials thus produced.



By solid material 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.

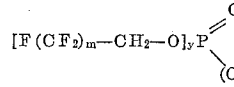
It is a primary object of this invention to provide a novel means of imparting oil-repellency to water-insoluble solid materials which is applicable to said material from an aqueous treating bath. Another object is to provide a novel means as aforesaid which is applicable from aqueous baths by ordinary means such as padding, dipping, impregnation, spraying, etc.

A special further object of this invention is to modify the mode of application of certain types of oil-repellency agents whereby to intensify their quality of exhausting from an aqueous treatment bath onto the solid material being treated. A particular further object, which is in effect a corollary of the last mentioned object, is to provide a method for rendering paper oil-repellent which can be applied to the paper pulp prior to sheet formation, whereby a more uniform, more effective and more economical impregnation may be achieved. Another corollary object is to provide as a novel article oil-repellent paper in which the oil-repellent factor is distributed essentially uniformly throughout the volume of the paper instead of being restricted to the surface or superficial layers thereof. Other objects and achievements of this invention will become apparent as the description proceeds.

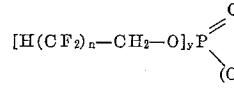
Oil-repellency in articles such as wearing apparel, cardboard boxes, paper bags or wrapping paper is a relatively young and not fully developed art. The demand for such articles is perhaps old enough. The advantages of having for instance grease-repellent overalls for mechanics, wallpaper that does not stain easily, oil-repellent paper bags for bakery goods, or—on the contrary—containers which will keep the contents safe

against contamination with greasy soil from the outside, are so obvious as not to require much elaboration. Hitherto, however, the solution to this problem has not been entirely satisfactory from the economical viewpoint. Some of the oil-repellency agents hitherto used or suggested are complicated and costly chemicals. Others can be applied only from an organic solvent. Still others are relatively inefficient and require application of large quantities thereof with respect to the weight of the fiber or solid material being treated therewith.

In the copending application of Werner V Cohen, filed on the same date herewith, it is taught that highly effective oil-repellency effects can be produced on solid materials such as above indicated by applying to the same an aqueous solution of a polyfluoroalkyl phosphate of the group defined by the general formulas:


(I)

and


(II)

wherein m is an integer from 3 to 12, n is an integer from 6 to 12, y is a number of average value from 1.0 to 2.5, and Z is a member of the group consisting of hydrogen and water-solubilizing cationic ions. The treated material is then dried, whereby to form in intimate contact therewith an evenly distributed deposit of said polyfluoroalkyl phosphate.

As examples of water-solubilizing cations in the definition of Z above, are mentioned in said copending application the alkali-metals (Na, K, Li), ammonium, diethanolammonium, triethanolammonium, morpholinium, and the like.

Compounds falling within the above general formulas are disclosed in U.S.P. 2,597,702 and 2,559,749, which assign to them the special property of being excellent dispersing agents. But their quality as oil-repellency agents has apparently not been recognized heretofore.

According to said application, however, it has been found that the above defined polyfluoroalkyl phosphates not only possess the desirable quality of imparting oil-repellency to solid bodies, but some of them are highly potent in this respect. This is particularly true of compounds of the above formulas wherein y is 2. And inasmuch as the synthesis of these phosphates naturally results in a mixture of phosphates of different degrees of esterification, it is taught in said application that mixtures of bis- and mono-polyfluoroalkyl phosphates in which the bis compounds predominate constitute the most desirable agents for practical use. Expressed in different words, they are mixtures of compounds falling within one or the other of the above formulas and wherein y has an average value from 1.0 to 2.5 with a preferred range of 1.5 to 2.0.

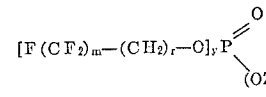
Furthermore, the mixtures can be practicably separated, and where the intended use justifies the added cost of separation, the compounds wherein y equals 2 constitute the preferred agents.

The above compounds possess also other valuable properties for the purpose intended. For instance, their water-solubility adapts them for application from a purely aqueous bath or, if desired, from an aqueous bath containing acetone, alcohol, or any other water-miscible, volatile adjuvant.

The compounds defined have also the quality of versatility, being applicable to a wide variety of textile fibers, including cotton, viscose, cellulose acetate, wool, silk, nylon, acrylic fiber and polyester fiber. They are also

applicable to leather, paper, wood and unglazed earthenware.

