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Description

[0001] The present invention relates to the use of phosphonates / phosphinates in aqueous formulations as carriers for improving the absorption of the compounds present in said formulations, into porous wettable materials, such as paper, wood, masonite and plaster.

[0002] More particularly, the present invention relates to the use of low molecular weight phosphonates and/or phosphinates, soluble in aqueous formulations in order to improve impregnation capacity as shown by the substantial absence of any blooming phenomena.

[0003] Even more particularly, the present invention relates to the use of phosphonates and/or phosphinates in the application of aqueous solutions onto ligneous materials.

[0004] Compositions comprising phosphonates and phosphinates for applications onto substrates of plant origin are known in the art. US patent 6,423,251 describes a composition for ligneous materials which may be in solid, aqueous or aqueous emulsion form, based on the condensation products between urea and boron oxyacids, and optionally containing carbonization catalytic agents (carbonization auxiliaries). Said catalytic agents may be acidic compounds such as boric, sulphuric or phosphoric acids, and salts thereof. Furthermore, other phosphorous compounds are indicated as being suitable for use as "carbonization auxiliaries" such as for example, phosphoric acid salts with nitrogen containing compounds and organo-phosphor compounds such as for example phosphoric esters. In the patent, it is affirmed that in order to have good penetration into wood, the composition must be applied hot and that it is necessary to operate under pressure or vacuum, or using glycol, polyol or ethylene oxide type surfactants. This patent solves the problem of the absorption of aqueous compositions based on urea - boron oxyacid condensation products into wood through the use of particular composition application procedures, as indicated above. US patent 6,114,340 describes fungicidal compositions, particularly usable for phytopathogenic fungi, including a fungicidal compound together with a second compound, capable of increasing the activity of the first compound, said second compound being selected from among the following: phosphinates, diphenylphosphinates, phosphonates and diphenylphosphonates. Such phosphorus compounds contain three aliphatic C_6-C_20 chains within the molecule, and hence possess high molecular weights. Furthermore, said phosphino-phosphonates are insoluble in water, but are emulsionable. In the examples, the use of such compositions for spraying wheat fields inoculated with a pathogenic fungus is described. Hence the patent does not refer to applications onto wood.

[0005] WO 9304585 describes a herbicidal composition which comprises a phosphate or phosphinate.

[0006] The need was felt for the availability of water soluble compounds for use as carriers in order to improve the absorption of aqueous compositions, preferably aqueous solutions, into porous wettable materials, such as paper, wood, masonite, plaster, preferably wood, so as to obtain the following combination of properties:

- the application of the aqueous formulation at room temperature;
- improved substrate impregnation capacity, thus avoiding the addition of solvents and surfactants, even when the dry percentage is high and there are additives, such as for example biocides, present;
- applicability using simple impregnation techniques, such as for example spraying or application by brushing;
- improved environmental impact.

[0007] A class of compounds overcoming the above mentioned drawbacks has now been surprisingly and unexpectedly found by the Applicant.

[0008] The use of water soluble neutral esters of acids of phosphorous of general formula (I) as carriers for the improved absorption of aqueous compositions, preferably aqueous solutions, into porous wettable materials such as paper, wood, masonite, plaster, preferably wood, constitutes a subject of the present invention:

\[
\begin{align*}
O \\
\| \\
R_1-P-O-R_3 \\
\| \\
R_2
\end{align*}
\]

wherein:

R_1 and R_3, being identical or different, are linear or branched C_1-C_4 alkyls, preferably C_1-C_3;
R₂ is linear or branched C₁-C₄ alkyl or oxyalkyl, preferably C₁-C₃; R₃ and R₂, when R₂ is oxyalkyl taken together may form a ring having 5 to 6 atoms, including 2 or 3 carbon atoms.

[0009] Preferably, R₂ is oxyalkyl.

[0010] The compounds of formula (I) which may be cited are diethylethylphosphonate, dimethylmethylphosphonate and cyclic phosphonates.

[0011] The quantities of the compounds of formula (I) in the aqueous formulations varies, as a percentage by weight over the total, from 0.1 % to 15%, preferably from 1% to 10%, even more preferably from 1% to 8%.

[0012] Application of the aqueous formulations of the invention is achieved through the impregnation of said substrates while operating within a temperature interval of from 5°C to 80°C, preferably at a temperature of less than 40°C.

[0013] Application may be performed using even simple impregnation methods, such as for example application by spraying, by roller or by brushing.

[0014] The Applicant has surprisingly and unexpectedly found that the aqueous formulations containing compounds of formula (I) allow the carrying of both ionic and non-ionic additives, and also polymeric additives, such as for example urea formaldehyde condensates, into porous substrates. Furthermore, the presence of solvents and surfactants is not required in the formulations.

[0015] The additives which may be carried using the compounds of formula (I) are for example the following:

A) flame retardants, such as for example ethylenediamine monophosphate, guanidine phosphate, triethylphosphate, guanyleurea phosphate, trihydroxyethyl isocyanurate phosphates, melamine pentaerythritol phosphate, urea phosphate, neutral phosphates of polyethylene oxides, diethyl-N,N-bis[2-hydroxyethyl]amino-methylphosphonate, neutral phosphates of oligomeric alcohols, dicyandiamide phosphate, condensation products between melamine, urea formaldehyde and phosphoric acid described in USP 3.832.316; mono- and di-ammonium phosphate; ammonium polyphosphates; mono- and di-melamine phosphate; melamine polyphosphate; glucose and phosphoric acid based condensates (USP 2.719.179) commercially known by the brand Budit®; glucose phosphoric acid and formaldehyde based condensates; dextrin and phosphoric acid based condensates; guanidine, formaldehyde phosphoric acid condensation products described in USP 4.219.456; the product of the condensation between formaldehyde, urea, dicyandiamide and phosphoric acid described in USP 3.887.511, the condensate may be obtained through the reaction of the above mentioned substances using the following amounts:

- from 1 to 10 moles of urea;
- from 1 to 11 moles of dicyandiamide;
- from 1.2 to 3 moles of formaldehyde for each mole of urea + dicyandiamide;
- from 0.5 to 2 moles of phosphoric acid for each mole of urea + dicyandiamide;

the condensation compound is prepared by adding a urea and dicyandiamide mixture to an aqueous solution of formaldehyde, at a temperature of between 60°C and 90°C, whilst keeping the temperature constant until the solution becomes clear; the temperature is then lowered to less than 50°C and phosphoric acid is added whilst stirring; the quantity of flame retardants, as a percentage by weight, varies from 1% to 35%, preferably from 5% to 25%, with the total percentage sum of the components present being equal to 100;

B) biocide additives, for example boron based salts, preferably selected from sodium borate, borax pentahydrate, borax decahydrate (Na₂B₄O₇·10H₂O), sodium octaborate tetrahydrate, boric acid or mixtures thereof. The quantities of biocide additives are generally from 0.5% to 23%, preferably from 1% to 10%, in reference to the total weight of the composition.

