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**[54] PHOSPHORUS COMPOUNDS CONTAINING
AMIDE GROUPS****[75] Inventors:** Walter Dürsch, Schneidhain,
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Frankfurt am Main, Germany**[22] Filed:** Oct. 29, 1973**[21] Appl. No.:** 410,779**[30] Foreign Application Priority Data**

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260/968; 260/970; 260/982**[51] Int. Cl.**..... C07f 9/24**[58] Field of Search** 260/928, 929, 970, 968,
260/982

[56]

References Cited**UNITED STATES PATENTS**

3,036,109	5/1962	Walsh	260/982
3,265,774	8/1966	Friedman	260/982 X
3,374,292	3/1968	Zahir	260/970 X

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[57]

ABSTRACT

Condensation products of dialkylphosphites or alkylphosphonites and phosphorus containing polyols are capable of rendering fibrous materials flame-proof or flame-retardant. The flame-proof finish is fast to washing and dry-cleaning and is effective on natural and synthetic fibrous material.

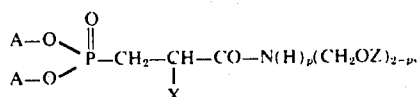
14 Claims, No Drawings

PHOSPHORUS COMPOUNDS CONTAINING AMIDE GROUPS

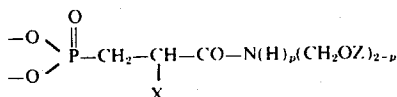
For the flameproofing finish of cellulose fibre materials in addition to a content of chemically bound phosphorus of at least about 0.5 % by weight a certain content of chemically bound nitrogen on the fibre material is required.

It is generally not important whether the nitrogen is contained in the same molecule as the phosphorus or admixed in the form of compounds abounding in nitrogen such as for example the methylol derivatives of urea or of amino-1,3,5-triazines, preferably of melamine. On the contrary, for flameproofing finishes of synthetic, especially totally synthetic fibre materials, a high content of halogen or phosphorus in the flameproofing agents is above all important, whereas the content of nitrogen is of secondary importance. Thereof, there is an interest in compounds having a large field of application, which have a low content of nitrogen and are, therefore, less expensive, but which are nevertheless able to react chemically with cellulose.

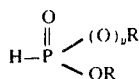
The preparation of compounds of the type



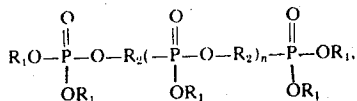
wherein A may represent for example lower alkyl radicals or alkylene radicals, the free valence of which is bound again to a group



X is hydrogen or CH₃, p is 0, 1 or 2 and Z is hydrogen or alkyl having 1 to 6 carbon atoms, and their use for rendering textile material flameproof is known (German Offenlegungsschrift No. 1,469,281). Since in these compounds per each phosphorus atom one nitrogen atom is contained, the content of nitrogen being, thus, relatively high, they are not completely satisfying for economical reasons. It has now been found that inexpensive flameproofing agents containing carbonamide groups can be prepared by reacting in a first step dialkyl phosphites or alkyl phosphinites of the general formula I



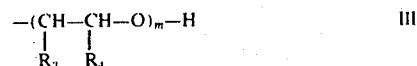
wherein y is zero or 1 and R represents identical or different hydrocarbon radicals with 1 to 4 carbon atoms, preferably alkyl groups with 1 to 4 carbon atoms or alkanyl groups with 3 or 4 atoms, with organic phosphorus compounds of the general formula II



wherein R₁ is halogenalkyl and/or hydroxyalkyl having 1 to 4 carbon atoms with the proviso that at least one R₁ represents halogenalkyl and at least one R₁ represents hydroxyalkyl, and n is an integer of zero to 4, subsequently, in a second step, further reacting the reaction product so-obtained with acrylamide or methacrylamide and, optionally, methylolizing the so-obtained product with 1 to 2 mols of formaldehyde per mole of (meth-)acrylamide used.

In the compounds of the general formula II the halogenalkyl groups preferably contain chlorine and/or bromine. Preferred are compounds which contain 2 to 3 carbon atoms and 1 or 2 halogen atoms, which are chlorine and/or bromine. The 2-chloroethyl-, 2,3-dichloropropyl- and the 2,3-dibromopropyl groups are especially preferred.

The hydroxyalkyl groups have the general formula III



wherein m is 1 to 10, preferably 1 to 4. R₃ and R₄ represent hydrogen atoms or an optionally chlorinated or brominated alkyl radical having 1 to 4 carbon atoms. R₃ and R₄ are preferably hydrogen, methyl or chloromethyl with the proviso that at least one of the radicals R₃ and R₄ is hydrogen.

R₂ represents independently from R₁ a radical of the general formula IV



wherein R₃, R₄ and m have the above meanings. The compounds of the formula II can be prepared according to German Offenlegungsschrift No. 2,036,595 (German Offenlegungsschrift No. 2,036,595 corresponds to U.S. patent application Ser. No. 163,098, filed July 15, 1971, by Werner Klose allowed May 8, 1973 and now U.S. Pat. No. 3,767,732.) by treating mixtures of trihalogenalkyl, phosphorus pentoxide and polyphosphoric acid, preferably in weight ratios of from 10:2:1 to 10:0:6 in the presence of 0.1 to 2 % by weight of phosphorus acid and 0.1 to 2 % by weight of disodium phosphate at temperatures of from 20° to 180°C, preferably 60° to 160°C, and subsequently reacting the so-obtained product with an epoxide of the general formula V



at temperatures of from 60° to 120°C.