Now, according to my present invention, I have firstly augmented the list of phosphates available for producing oil-repellency, by the discovery that polyfluoroalkyl compounds wherein the perfluoroalkyl radical is separated from the P-atom by more than one CH_2 group are equally potent and effective for the above purpose. This is rather surprising when it is considered that in the analogous case of water-repellency agents wherein stearamidomethyl pyridinium chloride was at one time the most popular practical agent on the market for said purpose, it was learned that analogous compounds in which the stearamido radical was separated from the nitrogen atom of the pyridinium radical by a link of 2 or more CH_2 groups (e.g. ethylene) were totally ineffective. Accordingly, the compounds which this invention adds to the teachings of said copending application of Werner V. Cohen are compounds of the general formula



(III)

wherein *m*, *y* and Z have the same significance as in Formulas I and II above, while *r* is an integer from 2 to 16. Many of these are novel compounds, and are claimed in the copending application of Neal O. Brace and myself, Ser. No. 158,128, filed December 8, 1961.

Secondly, I have found that the polyfluoroalkyl phosphates hereinabove discussed (including Formulas I, II and III) possess in themselves the quality of exhaustion from an aqueous bath onto textile fiber, leather or paper. This is a very valuable practical quality, and enables for instance the treatment of paper stock in the pulp stage, prior to sheet formation, as will be more fully explained below.

Furthermore, according to a further feature of this invention, I have found that the exhausting qualities of any of the compounds hereinabove discussed for fibrous materials such as textile yarn or fabric, paper or leather can be immensely increased (or that the quality of exhaustibility can be essentially created where it did not exist before) by further treating said fibrous materials with an aqueous bath comprising a water-soluble linear polymer containing cationic N-atoms, said polymer being present in sufficient quantity to desposit thereof on said fibrous material a quantity corresponding to from 0.05 to 10% by weight. Said further treatment may be done prior to treatment with said polyfluoroalkyl phosphates, after such treatment, or simultaneously therewith, provided in the last case that very rapid contact of both agents with the fiber is assured.

To shed more light on this subject, treatments of textile fibers with aqueous baths generally proceed under two major categories: Padding and exhaustion.

In padding, a concentrated aqueous bath is generally employed. The fabric is impregnated with the treatment bath and then squeezed until there remains a definite amount of the aqueous liquors in proportion to the weight of the fiber. For instance, the fiber may be squeezed to a 100% pickup. In such event, the fiber picks up an equal weight of the treatment bath, and when the padded fiber is dried, there remains inside it (or on it) a percentage weight of the treating agent equal to its original concentration in the treatment bath.

If, on the other hand, the fiber does have affinity for the treating agent, as is more commonly the case in dyeing cellulosic fiber or wool with compounds which are true dyes (as distinguished from pigments), the fabric generally extracts the treating agent from the bath, until the latter becomes essentially exhausted. The quantity of agent absorbed by the fiber (provided a sufficient quantity of fiber has been used) is then essentially the entire quantity of agent that had been added to the bath. The quantity of agent, therefore, is independent of the quantity of water picked up by the fiber (with or without squeezing). In such cases, the quantity of agent initially added to the bath is calculated in advance "O.W.F.," that is, on the weight of the dry fiber.

It will be readily seen that exhaust treatments are more economical than padding treatments; they permit the use of dilute aqueous baths and are often adapted for use in fields where padding procedures are inapplicable.

A practical illustration on this point is the problem of rendering paper oil-repellent. Hitherto, this problem has invariably been solved by applying the chosen oil-repellency agent to the finished paper sheet by spraying, dipping or transfer from a moistened roll. Although treatment of the pulp prior to sheet formation has several obvious advantages (for instance, uniform distribution of the agent throughout the mass of the paper sheet as opposed to superficial saturation), it has not been practicably possible heretofore to apply the agent at this stage, because the paper pulp as prepared in ordinary paper-making machines is generally obtained in the form of a highly dilute aqueous suspension, of at most a few percent by weight. If the oil-repellency agent be now added in a quantity corresponding to a few percent by weight of the paper pulp, it is obvious that its concentration in the aqueous mass will be exceedingly low. So unless the fiber has the quality of "drawing" the agent out of solution, it is clear that the desired percentage deposit on the fiber cannot practicably be achieved.