[0016] Other additives which may be carried using the compounds of formula (I) include the following: colorants, pigments, gelling agents, waxes, proteins, surfactants, silanes, siloxanes, cellulose, halogens, additives for improving the mechanical or aesthetic characteristics of porous items such as for example vinyl latexes.

[0017] The useable aqueous formulations are in the form of aqueous solutions or dispersions, preferably aqueous solutions. In the case of aqueous dispersions then preferably emulsions are used if it is possible to obtain them with the components of the formulation.

[0018] The preferred aqueous compositions of the present invention include:

- diethylethylphosphonate, dimethylmethylphosphonate as compounds of formula (I), with the quantities as a percentage by weight of the total being from 1% to 8%;

A) phosphates selected from guanidine phosphates, guanidine urea phosphate and urea phosphate; condensation products between formaldehyde, urea, dicyandiamide and phosphoric acid described in USP 3,887,511.
The condensate may be obtained through the reaction of the above indicated substances using the following amounts:

- from 1 to 10 moles of urea;
- from 1 to 11 moles of dicyandiamide;
- from 1.2 to 3 moles of formaldehyde for each mole of urea + dicyandiamide;
- from 0.5 to 2 moles of phosphoric acid for each mole of urea + dicyandiamide; the condensation compound is prepared by adding a urea and dicyandiamide mixture to an aqueous solution of formaldehyde, at a temperature of between 60°C and 90°C, whilst keeping the temperature constant until the solution becomes clear; the temperature is then lowered to less than 50°C and phosphoric acid is added whilst stirring; condensation products between melamine, urea formaldehyde and phosphoric acid described in USP 3,832,316; with the percentage by weight of component A) being from 5% to 25%;

B) biocides, preferably borax decahydrate (Na₂B₄O₇·10H₂O), boric acid or mixtures thereof; in quantities as percentages by weight from 1% to 10%;

[0019] The percentage by weight of the various components is in reference to the total weight of the composition; with the total sum of the components present being equal to 100%.

[0020] The percentage dry weight of the aqueous compositions according to the present invention is from 3% a 50%, preferably from 10% to 40%.

[0021] It has been surprisingly and unexpectedly found by the Applicant that using the above indicated quantities of the compounds of formula (I) it is possible to achieve the absorption into the substrate of aqueous formulations, even oligomeric or polymeric in nature, having a high dry content. For example, it is possible to mention to the condensation products belonging to a) such as neutral polyethylene oxide phosphates, neutral phosphates of oligomeric alcohols, condensation products between melamine, urea formaldehyde and phosphoric acid described in USP 3.832.316; or the condensation product between formaldehyde, urea, dicyandiamide and phosphoric acid described in USP 3.887.511.

The condensate may be obtained through the reaction of the above indicated substances using the following amounts:

- from 1 to 10 moles of urea;
- from 1 to 11 moles of dicyandiamide;
- from 1.2 to 3 moles of formaldehyde for each mole of urea + dicyandiamide;
- from 0.5 to 2 moles of phosphoric acid for each mole of urea + dicyandiamide;

the condensation compounds are prepared by adding a urea and dicyandiamide mixture to an aqueous solution of formaldehyde, at a temperature of between 60°C and 90°C, whilst keeping the temperature constant until the solution becomes clear; the temperature is then lowered to less than 50°C and phosphoric acid is added whilst stirring.

[0022] The aqueous formulations of the invention may also have high dry content, generally even greater than 40%, preferably even up to 50% by weight of the formulation.

[0023] The Applicant has found that aqueous formulations marketed for applications to the above mentioned porous supports leave unabsorbed residues, and that it is possible to avoid such drawbacks by the addition of the compounds of formula (I). This way the unabsorbed residues are made to completely penetrate the porous material without leaving any deposits. Hence, the presence of compounds of formula (I) in the aqueous compositions containing the additives to be carried, allows the improvement of absorption, even when the additive would only be partially absorbed or not absorbed into the porous substrate as it is.

[0024] Use of the compounds of formula (I) according to the present invention has particular importance for applications involved in the restoration of wooden materials, where the following requirements must also be taken into consideration:

- the treatment of the item must not alter its outward appearance;
- the composition must have good biocide effectiveness and good resistance to fire;
- the neutrality of the composition.

[0025] Application of the compositions onto porous materials is simple and may even be performed using conventional impregnation methods such as for example by immersion at atmospheric pressure or by using repeated cycles including depressurisation, immersion and pressurisation stages. Preferably the composition is applied onto the surface to be treated by using, as already mentioned, techniques such as application by brushing, by roller or by spraying, which are simpler and less costly than those indicated above.

[0026] Independently from the technique of application, following evaporation of the aqueous solvent, the ligneous material treated with the composition of the present invention shows essentially no blooming due to the surface crystal-
Using the compounds of formula (I) it is possible to apply overall quantities of additives varying from 200 g/m² to 2,000 g/m², preferably between 300 g/m² and 1,000 g/m² onto substrates, without detecting any blooming phenomena on the treated surface.

Depending on the porosity of the material to be treated and also using a simple application technique, such as that of brushing, absorption of the required quantity of composition is already obtained after just a few applications, even in the case of applications onto smooth, low porosity, unseasoned wood.

The following examples are given herein by way of non-limiting illustration of the present invention.

**EXAMPLES**

In the following examples, dry components have been calculated as % by weight of all components, excluding water, over the composition total.

**EXAMPLE 1**

Preparation of an aqueous solution containing boric acid, borax, diethyl ethylphosphonate and neutral condensation products between formaldehyde, urea, dicyandiamide and phosphoric acid.

Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 71 g of an aqueous solution containing 15% by weight of boric acid, 20% by weight of borax decahydrate;
- 71 ml of water;
- 143 g of a condensate in aqueous solution, containing urea dicyandiamide and phosphoric acid, prepared according to USP 3,887,511 (example 7), having the following characteristics:
  - the urea, dicyandiamide, formaldehyde, phosphoric acid molar ratio was 1.0/1.5/2.0/0.8,
  - dry content = 57%,
  - pH of approx. 7;
- 15 g of diethyl ethylphosphonate.

The dry content was 41 % by weight. After a few minutes stirring at 1500 r/min the composition was clear and colourless and remained stable for many days.

