ABSTRACT: Heterocyclic phosphorus compounds with a hetero-ring containing eight ring members, namely two carbon, two nitrogen and two oxygen atoms are provided. These compounds are manufactured by reacting 2 mols of at least one phosphonicarboxylic acid amide with at least 4 mols of anhydrous formaldehyde in the presence of an acid catalyst and in the absence of water. The phosphorus compounds are used for flameproofing and creaseproofing cellulose-containing textile material. They may be optionally used together with an aminoplast precondensate.
HETEROCYCLIC PHOSPHORUS COMPOUNDS AND PROCESS FOR THEIR MANUFACTURE

The subject of the invention are heterocyclic phosphorus compounds with a heteroring, containing 8 ring members, of formula

\[
\begin{align*}
R_1 &- \begin{array}{c}
\text{O} \\
\text{N}
\end{array} \\
\text{X} &- \begin{array}{c}
\text{O} \\
\text{N}
\end{array}
\end{align*}
\]

wherein \( R_1 \), \( R_2 \), \( R_1' \), and \( R_2' \) each denote an alkyl, halogenalkyl or alkenyl residue with at most four carbon atoms each and X and X' each represent a methyl residue or preferably a hydrogen atom.

Preferred compounds are symmetrical phosphorus compounds of formula

\[
\begin{align*}
R_1 &- \begin{array}{c}
\text{O} \\
\text{N}
\end{array} \\
\text{X} &- \begin{array}{c}
\text{O} \\
\text{N}
\end{array}
\end{align*}
\]

wherein \( R_1 \) and X have the indicated significance.

Compounds of particular interest are phosphonocarboxylic acid amides of formula

\[
\begin{align*}
R_1 &- \begin{array}{c}
\text{O} \\
\text{N}
\end{array} \\
\text{X} &- \begin{array}{c}
\text{O} \\
\text{N}
\end{array}
\end{align*}
\]

wherein \( R_4 \) represents a methyl or ethyl residue.

3-(Dimethylphosphino)-propionic acid amide is used to manufacture the particularly suitable compound of formula (1).

The reaction is advantageously carried out at elevated temperature, preferably 80° to 150° C. The usual agents which split off water, such as for example sulfuric acid, phosphoric acid or especially p-toluenesulfonic acid are used as acid catalysts required for this reaction. In certain cases it proves advantageous to carry out the reaction in the presence of a solvent which is inert towards the reagents, such as for example benzene, toluene, xylene or methanol. On the other hand the reaction can also be carried out in the melt, that is to say without solvents.

The phosphonocarboxylic acid amides of formula (5) used for the manufacture of the phosphorus compounds of formula (1) to (4) are in themselves known and can be manufactured according to known methods.

The reaction of the phosphonocarboxylic acid amides of formula (5) with formaldehyde probably takes place via two, and possibly three, stages by these phosphonocarboxylic acid amides first being dimethylolated at the amide nitrogen atom and two molecules of these dimethylol compounds thereafter forming an eight-membered heteroring, with water being split off.
In order to manufacture the phosphorus compounds of formulas (1) to (4), it is also possible to proceed by starting from 2 mols of the dimethylated compounds of formula (5), dissolving these in an inert organic solvent and effecting the ring closure between two molecules of the dimethylol compounds at a time at elevated temperature in the presence of an acid catalyst and with water being split off.

The invention also relates to a process for the flameproofing and creaseproofing of cellulose-containing fiber materials characterized in that an aqueous preparation which contains at least one phosphorus compound of one of the formulas (1) to (4) and optionally a curable aminoplast precondensate to these materials, thereafter drying the materials and subjecting them to a treatment at elevated temperature.

In particular, the phosphorus compounds of formula (1) are used for flameproofing and creaseproofing cellulose-containing textile material. Phosphorus compounds of formulas (2) and (3) are preferred, and the process for flameproofing and creaseproofing is of very particular interest if the compound of formula (4) is used.