According to my present invention, however, further treatment of the fiber with cationic polymers as above set forth endows it somehow with the quality of drawing polyfluoroalkyl oil-repellency compounds out of aqueous solution, and treatment of paper in the pulp stage becomes a highly practical matter.

As examples of commercially available cationic polymeric materials suitable for the aforesaid pretreatment may be mentioned:

(*a*) The polymers or copolymers of quaternary or acid salts of esters of a dialkylamino alcohol and acrylic acid or methacrylic acid.

Specific dialkylamino alcohols coming into consideration for this purpose include 2-(dimethylamino)ethanol, 2-(diethylamino)ethanol, 2-(dipropylamino)ethanol, 2-(N-methyl-N-cyclohexylamino)ethanol, 2-morpholinoethanol, 2-(diisobutylamino)ethanol, 3-(diethylamino)propanol and 4-(diethylamino)butanol. The esters are prepared according to the method set forth in U.S.P. 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.P. 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 which possess cationic N-atoms, for instance one prepared from urea, formaldehyde, tetraethylenepentamine, and hydrochloric acid as described by Suen, in "Polymer Processes," edited by Schildknecht (Interscience, 1956), page 343.

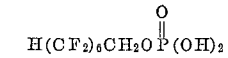
(*c*) Melamine-formaldehyde resins which possess cationic N-atoms, for instance the acid colloid prepared from formaldehyde, melamine, and hydrochloric acid as described by Suen, loc. cit., at pages 315, 344.

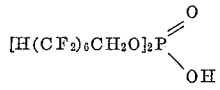
(*d*) The quaternized or acid salts of polymerized ethyleneimine, for instance those having a molecular weight of 30,000 to 40,000.

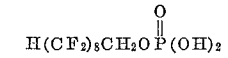
(*e*) Cationically modified nitrogen-containing starches, certain representatives of which occur in commerce.

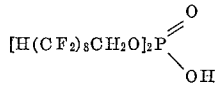
Returning now to the polyfluoroalkyl phosphates de-

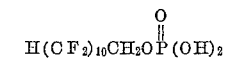
fined by the general Formulas I, II and III hereinabove, the following table indicates, by formula, a number of practical illustrations thereof in the free acid state:

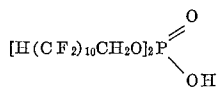
(1) 

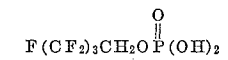
(2) 

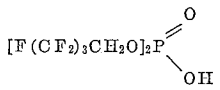
(3) 

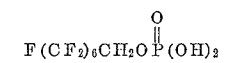
(4) 

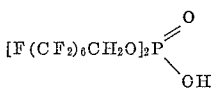
(5) 

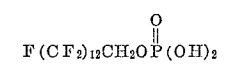
(6) 

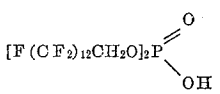
(7) 

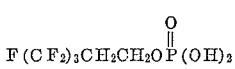
(8) 

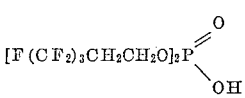
(9) 

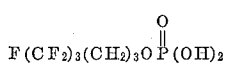
(10) 

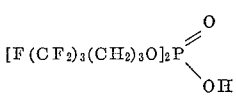
(11) 

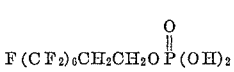
(12) 

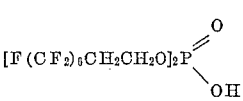
(13) 

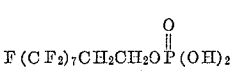
(14) 

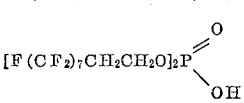
(15) 

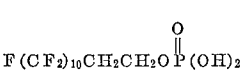
(16) 

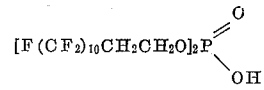
(17) 

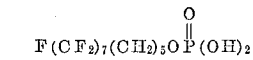
(18) 

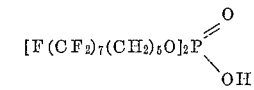
(19) 

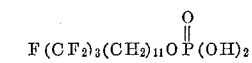
(20) 

