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3,709,940

# PHOSPHORUS COMPOUNDS FOR FLAME-PROOFING FABRICS

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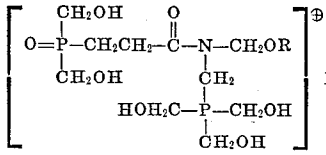
Int. Cl. C07c *103/30*
U.S. Cl. 260—561 P 7 Claims

## ABSTRACT OF THE DISCLOSURE

Organic phosphorus compounds of the general formula



(I)

in which R is H or $C_{1-3}$ alkyl and X is halogen or OH, are useful for flameproofing textiles, especially textiles including cellulosic fibres.

This invention relates to new organic phosphorus compounds, and to the treatment of textile materials therewith for flameproofing.

It is known to treat textiles, particularly textile materials of cellulose containing fibre, with difficultly inflammable materials, which are known collectively as "organic phosphorus compounds." Known materials of this type are for example aziridinyl phosphine oxide (APO), dialkylphosphonocarboxylalkylolamide, phosphoronitrilechloride, tetrahydroxymethylphosphonium chloride (THPC) as well as reaction products of THPC and various nitrogen containing compounds (compare German specification 1,045,098).

Particular difficulties arise in flameproofing textiles of mixed fibre goods, e.g., fibre goods of cellulose fibes and synthetic fibres such as polyamide or polyester fibres.

A process for flameproofing fibre goods made from mixtures of polyester fibres and cellulose fibres is known in which the fibrous material is impregnated with solutions of ammonium salts of bis-hydroxymethylphosphinic acid. Such an impregnation is not satisfactory from all points of view in practice especially having regard to permanency and toxicological harmlessness.

Finally, a process for improving textile of natural and artificial cellulose containing fibres, as well as from mixed fibre of cellulose containing fibres and synthetic fibres, has been suggested in which the textiles are subjected to the combined action of tetrahydroxymethylphosphonium salts and halogenated alcohols, aldehydes, amines, ketones and/or carboxylic acids or their derivatives or non-volatile halogenated hydrocarbons. Optionally, in this process there can also be included as well as the flameproofing substances compounds containing primary and/or secondary amino groups including their methylol compounds. Polymerisable compounds such as acrylamide can also be used, which are reactable with the methylol groups of the tetrahydroxymethylphosphonium salt or trishydroxymethylphosphine oxide. If desired the treated textiles can be subjected to the effect of heat, especially in the region of about 40 to 170° C. By the additional treatments a water or solvent resistance can be obtained.

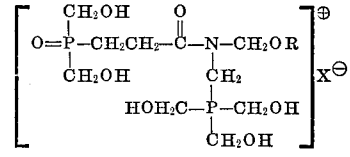
The object of the invention is the provision of a material for improving textiles, especially for making them flameproof, which in use gives the textiles not only a high flame resistance but also a particular permanency of the effect of the treatment, wherein the textile properties



of the treated goods are retained and their technological properties are practically not adversely influenced.

It has been found that certain organic phosphorus compounds give good permanent treatment effects on textiles of natural or artificial cellulose containing fibres, especially mixed fibre goods of cellulose containing fibres and synthetic fibres with a synthetic fibre content up to about 70%.

The organic phosphorus compounds according to the invention have the general formula



(I)

in which R is hydrogen or an alkyl residue of 1–3 carbon atoms and X is halogen, particularly chlorine, or OH.

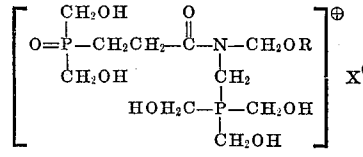
In order to increase the permanency and at the same time improve the creasing properties of such treatments, it can in some cases be of value to use therewith additional wetting agents such as polymethylolmelamine or alkyl ethers thereof. Furthermore it is possible, by using as well carboxylic acid modified alkylol compounds of melamine, cyclic urea etc., to obtain a permanent flameproof and water repellent effect.

With the treatments provided according to the invention, according to the type of organic phosphorus compound used and according to the type of fibrous material, a loading of 15–30% of treatment agent is necessary in order to make the treated textiles flameproof as required by DIN 53906.

In the practical use of organic phosphorus compounds according to the invention for treating textiles, it is important that the organic phosphorus compounds are substantially wetted with respect to the fibrous materials; this can suitably take place by condensation at temperatures in the range of 120–180° C., especially 140–160° C., and suitably also in the presence of a reaction accelerator such as o-phosphoric acid, ammonium salts or the like. The length of time for the heating depends on various factors, inter alia on the type of fibrous material to be treated, the temperature used, and the construction of the condensation plant or apparatus used. Generally good results are achieved with condensation times in the region of 1–10 minutes. In some cases it can be necessary to extend this time somewhat.