**EXAMPLE 1a**

Application of the composition of example 1 onto wood

A white pine board having dimensions 80 x 15.5 cm and a thickness of 2 cm was impregnated by brushing using 1,000 g/m² of composition on average.

The product was rapidly absorbed. Following application, it was noted that the appearance of the treated surface was indistinguishable from that of the untreated wood.

**EXAMPLE 2 (Comparison)**

Preparation of a composition like that of example 1 but omitting diethyl ethylphosphonate.

Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 71 g of an aqueous solution containing 15% by weight of boric acid, 20% by weight of borax decahydrate;
- 71 ml of water;
- 143 g of a condensate in aqueous solution, containing urea dicyandiamide and phosphoric acid, prepared according to USP 3,887,511 (example 7), having the following characteristics:
  - the urea, dicyandiamide, formaldehyde, phosphoric acid molar ratio was 1.0/1.5/2.0/0.8;
  - dry content = 57%;
  - pH of approx. 7.
EXAMPLE 2a (Comparison)

[0037] Application of the composition of comparative example 2 onto wood.
[0038] Example 1a was repeated but with the use of the composition of example 2. Following application of the composition and evaporation of the aqueous solvent, the presence of evident quantities of solid residues was observed on the surface of the wood.

EXAMPLE 3

[0039] Preparation of an aqueous solution as in example 1 but containing dimethyl methylphosphonate instead of diethyl ethylphosphonate.
[0040] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 71 g of an aqueous solution containing 15% by weight of 15% boric acid and 20% by weight of borax decahydrate;
- 71 ml of water;
- 100 g of a condensate in aqueous solution, containing urea dicyandiamide and phosphoric acid, prepared according to USP 3,887,511 (example 7), having the following characteristics:
  - the urea, dicyandiamide, formaldehyde, phosphoric acid molar ratio was 1.0/1.5/2.0/0.8;
  - dry content = 57%;
  - pH of approx. 7;
- 15 g of dimethyl methylphosphonate.

The dry content was 37.6% by weight. After a few minutes stirring at 1,500 r/min the composition was clear and colourless and remained stable for many days.

EXAMPLE 3a

[0041] Application of the composition of example 3 onto wood.
[0042] Example 1a was repeated but with the use of the composition of example 3.
[0043] The product was rapidly absorbed. After application, it was noted that the appearance of the treated surface was indistinguishable from that of the untreated wood.

EXAMPLE 4 (Comparison)

[0044] Preparation of an aqueous solution like that of example 3 but omitting dimethyl methylphosphonate.
[0045] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 71 g of an aqueous solution containing 15% by weight of 15% boric acid and 20% by weight of borax decahydrate;
- 71 ml of water;
- 100 g of a condensate in aqueous solution, containing urea dicyandiamide and phosphoric acid, prepared according to USP 3,887,511 (example 7), having the following characteristics:
  - the urea, dicyandiamide, formaldehyde, phosphoric acid molar ratio was 1.0/1.5/2.0/0.8;
  - dry content = 57%;
  - pH of approx. 7.

EXAMPLE 4a (Comparison)

[0046] Application of the composition of comparison example 4 onto wood.
[0047] Example 1a was repeated but with the use of the composition of example 4. Following application of the composition and evaporation of the aqueous solvent, the presence of evident quantities of solid residues was observed on the surface of the wood.

EXAMPLE 5

[0048] Preparation of an aqueous solution containing boric acid, borax and diethyl ethylphosphonate.
[0049] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 71 g of an aqueous solution containing 15% by weight of boric acid, 20% by weight of borax decahydrate;
- 15 g of diethyl ethylphosphonate;
- 114 g of water.

The dry content was 20% by weight. After a few minutes stirring at 1,500 r/min the composition was clear and colourless and remained stable for many days.

EXAMPLE 5a

[0050] A white pine board having dimensions 80 x 15.5 cm and a thickness of 2 cm was impregnated by brushing using 2.000 g/m² of composition on average.

[0051] The product was rapidly absorbed. The same results as for example 1a were obtained.

EXAMPLE 6 (Comparison)

[0052] Preparation of an aqueous solution like in example 5 but omitting diethyl ethylphosphonate. Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 71 g of an aqueous solution containing 15% by weight of boric acid and 20% by weight of borax decahydrate;
- 114 g of water.

After a few minutes stirring at 1,500 r/min the composition was clear and colourless.

EXAMPLE 6a (Comparison)

[0053] Example 5a was repeated but with the use of the composition of example 6. Following application of the composition and evaporation of the aqueous solvent, the presence of evident quantities of solid residues (borates) was observed on the surface of the wood.

EXAMPLE 7

[0054] Preparation of a composition containing boric acid, borax, urea phosphate and diethyl ethylphosphonate

[0055] Into a mixer with a nominal volume of 250 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 25 g of urea phosphate;
- 150 ml of water;
- 15 g of boric acid;
- 15 g of diethyl ethylphosphonate;

The dry content was 26.8% by weight. The pH was adjusted to neutrality using borax decahydrate. After a few minutes stirring at 1,500 r/min the composition was clear and colourless and remained stable for many days.

EXAMPLE 7a

[0056] Example 5a was repeated but with the use of the composition of example 7.

[0057] The product is rapidly absorbed. The same results as for example 1a were obtained.

EXAMPLE 8 (Comparison)

[0058] Preparation of an aqueous solution like in example 7 but omitting diethyl ethylphosphonate.

[0059] Into a mixer with a nominal volume of 250 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 25 g of urea phosphate;
- 150 ml of water;
- 15 g of boric acid.
The pH is adjusted to neutrality using borax decahydrate. After a few minutes stirring at 1,500 r/min the composition was clear and colourless.

EXAMPLE 8a (Comparison)

[0060] Example 5a was repeated but with the use of the composition of example 8. Following application of the composition and evaporation of the aqueous solvent, the presence of evident quantities of solid residues was observed on the surface of the wood.

EXAMPLE 9

[0061] Preparation of an aqueous solution containing diethyl ethylphosphonate and a glucose and phosphoric acid based condensate

[0062] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 113 g of water;
- 36 g of Budit® 380 (Budenheim, glucose and phosphoric acid based condensate having the following mean composition by weight: 68% H₃PO₄, 13% glucose, 19% water);
- 15 g of diethyl ethylphosphonate.

The dry content was 26.8% by weight. After a few minutes stirring at 1,500 r/min the composition was clear and colourless.

EXAMPLE 9a

[0063] Example 1a was repeated but with the use of the composition of example 9.

[0064] The product was rapidly absorbed. The same results as for example 1a were obtained.

EXAMPLE 10 (Comparison)

[0065] Preparation of an aqueous solution like in example 9 but omitting diethyl phosphonate.