During the oxalkylation process taking place in this way the epoxide reacts with free P—OH groups or is inserted into P—O—P-groups in a statistical distribution, expressed by the variable values of m, the average value of which depends on the amount of epoxide used and incorporated. In general, 30 to 100 % by weight of epoxide, calculated on the phosphate/phosphoric acid mixture, are reacted.

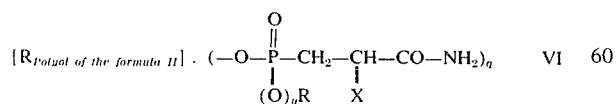
From the reaction product thus obtained described by the formula II, the phosphorus content of which is between about 10 and 15 % by weight and the content of hydroxy groups of which is between 2 and 7 % by weight, 0.9 to 2.1, preferably 1.0 to 1.5 equivalents—calculated on the free hydroxy groups present—are reacted with one mol of a phosphite or phosphonite of the formula I, subsequently with 1.0 to 1.1 mol of (meth)-acrylamide and optionally subsequently with 1 to 2, preferably 1.0 to 1.2 mol of formaldehyde.

As dialkyl-phosphites or alkylphosphonites of the formula I are suitable for example di-n-butyl-phosphite, diisobutylphosphite, di-n-propyl-phosphite, diallyl-phosphite, methyl-ethyl-phosphite, methane-phosphinous acid methyl ester, methane-phosphonous acid-isobutyl ester, ethane-phosphonous acid ethyl ester, n-butane-phosphonous acid methyl ester and, for economical reasons, especially diethyl or dimethyl phosphite.

The reaction between the polyols of the formula II and the phosphorus compounds of the formula I takes place in the way of a transesterification reaction, while splitting off at least 1 mol of the easily volatile alcohol ROH per mol of dialkyl phosphite or alkyl phosphinite. The reaction is carried out in a pH-range of about 4 to 11, preferably 5 to 9, preferably in the presence of 0.005 to 4.0, preferably 0.05 to 2 % by weight of alkaline catalysts, such as for example alkali metals or the compounds thereof such as methylates, ethylates, carbonates, hydrogencarbonates or tertiary phosphates, wherein the term "alkali metal" especially refers to the elements lithium, sodium and potassium.

The reaction temperatures range between about 0° and 160°C, preferably between 20° and 120°C and depend on the boiling point of the separated alcohol. Since the dialkyl phosphites or alkyl phosphinites have the tendency, especially in the heat, to form acid by-products, it is advisable to operate with temperatures as low as possible. To remove the alcohols from the reaction equilibrium even at temperatures below their boiling points, it is necessary to operate under reduced pressure, for example, at about 0.1 to 400 mm mercury, preferably 1 to 100 mm mercury. The course of the transesterification can be observed for example by gravimetric analysis after collecting the alcohols in a refrigerating trap cooled with solid carbon dioxide or, for example, by determining the refraction index.

The phosphites or phosphinites formed by this reaction from the polyols are further reacted, expediently in the same vessel, with acrylamide or methacrylamide, to give phosphoric or phosphonic acid esters containing carbonamido groups and corresponding approximately to the following formula VI

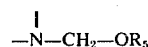


wherein q represents the number of the molecules of the compound of the formula I added to one molecule of the polyol and X represents either H or CH_3 and y is 0 or 1.

Since the polyols obtained according to the Examples, of the above cited German Offenlegungsschrift contain predominantly two hydroxy groups per molecule, these polyols have been termed in the following Examples as "diols", for reasons of simplicity, and as a consequence, also simplified, two carbonamide groups per mol have been assigned to them, whereas, strictly speaking, the polyols of the formula II are statistic mixtures of molecules of different sizes and different degrees of hydrolization.

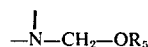
The most favorable reaction temperatures for the reaction to give the compounds VI are between 20° and 100°C, preferably 40° and 70°C. In this case the use of alkaline catalysts, as mentioned above, is necessary, for example of alkali alcoholates. Due to their good dosability, solutions of sodium methylate in methanol have proved to be very favorable. The concentrations of these alkaline catalysts are in the same range as indicated above.

The phosphoric or phosphonic acid esters of the formula VI thus obtained containing carbonamide groups can be used directly for the flameproofing of textiles, in combination with N-methylol derivatives of amino-1,3,5-triazines, ureas or cyclo-ureas, especially cycloalkylene ureas, imidazolidones(2), and hexahydrotriazones-(2) as well as compounds with at least 2 carbamate groups, wherein these compounds mentioned contain at least two groups of the formula



wherein R_5 is hydrogen or a hydrocarbon radical having 1 to 4 carbon atoms, and while using the usual acidic cross-linking catalysts as indicated below.

It is also possible to convert the reaction products first into the corresponding methylol compounds according to known processes with at least one mol of formaldehyde per mol of (meth)-acrylamide added, in known manner at 20°–100°C, preferably 30° to 70°C, and at pH 7 to 11, preferably 8 to 10. These methylol compounds can be used individually or, for an improved resistance to washing, also in combination with the above-mentioned N-methylol derivatives, which contain at least two groups of the formula



and in the presence of acidic cross-linking catalysts in known manner to obtain flameproof finishes.