It can further be desired that the flameproofed textiles are treated after condensation with an oxidative agent or an oxidising rinsing treatment, in order to remove insufficiently fixed organic phosphorus compound and to make the treated goods wholly non-odorous.

The invention includes also a process for the manufacture of organic phosphorus compounds of the general formula

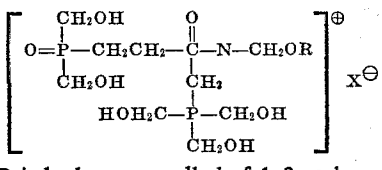


(I)

in which R is hydrogen or alkyl of 1–3 carbon atoms and X is halogen, particularly chlorine, which is characterised in that 2 mol. tetrahydroxymethylphosphonium salt are recated with 1 mol N-methylolacrylamide at a pH value of 4–8, particularly 6–7, and at temperatures of 100–140° C., particularly 120–130° C., preferably under reduced pressure, e.g. in the range of 10–50 torr.

The resulting product can be extracted from the reaction mixture without isolation with a 1–3 carbon atom alcohol at room temperature or slightly elevated temperature up to 50° C. in acid conditions (pH value of 1–5).

The invention further includes a process for the manufacture of organic phosphorus compounds of the general formula



(I)

in which R is hydrogen or alkyl of 1–3 carbon atoms and X is OH, in which tetrahydroxymethylphosphoniumhalide, particularly tetrahydroxymethylphosphoniumchloride (THPC) is reacted under such conditions that the entire amount of halide ions, particularly chloride ions, are removed from the reaction mixture and replaced by hydroxyl ions.

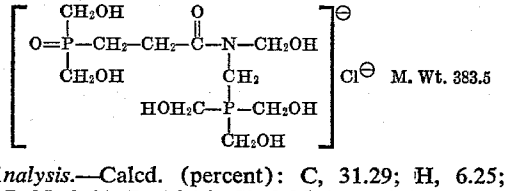
A useful embodiment of the process according to the invention is characterised in that 1 mol tetrahydroxymethylphosphonium salt, particularly 1 mol THPC, is neutralized in aqueous alcoholic solution with sodium carbonate at 20–40° C., the sodium halide, particularly NaCl, separated off, the alcohol containing filtrate is reduced under vacuum and the viscous solution is reacted with stirring and intense cooling with half a mol of N-methylolacrylamide added in portions, the reaction being carried out under reduced pressure, particularly from 10–50 torr and then heated to about 100° C.

For the manufacture of organic phosphorus compounds according to the invention tetrahydroxymethylphosphoniumchloride or bromide are particularly suitable.

The invention is subsequently described with reference to the following specific examples.

## EXAMPLE 1

240 grams of an 80% aqueous solution of THPC (1 mol) and 50.5 grams N-methylolacrylamide (0.5 mol) were stirred together and treated with about 10 grams $Na_2CO_3$ in portions of 1–2 grams, until a pH value of 6–7 was obtained. This mixture was then dewatered under reduced pressure (20 torr) and slowly increasing temperature and brought to reaction. In this way the temperature of the reaction mix is brought to 125° C. and is held at this temperature for about 2 hours. After removal of the by-products formed (essentially NaCl) a water soluble condensation product which at this temperature was viscous, of the following constitution resulted.



M. Wt. 383.5

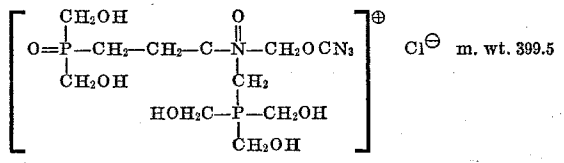
*Analysis.*—Calcd. (percent): C, 31.29; H, 6.25; O, 33.37; N, 3.64; P, 16.16; Cl, 9.25. Found (percent): C, 30.80; H, 6.35; O, 32.80; N, 3.60; P, 15.80; Cl, 10.60.

Yield: 180 grams=95% of theoretical.

This reaction product was diluted with water to a concentration of about 80% in order to give the necessary handleability in practice.

## EXAMPLE 2

180 grams of the pure organic phosphorus compound manufactured according to Example 1 was converted into the corresponding N-methoxymethyl compound by treatment with 100-gram methanol in the presence of 10 ml. hydrochloric acid (concentrated) at 22–50° C. for 30 minutes. After the termination of etherification the reaction mixture was again adjusted to a pH value of 7.0 with about 5 gram $Na_2CO_3$, the excess methanol was removed under vacuum, and the mixture filtered. A viscous water soluble compound of the following constitution resulted:



m. wt. 399.5

*Analysis.*—Calcd. (percent): C, 33.2; H, 6.54; O, 32.20; N, 3.52; P, 15.57; Cl, 8.93. Found (percent): C, 32.7; H, 6.6; O, 31.1; N, 3.4; P, 15.3; Cl, 10.9.