[0066] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 113 g of water;
- 36 g of Budit® 380 (Budenheim, glucose and phosphoric acid based condensate having the following mean composition by weight: 68% H₃PO₄, 13% glucose, 19% water).

After a few minutes stirring at 1,500 r/min the composition was clear and colourless.

EXAMPLE 10a (Comparison)

[0067] Example 1a was repeated but with the use of the composition of comparison example 10.

[0068] Following application of the composition and evaporation of the aqueous solvent, significant quantities of sticky and hygroscopic solid residues were observed on the surface of the wood.

EXAMPLE 11

[0069] Preparation of an aqueous solution containing guanidine urea phosphate and diethyl ethylphosphonate

[0070] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 7.5 g of guanidine urea phosphate;
- 100 g of water;
- 5.0 g of diethyl ethylphosphonate.

The dry content is 11.2% by weight.

[0071] The pH is adjusted to neutrality using aqueous KOH. After a few minutes stirring at 1,500 r/min the composition was clear and colourless and remained stable for many days.
EXAMPLE 11a

[0072] A white pine board having dimensions 80 x 15.5 cm and a thickness of 2 cm was impregnated by brushing using 500 g/m² of composition on average.

[0073] The product was rapidly absorbed. After the application, it was noted that the appearance of the treated surface was indistinguishable from that of the untreated wood.

EXAMPLE 12 (Comparison)

[0074] Preparation of an aqueous solution like in example 11 but omitting diethylethylphosphonate into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 7.5 g of guanidine urea phosphate;
- 100 g of water.

The pH is adjusted to neutrality using aqueous KOH.

After a few minutes stirring at 1,500 r/min the composition was clear and colourless.

EXAMPLE 12a (Comparison)

[0075] Example 11a was repeated but with the use of the composition of comparison example 12. After the application of the composition and evaporation of the aqueous solvent, evident amounts of solid residues were observed on the surface of the wood.

EXAMPLE 13

[0076] Preparation of an aqueous solution containing diguanidine phosphate, boric acid, diethyl ethylphosphonate, alkyltrialkoxysilane and phosphoric acid.

[0077] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 60.9 g of diguanidine phosphate;
- 13.5 g of boric acid;
- 3.6 g of phosphoric acid (75%)

The composition was heated until all guanidine was fully solubilized. It was then cooled down and the following ingredients were introduced:

- 192 g of water
- 15 g of diethyl ethylphosphonate
- 15 g of octyl trietoxysilane

[0078] The dry content was 33.1 % by weight. After a few minutes stirring at 1,500 r/min the composition was clear and colourless and remained stable for many days.

EXAMPLE 13a

[0079] A white pine board having dimensions 80 x 15.5 cm and a thickness of 2 cm was impregnated by brushing using 500 g/m² of composition on average.

[0080] The product was rapidly absorbed. After the application, it was noted that the appearance of the treated surface was indistinguishable from that of the untreated wood.

EXAMPLE 14 (Comparison)

[0081] Preparation of an aqueous solution like in example 13 but omitting diethylethylphosphonate.

[0082] Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 60.9 g of diguanidine phosphate;
- 13.5 g of boric acid;
3.6 g of phosphoric acid (75%)

The composition was heated until all guanidine was fully solubilized. It was then cooled down and the following ingredients were introduced:

- 207 g of water
- 15 g of octyl triethoxysilane

The dry content was 28.1 % by weight.

EXAMPLE 14a (Comparison)

Example 13a was repeated but with the use of the composition of comparison example 14. After the application of the composition and evaporation of the aqueous solvent, evident amounts of solid residues were observed on the surface of the wood.

EXAMPLE 15

Preparation of an aqueous solution containing boric acid, borax, diethyl ethylphosphonate, halogenides and cellulose.

Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 148.8 g of an aqueous solution containing 15% by weight of boric acid, 20% by weight of borax decahydrate;
- 2.1 g of ammonium bromide;
- 68 g of water;
- 0.9 g of low molecular weight cellulose (viscosity Brookfield, 25°C, 15 mPa · s)

The composition is heated until cellulose is fully solubilized; then, after cooling down, 15 g of diethyl ethylphosphonate were introduced.

After a few minutes stirring at 1,500 r/min the composition was clear and colourless and remained stable for many days.

EXAMPLE 16 (Comparison)

Preparation of an aqueous solution like in example 15 but omitting diethylethylphosphonate.

Into a mixer with a nominal volume of 500 ml, fitted with a mechanical turbine stirrer, were introduced in order:

- 148.8 g of an aqueous solution containing 15% by weight of boric acid, 20% by weight of borax decahydrate;
- 2.1 g of ammonium bromide;
- 68 g of water;
- 0.9 g of low molecular weight cellulose (viscosity Brookfield, 25°C, 15 mPa · s)

After a few minutes stirring at 1,500 r/min, the composition was heated until cellulose was fully solubilized. The solution was clear and colourless and remained stable for many days.

EXAMPLE 16a (Comparison)

Example 15a was repeated but with the use of the composition of comparison example 14. After the application of the composition and evaporation of the aqueous solvent, evident amounts of solid residues were observed on the surface of the wood.

Claims

1. Use of water soluble neutral esters of acids of phosphorous of general formula (I) as carriers for improving the absorption of aqueous compositions, preferably aqueous solutions, into porous wettable materials such as paper, wood, masonite, plaster, preferably wood:
1. Use according to claim 1, wherein R₂ and R₃, being identical or different, are linear or branched C₁-C₄ alkyls, preferably C₁-C₃.

2. Use according to claim 1, wherein in formula (I) R₂ is preferably oxyalkyl.

3. Use according to claims 1-2, wherein the compounds of formula (I) are selected from diethylethylphosphonate, dimethylmethylphosphonate and cyclic phosphonates.

4. Use according to claims 1-3, wherein the quantities of the compounds of formula (I) vary, as a percentage by weight of the total, from 0.1 % to 15%, preferably from 1% to 10%, even more preferably from 1 % to 8%.