The pH value of the aqueous preparations containing the compounds of formula (1) is advantageously less than 5, in particular less than 3. In order to achieve this, mineral acids such as sulfuric acid, nitric acid, orthophosphoric acid or hydrochloric acid are added to the preparations. Instead of the acids themselves, especially hydrochloric acid, it is also possible to use compounds from which the corresponding acids are easily, for example even without warming, formed in water by hydrolysis. As examples, there may here be mentioned phosphorus trichloride, phosphorus pentachloride, phosphorus oxychloride, thionyl chloride, sulfuryl chloride, cyanuric chloride, acetyl chloride and chloracetyl chloride. These compounds exclusively yield acid decomposition products, for example cyanuric acid and hydrochloric acid, on hydrolysis. Now it can be advantageous to use the acid mixtures corresponding to the hydrolysis products of one of the compounds just mentioned in place of one of the strong acids mentioned, that is to say for example to use, instead of hydrochloric acid or orthophosphoric acid alone, a mixture of hydrochloric acid and orthophosphoric acid which corresponds to phosphorus pentachloride, appropriately in a molecular ratio of 5:1.

The preparations for flameproofing and creaseproofing can also contain a latent acid catalyst for accelerating the cure of the aminoplast precondensate which is optionally present and for cross-linking the compounds of formula (1). As latent acid catalysts it is possible to use the catalysts which are known for curing aminoplasts on cellulose-containing material, for example ammonium chloride, ammonium dihydrogen orthophosphate, magnesium chloride, zinc nitrate and others.

Apart from the compounds of formula (1) and the additives which are required for adjusting the pH value, the preparations to be used according to the invention can contain yet further substances. An addition of aminoplast precondensates is advantageous for achieving a good wash-resistant flameproof finish, but is not necessary.

By aminoplast precondensates there are understood addition products of formaldehyde to nitrogen compounds which can be methylolated. 1,3,5-Amino-triazines such as N-substituted melamines, for example N-butylmelamine, N-trihalogenomethylmelamines, as well as ammeline, guanamines, for example benzoguanamine, acetoacuanime or also diguanamines may be mentioned. Further possible substances are: alkylureas or arylureas and alkylthioureas or arylthioureas, alkylenureas or alkylenediureas, for example ethyleneurea, propyleneurea, acetyleneurea, or especially 4,5-dihydroxyimidazolinedione-2 and derivatives thereof, for example the 4,5-dihydroxyimidazolinedione-2 which is substituted in the 4-position at the hydroxy group by the residue —CH₂CH₂CO—NH—CH₂OH. The methylol compounds of a urea, an ethyleneurea or of melamine are preferred. Particularly valuable products are in general provided by products which are as highly methylolated as possible. Suitable aminoplast precondensates are both predominantly monomolecular and also highly precondensed aminoplasts.

It is also possible to use the ethers of these aminoplast precondensates together with the compounds of formula (1). Advantageous compounds are for example the ethers of alkanols such as methanol, ethanol, n-propanol, isopropanol, n-butanol or pentanols. It is however appropriate for these aminoplast precondensates to be water soluble, for example pentamethylolmelamine-dimethyl-ether.

It can also be advantageous for the preparations to contain a copolymer, obtainable by polymerization in aqueous emulsion, of (a) 0.25 to 10 percent of an alkaline earth salt of an α,β-ethylenically unsaturated monocarboxylic acid, (b) 0.25 to 30 percent of a N-methylolamide or N-methylolamid-ether of an α,β-ethylenically unsaturated monocarboxylic or dicarboxylic acid and (c) 99.5 to 60 percent of at least one other copolymerizable compound. These copolymers and their manufacture are also known. The tear resistance and scorching resistance of the treated fiber material can be advantageously influenced by the copolymer.

As further additive which is of advantage in some cases, a plasticizing dressing should be mentioned, for example an aqueous polyethylene emulsion or ethylene copolymer emulsion.

It can also prove appropriate to add an emulsifier, for example a nonionic emulsifier, to the preparations.

The content of compound of formula (1) in the aqueous preparation is appropriately such that 10 to 28 percent is applied to the material to be treated. Here it is necessary to take into account that the commercially available textile materials of native or regenerated cellulose can take up between 50 and 120 percent of an aqueous preparation. As a rule the aqueous preparations contain 100 to 500 g/l, preferably 250 to 400 g/l, of phosphorus compound of formula (1). The amount of the additive required to adjust the hydrogen ion concentration to a value of less than 5 depends on the selected value itself and on the nature of the additive, though in any case it is not possible to go below a certain minimum. A certain excess above this minimum amount is generally to be recommended. Large excesses offer no advantages and can even prove harmful.

If a polymer of the indicated nature is further added to the preparation, then this is preferably done in small amounts, for example 1 to 10 percent relative to the amount of the compound of formula (1). The same is true of a possible plasticizer, where the appropriate amounts can again be 1 to
The preparation is now applied to the cellulose-containing fiber material, for example linen, cotton, acetate rayon, viscose rayon or fiber mixtures of such materials and others such as wool, polyamide or polyester fibers, and this can be carried out in a manner which is in itself known. Preferably, piece goods are used and these are impregnated on a padder of the usual construction which is fed with the preparation at room temperature.