The yield amounted to: 170 g.=85% theoretical.

This reaction product was diluted with water to the necessary concentration for practical handleability of about 80%.

## EXAMPLE 3

A web (140-gram/m.²) of a polyester cotton mixed fibre yarn (50:50) was treated on the foulard with the following bath:

500 g./l. of an 80% aqueous solution of the reaction product of THPC and N-methylolacrylamide (made according to Example 1);

50 g./l. trimethylolmelaminetrimethylether (60% aqueous solution);

50 g./l. orthophosphoric acid (as catalyst);

30 g./l. polyethylene softening agent.

After squeezing out to 80% liquid take-up, the web was dried and condensed at about 140° C. Finally it was subjected at about 60° C. to a weakly alkaline peroxide or percarbonate containing wash, rinsed out and dried.

A material resulted which was loaded to about 30% by the treatment agent.

The so treated web was flameproof according to DIN 53906 and according to the so-called match test (British Standard 2963, method A). The flameproof effect according to DIN 53906 still remained also after 30 machine washes at 60° C.

The textile properties of the flameproofed material were exceptional, the feel of the goods being practically nonchanged compared to the non-treated goods. The technological properties were good; the "wash and wear" properties were substantially improved.

## EXAMPLE 4

A web (160-gram/m.²) of pure cotton was treated on the foulard with the following bath:

500 G./l. an 80% aqueous solution of the reaction product of THPC, N-methylolacrylamide and methanol (manufactured according to Example 2);

40 g./l. tetramethylolmelamine;

10 g./l. monoammonium phosphate (as catalyst);

30 g./l. polyethylene agent.

After squeezing out to 90% liquid take-up the fabric was dried and condensed at about 160° C. Thereafter it was treated at about 60° C. with a weakly alkaline peroxide or percarbonate containing afterwash, rinshed and dried.

A web resulted with a take-up of treatment agent of about 25–30%.

The so-treated web was flameproof (according to DIN 53906 and match test). The flameproof effect still remained even after 13 machine washes at 90° C.

The technological properties of the treated material were satisfactory; the wash and wear ability was substantially improved.

## EXAMPLE 5

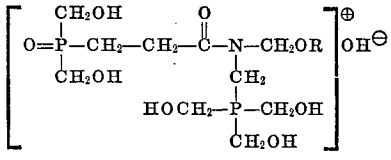
240 grams of an 80% aqueous solution of THPC (1 mol) were evaporated under vacuum to about 100% and diluted with about 100 ml. methanol, and the methanolic solution was neutralized with stirring with about 50 g. sodium carbonate at 22–40° C. The NaCl arising was separated. The methanol containing filtrate was reduced

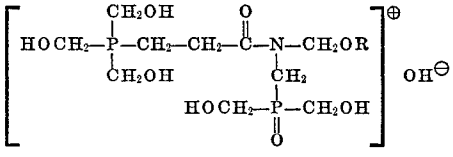
under vacuum at temperatures of 20–50° C. and under reduced pressure (10–50 torr). The viscous solution was then reacted with 50.5 g. (half mol) N-methylol-acrylamide, the N-methylolacrylamide being introduced in portions (2–5 g.) with striring and intensive cooling at 20–50° C. Thereafter vacuum was applied, and the temperature rose within 2½ hours to 100° C. A viscous end product resulted (about 182 grams) which was diluted with about 80 grams water to a 70% solution for better handleability.

Yield: 260-gram, 70% solution, ≧98% of theory.

The analysis gave the following values: Calcd. (percent): C, 32.90, H, 6.86; O, 39.40; N, 3.84; P, 17.00. Found (percent): C, 33.10; H, 7.10; O, 39.10; N, 3.80; P, 16.90.

For the organic compound according to the invention in which, in the general Formula 1, X is a hydroxyl ion, the following formulae result





in which R is hydrogen or alkyl of 1–3 carbon atoms. Molecular weight 365.

## EXAMPLE 6

A web (140-gram/m.²) of a polyester/cotton mixed fibre yarn (50:50) was treated on the foulard with the following bath:

500 g./l. of a 70% aqueous solution of the organic phosphorus compound made according to Example 5;

80 g./l. trimethylolmelaminetrimethylether (60% aqueous solution);

30 g./l. orthophosphoric acid (as catalyst);

30 g./l. polyethylene softening agent.

After squeezing to about 80% liquid take-up, the web was dried and condensed at about 140° C. Then it was treated at about 30° C. with a weakly alkaline, peroxide or percarbonate containing afterwash, rinsed and dried.

