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COMPOSITIONS FOR AND METHODS OF FINISHING TEXTILE MATERIALS

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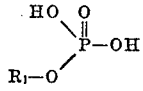
11 Claims. (Cl. 117—121)

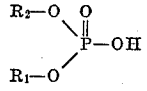
This invention relates to compositions for and methods of finishing textile materials, and more particularly to methods of making textile materials water-repellent by impregnating them with a composition containing organic esters of phosphoric acid and organic amido-compounds.

I have found that textile materials can be rendered water-repellent by impregnating them with aqueous solutions containing acid esters formed by esterifying phosphoric acid with high-molecular alcohols and phenols.

Acid esters of the above type which may advantageously be employed to make textiles water-repellent in accordance with my invention include mono-esters having the general structural formula



wherein R_1 is a hydrocarbon radical containing at least 6 carbon atoms selected from the group consisting of high-molecular alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals, and di-esters having the general structural formula



wherein R_1 is a hydrocarbon radical as defined above and R_2 is also a hydrocarbon radical containing at least 6 carbon atoms, selected from the group consisting of alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals. In the di-ester formula, R_1 and R_2 may be identical radicals or radicals of different structure; in other words, the di-esters can be simple or mixed di-esters. R_1 and R_2 may also carry substituents or may be interrupted by oxygen, sulfur or nitrogen atoms or by heteroatom groups derived therefrom.

Specific illustrative examples of phosphoric acid esters which can be used to impart water-repellent properties to textile materials in accordance with my invention are the following:

Phosphoric acid dihexyl ester
Phosphoric acid dioctyl ester
Phosphoric acid didodecyl ester
Phosphoric acid dioleyl ester
Phosphoric acid dimontanyl ester
Phosphoric acid dimethylcyclohexyl ester
Phosphoric acid dinaphthenyl ester
Phosphoric acid diabietyl ester
Phosphoric acid dibenzyl ester
Phosphoric acid dimenaphthyl ester

as well as di-alkylphenyl esters wherein the alkyl radicals contain from 3 to 18 carbon atoms, mixed esters corresponding to the above simple esters, mono-esters of these alcohols or phenols, and mixtures of any of these esters.

The above-described acid esters of phosphoric acid are

water-soluble or at least dispersible in water; the esters wherein R_1 and/or R_2 contain from 6 to 18 carbon atoms are readily water-soluble, while those wherein R_1 and/or R_2 contain more than 18 carbon atoms are relatively insoluble, but may be dispersed in water with the aid of low-molecular alcohols such as ethylalcohol and isopropylalcohol, ketones such as 2-butanone, ethers such as glycerin monoalkyl ethers, or etheralcohols such as tetrahydrofurfurylalcohol, acting as solubilizing agents.

In a few special cases it is possible to partially neutralize the particular acid phosphoric acid esters with volatile inorganic alkaline substances such as ammonia, or with organic alkaline compounds such as alkylamines, alkylpiperidines and the like.

In practicing my invention, I first immerse the textile material in an aqueous solution containing from 1 to 20 gm./liter of any one of the above mono- or di-esters of phosphoric acid. Thereafter, I pass the treated material through a wringer to remove excess amounts of solution, and then dry and heat the wet impregnated material at a temperature in excess of 90° C. to remove the water while leaving the phosphoric acid ester compound affixed to the textile fibers.

The water-repellent effect created on textiles by the above procedure can be further improved by treating the dried fabric with dilute solutions of salts of bivalent, trivalent or tetravalent metals, particularly of aluminum salts, or by simply rinsing the dried cloth in hard water.

I have further found that the process of rendering textile materials water-repellent, in accordance with my invention, as above set forth, can be materially improved by impregnating such textile materials with an aqueous solution containing not only the above-described acid esters of phosphoric acid, but also amido-compounds which contain at least one amino-group bonded to a CO—, CS—, C(NH)—, or CN-group, said amino group containing at least one replaceable hydrogen atom.

Amido-compounds of this type are, for example, the following: Urea, thiourea, alkylated urea, methylenediurea, methane, guanidine, alkylated guanidine, cyanamide, dicyandiamide, dicyandiamidine, as well as cyclic compounds such as methyldiaminotriazine, triaminotriazine (melamine), melam, melem, mellone, ammeline and the like.

In practicing the improved method of my invention, I first prepare an aqueous solution containing from 1 to 20 gm./liter of the acid phosphoric acid ester, and if desired also, from 1 to 20 gm./liter of the amino-compound. I then pass the textile material into this solution, subsequently run the material through a wringer to remove excess solution, and finally dry the wet fabric at a temperature above 90° C.

