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3,560,479

FIRE-RETARDANT CELLULOSIC COMPOSITIONS

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U.S. Cl. 260-212

6 Claims

ABSTRACT OF THE DISCLOSURE

A flame-retardant composition comprised of a cellulosic composition and a bis- β , β -(dialkylphosphono)propionic acid derivative integrally attached to the cellulosic polymer chain of the cellulosic composition.

BACKGROUND OF INVENTION

Prior to this invention, there were numerous methods of treating cellulosic compositions to impart flame-retardant characteristics thereto. Perhaps the most efficient and well-known manner of providing flame-retardant properties to cellulosic was to add chlorinated hydrocarbons as well as antimony oxide as a rinse on the cellulosic fabric or sheet to deposit the flame-retardant compound on the surface thereof. The fabric or sheet was thereby rendered less flammable than it was prior to treatment.

In recent years, phosphorus compounds have been utilized to enhance the fire-retardant characteristics of cellulosic materials and some of the phosphorus compounds have been chemically reacted with cellulosic composition to provide a degree of flame-retardant characteristics to the cellulosic composition. One such treatment is set forth in United States Pat. 3,374,292 issued to Zahir. This patent sets forth a treatment of cellulosic materials with substituted phosphono amides as the reactant.

The aforementioned patent discloses a chemical combining of a flame-retardant compound with a cellulosic composition which has been found to be superior to the blending of flame-retardant components with cellulosic compositions. The use of the phosphorus compound set forth in Pat. 3,374,292 is, however, somewhat limited in its effect on the flame-retardant characteristics of a cellulosic composition because it utilizes only one phosphono group in the phosphorus containing compound.

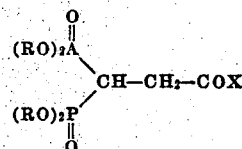
SUMMARY OF INVENTION

The present invention is direct to flame retardant cellulosic compositions provided by treating the cellulosic composition with a disubstituted phosphono compound which is generally referred to as a bis- β , β -(dialkylphosphono)propionic acid derivative. The propionic acid derivative is integrally combined with the polymeric cellulosic chain and becomes an integral part of the cellulose molecule. Thus, the treating compound is not washed out of a fabric or from a given cellulosic composition after treatment, even though there may be repeated washings.

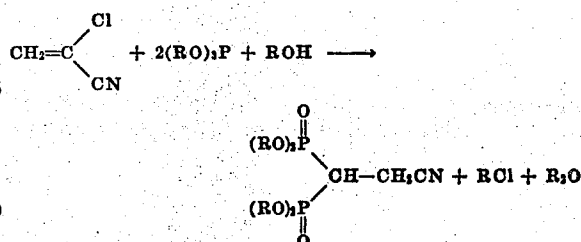
The compounds of this invention are generally described

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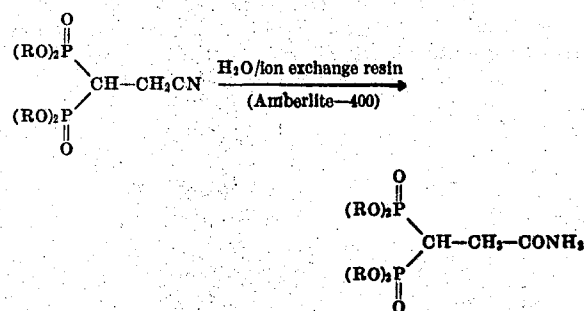
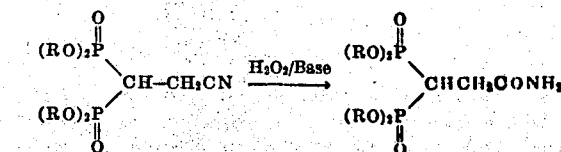
as bis- β , β -(dialkylphosphono)propionic acid compounds which are generically described by the formula:



wherein R is an alkyl group containing from 1 to 8 carbon atoms and X is selected from the group consisting of OR' wherein R' is C₁-C₈ alkyl, NH₂ and NH-CH₂OH. The compounds may be prepared by reacting α -chloroacrylonitrile, trialkyl phosphite and alcohol in accordance with the equation set forth herein below:

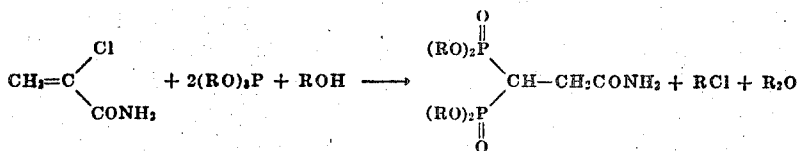
**EQUATION I**

The cyano compounds prepared as set forth in Equation I above may be converted to the amido compound by either Equation II or Equation III as set forth herein below:

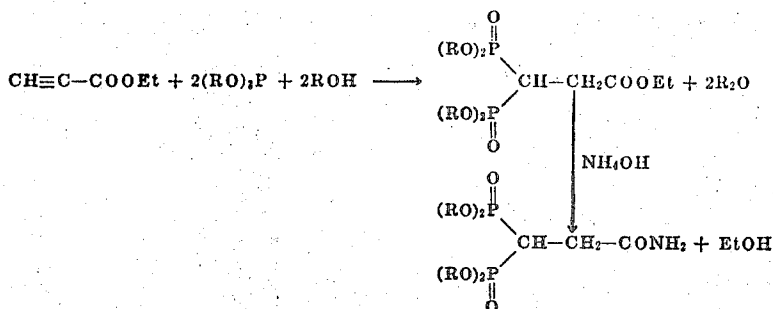
**EQUATION II**

3 EQUATION III

The amido compound set forth in Equation II may also be prepared in accordance with Equations IV and V set forth herein below:



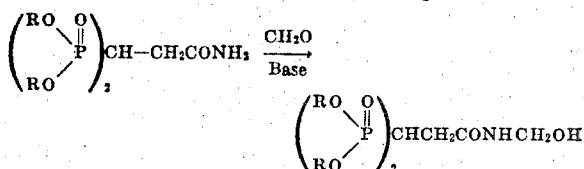
EQUATION IV



EQUATION V

As set forth above, Equation IV shows the compounds as prepared from ethyl α -chloroacrylate Equation V from α -chloroacrylamide and Equation VI from ethyl propionate.