Such N-methylol compounds for improving the resistance to washing can be for example: derivatives of amino-1,3,5-triazines, such as trimethylol-melamine, hexamethylol-melamine, trimethylol-melamine-dimethyl ether, hexamethylol-melamine-pentamethyl ether, trimethylol-melamine-tri-isobutyl ether, dimethylol-acetoguanamine, furthermore derivatives of urea, such as dimethylol-urea, dimethylol-urea dimethyl ether, dimethylol-urea-dibutyl ether, dimethylol-cycloethylene-urea, dimethylol-cyclo-propylene-urea, dimethylol-4-methoxy-5-dimethyl-propylene-urea, dimethylol-5-hydroxy-propylene-urea, 1,3-dimethylol-4,5-dihydroxy-imidazolidone-(2), 1,3-dimethylol-5-hydroxyethyl-hexahydrotriazinone-(2), dimethylol-urone and N,N'-dimethylol-dicarbamates

such as N,N'-dimethylol-alkylene-biscarbamates having 2 to 6 carbon atoms in the alkylene radical, for example N,N'-dimethylol-butylene-1,4-bis-carbamate.

Especially interesting compounds of this type are the melamine derivatives, such as above all hexamethylol-melamine-pentamethyl ether.

As cross-linking catalysts are generally used about 0.2 to 5 % by weight, preferably 0.4 to 3 % by weight, of organic or inorganic acids or the salts thereof, which set free acid by hydrolysis or by heat treatment, such as for example sulfuric acid, hydrochloric acid, phosphoric acid, oxalic acid, glycolic acid, monochloroacetic acid, trichloroacetic acid, maleic acid, tartaric acid, citric acid or salts with ammonia, amines or polyvalent metals with strong or medium-strong acids, such as ammonium sulfate, ammonium chloride, mono- and diammonium oxalate, ammonium nitrate, magnesium chloride, aluminum chloride, zinc chloride, zinc nitrate, zinc fluoroborate, ethanol-ammonium chloride, 2-amino-2-methyl-propanol hydrochloride.

The cross-linking catalysts may be added to the finishing baths individually or in admixture with one another. In general, these finishing baths usually contain 2 to 5 % by weight, preferably 3 to 4.5 % by weight of phosphorus, the carriers of which are the compounds of the formula VI, furthermore 5 to 10 % by weight, preferably 7 to 9 % by weight, of substances capable of being cross-linked, in addition to 0.2 to 5 % by weight of cross-linking catalysts as described above, as well as, if described, 5 to 25 % by weight, preferably 10 to 20 % by weight of high-polymer plastics, as mentioned further below, preferably in the form of plastics dispersions.

The reaction product of the process described above, i.e. compounds of the formula VI, are obtained as water-soluble products or products capable of being suspended in water; the corresponding methylol compounds are mostly obtained in the form of an aqueous solution, due to their preparation, and they can be used directly for preparing finishing baths for the flameproof finish of textiles, as they are described below.

Therefore, the invention further relates to a process for the flameproofing finish of textiles with the compounds according to the formula VI and the methylolization products or aqueous solutions thereof obtained by the reaction of polyols according to German Offenlegungsschrift No. 2,036,595 with phosphorus compounds of the formula I, by subsequent reaction with (meth-)acrylamide and, optionally, with formaldehyde.

In contradistinction to carbonamides containing phosphorus hitherto known the products of the invention have the advantage of a higher P:N-ratio above 2, whereas it is 2 in the case of the known carbonamides due to the molecular structure. Nevertheless, the flameproofing agents of the invention can be fixed on synthetic materials and on textiles containing cellulose, yielding an improved fastness to washing and excellent flameproof properties.

Textile fibre materials are on the one hand fibres or fabrics of natural or regenerated cellulose or the mixtures thereof. Surprisingly, however, excellent permanent flameproofing effects are obtained on the other hand even on totally synthetic fibre materials, especially on mixed fibre materials. As totally synthetic or mixed fibre material are especially suitable non-woven fabrics, for example needle felts for wall and floor coverings having very different compositions, such as for

example needle felts consisting of polyester/polyamide-6-fibres in a weight ratio of 50/50, polyamide fibres and viscose rayon 50/50, polyester fibres/viscose rayon 50/50, polyamide fibres/viscose rayon 75/25, polyester fibres/viscose rayon 75/25, polyamide/polyacrylonitrile and polyester fibres 50/25/25, polyamide/jute fibres 50/50 etc.

Non-woven fabrics are also fibre fleeces bonded by binding agents, as they are used for insulating purposes (for example as inserts) and for wet and dry filters. In this case either pure totally synthetic fibres of polyesters or polyamide-6 or -66 or mixtures of these fibres with one another or with fibres of native or regenerated cellulose such as for example viscose rayon are considered.

The flameproofing process according to the invention is carried out under the conditions of application usual in textile industry. The fabrics or needle felts are treated with the aqueous finishing baths on a two roller or three roller foulard (padding mangle), squeezed off and subjected to a drying and/or condensation process. The fleeces bonded by binding agents are either finished also on a foulard or reinforced by spraying or foaming with a mixture of known binders with the flameproofing finish of the invention.

For the flame-proof finish of cellulose fibre fabrics, the action of heat can preferably be effected in 2 steps. At first the fabrics are dried at a temperature above about 50°C, preferably at about 100° to 120°C, in order to remove the water, except for a residual value of about 4 to 8 % and subsequently the condensation is effected at about 140° to 180°C during about 7 to 3 minutes.