5. Use according to claims 1-4, wherein the additives carried by the compounds of formula (I) are the following:

A) flame retardants, selected from ethylenediamine monophosphate, guanidine phosphate, triethylphosphate, guanylurea phosphate, trihydroxyisocyanurate phosphates, melamine pentaerythritol phosphate, urea phosphate, neutral phosphates of polyethylene oxides, diethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphonate, neutral phosphates of oligomeric alcohols, dicyandiamide-phosphate, products of condensation reactions between melamine, urea formaldehyde and phosphoric acid; mono- and di-ammonium phosphate; ammonium polyphosphates; mono- and di-melamine phosphate; melamine polyphosphate; glucose and phosphoric acid based condensates; glucose phosphoric acid and formaldehyde based condensates; dextrin and phosphoric acid based condensates; guanidine, formaldehyde phosphoric acid condensation products; condensation products between formaldehyde, urea, dicyandiamide and phosphoric acid obtainable through the reaction of the above mentioned substances using the following amounts:

- from 1 to 10 moles of urea;
- from 1 to 11 moles of dicyandiamide;
- from 1.2 to 3 moles of formaldehyde for each mole of urea + dicyandiamide;
- from 0.5 to 2 moles of phosphoric acid for each mole of urea + dicyandiamide;

said condensation compound being prepared by adding a urea and dicyandiamide mixture to an aqueous solution of formaldehyde, at a temperature of between 60°C and 90°C, whilst keeping the temperature constant until the solution becomes clear; the temperature is then lowered to less than 50°C and phosphoric acid is added whilst stirring. The quantity of flame retardants, as a percentage by weight, varies from 1% to 35%, preferably from 5% to 25%, with the total percentage sum of the components present being equal to 100;

B) biocide additives, for example boron based salts, preferably selected from sodium borate, borax pentahydrate, borax decahydrate (Na₃B₂O₇· 10H₂O), sodium octaborate tetrahydrate, boric acid or mixtures thereof. The quantities of biocide additives vary from 0.5% to 23%, preferably from 1% to 10%, in reference to the total weight of the composition.

6. Use according to claims 1-5, wherein the compositions include other additives selected from the following: colorants, pigments, gelling agents, waxes, proteins, surfactants, silanes, siloxanes, cellulose, halogens, additives for improving the mechanical or aesthetic characteristics of porous items such as for example vinyl latexes.

7. Use according to claims 5-6, wherein the aqueous compositions include:
diethylethylphosphonate, dimethylmethylphosphonate as compounds of formula (I), with the quantities, as a percentage by weight of the total, being from 1% to 8%;

A) phosphates selected from guanidine phosphates, guanidine urea phosphate and urea phosphate; condensation products between formaldehyde, urea, dicyandiamide and phosphoric acid obtainable through the reaction of the above substances using the following quantities:

- from 1 to 10 moles of urea;
- from 1 to 11 moles of dicyandiamide;
- from 1.2 to 3 moles of formaldehyde for each mole of urea + dicyandiamide;
- from 0.5 to 2 moles of phosphoric acid for each mole of urea + dicyandiamide; the condensation compound is prepared by adding a urea and dicyandiamide mixture to an aqueous solution of formaldehyde, at a temperature of between 60°C and 90°C, whilst maintaining the temperature constant until the solution becomes clear;
- it is then cooled to a temperature of less than 50°C and phosphoric acid added whilst stirring;
- condensation products between melamine, urea formaldehyde and phosphoric acid; with the percentage by weight of component A) being from 5% to 25%.

B) biocides, preferably borax decahydrate (Na₂B₄O₇·10H₂O), boric acid or mixtures thereof; in quantities as percentages by weight of from 1% to 10%; the percentage weight of the various components is in reference to the total weight of the composition, with the total sum of the components present being equal to 100%.

8. Use according to claims 1-7, wherein the percentage by weight of the dry components of the aqueous compositions varies from 3% to 50%, preferably from 10% to 40%.

9. Use according to claims 1-8, wherein overall quantities of additives varying from 200 g/m² to 2,000 g/m², preferably between 300 g/m² and 1,000 g/m² are applied onto the substrate.

10. Formulations for the treatment of porous wettable materials such as paper, wood, masonite, plaster, constituted of an aqueous solution comprising the following components:

   a) a carrier selected from neutral esters of acids of phosphorous of general formula (I)

\[
\begin{align*}
O & \\
\| & \\
R_1-P-O-R_3 & \\
| & \\
R_2
\end{align*}
\]

(I)

wherein:
R₁ and R₃, being identical or different, are linear or branched C₁-C₄ alkyls, preferably C₁-C₃;
R₂ is linear or branched C₁-C₄ alkyl or oxyalkyl, preferably C₁-C₃;
R₃ and R₂, when R₂ is oxyalkyl taken together may form a ring having 5 to 6 atoms, including 2 or 3 carbon atoms;

b) at least one carried additive selected from the following categories: flame retardants and biocide additives.

11. Formulation according to claim 10, wherein the flame retardant is selected from one or more of the following compounds: ethylenediamine monophosphate; guanidine phosphate; triethylphosphate; guanylurea phosphate; trihydroxyethyl isocyanurate phosphates; melamine pentaerythritol phosphate; urea phosphate; neutral phosphates of polyethylene oxides; diethyl-N,N-bis(2-hydroxyethyl)amino-methylphosphonate; neutral phosphates of oligomeric alcohols; dicyandiamide phosphate; condensation products between melamine, urea formaldehyde and phosphoric
acid; mono- and di-ammonium phosphate; ammonium polyphosphates; mono- and di-melamine phosphate; melamine polyphosphate; glucose and phosphoric acid based condensates commercially known by the brand Budit®; glucose phosphoric acid and formaldehyde based condensates; dextrin and phosphoric acid based condensates; guanidine, formaldehyde phosphoric acid condensation products; the product of the condensation between formaldehyde, urea, dicyandiamide and phosphoric acid.

12. Formulation according to claim 10 wherein the biocide additive is selected from one or more of the following compounds: sodium borate, borax pentahydrate, borax decahydrate \((\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O})\), sodium octaborate tetrahydrate, boric acid

13. Formulation according to claim 12, wherein the biocide additives are present in an amount comprised between 0.5 and 23 % by weight, preferably between 1 and 10 % by weight.

14. Formulation according to claims 10-13, further comprising one or more of the following compounds: colorants, pigments, gelling agents, waxes, proteins, surfactants, silanes, siloxanes, cellulose, halogens, additives for improving the mechanical or aesthetic characteristics of porous items such as for example vinyl latexes.

Patentansprüche

1. Verwendung wasserlöslicher neutraler Ester von Phosphorsäuren der allgemeinen Formel (I) als Trägerstoffe zur Verbesserung der Absorption von wässrigen Zusammensetzungen, vorzugsweise wässrigen Lösungen, in poröse, benetzbare Materialien wie Papier, Holz, Holzfaserplatten, Putzmörtel, vorzugsweise Holz:

```
      O
     /\  
    /   
   R_1-P-O-R_3  (I)
    \  |
      R_2
```

worin:

- \(R_1\) und \(R_3\), wobei sie identisch oder unterschiedlich sind, lineare oder verzweigte \(C_1-C_4\)-Alkyle, vorzugsweise \(C_1-C_3\), sind;
- \(R_2\) ein lineares oder verzweigtes \(C_1-C_4\)-Alkyl oder -Oxyalkyl, vorzugsweise \(C_1-C_3\), ist;
- \(R_5\) und \(R_2\), wenn \(R_2\) ein Oxyalkyl ist, zusammen genommen einen Ring mit 5 bis 6 Atomen, 2 oder 3 Kohlenstoffatome umfassend bilden können.