Both the treatment with the solutions of acid phosphoric acid esters alone and with the mixed solution of the phosphoric acid ester and the amido-compound can be applied to textile materials in the form of threads, strips, and fabrics. For example, it may be applied to cotton, regenerated cellulose, rayon, jute, linen, wool, silk, as well as 100%-synthetic fibers.

The following examples will further illustrate my invention and enable others skilled in the art to understand my invention more completely. However, it is understood that there is no intention on my part to limit the invention to these particular examples.

Example I

Cotton poplin fabric was wetted with a solution containing 3 gm./liter of the monocetyl ester of phosphoric acid. The wetted fabric was then removed from the solution and passed through a wringer where all of the solution was removed which was in excess of the amount required to bring the weight of the wet cloth up to 100%

above the weight of the dry cloth. Thereafter, the wet cloth was dried at 90° C. The finished dry cloth was found to be adequately water-repellent.

Example II

Unbleached cotton cloth was immersed in a solution containing 3 gm./liter of the monocetyl ester of phosphoric acid and 0.5 gm./liter of ammonia. The treated fabric was then removed from the solution, passed through a wringer to remove excess solution as in Example I, and dried at 100° C. Subsequently, the dry fabric was rinsed for one hour in hard water, and again dried. Unbleached cotton cloth treated in this manner was found to be satisfactorily water-repellent.

Example III

Cotton poplin cloth was passed into a solution containing 15 gm./liter of the monododecylester of phosphoric acid and 7.5 gm./liter of cyanamide. The treated fabric was then removed from the solution and passed through a wringer where all of the solution was removed in excess of the amount required to bring the weight of the wet cloth up to 100% above the weight of the dry cloth. Thereafter, the wet cloth was dried at 60° C. and then exposed to a temperature of 120° C. for 10 minutes. The treated cloth exhibits good water-repellent properties which can be improved by washing the treated cloth under mild conditions at 45° C. The water-repellent effect also survived repeated laundering of the treated fabric.

Example IV

Unbleached cotton cloth was inserted into a solution containing 2 gm./liter of a dialkyl ester of phosphoric acid, wherein the alkyl radicals contained from 16 to 18 carbon atoms, and 1 gm./liter of cyanamide. The wetted fabric was then removed from the solution and wrung out and dried as described in Example III. The result was a hydrophobic textile fabric which retained its water-repellent properties even after repeated laundering.

Example V

Cotton fabric was passed into a solution which contained 10 gm./liter of a monoalkylester of phosphoric acid, wherein the alkyl radical contained from 16 to 18 carbon atoms, 3 gm./liter of melanine and 50 gm./liter isopropanol. The wetted fabric was then removed from the solution and wrung out and dried as in Example III. The result was a hydrophobic fabric which retained its water-repellent properties even after repeated laundering.

Example VI

Nylon fabric was inserted into an aqueous dispersion containing 20 gm./liter of mono-dodecylphenylester of phosphoric acid, 0.5 gm./liter of ammonia, and 2 gm./liter of methylenediurea. Excess dispersion was removed, and the wet fabric was dried at 95° C. Subsequently, the dry fabric was rinsed for half an hour in a solution containing 5 gm./liter of aluminium formate, and again dried. Nylon fabric treated in this manner was found to exhibit good water-repellent properties.

Example VII

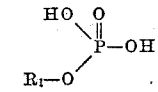
Wool cloth was passed at 60° C. into a dispersion containing 10 gm./liter of a mixture of mono- and di-octadecylester of phosphoric acid, 15 gm./liter of cyanamide, and 100 gm./liter of isopropanol. The treated cloth was then removed from the dispersion, passed through a wringer to remove excess solution and dried at 105° C. The finished dry cloth was found to be satisfactorily water-repellent. The water-repellent effect survived repeated laundering.

In certain cases it may be that the acid esters of phosphoric acid, used according to the invention, are not sufficiently water-soluble. Then it is possible to use them in aqueous dispersion. For improving the solubility it is useful to add small amounts of volatile inorganic or organic bases as described, which are removed during the drying process of the impregnated cloth. Under certain conditions it may be advantageous to use the acid esters in organic solvents such as halogen hydrocarbons or benzene.

While I have disclosed certain specific embodiments of my invention, I wish it to be understood that my invention is not limited to such embodiments, and that changes and modifications may be made therein without departing from the spirit of my invention or the scope of the following claims.

I claim:

1. The method of rendering textile materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid esters of phosphoric acid having the general structural formulas



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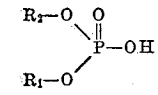
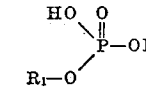


wherein R_1 and R_2 are hydrocarbon radicals containing at least 6 carbon atoms selected from the group consisting of high-molecular alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals, and drying said materials at a temperature above 90° C.