The needle felt material for wall-to-wall carpets can also be dried and condensed according to the 2-step process. Cross-linking preferably takes place in a one-step drying or condensation process at about 120° to about 180°C, mostly at 145°-160°C. On the average, the heat treatment takes about 10 to about 60, preferably 20 to 30 minutes. The action of heat takes place in drying cabinets, on stretching frames, hotflues or condensation frames. Further finishing agents such as textile softening agents, hydrophobing products, oleophobic agents or anti-microbial finishing products may be added to the finishing baths.

To get a good handle of cellulose fibre fabrics, to obtain a good dimensional stability, to improve the abrasion and the scuff-resistancy of the needle felt carpet material, high-polymer plastics preferably in the form of plastics dispersions may be added to the finishing baths, for example on the basis of polyvinyl acetate, polyvinyl-acetate with plasticisers, such as dibutylphthalate, mixed polymers of vinyl acetate with maleic acid dibutyl ester, mixed polymers of acrylic acid butyl ester with N-methylolacrylamide, mixed polymers of acrylic acid butyl ester, N-methylol-acrylamide and acrylic acid, mixed polymers of acrylic acid butyl ester, N-methylol-acrylamide and/or N-methylolmethacrylamide and acrylic acid, mixed polymers of acrylic acid butyl ester, methacrylic acid methyl ester and methylol-methacrylamide, mixed polymers of acrylic acid butyl ester, acrylonitrile, N-methylol-acrylamide and methacrylic acid, mixed polymers of acrylic acid butyl ester, acrylic acid ethyl ester, acrylonitrile, N-methylol-methacrylamide and acrylic acid, mixed polymers of acrylic acid butyl ester, styrene, acrylonitrile and N-methylol-methacrylamide, N-methylol-

methacrylamide and butane-diol-diacrylate, mixed polymers of acrylic acid methyl ester and acrylic acid butyl ester, mixed polymers of ethylacrylate, acrylonitrile and N-methylolacrylamide, mixed polymers of butyl-acrylate, vinyl acetate with N-methylolacrylamide, mixed polymers of butyl-acrylate, acrylonitrile and N-methylolacrylamide, mixed polymers of styrene, butylacrylate and acrylic acid, natural latex or synthetic latices from styrene with butadiene.

Needle felts having a flame-proof finish according to the present invention to which are applied, as already mentioned, besides the flame-proof component, plastics dispersions, show, in wear tests a considerably reduced tendency to soiling compared with needle felts which have been treated only with plastics dispersions to improve the dimensional stability.

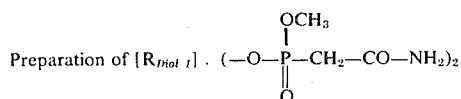
The needle felts finished according to the invention also show a reduced electrostatic charge as compared with the fleeces non-treated or treated only with plastics dispersions.

In contradistinction to the commercial flame-proofing agents on the basis of 3-(dimethyl-phosphono)-propionic acid amide the products of the present invention have great advantages especially with regard to the permanence of the finishes obtained on synthetic "non-wovens", for example needle felts having different fibre components.

In the following examples percentages and ratios are by weight, unless otherwise stated.

EXAMPLES FOR PREPARING NOVEL COMPOUNDS

EXAMPLE 1



1251.6 g (4.2 OH-equivalents) of a diol containing phosphoric acid ester groups obtained according to Example 2 of German Offenlegungsschrift No. 2,036,595 ($m=2$), in the following called diol, having a content of P_2O_5 of 24.8 % by weight, a content of chlorine of 15.5 % by weight and a hydroxyl number of 212 (mg KOH/g) and 440 g (4 mols) of freshly distilled dimethyl phosphite were weighed into a 2-liter four-necked flask. After carefully adding portionwise 4 g of sodium methylate, methanol was distilled off at a reduced pressure of 10 mm mercury at 40°–60°C. After 4 hours further 2 g of sodium methylate were added. Thus, after a total of 8 hours, 134 g (3.85 mols of methanol) of distillate were obtained in a refrigerating trap cooled with CO_2 /methanol, which also contained according to the gas chromatogram, in addition to 93 % of methanol, small amounts of dimethyl phosphite, a small amount of 2-chloroethanol and 1,2-dichloro-ethane. There remained 1565 g of polyolphosphite having a refraction index of $n_{22}=1.4664$.

At 50°–60°C this compound was converted within 50 minutes into the corresponding phosphonic acid ester carbonamide of the formula VI ($q=4$) by portionwise addition of 284 g (4 mols) of acrylamide and simultaneous addition of 75 g of a 33 % solution of sodium methylate in methanol to maintain a pH-value of about 7 to 9 (determined with moist "Merck-Universalindikatorpapier"=universal indicator paper).

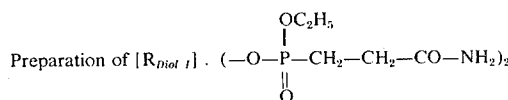
About 1927 g of a colorless oil were obtained which solidified after some time at room temperature and had a content of phosphorus of about 14 % and a content of nitrogen of about 3 %.