The fiber material impregnated in this way must now be dried, and this is appropriately done at temperatures of up to 100°C. Thereafter it is subjected to a dry heat treatment at temperatures above 100°C, for example between 130° and 200°C, and preferably between 150° and 180°C, the duration of which can be the shorter, the higher the temperature. This duration of warming is for example 2 to 6 minutes at temperatures of 150° to 180°C.

Rinsing with an acid-binding agent, preferably with aqueous sodium carbonate solution, for example at 40°C to boiling temperature, and for 3 to 10 minutes, is advisable in the case of a strongly acid reaction medium.

As already indicated, it is possible to obtain flameproofing and creaseproofing finishes by the present process which largely remain preserved even after repeated washing or drycleaning and which do not cause any intolerable reduction in the mechanical textile properties of the treated material.

A particular advantage of the present process is the fact that the treated cellulose-containing fiber materials are simultaneously flameproof and creaseproof, even without the conjoint use of aminoplast precondensates. In particular, alongside the flameproof finish, the wet creaseproof properties of the treated fiber materials are significantly improved. A distinct improvement in the dry creasing angle can also be observed.

It is furthermore also possible to incorporate the phosphorus compounds of formula (1) into the spinning composition, for example of cellulose-2acetate, provided they exhibit adequate solubility in organic solvents such as acetone. The incorporation is simple, the spinning poses no difficulties, and fabrics manufactured therefrom are thus flameproofed in a simple manner.

The percentages and parts in the examples which follow are units by weight, unless otherwise stated. The relationship of parts by volume to parts by weight is as of milliliter to gram.

**EXAMPLE 1**

One hundred and eighty-one parts (1 mol) of 3-(dimethylphosphono)-propionic acid amide, 120 parts (4 mols) of paraformaldehyde, 700 ml. of methanol as the solvent and 0.9 parts of p-toluene sulfonic acid as the catalyst are introduced into a stirred flask equipped with a reflux condenser and internal thermometer. This mixture is heated to the boil and left to react until no further 3-(dimethylphosphono)-propionic acid amide can be detected by means of a thin layer chromatogram. The reaction mixture is filtered while still hot and the filtrate is concentrated in vacuo on a water bath. A slightly yellowish viscous oil remains as the reaction product and can be used without further purification. Yield: 205 parts = 91.9 percent of theory.

The reaction product corresponds to formula (4). For further purification, the reaction product is distilled with the same volume of water. Thereafter it is extracted with n-hexane for 72 hours, in the course of which mainly the compound of formula (5) is extracted. For yet further purification, the reaction product is distilled, with the main fraction being collected between 252°C and 260°C. The structure of formula (4) can be confirmed by means of mass spectrometry and infrared spectroscopy.

The compounds of examples 2 to 7 can also be purified and identified in an analogous manner.

**EXAMPLE 2**

One hundred and eighty-one parts (1 mol) of 3-(dimethylphosphono)-propionic acid amide, 123 parts (4 mols) CH₃O) of 97.5 percent strength paraformaldehyde and 0.9 part of p-toluene sulfonic acid monohydrate are warmed to 100°C. Internal temperature, while stirring, in a 500 parts by volume stirred flask which is equipped with a condenser and thermometer, and are kept at this temperature for 6 hours.

After this time, a sample of the reaction product shows, in a thin layer chromatogram, that practically all the 3-(dimethylphosphono)-propionic acid amide has reacted. The mixture is cooled to 60°C, 300 parts of methanol are added, and the whole cooled to 15°C with rapid stirring. Thereafter the free paraformaldehyde is filtered off and the methanol is removed in vacuo.

Two hundred and forty-six parts of a yellowish clear product of low viscosity, corresponding to formula (4), are obtained.

**EXAMPLE 3**

1,357.5 parts (7.5 mols) of 3-(dimethylphosphono)-propionic acid amide, 922.5 parts (30 mols) of 97.5 percent strength Paraformaldehyde and 6.75 parts of p-toluene sulfonic acid monohydrate in 1,500 parts of toluene are stirred for 3 hours at reflux temperature (100°C) in a 5,000 parts by volume stirred flask equipped with a condenser and thermometer. Thereafter the mixture is cooled to 60°C, the toluene is decanted, 1,500 parts of methanol are added, the whole is cooled to 15°C with rapid stirring, and free paraformaldehyde is filtered off. The methanol is then removed in vacuo.