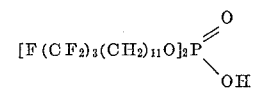
(21) 

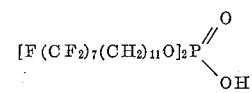
(22) 

(23) 

(24) 

(25) 

(26) 

(27) 

The nomenclature of these compounds is rather complicated, but is typified by the following samples:

Item 1: 1H,1H,7H-dodecafluoroheptyl phosphate
Item 2: bis(1H,1H,7H-dodecafluoroheptyl) phosphate
Item 9: 1H,1H,tridecafluoroheptyl phosphate
tIem 12: bis(1H,1H-pentacosafluorotridecyl) phosphate
Item 16: bis(1H,1H,2H,2H,3H,3H-heptafluorohexyl) phosphate
Item 26: bis(12 through 14-heptafluorotetradecyl) phosphate

They can also be named as typified by the following samples:

Item 17: Mono(2-perfluorohexyl-ethyl) ester of phosphoric acid
Item 27: bis(11-perfluoroheptyl-1-undecyl) ester of phosphoric acid

Some of the compounds in the above table which are not named in U.S.P. 2,559,749 and 2,597,702 may be prepared by methods analogous to those indicated in said patents. This is true of all the compounds of Formulas I and II above. Of the compounds of Formula III above, those which are new may be prepared by procedures analogous to the one set forth hereinbelow for a typical member of this group:

One mole of vinyl acetate and about 1.05 moles of 1-iodopentadecafluoroheptane are heated together at 80° to 90° C. in the presence of 2,2'-azodiisobutyronitrile for seven hours. The excess of 1-iodopentadecafluoroheptane is then distilled off under a vacuum, and 550 parts (by weight) of the residual liquid, which is essentially 1H,2H,2H-1-iodopentadecafluorononyl acetate, are reacted in 1200 parts of ethanol with 200 parts of zinc dust and 200 parts of concentrated HCl. The reaction mass is cooled and drowned in water, and the oily layer is drawn off.

The oily product is then treated with a 10% ethanol solution of potassium hydroxide, then drowned in water and extracted with chloroform. The extract is dried over anhydrous magnesium sulfate, and the chloroform is stripped off, leaving behind 2-perfluoroheptyl-ethanol, which is a colorless liquid, of B.P. 84° C. at 10 mm. pressure. It has a refractive index (n_D^{25}) of 1.3164. When this alcohol is reacted in molar proportions with $POCl_3$ in benzene in the presence of pyridine, it yields a dichlorophosphate which upon hydrolysis with pyridine and water yields the compound of Formula 19 above. If two moles of the alcohol are reacted with one mole of $POCl_3$ and hydrolyzed, the bis compound of Formula 20 is obtained.

Phosphates of polyfluoroalcohols having the structure $F(CF_2)_o(CH_2)_rOH$ where r is greater than 2 are prepared by similar procedure, from 1-iodopolyfluoroalkanes

and higher omega-alkenyl acetates such as 4-pentenyl acetate, 10-undecenyl acetate and the like.

Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight. The oil-repellency tests referred to in these examples are of two types, depending on whether the material tested has been prepared by surface treatment or it is paper made by treating the pulp. The former test is known in the art, and its essential features are as follows:

A. TESTING OF SURFACE-TREATED, SHEET MATERIAL

This test is based on the different penetrating properties of mineral oil ("Nujol") and n-heptane. Mixtures of these two hydrocarbon liquids, which are miscible in all proportions, show penetrating properties proportional to the amount of n-heptane in the mixture.

To measure oil repellency of a treated fabric, 8" x 8" swatches of the fabric are placed on a table and a drop of one of several test-mixtures of the above hydrocarbons is gently placed onto each fabric surface. After 1 minute, the fabrics are inspected to determine the mixture of highest heptane percentage which did not wet the fabric under the drop. According to said highest heptane percentage, the fabric is assigned a rating as set forth in the following table:

Oil-Repellency Rating	Percent by Volume Heptane	Percent by Volume "Nujol"
100(+)	60	40
100	50	50
90	40	60
80	30	70
70	20	80
50	0	100

(No resistance to "Nujol"; i.e. penetration within 3 minutes)

Usually, acceptable ratings are 70 and above, although beneficial effect to oil staining is sometimes obtained with ratings as low as 50.