EXAMPLE 2

Preparation of the N-methylol compound of the carbonamide of Example 1

1927 Grams of the reaction product obtained according to Example 1 were mixed at room temperature with 340 g (4.2 mols) of an aqueous 37 % by weight formaldehyde solution. By portionwise addition of altogether 115–120 g of a 33 % sodium hydroxide solution, the pH-value was adjusted several times to 9–10 for 60 minutes. Every time, especially in the beginning, the temperature increased considerably as long as the pH-value was above 7 to 8. By cooling, the temperature was maintained at 35°–45°C. About 2385 g of a colorless solution were obtained which had a pH-value of 5 to 6, a content of phosphorus of 11.4 % and a content of nitrogen of 2.3 %.

EXAMPLE 3



312.9 Grams (1.05 OH- equivalent) of the diol of Example 1 containing phosphoric acid ester groups, 138 g (1 mol) of diethyl phosphite and 6.8 g of sodium ethylate were heated at a pressure of 50 mm mercury for about 11 hours to 60°–90°C. 47 Grams of volatile material were distilled off and condensed in a refrigerating trap. The refraction index of the residue was $n_{22}=1.4648$, the pH-value at 4–5 (measured with moist "Merck-Universalindikatorpapier").

At 50°–60°C, within 30 minutes, 71 g (1 mole) of acrylamide and simultaneously 19 g of a 33 % solution of sodium methylate in methanol were added in a way that a pH-value of 7 to 9 was always maintained. Stirring was then continued for further 30 minutes. Yield: 500 g, content of P about 14 %, content of N 2.8 %.

EXAMPLE 4

Preparation of the N-methylol compound of the carbonamide of Example 3

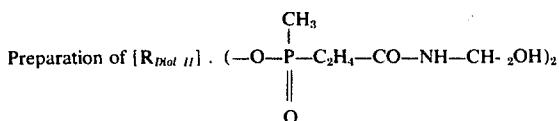
250 Grams of the reaction product of Example 3 were mixed with 42.5 g (0.525 mol) of an aqueous 37 % by weight formaldehyde solution and methylolized by addition of altogether 8 g of a 33 % sodium hydroxide solution at 35°–40°C and a pH-value of 7 to 20. Yield: 309 g, content of P 11.3 %, content of N 2.3 %.

EXAMPLE 5

The process was carried out as in Example 3 with the modification that instead of 6.8 g of sodium ethylate 10.6 g (1/10 mol) of anhydrous sodium carbonate were used as a catalyst. The properties of the reaction product corresponded to those of the product of the Example 3.

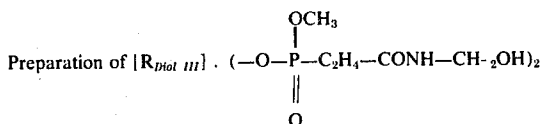
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EXAMPLE 6



154 Grams (0.5 OH-equivalent) of a polyol obtained in analogy to Example 2 of German Offenlegungsschrift No. 2,036,595, called in the following diol_{II}, having the analytical values C=30.1 %, H=5.4 %, Cl=17.0 %, P=11.9 % and OH-number=173 (mg KOH/g), 71.5 g (0.5 mol) of an about 95 % methanephosphonic acid isobutyl ester and 1 g of sodium methylate were heated at a pressure of 15 to 20 mm mercury for 11 hours. After this time 39 g of distillate consisting mostly of isobutanol, were weighed out in a refrigerating trap cooled with CO₂/methanol. Subsequently, at 50°–60°C, within 30 minutes, 35.5 g (0.5 mol) of acrylamide were introduced and simultaneously 7.5 g of a 33 % solution of sodium methylate in methanol were added dropwise in the way that the reaction mixture had a pH-value of 7 to 9. Stirring was continued for 10 minutes, and the whole was reacted at 30°–40°C with 44.5 g (0.55 mol) of an aqueous 37 % formaldehyde solution and 50 g of a 33 % sodium hydroxide solution at pH 8 to 9. Yield: 326 g, content of P 10.4 %.

EXAMPLE 7



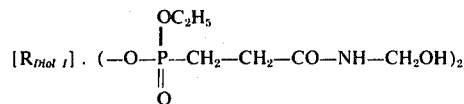
362 Grams (0.736 OH-equivalent) of a diol containing phosphorus and prepared according to German Offenlegungsschrift No. 2,036,595, Example 1 (P₂O₅=29.5 %, Cl=23.7 %, OH-number=114 (mg KOH/g), acid number = 2.5), in the following called diol_{III}, were mixed at room temperature at a pressure of 0.1 to 0.2 mm mercury with 55 g (0.5 mol) of dimethyl phosphite and 2.5 g of a 33 % solution of sodium methylate in methanol. 18 Grams distilled off into a refrigerating trap cooled with CO₂/methanol. A residue of 401 g remained. From this amount 398 g (corresponding to 0.48 pH-gram equivalents) were converted into the corresponding phosphonic acid ester carbonamide at 45°–55°C in 60 minutes, by introducing slowly 34.0 g (0.48 mol) of acrylamide. As a catalyst altogether 15 g of a 33 % solution of sodium methylate in methanol were added. Then 48.8 g (0.6 mol) of an aqueous 37 % formaldehyde solution were added and methylolization was carried out at 35°–40°C. To maintain the pH-value altogether 40 g of a 33 % sodium hydroxide solution were consumed. Yield: 541 g of an aqueous solution which had a content of P of 11.2 %.