2. The method of rendering textile materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid esters of phosphoric acid having the general structural formulas



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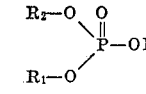
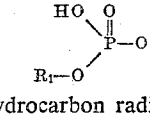


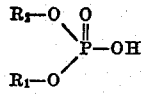
wherein R_1 and R_2 are hydrocarbon radicals containing at least 6 carbon atoms selected from the group consisting of high-molecular alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals, said solution also comprising at least one amido-compound containing at least one amino-group bonded to an atom group selected from the group consisting of CO—, CS—, C(NH)—, and CN-groups, said amino group also containing at least one replaceable hydrogen atom, and drying said materials at a temperature above 90° C.

3. The method of rendering textile materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid mono-esters of phosphoric acid having a structural formula



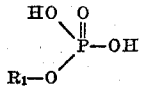
wherein R_1 is a hydrocarbon radical containing at least 6 carbon atoms selected from the group consisting of alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals, said solution also comprising at least one amido-compound containing at least one amino-group bonded to an atom group selected from the group consisting of CO—, CS—, C(NH)—, and CN-groups, said amino-group also containing at least one replaceable hydrogen atom, and drying said materials at a temperature above 90° C.

4. The method of rendering textile materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid di-esters of phosphoric acids having the general structural formula



wherein R_1 and R_2 are hydrocarbon radicals containing at least 6 carbon atoms selected from the group consisting of high-molecular alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals, and drying said materials at a temperature above 90° C.

5. The method of rendering textile fabric materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid mono- and di-esters of phosphoric acid having the general structural formula



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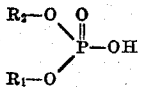


respectively, wherein R_1 and R_2 are hydrocarbon radicals selected from the group consisting of alkyl, cycloalkyl, alkylcycloalkyl, and alkylaryl radicals, said radicals containing at least 6 carbon atoms, and drying said materials at a temperature above 90° C.

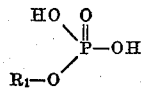
6. The method of rendering textile materials water-repellent as in claim 1, comprising the additional step of removing excess amounts of impregnating solutions from the impregnated materials prior to drying said materials.

7. The method of rendering textile materials water-repellent as in claim 1, comprising the additional step of partially neutralizing the ester with a compound selected from the group consisting of inorganic and organic alkaline compounds.

8. The method of rendering textile materials water-repellent as in claim 1, comprising the additional step of adding to the aqueous solution a solubilizing agent selected from the group consisting of water-soluble and water-dispersible organic solvents.

9. The method of rendering textile materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid mono- and

di-esters of phosphoric acid having the general structural formula



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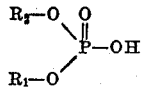
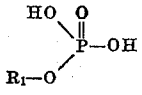


respectively, wherein R_1 and R_2 are hydrocarbon radicals selected from the group consisting of alkyl, cycloalkyl, alkylcycloalkyl, alkylaryl radicals, said hydrocarbon radicals containings at least 6 carbon atoms, drying said impregnated materials at a temperature above 90° C., and contacting said dried impregnated materials with an aqueous solution of salts of metals selected from the group consisting of bivalent, trivalent and tetravalent metals.

10. The method of rendering textile materials water-repellent which comprises impregnating said materials with an aqueous solution of at least one compound selected from the group consisting of acid mono- and di-esters of phosphoric acid having the general structural formula



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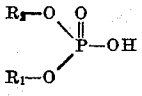

respectively, wherein R_1 and R_2 are hydrocarbon radicals selected from the group consisting of alkyl, cycloalkyl, alkylcycloalkyl, alkylaryl radicals, said hydrocarbon radicals containing at least 6 carbon atoms, drying said impregnated materials at a temperature above 90° C., and rinsing said dried impregnated materials in hard water.

11. As a product of manufacture, a textile material rendered water-repellent according to the process of claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,173,638	Rozenbroek et al.	Sept. 19, 1939
2,406,423	Woodstock	Aug. 27, 1946
2,482,755	Ford et al.	Sept. 27, 1949
2,519,388	Loukomsky et al.	Aug. 22, 1950
2,634,270	Nielsen	Apr. 7, 1953
2,656,372	Ernst et al.	Oct. 20, 1953
2,678,329	Gamrath	May 11, 1954
2,730,498	Fortess	Jan. 10, 1956
2,743,193	Donaldson	Apr. 24, 1956