B. TESTING OF PAPER MADE FROM TREATED PULP

This test is effected by cementing to the surface of a sheet of the paper to be tested and to a sheet of untreated control paper, four metal cylinders, one inch in diameter and one-half inch high. The sheets of paper are supported on glass so that the under surface can be observed. To each metal cylinder is then added about 1 ml. of oil, and the time until the first trace of oil penetration can be seen on the under surface on the paper is observed. A comparison of the average times for penetration by the oil of the treated and untreated papers indicates the order of magnitude of the oil repellency that has been attained.

Example 1

Four parts of dry bleached kraft pulp are agitated vigorously in a vessel containing 300 parts of water, and 4 parts of an aqueous 1% solution of polymerized 2-(diethylamino)ethyl methacrylate acetic acid salt are added (1% of the polymer on the dry weight of the pulp). Agitation is continued for five minutes (or more), and then 20 parts of an aqueous 1% solution of a mixture of mono- and bis(1H,1H,7H-dodecafluoroheptyl) phosphate, morpholine salt, having a *y*-value of about 1.5, are added. (This quantity calculates to 5% O.W.F.) After additional stirring for five minutes or more, the aqueous pulp is conveyed to the screen of a paper making machine, and the process of forming a paper sheet is proceeded with and finished in ordinary manner.

In an actual procedure as above described, carried out on laboratory-size paper making equipment, a sheet of paper was formed which under Test B above described, using peanut oil, required 5 minutes for the first observable penetration of the oil to the underside of the paper. In another sheet of paper made on the same equipment but without the addition of the aforementioned agents to the pulp, the penetration by peanut oil was essentially instantaneous.

In other experiments carried out according to the above procedure in laboratory-size equipment, the adjuvants and quantities were varied as in the examples below, with the results there indicated.

Example 2

Stock: Unbleached kraft pulp.
Cationic polymer: A commercial cationically modified starch. Quantity: 6 parts of a 1% solution (calculated to give 1.5% O.W.F.).
Polyfluoroalkyl phosphate: A mixture of mono- and bis-(1H,1H,9H-hexadecafluorononyl) phosphate, triethanolamine salt containing 48.6% of the mono phosphate ester. Quantity: 2 parts of a 1% solution (0.5% O.W.F.).
Oil penetration test:
Oil used—a light mineral oil.
Penetration time—30 minutes for the treated sample; almost instantaneous for the control (i.e. sample made from untreated pulp).

Example 3

Stock: Unbleached kraft pulp.
Cationic polymer: Polymer of dimethyl-sulfate-quaternized 2-diethylaminoethyl methacrylate. Quantity: 0.3% O.W.F.
Polyfluoroalkyl phosphate: Ammonium bis(1H,1H,9H-hexadecafluorononyl) phosphate. Quantity: 0.3% O.W.F.
Oil penetration test:
Oil used—peanut oil.
Penetration time—treated sample—30 minutes. Control—almost immediately.

Example 4

Stock: Bleached sulfite pulp beaten to a freeness of 480.
Cationic polymer: Same as in Example 3. Quantity: 0.2 part of a 1% solution (i.e. 0.05% O.W.F.).
Polyfluoroalkyl phosphate: A mixture of mono- and bis-(1H,1H-pentadecafluorooctyl) phosphate containing 77.3% of the mono phosphate ester; 0.3% O.W.F.
Oil penetration test:
Oil used—coconut oil.
Penetration time—treated sample—5 minutes. Control—within a few seconds.

Example 5

Stock: Unbleached kraft pulp.
Cationic polymer: Same as in Example 3; 0.5% O.W.F.
Polyfluoroalkyl phosphate: A mixture of mono- and bis-(1H,1H,2H,2H-heptafluoropentyl) phosphate containing 20% of the mono ester; 5% O.W.F.
Oil penetration test:
Oil used—peanut oil.
Penetration time—treated paper—30 minutes. Control—immediately.

Example 6

Stock: Unbleached kraft pulp.
Cationic polymer: Same as in Example 3; 0.5% O.W.F.
Polyfluoroalkyl phosphate: Ammonium salt of a mixture of mono- and bis(12 through 18 pentadecafluorooctadecyl) phosphate. Quantity: 1.6 parts of a 1% acetone solution (=0.4% O.W.F.).
Oil penetration test:
Oil used—peanut oil.
Penetration time—treated sample—30 minutes. Control—immediately.