EXAMPLES OF APPLICATION

EXAMPLE 8

A cotton fabric dyed with Indanthrene dyestuffs (Registered Trademark) having a square meter weight of 320 g was treated on a two-roller foulard (padding mangle) with an aqueous solution, which contained 400 g/l of a reaction product obtained according to Example 4

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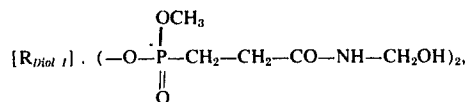
as well as 40 g/l of hexamethylol-melamine-pentamethyl ether and 5 g/l of ammonium chloride. After squeezing off the liquor pick-up was about 75 % and the impregnated fabric was pre-dried at 120°C to a residual moisture content of about 7 %. Condensation was effected for 4 minutes at 170°C. Then the fabric was after-treated with 2 g/l of a sodium carbonate solution at 90°C and rinsed until free of alkali.

The fabric thus finished showed a very good flameproofing effect after the flame-proof test DIN 53 906. (German Industrial Standard corresponding to AATCC 34.1966 and ASTM D 1230.61). The flame resistance endured a three hours' washing at the boil with 2 g/l of a commercial heavy-duty detergent or several washings at the boil in the washing machine. Burning lengths in cm according to DIN 53 906:

Initial effect	8.5
3 hours washing at the boil	9.5
3 machine washing cycles at the boil	9.0
non-treated fabric	burned completely

EXAMPLE 9

The cotton fabric described in Example 8 was also treated on a two-roller foulard. The impregnation solution contained 380 g/l of a reaction product obtained according to Example 2.



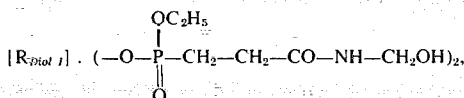
as well as 45 g/l of hexamethylol-melamine-pentamethyl ether and 4.5 g/l of ammonium chloride. The liquor pick-up was 75 %. The fabric thus treated was pre-dried at 100°C to a residual moisture content of about 6 %. Subsequently condensation was effected for 4 minutes at 170°C. The fabric was after-treated with a dilute sodium carbonate solution as described in Example 8.

The fabric was distinguished by a very good permanent flameproofing effect. The feel was soft and flowing. The flameproofing test was carried out according to DIN 53 906. Burning length in cm after the flame exposure:

Initial effect	8.0
3 hours washing at the boil	9.4
3 machine cycles at the boil	9.0
non-treated fabric	burned completely

EXAMPLE 10

A furnishing material of 100 % of cotton (250 g/m²) printed with Indanthrene dyestuffs was treated as in Example 8 with an aqueous solution which contained 400 g/l of the reaction product of Example 4



5

as well as 40 g/l of hexamethylol-melamine-pentamethyl ether, 10 g/l of urea and 5 g/l of ammonium chloride.

The content of moisture after the treatment on the foulard was 70 %. The fabric was pre-dried as in Example 8 and condensed. After-washing was effected with 2 g/l of sodium carbonate solution for 10 minutes at 90°C. After rinsing the fabric to free it from alkali it was dried again at 100°C.

The furnishing material was distinguished by a good and permanent flameproofing effect in washing and dry cleaning. The feel was soft. Moreover, the fabric showed an improved crease recovery in the dry and wet state.

The flameproofing test was carried out according to DIN 53 906, burning length in cm.

Initial effect	9.5
dry cleaning, three times	8.9
three machine washing cycles at 60°C	8.8
non-treated fabric	burned completely

EXAMPLE 11

The cotton fabric described in Example 8 was treated with an impregnation solution (water/ethanol 1:1), which contained 320 g/l of the condensation product obtained according to Example 7 (of 1 mol of dimethyl phosphite, 1.2 OH-equivalents of diol III, 1 mol of acrylamide and 1.25 mol of CH₂O), 40 g/l of hexamethylol-melamine-pentamethyl ether and 4.5 g/l of ammonium chloride. The liquor content after squeezing off was about 70 %. The fabric was pre-dried and condensed as in Example 1. Then it was after-washed for 6 minutes with a 2 g/l sodium carbonate solution at 90°C.

The fabric showed a good permanent flameproof effect, which endured several dry cleaning processes.

Flameproofing test according to DIN 53 906, burning length in cm.

Initial effect	10
5 dry cleaning processes	9.6

EXAMPLE 12

A flameproofing effect was obtained on the cotton fabric described in Example 8, when the fabric was treated with an aqueous finishing bath, which contained 400 g/l of a reaction product obtained according to Example 6 (of 1 mol of methane-phosphonous acid-isobutyl ester, 1 OH-equivalent of diol II, 1 mol of acrylamide and 1.1 mol of CH₂O), 45 g/l of hexamethylol-melamine-pentamethyl ether and 4 g/l of NH₄Cl. The fabric was treated as described in Example 8 with the finishing bath on a two-roller foulard. After-washing was carried out as already described with 2 g/l of sodium carbonate solution for 7 minutes at 90°C.

The fabric was distinguished by a good flameproofing effect which was resistant to dry cleaning.

Flameproofing test according to DIN 53 906.

Initial effect	8.5
3 dry cleaning processes	9.8
non-treated fabric	burned completely

EXAMPLE 13

A needle felt carpet material (wall to wall carpet) consisting of a fibre mixture (50 % of polyamide-6 and 50 % of polyester fibres) was treated on a two-roller foulard with an aqueous solution which contained 340 g/l of the carbonamide of Example 3, 85 g/l of hexamethylol-melamine-pentamethyl ether, 5 g/l of ammonium chloride and 200 g/l of a 40 % plastics dispersion of ethyl acrylate/acrylonitrile/N-methylolacrylamide in the ratio of 6:3:1. The liquor content after squeezing off was 100 %. Subsequently the fabric was dried for 25 minutes at 150°C.