2. Verwendung gemäß Anspruch 1, worin in Formel (I) \(R_2\) vorzugsweise Oxyalkyl ist.

3. Verwendung gemäß den Ansprüchen 1-2, worin die Verbindungen der Formel (I) ausgewählt sind aus Diethylthylphosphonat, Dimethylmethylphosphonat und cyclischen Phosphonaten.

4. Verwendung gemäß den Ansprüchen 1-3, worin die Mengen der Verbindungen der Formel (I) als Gewichtsprozentanteil der Gesamtmenge von 0,1 % bis 15 %, vorzugsweise von 1 % bis 10 % und noch bevorzugter von 1 % bis 8 % variieren.

5. Verwendung gemäß den Ansprüchen 1-4, worin die von den Verbindungen der Formel (I) mitgeführten Additive folgende sind:

A) Flammschutzmittel, ausgewählt aus Ethyldiaminmonophosphat, Guanidinphosphat, Triethylphosphat, Guanylnarnstoffphosphat, Trihydroxyethylisocyanuratphosphate, Melaminpentaerythritolphosphat, Harnstoffphosphat, neutrale Phosphate von Polyethylenoxiden, Diethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphonat, neutrale Phosphate oligomerer Alkohole, Dicyandiamidphosphat, Produkte von Kondensationsreaktionen
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zwischen Melamin, Harnstoffformaldehyd und Phosphorsäure; Mono- und Diammoniumphosphat; Ammoniumpolyphosphate; Mono- und Dimelaminphosphat, Melaminpolyphosphat; auf Glucose und Phosphorsäure basierende Kondensate; auf Glucose-Phosphorsäure und Formaldehyd basierende Kondensate; auf Dextrin und Phosphorsäure basierende Kondensate; Guanidin-, Formaldehyd-Phosphorsäure-Kondensationsprodukte; Kondensationsprodukte zwischen Formaldehyd, Harnstoff, Dicyandiamid und Phosphorsäure erhältlich aus der Reaktion der oben erwähnten Substanzen unter Verwendung der folgenden Mengen:

- von 1 bis 10 Mol Harnstoff;
- von 1 bis 11 Mol Dicyandiamid;
- von 1,2 bis 3 Mol Formaldehyd für jedes Mol Harnstoff + Dicyandiamid;
- von 0,5 bis 2 Mol Phosphorsäure für jedes Mol Harnstoff + Dicyandiamid;

wobei besagte Kondensationsverbindung hergestellt wird durch die Zugabe einer Harnstoff- und Dicyandiamid-Mischung zu einer wässrigen Formaldehydlösung bei einer Temperatur zwischen 60°C und 90°C, während die Temperatur so lange konstant gehalten wird, bis die Lösung klar wird; die Temperatur wird dann auf weniger als 50°C abgesenkt und Phosphorsäure wird unter Rühren hinzugegeben. Die Menge der Flammenschutzmittel als Gewichtsprozentsanteil variiert von 1 % bis 35 %, vorzugsweise von 5 % bis 25 %, wobei die Gesamtprozentsumme der vorhandenen Komponenten gleich 100 ist;

B) Biozid-Additive, zum Beispiel Salze auf Borbasis, vorzugsweise ausgewählt aus Natriumborat, Borax-Pentahydrat, Borax-Decahydrat (Na₂B₄O₇·10H₂O), Natriumoctaborat-Tetrahydrat, Borsäure oder Mischungen davon. Die Mengen der Biozid-Additive variieren von 0,5 % bis 23 %, vorzugsweise von 1 % bis 10 %, mit Bezug auf das Gesamtgewicht der Zusammensetzung.


7. Verwendung gemäß den Ansprüchen 5-6, worin die wässrigen Zusammensetzungen umfassen:

Diethylethylphosphonat, Dimethylmethylphosphonat als Verbindungen der Formel (I) in den als Gewichtsprozentsanteil des Gesamtgewichtes von 1 % bis 8 % betragenden Mengen;

A) aus Guanidinphosphaten, Guanidinharnstoffphosphat und Harnstoffphosphat ausgewählte Phosphate; Kondensationsprodukte zwischen Formaldehyd, Harnstoff, Dicyandiamid und Phosphorsäure, erhältlich aus einer Reaktion der obigen Substanzen unter Verwendung der folgenden Mengen:

- von 1 bis 10 Mol Harnstoff;
- von 1 bis 11 Mol Dicyandiamid;
- von 1,2 bis 3 Mol Formaldehyd für jedes Mol Harnstoff + Dicyandiamid;
- von 0,5 bis 2 Mol Phosphorsäure für jedes Mol Harnstoff + Dicyandiamid;

die Kondensationsverbindung wird hergestellt durch Zugabe einer Harnstoff- und Dicyandiamid-Mischung zu einer wässrigen Formaldehydlösung bei einer Temperatur zwischen 60°C und 90°C, wobei die Temperatur so lange konstant gehalten wird, bis die Lösung klar wird; dann wird auf eine Temperatur von weniger als 50°C abgekühlt und Phosphorsäure wird unter Rühren hinzugegeben; Kondensationsprodukte zwischen Melamin, Harnstoffformaldehyd und Phosphorsäure; wobei der Gewichtsprozentsanteil der Komponente A) von 5 % bis 25 % beträgt,

B) Biozide, vorzugsweise Borax-Decahydrat (Na₂B₄O₇·10H₂O), Borsäure oder Mischungen davon; in Mengen als Gewichtsprozentsanteile von 1 % bis 10 %; der Gewichtsprozentsanteil der verschiedenen Komponenten bezieht sich auf das Gesamtgewicht der Zusammensetzung, wobei die Gesamtsumme der vorhandenen Komponenten gleich 100 % ist.

8. Verwendung gemäß den Ansprüchen 1-7, worin der Gewichtsprozentsanteil der trockenen Komponenten der wässrigen Zusammensetzungen von 3 % bis 50 % variiert, vorzugsweise von 10 % bis 40 %.

9. Verwendung gemäß den Ansprüchen 1-8, worin von 200 g/m² bis 2.000 g/m², vorzugsweise zwischen 300 g/m² und 1.000 g/m² variierende Gesamt mengen von Additiven auf das Substrat aufgetragen werden.