A web resulted loaded to about 30% with the treatment agent.

The so-treated web was flameproof according to DIN 53906 and according to the so-called match test (British Standard 2963, method A). The flameproof effect according to DIN 53906 still remained after 30 machine washes at 60° C.

The textile properties of the flameproofed web were very good, and the feel of the goods compared to non-treated goods was practically unchanged. The technological properties were good; "wash and wear" was substantially improved.

## EXAMPLE 7

A web (160-g./m.²) of pure cotton was treated on the foulard with the following bath:

500 g./l. 70% aqueous solution of the organic phosphorus compound made according to Example 5;

80 g./l. tetramethylolmelamine;

10 g./l. monoammonium phosphate (as catalyst);

30 g./l. polyethylene softening agent.

After squeezing out the 90% liquid take-up the web was dried and condensed at about 160° C. Thereafter it was treated at about 60° C. with a weakly alkaline, peroxide or percarbonate containing afterwash, rinsed and dried.

A web loaded with 25–30% treatment agent resulted.

The so-treated web was flameproof (according to DIN 53906 and the match test). The flameproof effect still remained after 30 machine washes at 90° C.

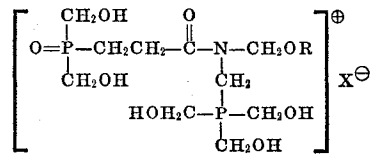
The technological properties of the treated web were good; "wash and wear" properties were substantially improved.

The loss in tear strength was surprisingly small; it amounted to only 0–20%.

While, in the treatment of webs of a mixed polyester/cotton fibre yarn (50:50) with compounds according to general Formula 1, in which X=OH, compared to treatment with these webs with compounds of general Formula 1 in which X is halogen, particularly chlorine, just as good flameproof properties can be obtained, and only small variations in the technological properties, in particular tear strength, in the treatment of webs of cellulose containing fibres, and indeed both of natural and regenerated cellulose fibres, with compounds of the first noted type, very surprising effects are obtained. The loss in tear strength when using the organic phosphorus compound in which X=OH amounts to 0–20% while in the use of the organic compound in which X is halogen on cotton webs it is somewhat higher.

I claim as my invention:

**1.** An organic phosphorus compound of the general formula:

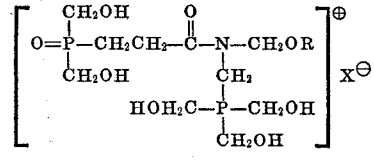


(I)

in which R is selected from the class consisting of hydrogen and alkyl of 1 to 3 carbon atoms, and X is selected from the class consisting of halogen and hydroxyl.

**2.** An organic phosphorus compound according to claim **1** wherein X is chlorine.

**3.** In the process for the production of an organic phosphorus compound of the general formula:



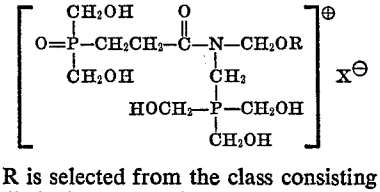
(I)

in which R is selected from the class consisting of hydrogen and alkyl of 1 to 3 carbon atoms, and X is halogen, the step of reacting 2 mol of tetrahydroxymethylphosphonium salt with 1 mol N-methylolacrylamide at a pH value of 4 to 8 and at a temperature of 100–140° C.

**4.** The process of claim **3** wherein the reaction is carried out at a pH value of 6 to 7, a temperature of 120–130° C., and under reduced pressure.

**5.** The process of claim **4** wherein the reduced pressure is 10–50 torr.

**6.** The process for the production of an organic phosphorus compound of the general formula:



(I)

in which R is selected from the class consisting of hydrogen and alkyl of 1 to 3 carbon atoms, and X is hydroxy, wherein 1 mole tetrahydroxymethyl phosphonium salt is neutralised in aqueous alcoholic solution at 20–40° C. with sodium carbonate, the sodium halide formed is

removed, the alcohol-containing filtrate is reduced under vacuum, and the viscous solution is reacted with ½ mol N-methylolacrylamide added in portions with stirring and intense cooling, and is heated under reduced pressure to about 100° C.

7. The process of claim 6 wherein the reduced pressure is 10–50 torr.



No references cited.

LEWIS GOTTS, Primary Examiner
E. G. LOVE, Assistant Examiner

U.S. Cl. X.R.
117—136

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,709,940 Dated January 9, 1973

Inventor(s) Wilhelm FLUGEL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 5, that portion of the formula reading

$-CH_2OCN_3$ should read $-CH_2OCH_3$

Signed and sealed this 23rd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.