The needle felt showed a very good elastic dimensional stability and a very good permanent flame resistance, which endured several shampoos and washing processes for delicate materials at 50°C.

The flameproofing test was carried out according to U.S. motor vehicle safety norm No. 302, inflammability of materials in motor cars having passenger compartments, in motor cars for various purposes, trucks and buses. Flame exposure time: 15 seconds.

The test specimen finished with only 200 g/l of the plastics dispersion mentioned in the Example continued to burn in a large front after removing the flame. The flame front ran over a test distance of 10 cm in 3 minutes and 10 seconds. However, the needle felt finished according to the invention did not continue to burn after removing the test flame. Only an after-glowing of 5 seconds could be observed. After a washing process for delicate materials with 2 g/l of a commercial light-duty detergent (duration of washing 15 minutes at 40°C) the needle felt did not continue to burn either after the flame exposure. The after-glowing time had only increased to 40 seconds.

After 5 shampooing processes the flameproof effect was also maintained. The needle felt did not continue to burn after exposure to the flame. After removing the flame only an after-glowing time of 50 seconds was observed.

EXAMPLE 14

A needle felt consisting of 50 % of polyamide-6 fibres and 50 % of viscose rayon was treated with an aqueous impregnation solution on a two-roller foulard (100 % liquor content after squeezing off) which had the following composition:

320 g/l of carbonamide of Example 1,
90 g/l of hexamethylol-melamine-pentamethyl ether,
150 g/l of a 40 % plastics dispersion consisting of butyl acrylate/vinyl acetate/N-methylol acrylamide (35:55:10) and
6 g/l of ammonium chloride.

The material was dried for 25 minutes at 150°C.

The needle felt showed a good permanent flameproofing effect which endured several shampooing processes or wet treatments (for example three washing processes for delicate materials at 40°C). The needle felt showed a very elastic feel.

EXAMPLE 15

The needle felt described in Example 13 was treated

with an impregnation solution which had the following composition:

400 g/l of the N-methylol-carbonamide solution of Example 4,

85 g/l of hexamethylol-melamine-pentamethyl ether, 200 g/l of the 40 % plastics dispersion mentioned in Example 13 and 5 g/l of ammonium chloride.

Impregnation was carried out again on a two-roller foulard (liquor content 100 %); then the fabric was dried for 20 minutes at 155°C.

The needle felt showed a good permanent flameproofing effect. The flameproofing test was effected according to U.S. motor vehicle safety norm No. 302.

As a comparison a sample was used which was finished not with a flameproofing agent, but with 200 g/l of the plastics dispersion. The burning time was 3 minutes and 10 seconds per 10 cm of test distance.

The needle felt provided with the instant flameproof finish did not continue to burn after removing the test flame. Only an after-glowing time within the zone exposed to the flame of 40 seconds could be observed. After three shampooing processes the good flameproof effect was maintained. The afterflowing time was 60 seconds.

EXAMPLE 16

A needle felt consisting of 75 % of polyester and 25 % of polyamide-6- fibres having a square meter weight of 750 g was treated on a two-roller foulard with a finishing bath which contained 380 g/l of an N-methylol-carbonamide solution obtained according to Example 2, 170 g/l of hexamethylolmelamine-pentamethyl ether, 200 g/l of a 40 % plastics dispersion of ethyl acrylate/acrylonitrile/N-methylol-acrylamide in the ratio of 6:3:1 and 5 g/l of NH_4Cl . The liquor content was 105 %. The material was dried for 25 minutes at 155°C.

The flameproofing test was carried out again according to U.S. motor vehicle safety norm No. 302. Flame exposure time: 15 seconds.

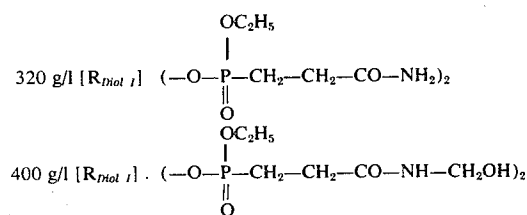
The sample which was only finished with the above-mentioned plastics dispersion burned with a burning time of 1 minute and 30 seconds per 10 cm.

However, the test specimen provided with the instant flameproof finish did not continue to burn after removing the flame. After a washing process for delicate materials the sample did not continue to burn either, but an after-glowing time of 30 seconds was observed. The needle felt showed a good dimensional stability.

The following comparative tests show the considerably improved permanence of the flameproofing process described in the specification and the possibility of using such processes for the flameproof finish of plane fibrous articles with regard to the feel, as compared with a commercial product on the basis of 3-(dimethylphosphono)-propionic acid imide:

A needle felt carpet material (wall to wall carpet), 900 g/m², which contained 50 % of polyamide-6 and 50 % of polyester fibres was finished, as described in Example 13, on a two roller foulard with 4 different flameproof products, furthermore with a plastics dispersion according to Example 13, with hexamethylol-melamine-pentamethyl ester as resin precondensate under addition of NH_4Cl as a catalyst. Products used:

I.



according to example 3

II.

according to Example 4

III. 267 g/l of 3-(dimethyl-phosphono)-propionic acid amide

IV. 400 g/l of N-methylol-3-(dimethylphosphono)-propionamide (commercial product)

The flameproofing test was carried out according to U.S. motor vehicle safety norm No. 302.