Example 7

Stock: Unbleached kraft pulp.

Cationic polymer: A polyethyleneimine of M.W. between 30,000 and 40,000, quaternized with dimethyl sulfate. (A commercial product.) Quantity: 2.5% O.W.F.

Polyfluoroalkyl phosphate: Same as in Example 3; 0.4% O.W.F.

Oil penetration test:

Oil used—peanut oil.

Penetration time—treated paper—30 minutes. Control—immediately.

Example 8

[Omitting the cationic agent]

Four parts of dry bleached kraft pulp are agitated vigorously in a vessel containing 300 parts of water, and 8 parts of an aqueous 1% solution of ammonium bis-(2-perfluoroheptyl-1-ethyl) phosphate (2% O.W.F.) are added. After stirring for 5 minutes or more, the aqueous pulp is conveyed to the screen of a paper making machine, and the process of forming a paper sheet is proceeded with and finished in ordinary manner. When the resulting paper is subjected to Test B, using peanut oil, it takes about 30 minutes for the first observable penetration compared with essentially immediate penetration for an untreated control.

Example 9

100 parts of cotton fabric are dipped into an aqueous bath containing 1000 or more parts of water and 1 part by weight (i.e. 1% O.W.F.) of a polymer obtained from the dimethyl-sulfate quaternary salt of 2-diethylaminoethyl methacrylate. After agitating for 5 minutes or more, the fabric is removed, squeezed and reimmersed in a bath containing 1000 parts or more of water and 1 part (i.e. 1.0% O.W.F.) of ammonium bis(1H,1H,9H-hexadecafluorononyl) phosphate. After agitating in said bath for 5 minutes or more, the fabric is removed, squeezed and air-dried.

The above procedure is applicable likewise to other fabrics, such as wool, nylon, polyester fabric, acrylic fabric, to the corresponding materials in the form of yarn, as well as to leather.

In a series of actual experiments according to the above procedure followed by oil-repellency Test A hereinabove described, the following results were obtained.

Material:	Oil-repellency rating
Cotton (sateen)	70
Wool (worsted)	70
Nylon	70–80
Acrylic fiber	80
Polyester fiber	80
Cellulose triacetate fiber	80
Retanned suede leather	50

In another series of experiments following the same procedure as above except for omitting the first dip (i.e. eliminating the treatment with the cationic polymer), the oil-repellency rating obtained was 50 on all fabrics. When, however, the same set of experiments is repeated except for increasing the concentration of the polyfluoroalkyl phosphate to 2% O.W.F., ratings as high at 80 are obtained.

Example 10

Six pounds of unbleached kraft stock was beaten to a Canadian Standard freeness of 450 and the pulp transferred to the machine chest of an 8½-inch laboratory Fourdrinier paper machine. The concentration of fibers in the pulp in the chest was about 0.6%. A solution of 13.6 g. of ammonium bis(1H,1H,9H - hexadecafluorononyl) phosphate, $[H(CF_2)_8CH_2O]_2P(O)ONH_4$, in about ½ gallon of water was added over a period of about 15 minutes to the pulp in the chest with agitation. The paper machine was then started and run at about

11 feet per minute to produce a sheet of 50 pounds (24" x 36" x 500) basis weight. After a steady state condition of machine operation had been reached, a 1.5% solution of poly[2-(diethylmethylammonio)ethyl methacrylate methosulfate] was metered continuously to the machine headbox by a metering pump at a rate to give 0.5% of the polymeric material based on the dry weight of the pulp. This solution was added at a point where turbulence insured an even distribution of the polymer throughout the polyfluoroalkyl phosphate-treated pulp. The paper was produced by the usual operation of the Fourdrinier machine, except that the sheet was not calendered.

Paper so produced exhibited greater than 30 minutes' holdout to peanut oil. A sheet run under similar conditions but containing no additives was found to have essentially no holdout to peanut oil.