10. Verwendung gemäß den Ansprüchen 1-9, worin die wässrigen Zusammensetzungen einen Gewichtsprozentsanteil von 3 % bis 50 % variiert, vorzugsweise von 10 % bis 40 %.

11. Verwendung gemäß den Ansprüchen 1-9, worin von 200 g/m² bis 2.000 g/m², vorzugsweise zwischen 300 g/m² und 1.000 g/m² variierende Gesamt mengen von Additiven auf das Substrat aufgetragen werden.
10. Zubereitungen für die Behandlung von porösen, benetzbar Materialien wie Papier, Holz, Holzfaserstoff, Putzmörtel bestehend aus einer wässrigen Lösung die folgenden Komponenten enthaltend:

a) einen Trägerstoff ausgewählt aus neutralen Estern von Phosphorsäuren der allgemeinen Formel (I)

\[
\text{O} \quad 
\begin{array}{c}
\text{R}_1 \cdot \text{P} \cdot \text{O} \cdot \text{R}_3 \\
\text{R}_2
\end{array}
\]

wirin:
R₁ und R₃, wobei sie identisch oder unterschiedlich sind, lineare oder verzweigte C₁-C₄-Alkyle, vorzugsweise C₁-C₃, sind;
R₂ ein lineares oder verzweigtes C₁-C₄-Alkyl oder -Oxyalkyl, vorzugsweise C₁-C₃, ist,
R₃ und R₂, wenn R₂ ein Oxyalkyl ist, zusammen genommen einen Ring mit 5 bis 6 Atomen, 2 oder 3 Kohlenstoffatome umfassend bilden können;

b) mindestens ein mitgeführt Additiv ausgewählt aus den folgenden Kategorien: Flammschutzmittel und Biozid-Additive.

11. Zubereitung gemäß Anspruch 10, worin das Flammschutzmittel ausgewählt ist aus einer oder mehrerer der folgenden Verbindungen:

- Ethylendiaminmonophosphat
- Guanidinphosphat
- Triethylphosphat
- Guanylharnstoffphosphat
- Trihydroxyethylisocyanuratphosphate
- Melaminpentaerythritolphosphat
- Harnstoffphosphat
- neutrale Phosphate von Polyethylenoxid
- Diethyl-N,N-bis(2-hydroxyethyl)aminomethylphosphonat
- neutrale Phosphate oligomerer Alkohole
- Dicyandiamidphosphat
- Kondensationsprodukte zwischen Melamin, Harnstoffformaldehyd und Phosphorsäure
- Mono- und Diammoniumphosphat
- Ammoniumpolyphosphate
- Mono- und Dimelaminphosphat, Melaminpolyphosphat
- im Handel unter der Marke Budit® bekannte auf Glucose und Phosphorsäure basierende Kondensate
- auf Glucose-Phosphorsäure und Formaldehyd basierende Kondensate
- auf Dextrin und Phosphorsäure basierende Kondensate
- Guanidin-, Formaldehyd-Phosphorsäure-Kondensationsprodukte
- das Kondensationsprodukt zwischen Formaldehyd, Harnstoff, Dicyandiamid und Phosphorsäure.

12. Zubereitung gemäß Anspruch 10, worin das Biozid-Additiv ausgewählt ist aus einer oder mehrerer der folgenden Verbindungen: Natriumborat, Borax-Pentahydrat, Borax-Decahydrat (Na₂B₄O₇·10H₂O), Natriumoctaborat-Tetrahydrat, Borsäure.

13. Zubereitung gemäß Anspruch 12, worin die Biozid-Additive in einer Menge zwischen 0,5 % und 23 % Gewichts-%, vorzugsweise zwischen 1 und 10 Gewichts-% vorhanden sind.


Reivendications

1. Utilisation d’esters neutres solubles dans l’eau d’acides du phosphore représentés par la formule générale (I) en tant que supports pour améliorer l’absorption de compositions aqueuses, de préférence, de solutions aqueuses, dans des matériaux mouillables poreux tels que le papier, le bois, la masonite, le plâtre, de préférence, le bois :
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R₁⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻ -= O

\[ \text{R}_1 \cdots \text{P} \cdots \text{O} \cdots \text{R}_3 \quad \text{(I)} \]

\[ \text{R}_2 \]

1. Utilisation selon la revendication 1, dans laquelle, dans la formule (I), R₂ représente, de préférence, oxyalkyle.

2. Utilisation selon la revendication 1, dans laquelle, dans la formule (I), R₂ représente, de préférence, oxyalkyle.

3. Utilisation selon l’une des revendications 1 et 2, dans laquelle les composés représentés par la formule (I) sont choisis parmi le diéthyléthylphosphonate, le diméthylméthylphosphonate et les phosphonates cycliques.

4. Utilisation selon l’une des revendications 1 à 3, dans laquelle les quantités des composés représentés par la formule (I) varient, exprimées en pourcentage en poids du total, de 0,1% à 15%, de préférence, de 1% à 10%, et de façon encore plus préférée, de 1% à 8%.

5. Utilisation selon l’une des revendications 1 à 4, dans laquelle les additifs supportés par les composés représentés par la formule (I) sont les suivants :

A) des retardateurs de flamme, choisis parmi le monophosphate d’éthylènediamine, le phosphate de guanidine, le triéthylphosphate, le phosphate de guanylurée, les phosphates de trihydroxyéthyl isocyanurate, le phosphate de mélamine pentaérythritol, le phosphate d’urée, les phosphates neutres d’oxydes de polyéthylène, le phosphonate de diéthyl-N,N-bis(2-hydroxyéthyl)aminométhyle, les phosphates neutres d’alcools oligomères, le dicyandiamide-phosphate, les produits de réactions de condensation entre la mélamine, l’urée-formaldéhyde et l’acide phosphorique ; le phosphate de mono- et di-ammonium ; les polyphosphates d’ammonium ; le phosphate de mono- et di-mélamine ; le polyphosphate de mélamine ; les condensats à base de glucose et d’acide phosphorique ; les condensats à base de glucose, d’acide phosphorique et de formaldéhyde ; les condensats à base de dextrine et d’acide phosphorique ; les produits de condensation de guanidine, de formaldéhyde, d’acide phosphorique ; les produits de condensation entre le formaldéhyde, l’urée, le dicyandiamide et l’acide phosphorique pouvant être obtenus par la réaction des substances mentionnées ci-dessus à l’aide des quantités suivantes :