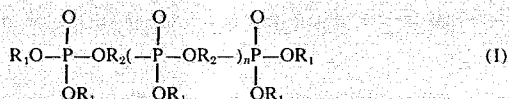
TABLE

Finishing Agents in g/l								
I	320	320						
II			400	400				
III					267	267		
IV							400	400
plastics dispersion	200	200	200	200	200	200	200	200
resin								
precondensate	170	250	170	250	170	250	170	250
NH_4Cl	6	6	6	6	6	6	6	6
Flameproofing test U.S. safety norm No. 302: after burning x'' = sample burns for x seconds x'y''(10) = the test distance of 10 cm burns in x minutes and y seconds								
Initial effect	does not burn	does not burn	does not burn	does not burn	does not burn	does not burn	does not burn	does not burn
after washing (delicate material)	after-burning 25''	after-burning 30''	does not burn	does not burn	burns	3'50''(10)	burns	3'30''(10)
Feel (initial)	stiffened	stiffened	stiffened	stiffened	stiffened	very stiff	stiffened	very stiff
after washing (delicate material)	stiffened	stiffened	stiffened	stiffened	slightly stiffened	stiffened	soft	stiffened

The needle felts stiffened are suitable for carpet material with regard to the feel. The very stiff needle felts are not suitable as carpet material (not elastic) Estimation: soft or slightly stiffened feel shows the insufficient fixation of the flameproofing agent.

What is claimed is:

1. A compound obtained by
a. heating a compound of the formula



wherein n is a number from 0 to 4, R_1 is haloalkyl and hydroxyalkyl or either each with 1 to 4 carbon atoms with the proviso that at least one R_1 is haloalkyl and at least one R_1 is hydroxyalkyl, R_2 is a group of the formula

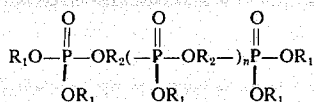


wherein R_3 and R_4 are hydrogen or haloalkyl with 1-4 carbon atoms with the proviso that at least one of the radicals R_3 and R_4 is hydrogen and m is a number from 1 to 10 with a compound of the formula



wherein y is 0 or 1 and R_5 are equal or different alkyl or alkenyl with 1 to 4 carbons; at 0° to 160°C at a pH value from 4 to 11 optionally in the presence of 0.005 to 4% by weight of an alkaline catalyst,

- b. adding (meth)acrylamide and heating at 20° to 100°C in the presence of 0.005 to 4% by weight of an alkaline catalyst and
c. optionally adding formaldehyde and heating at 20° to 100°C at a pH value from 7 to 11.
2. A compound according to claim 1 wherein a compound of the formula



wherein n is a number from 0 to 4, R_1 is tri-chloro ethyl and hydroxyethyl or either with the proviso that at least one R_1 is tri-chloro ethyl and at least one R_1 is hydroxyethyl, R_2 is a group of the formula



wherein m is a number from 1 to 10, characterized by the following analysis:

$\text{P}_2\text{O}_5=24.8\%$ by weight

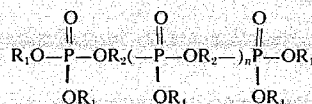
$\text{Cl}=15.5\%$ by weight

- 5 and an OH-value of 212 mg KOH/g is first reacted with diethylphosphite and then with acrylamide, said compound being characterized by the following analysis:

$\text{P}=14\%$ by weight

$\text{N}=2.8\%$ by weight.

- 10 3. A compound according to claim 1 wherein a compound of the formula



wherein n is a number from 0 to 4, R_1 is tri-chloro ethyl and hydroxyethyl or either with the proviso that at least one R_1 is tri-chloro ethyl and at least one R_1 is hydroxyethyl, R_2 is a group of the formula



wherein m is a number from 1 to 10, characterized by the following analysis:

$\text{P}_2\text{O}_5=24.8\%$ by weight

$\text{Cl}=15.5\%$ by weight

and an OH-value of 212 mg KOH/g is first reacted with dimethylphosphite and then with acrylamide, said compound being characterized by the following analysis:

$\text{P}=14\%$ by weight

$\text{N}=3\%$ by weight.

4. Compounds according to claim 1, wherein the NH_2 - group is substituted by one or two methylol groups.

5. Compounds according to claim 1, wherein the halogen of the haloalkyl is chlorine and bromine or either.

6. Compounds according to claim 5, wherein the haloalkyls have 2 or 3 carbons and 1 or 2 halogen atoms.

7. Compounds according to claim 6, wherein R_1 is 2-chloroethyl.

8. Compounds according to claim 6, wherein R_1 is 2,3-dibromopropyl or 2,3-dichloropropyl.

9. Compounds according to claim 5, wherein R_3 or R_4 is chloromethyl.

10. Compounds according to claim 5, wherein R_3 and R_4 are hydrogen.

11. Compounds according to claim 5, wherein m is a number from 1 to 4.

12. Compounds according to claim 5, wherein R_5 is alkyl with 1 to 4 carbons.

13. Compounds according to claim 12, wherein R_5 is methyl or ethyl.

14. Compounds according to claim 5, wherein R_5 is alkenyl with 3 or 4 carbons.

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