Example 11

1000 pounds of bleached kraft furnish was beaten to a freeness of 600. 0.25 oz. of a blue direct azo dye was added to tint or whiten the paper. The charge was dropped to the beater chest. The pulp consistency was about 3.5% and the pH 7.5. 15 lbs. of a 30% solution of polymerized dimethyl-sulfate-quaternized 2-diethylaminoethyl methacrylate were mixed with 50 gallons of water and the resultant solution was added over a 40-minute period to the pulp in the beater chest. The pulp pH was then 5.8. The stock was transferred to the beater chest through a jordan. 6 lbs. of ammonium bis(1H,1H,9H-hexadecafluorononyl) phosphate were dissolved in 6 lbs. of acetone, diluted to 50 gallons with water, and the solution was added to the pulp in the beater chest over a 20-minute period. The pulp was again jordaned, diluted to machine consistency in the fan pump and fed to a 108-inch Fourdrinier machine.

The paper-making process was then completed in the usual manner. When subjected to Test B, using a light mineral oil, this paper required about 30 minutes for the first observable penetration to the underside.

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

Thus, while in most of the above examples the agents have been added in the form of 1% aqueous solutions, solutions of other concentrations may, obviously, be employed. Moreover, in the case of the polyfluoroalkyl phosphates, preparation of the aqueous solution may be facilitated by first dissolving the 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 as aforenoted may be diluted with an aqueous amine or ammonia solution.

The quantities of materials added may vary from 0.05 to 3% O.W.F. for the cationic polymer and from 0.05 to 10% O.W.F. for the phosphate. The optimum amount will depend upon such factors as the nature of the pulp, the particular nitrogen-containing polymeric 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.

In the phosphates, the ammonium salts or amine-addition products are more effective than the free phosphoric acid, and the ωF-compounds (Formula I) are more potent than the ωH-compounds (Formula II). Moreover, with either kind, the bis-fluoroalkyl phosphates are immensely more effective than the mono compounds, and where mixtures are unavoidable, it is preferred to use such mixtures wherein the bis-fluoroalkyl compounds predominate (i.e. y has an average value greater than 1.5). Fully alkylated phosphates (i.e. $y=3$) are inoperable, but where a mixture is readily available, they constitute an inert, but harmless diluent to the active bis-

compounds. Therefore, mixtures of polyfluoroalkyl phosphates having a y-value greater than 2, say up to $y=2.5$, are tolerable. Altogether then, compounds wherein $y=2$ are preferred, but mixtures having an average y-value between 1.0 and 2.5 can be used.

The ωF-compounds (Formula I) may be generically referred to as (perfluoroalkyl-alkyl) phosphates. It follows from the aforegoing discussion that the most potent compounds for the purposes of this invention, and therefore the most desirable from the practical viewpoint, are the bis(perfluoroalkyl-alkyl)ammonium phosphates.

Incidentally, the ωF-compounds possess the added advantage that they also impart water-repellence to the treated articles. Thus, while production of oil-repellent solid articles has been stressed throughout the above discussion as being the primary object of this invention, the porcess and means herein described, when ωF polyfluoroalkyl phosphates are employed, produce both oil-repellency and water-repellency on the article treated therewith, be it textile fiber, paper or any other water-insoluble, solid material.

The order of treatment of the solid material with the two principal agents of this invention (i.e. polyfluoroalkyl phosphate and cationic resinous 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 implies that the cationic agent may be applied first and after a little time, to allow for complete exhaustion of said agent onto the material being treated (say, an aqueous paper pulp), the polyfluoroalkyl phosphate may be applied. Or the reverse sequence may be applied, with a suitable time interval to allow for maximum exhaustion of the phosphate compound onto the fiber. Or again, the materials may be fed simultaneously from 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 either agent with the pulp, thus minimizing the frequency and time of contact between the two agents when not in contact with the pulp.

The process of this invention may be applied to many types and grades of pulp. These include unbleached kraft pulp, unbleached sulfite pulp, bleached draft pulp, bleached sulfite pulp, alpha pulp or rag stock from cotton fibers, such pulps being used alone or in mutual admixture, or again in admixture with ground-wood pulps.

The advantages of my invention will now be readily apparent. Firstly, new fields of utility and a new degree of potency are opened up for the polyfluoroalkyl phosphates when used as oil-repellency agents. Thus, the polyfluoroalkyl phosphates can now be made to exhaust onto fibrous material from dilute baths, and when so applied they are about 10 times as powerful, insofar as oil-repellency effects are concerned, as some other present-day commercial polyfluoro compounds. Secondly, the last mentioned quality in turn opens up the commercial feasibility of producing oil-repellent paper by treating the paper stock in the aqueous pulp stage. From this in turn flows a new commercial product, namely paper that is permeated uniformly throughout its mass with the oil-repellent agent.