- de 1 à 10 moles d’urée ;
- de 1 à 11 moles de dicyandiamide ;
- de 1,2 à 3 moles de formaldéhyde pour chaque mole d’urée + dicyandiamide ;
- de 0,5 à 2 moles d’acide phosphorique pour chaque mole d’urée + dicyandiamide ; ledit composé de condensation étant préparé par l’addition d’un mélange d’urée et de dicyandiamide à une solution aqueuse de formaldéhyde, à une température entre 60°C et 90°C, tout en maintenant la température constante jusqu’à ce que la solution devienne transparente ; la température est ensuite abaissée à moins de 50°C et de l’acide phosphorique est ajouté sous agitation, la quantité de retardateurs de flamme, exprimée en pourcentage en poids, variant de 1% à 35%, de préférence de 5% à 25%, la somme totale des pourcentages des composants présents étant égale à 100 ;

B) des additifs biocides, par exemple des sels à base de bore, de préférence choisis parmi le borate de sodium, le pentahydrate de borax, le décahydrate de borax (Na₃B₄O₇·10H₂O) l’octaborate-tétrahydratde de sodium, l’acide borique ou leurs mélanges, les quantités d’additifs biocides variant de 0,5% à 23%, de préférence, de 1% à 10%, en référence au poids total de la composition.

7. Utilisation selon l’une des revendications 5 et 6, dans laquelle les compositions aqueuses comprennent : du diéthyléthylphosphonate, du diméthylméthylphosphonate en tant que composés représentés par la formule (I), dont les quantités, exprimées en pourcentage en poids du total, sont de 1% à 8% ;

A) des phosphates choisis parmi les phosphates de guanidine, le phosphate de guanidine-urée et le phosphate d’urée ; les produits de condensation entre le formaldéhyde, l’urée, le dicyandiamide et l’acide phosphorique pouvant être obtenus par la réaction des substances mentionnées ci-dessus à l’aide des quantités suivantes :

- de 1 à 10 moles d’urée ;
- de 1 à 11 moles de dicyandiamide ;
- de 1,2 à 3 moles de formaldéhyde pour chaque mole d’urée + dicyandiamide ;
- de 0,5 à 2 moles d’acide phosphorique pour chaque mole d’urée + dicyandiamide ;

le composé de condensation étant préparé par l’addition d’un mélange d’urée et de dicyandiamide à une solution aqueuse de formaldéhyde, à une température entre 60°C et 90°C, tout en maintenant la température constante jusqu’à ce que la solution devienne transparente ;
étant ensuite refroidie à une température de moins de 50°C et de l’acide phosphorique étant ajouté sous agitation ;
des produits de condensation entre mélamine, urée formaldéhyde et acide phosphorique, le pourcentage en poids du composant A) étant de 5% à 25%,
B) des biocides, de préférence le décahydrate de borax (Na$_2$B$_4$O$_7$.10H$_2$O), l’acide borique ou leurs mélanges,
dans des quantités exprimées en pourcentages en poids de 1% à 10%, le pourcentage en poids des divers composants étant en référence au poids total de la composition, la somme totale des composants présents étant égale à 100%.

8. Utilisation selon l’une des revendications 1 à 7, dans laquelle le pourcentage en poids des composants secs des compositions aqueuses varie de 3% à 50%, de préférence, de 10% à 40%.

9. Utilisation selon l’une des revendications 1 à 8, dans laquelle des quantités globales d’additifs variant de 200 g/m$^2$ à 2 000 g/m$^2$, de préférence entre 300 g/m$^2$ et 1 000 g/m$^2$, sont appliquées sur le substrat.

10. Formulations pour le traitement de matériaux mouillables poreux, tels que le papier, le bois, la masonite, le plâtre, constituées d’une solution aqueuse comprenant les composants suivantes :

a) un support choisi parmi des esters neutres d’acides du phosphore représentés par la formule générale (I)

\[
\begin{align*}
&\text{O} \\
R_1 &-\text{P-O-R}_3 \\
&| \\
R_2 
\end{align*}
\]

dans laquelle :

- R$_1$ et R$_3$, étant identiques ou différents, représentent des alkyles en C$_1$-C$_4$, de préférence en C$_1$-C$_3$, linéaires ou ramifiés ;
- R$_2$ représente un alkylique oxyalkyle en C$_1$-C$_4$, de préférence en C$_1$-C$_3$, linéaire ou ramifié ;
- R$_3$ et R$_2$, si R$_2$ représente oxyalkyle, pris conjointement peuvent former un noyau ayant 5 à 6 atomes, comprenant 2 ou 3 atomes de carbone.
b) au moins un additif supporté choisi parmi les catégories suivantes : retardateurs de flamme et additifs biocides.

11. Formulation selon la revendication 10, dans laquelle le retardateur de flamme est choisi parmi un ou plusieurs des composés suivants : le monophosphate d'éthylènediamine ; le phosphate de guanidine ; le triéthylphosphate ; le phosphate de guanylurée ; les phosphates de trihydroxyethyl isocyanurate ; le phosphate de mélanime pentaérythritol ; le phosphate d'urée ; les phosphates neutres d'oxydes de polyéthylène ; le phosphonate de diéthyl-N,N-bis(2-hydroxyéthyl)aminométhyle, les phosphates neutres d'alcools oligomères ; le phosphate de dicyandiamide ; les produits de condensation entre la mélanime, l'urée formaldéhyde et l'acide phosphorique ; le phosphate de mono- et di-ammonium ; les polyphosphates d'ammonium ; le phosphate de mono- et di-mélanime ; le polyphosphate de mélanime ; les condensats à base de glucose et d'acide phosphorique connus dans le commerce par la marque Budif® ; les condensats à base de glucose, d'acide phosphorique et de formaldéhyde ; les condensats à base de dextrine et d'acide phosphorique ; les produits de condensation de guanidine, de formaldéhyde et d'acide phosphorique ; le produit de la condensation entre le formaldéhyde, l'urée, le dicyandiamide et l'acide phosphorique.

12. Formulation selon la revendication 10, dans laquelle l'additif biocide est choisi parmi un ou plusieurs des composés suivants : le borate de sodium, le pentahydrate de borax, le décahydrate de borax (Na₂B₄O₇·10H₂O), l'octaborate-tétrahydrate de sodium, l'acide borique

13. Formulation selon la revendication 12, dans laquelle les additifs biocides sont présents dans une quantité comprise entre 0,5% et 23% en poids, de préférence, entre 1% et 10% en poids.

14. Formulation selon les revendications 10-13, comprenant en outre un ou plusieurs des composés suivantes : colorants, pigments, agents gélifiants, cires, protéines, agents tensio-actifs, silanes, siloxanes, cellulose, halogènes, additifs pour l'amélioration des caractéristiques mécaniques ou esthétiques d'articles poreux, tels que, par exemple, des latex vinyliques.
REFERENCES CITED IN THE DESCRIPTION

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