One thousand eight hundred and thirty parts of a yellowish clear product of low viscosity corresponding to formula (4) are obtained.

**EXAMPLE 4**

One hundred and eighty-one parts (1 mol) of 3-(dimethylphosphono)-propionic acid amide are mixed with 96 parts (3 mols) of 97.5 percent strength paraformaldehyde and 0.6 parts of magnesium oxide in a stirred flask of 500 volumes capacity, equipped with a thermometer and reflux condenser, and kept at 100°C internal temperature for 30 minutes while stirring. After this time the content of bonded formaldehyde is 48.4 parts, corresponding to an 80 percent formation of the dimethylol compound. The total CH₃O found is 90 parts and the free CH₂O found is 41.6 parts.

Thereafter 6 parts of p-toluene sulfonic acid monohydrate are added and the mixture is treated at 100°C for a further 10 hours and then cooled. The total CH₂O found is still 51.5 parts and the free CH₂O found is still 30 parts. The 38% part of CH₂O can no longer be detected (as a result of ring closure), corresponding to a 64 percent formation of the product of formula (4).

The product is thereafter stirred with 250 parts of methanol and excess paraformaldehyde is filtered off. The methanol is finally removed in vacuo at 45°C. The reaction product of formula (4) is a yellow clear syrup which can be regarded as 100 percent strength active substance.

**EXAMPLE 5**

One hundred and thirty-nine parts (0.5 mol) of (bis-2-chloryl)-phosphonopropionic acid amide are mixed with 61.5 parts of 97.5 percent strength paraformaldehyde (2 mols), 0.5 parts of p-toluene sulfonic acid monohydrate and 200 parts of toluene in a stirred flask of 200 volumes capacity equipped with a thermometer and reflux condenser, and are treated for 5 hours at 100°C internal temperature. Thereafter the mixture is cooled, the toluene is separated off and the reaction product is stirred with 250 parts of methanol. Excess paraformaldehyde is filtered off and the methanol is removed in vacuo at 45°C. The residue is washed in 200 parts of water in a homogenizing apparatus and is adjusted to pH 6 with 30 parts of 2N sodium hydroxide solution. Thereafter the aqueous phase is separated off and the residue is again taken up in
methanol and clarified by filtration, after which the methanol is again removed in vacuo. A yellowish syrup containing 100 percent of active substance is obtained. This reaction product corresponds to the formula

\[ \text{Cl} - \text{CH}_2 - \text{CH}_2 \text{C} \]

\[ \text{Cl} - \text{CH}_2 - \text{CH}_2 \text{C}_\text{ON} \]

\[ \text{H}_2 \text{O} \]

\[ \text{CH}_2 \text{OH} \]

\[ \text{N} - \text{OC} \]

\[ \text{Cl} - \text{CH}_2 - \text{CH}_2 \text{C} \]

The reaction products of formulas

\[ \text{OH}_2 \]

\[ \text{PO} \]

\[ \text{CH}_2 \text{OH} \]

\[ \text{N} - \text{OC} \]

\[ \text{Cl} - \text{CH}_2 - \text{CH}_2 \text{C} \]

are obtained in an analogous manner.

**EXAMPLE 6**

116.6 parts (0.5 mol) of diallylphosphonopropionic acid amide, 61.5 parts (2 mol) of 97.5 percent strength paraformaldehyde, 0.2 part of hydroquinone, 0.5 part of p-toluensulfonic acid monohydrate and 200 parts of toluene are mixed in a stirred flask of 500 volumes capacity equipped with a thermometer and reflux condenser, and the mixture treated at 100°C internal temperature for 10 hours. Thereafter it is cooled, the toluene is separated off, and the reaction product is stirred with 250 parts of methanol. Excess formaldehyde is filtered off and the methanol removed in vacuo at 45°C. One hundred and forty parts of a yellowish clear syrup which can be regarded as 100 percent strength active substance are obtained. The product still contains 12 parts of total CH₂O. Furthermore, 20 parts of paraformaldehyde were recovered by filtration, so that 28 parts of CH₂O were no longer detectable. This corresponds to 93 percent formation of the product of formula

\[ \text{OH}_2 \]

\[ \text{PO} \]

\[ \text{CH}_2 \text{OH} \]

\[ \text{N} - \text{OC} \]

\[ \text{Cl} - \text{CH}_2 - \text{CH}_2 \text{C} \]