The novel paper thus produced itself has several important valuable qualities and advantages. Thus, while the paper may possess a high degree of oil-repellency, its appearance, feel, porosity and other physical qualities are not changed, and the paper may, furthermore, be given customary finishing treatments such as sizing, coating and the like, to improve the surface for printing or to provide water repellency. When the paper is creased it does not produce a break in the oil-repellent film, as is the case with surface-treated paper.

Furthermore, in certain processes of coating paper with waxy, or tarry coatings, as for instance in producing typewriter carbon paper, asphalt-laminated seed bags or water-proof containers in general, it has been found in the art advantageous to give the paper first an oil-repellency treatment, to prevent said coatings from penetrating deeply into the paper stock, with the result that both economy in the consumption of the coating material is achieved and the paper is prevented from becoming transparent. This remedy, however, often results in a tarry or waxy coating of weak adhesion; that is, it may readily flake off when the paper is flexed. Oil-repellent paper, however, which has been produced from treated pulp according to this invention has been found to be excellently adapted for further treatment with tarry or waxy coatings, giving consistently a superior product in respect to adhesion of the coating, opacity of the paper and economy of the process compared to other papers which have not been made oil-repellent at all or papers which have been made oil-repellent by surface treatment of the paper sheet.

I claim as my invention:

1. The process of rendering a water-insoluble solid material oil repellent which comprises treating said material with an aqueous bath containing a water-soluble polyfluoroalkyl phosphate in quantity sufficient to deposit thereof on said solid material from 0.05 to 3% by weight, and with an aqueous bath comprising a water-soluble linear polymer containing cationic N-atoms, said polymer being present in sufficient quantity to deposit thereof on said solid material a quantity corresponding to from 0.05 to 10% by weight, said treatments being effected in optional time relation to each other but under conditions whereby to minimize contact between said linear polymer and said phosphate except when either of them is in contact with the fiber, and removing excess moisture from the thus treated solid material.

2. A process as in claim 1, wherein said water-soluble linear polymer containing cationic nitrogen atoms is a member selected from the group consisting of cationic urea-formaldehyde resins, cationic melamine-formaldehyde resins, quaternary salts and acid salts of polymerized ethyleneimine, cationic starches and quaternary salts and acid salts of polymerized dialkylaminoalkyl acrylates and methacrylates.

3. A process as in claim 1, wherein said water-soluble linear polymer is the acetic acid salt of polymerized 2-diethylaminoethyl methacrylate.

4. A process as in claim 1, wherein said water-soluble linear polymer is the dimethyl-sulfate quaternization product of polymerized 2-diethylaminoethyl methacrylate.

5. A process of producing an oil-repellent paper, which comprises treating an aqueous paper pulp, in the stage prior to sheet formation, with an aqueous solution of a polyfluoroalkyl phosphate containing from 3 to 12 CF_2 groups per molecule whereby to exhaust onto said pulp from 0.05 to 3% of its weight of said polyfluoroalkyl compounds, further treating said aqueous pulp with an aqueous solution of a water-soluble linear polymer containing cationic N-atoms whereby to exhaust onto said pulp from 0.05 to 10% of its weight of said polymer, and forming paper sheet material from the pulp so treated.

6. The process of rendering a water-insoluble solid material oil repellent which comprises treating said material with an aqueous bath containing a water-soluble polyfluoroalkyl phosphate of the formula

wherein r is an integer from 2 to 16, m is an integer from 3 to 12, y is a number of average value from 1.0 to 2.5, and Z is a member of the group consisting of hydrogen and water-solubilizing cationic ions, and drying the material whereby to form in intimate contact therewith an

evenly distributed deposit of said polyfluoroalkyl phosphate.

7. A process as in claim 6, wherein the polyfluoroalkyl phosphate selected is a mixed product in which the dominant component is a compound whose *y*-value is 2.

8. As an article of manufacture, paper uniformly permeated throughout its body with a polyfluoroalkyl phosphate, said phosphate rendering said paper oil-repellent.

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