**EXAMPLE 7**

One hundred and thirty-three parts (0.5 mol) of 3-dibutylphosphonopropionic acid amide, 90.5 parts of 3-dimethylphosphonopropionic acid amide (0.5 mol), 123 parts (4 mol) of 97.5 percent strength parafomaldehyde and 1 part of p-toluensulfonic acid monohydrate are mixed in a stirred flask of 500 volumes capacity equipped with a thermometer and reflux condenser, and treated for 10 hours at 100°C internal temperature. Thereafter the mixture is cooled and the reaction product stirred with 250 parts of methanol, after which the excess parafomaldehyde is filtered off. Finally, the methanol is removed in vacuo at 45°C. Two hundred and seventy-five parts of a syrupy product which still contains 24 parts of total CH₂O and 5.6 parts of free CH₂O are obtained. The product is a mixture which predominantly corresponds to formula (13) but alongside this still contains compounds with free

\[ \text{OH}_2 \]

\[ \text{PO} \]

\[ \text{CH}_2 \text{OH} \]

\[ \text{N} - \text{OC} \]

\[ \text{Cl} - \text{CH}_2 - \text{CH}_2 \text{C} \]

**EXAMPLE 8**

A cotton fabric is padded with one of the aqueous liquors A to D of table I below. The liquor uptake is 80 percent. The fabric is dried at 70°C to 80°C, and thereafter cured for 4 ½ minutes at 160°C. The fabric is now post-washed at the boil for 5 minutes in a solution which per liter of water contains 2 g. of anhydrous sodium carbonate, rinsed and dried. A part of the fabric is boiled five times or 10 times for 30 minutes in a solution which contains 2 g. of sodium carbonate and 5 g. of soap per liter of water (=SNV-4 wash).

The individual pieces of fabric are then tested for their flameproof property, tear strength and crease resistance. The results of these tests are also summarized in table I.

<table>
<thead>
<tr>
<th>Constituents:</th>
<th>Untreated</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product according to Example 8, g./l.</td>
<td>280</td>
<td>330</td>
<td>2,2</td>
<td>2,2</td>
<td></td>
</tr>
<tr>
<td>NH₃ (g.), %</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>pH of the preparation</td>
<td>2,2</td>
<td>2,2</td>
<td>2,2</td>
<td>2,2</td>
<td></td>
</tr>
<tr>
<td>Flameproof property:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 1 SNV-4 wash:</td>
<td>Burns</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Burning time (sec.)</td>
<td>10</td>
<td>11</td>
<td>10</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Glowing time (sec.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Length of tear (cm.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Plus after 10 SNV-4 washes:</td>
<td>Burns</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Burning time (sec.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Glowing time (sec.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Length of tear (cm.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Crease resistance:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;Monsanto picture&quot; after single SNV-4 wash</td>
<td>1-2</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>&quot;Creating single&quot; dry (&lt;4%).</td>
<td>85</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Tear resistance:</td>
<td>100</td>
<td>85</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Warp, percent</td>
<td>100</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>Weft, percent</td>
<td>100</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>64</td>
</tr>
</tbody>
</table>

1 Vertical test according to DIN 53,005.
2 "Monsanto picture" according to AATCC S8A-1969T—rating 5: good freedom from creasing, rating 1: poor freedom from creasing.
3 Average of 20 measurements.
4 Breaking load according to SNV-98-461.
Thus a durable flameproofing and a good crease-free effect is simultaneously achieved with preparations A to D, and in particular without the addition of an aminoplastic percondensate. The mechanical textile properties of the fabrics are only insignificantly affected by the present finishes. The handle of the fabric finished in this way is also practically unchanged compared to the handle of the untreated fabric.

EXAMPLE 9

A cotton fabric is padded with one of the aqueous liquors E to I of Table II below. The liquor uptake is 80 percent. The fabric is dried at 80°C and curing is then carried out for 4½ minutes at 160°C. The fabric is now post-washed for 3 minutes at the boil in a solution which per liter of water contains 2 g. of anhydrous sodium carbonate, rinsed and dried.

The concentrations of preparations E to I are so chosen that 44.5 g/l of phosphorus is in each case contained in the bath.

The individual pieces of fabric are then tested for their flameproofing property in accordance with the vertical test DIN 53,906. The results of this test are also summarized in Table II.

<table>
<thead>
<tr>
<th>Constituents:</th>
<th>Percent phosphorus</th>
<th>Treated with preparation—</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product according to Ex-ample 1, g/l.</td>
<td>13.9</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product according to Ex-ample 2, g/l.</td>
<td>13.9</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product according to Ex-ample 4, g/l.</td>
<td>13.9</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product according to Ex-ample 6, g/l.</td>
<td>11.8</td>
<td>305</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product according to Ex-ample 7, g/l.</td>
<td>11.7</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Condensation product of 1 mol of p-tert.-octylyphenol and 9 mol of ethylene oxide, g/l.</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85% strength phosphoric acid, gl.</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH value of the preparation</td>
<td>2.2</td>
<td>2.0</td>
<td>1.0</td>
<td>2.1</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flameproof property:</td>
<td>Burns</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Burning time, sec</td>
<td>12.3</td>
<td>9.6</td>
<td>11.3</td>
<td>10.8</td>
<td>11.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLE 10

A product of formula (9) according to example 5, which is in the form of a highly viscous liquid, is incorporated into the spinning composition of cellulose-2½ acetate. The amount employed is 30 percent relative to the spinning composition. Films manufactured from the spinning composition show a pronounced flameproofing property.

An endless yarn is also manufactured from the spinning composition and is then further worked into a fabric in the form of a "stocking tube." This fabric also acquires good flameproofing in this way.

We claim:

1. A heterocyclic phosphorous compound of the formula

\[
\text{R}_1\text{H}_{\text{CH}}\text{CH} \xrightarrow{\text{O}} \text{CH}_2\text{O} \xrightarrow{\text{N}} \text{CH}_2\text{H} \xrightarrow{\text{O}} \text{R}_1' \xrightarrow{\text{O}} \text{R}_1''
\]

in which \( R_1 \) and \( R_1' \) each is alkyl, chloroalkyl or allyl with at most four carbon atoms each and \( X \) is methyl or hydrogen.

2. A phosphorous compound of the formula

\[
\text{R}_1\text{H}_{\text{CH}}\text{CH} \xrightarrow{\text{O}} \text{CH}_2\text{O} \xrightarrow{\text{N}} \text{CH}_2\text{H} \xrightarrow{\text{O}} \text{R}_1' \xrightarrow{\text{O}} \text{R}_1''
\]

in which \( R_1 \) is alkyl, chloroalkyl or allyl with at most four carbon atoms each and \( X \) is methyl or hydrogen.

5. A phosphorous compound according to claim 2 of the formula

\[
\text{CH}_2\text{H}_2\text{CH}_2\text{O} \xrightarrow{\text{CH}_2\text{H}_2\text{CH}_2\text{O}} \text{CH}_2\text{OH}_2\text{CH}_2\text{O} \xrightarrow{\text{CH}_2\text{OH}_2\text{CH}_2\text{O}} \text{OCH}_2\text{CH}_2\text{H}_2\text{CH}_2\text{O} \xrightarrow{\text{OCH}_2\text{CH}_2\text{H}_2\text{CH}_2\text{O}} \text{CH}_2\text{H}_2\text{CH}_2\text{O} \xrightarrow{\text{CH}_2\text{H}_2\text{CH}_2\text{O}} \text{OCH}_2\text{CH}_2\text{H}_2\text{CH}_2\text{O}
\]

6. A phosphorous compound according to claim 2 of the formula

\[
\text{Cl}_2\text{H}_2\text{CH}_2\text{O} \xrightarrow{\text{Cl}_2\text{H}_2\text{CH}_2\text{O}} \text{CH}_2\text{OH}_2\text{CH}_2\text{O} \xrightarrow{\text{CH}_2\text{OH}_2\text{CH}_2\text{O}} \text{OCH}_2\text{CH}_2\text{H}_2\text{CH}_2\text{O} \xrightarrow{\text{OCH}_2\text{CH}_2\text{H}_2\text{CH}_2\text{O}} \text{CH}_2\text{H}_2\text{CH}_2\text{O} \xrightarrow{\text{CH}_2\text{H}_2\text{CH}_2\text{O}} \text{OCH}_2\text{CH}_2\text{H}_2\text{CH}_2\text{O}
\]
8. A process for the manufacture of a phosphorus compound of the formula indicated in claim 1, which comprises reacting
a. 2 mols of at least one phosphonocarboxylic acid amide of the formula

in which R₆ and X have the significance indicated in claim 2, with
b. at least 4 mols of anhydrous formaldehyde in the presence of an acid catalyst used to split off water, in the absence of water, at 80° to 150° C.