The amido compounds may be converted into their N-hydroxymethyl analogue according to Equation VI.

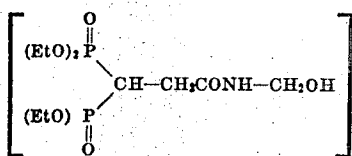


EQUATION VI

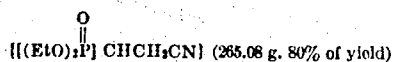
The compounds that are used to chemically combine with cellulosic materials in accordance with this invention may be prepared with a minimum of effort. The examples set forth hereinbelow illustrate the preparation of the compounds and all parts in the following examples are by weight unless otherwise indicated.

EXAMPLE I

Preparation of N-hydroxymethyl-bis- β,β -(diethylphosphono)propionamide



Triethyl phosphite (332 g.) was added to an ethanolic solution of α -chloroacrylonitrile (88.2 g. in 250 ml. ethanol). An exothermic reaction occurred. Upon complete addition of the α -chloroacrylonitrile, the reaction mixture was refluxed for six hours. On fractionation it yielded bis- β,β -(diethylphosphono)propionitrile.



IR and NMR spectra confirmed the structure. The B.P. of this compound was found to be 155° C./0.3 mm.

The above phosphono propionitrile was converted into the corresponding bis- β,β -(diethylphosphono)propionamide by using the following reaction:

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43.0 g. of bis- β,β -(diethylphosphono)propionitrile, 90.9 g. base ion exchange resin (Amberlite-400) and 250 ml. of water was refluxed under stirring for six hours. The ion exchange resin was filtered and the water was evaporated

from the filtrate. A viscous oil (27.0 g.) formed. IR of

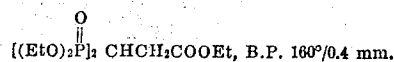
this oil confirmed the formation of bis- β,β -(diethylphosphono)propionamide.

The above propionamide (25.0 g.) was added to formalin (37% 15.0 g.) at 50–60° C., the pH of the mixture was maintained at 8.0 by adding aqueous sodium hydroxide solution drop by drop. After stirring for 1½ hours, the mixture was cooled to room temperature. On evaporation of the volatile fraction under reduced pressure, N-hydroxymethyl-bis- β,β -(diethylphosphono)propionamide was obtained.

EXAMPLE II

Preparation of N-hydroxymethyl bis- β,β -(diethylphosphono)propionamide from ethyl α -chloroacrylate

Triethyl phosphite (220 g.) was added to an ethanolic solution of ethyl α -chloroacrylate (80 g. in 250 ml. ethanol). An exothermic reaction occurred. Upon complete addition of triethyl phosphite, the reaction mixture was refluxed for six hours. On fractionation it yielded 140 g. of ethyl bis- β,β -(diethylphosphono)propionate.



The compound was characterized by its IR and NMR spectra.

183 g. of the above propionate was added to aqueous ammonium hydroxide in ethanol (7.50 ml. of 30% aqueous ammonium hydroxide). The reaction mixture was allowed to stand for three days at room temperature and the water, alcohol and excess ammonia were evaporated off. A thick viscous mass was obtained which was identified by its IR and NMR spectra as bis- β,β -(diethylphosphono)propionamide.

The bis- β,β -(diethylphosphono)propionamide was converted into N-hydroxymethyl bis- β,β -(diethylphosphono)propionamide as described in Example 1.

EXAMPLE III

Preparation of N-hydroxymethyl bis- β,β -(diethylphosphono)propionamide from α -chloroacrylamide (Equations IV and VI)

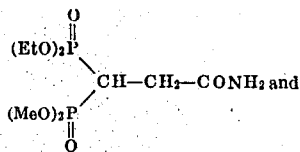
Triethylphosphite (83.0 g.) was added to a solution of α -chloroacrylamide (26.0 g.) in ethanol (150 ml.). The reaction mixture was refluxed for six hours. Excess ethanol was evaporated from the solution leaving bis- β,β -(diethylphosphono)propionamide as a viscous colorless liquid (78 g.). IR spectra confirmed the structure.

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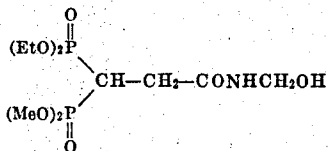
This amide was converted to its N-hydroxymethyl derivative as described in Example I.

EXAMPLE IV

Preparation of β -(diethylphosphono)- β -(dimethylphosphono)propionamide and its N-hydroxymethyl derivative

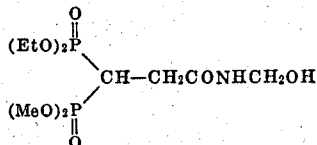
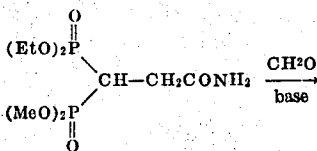
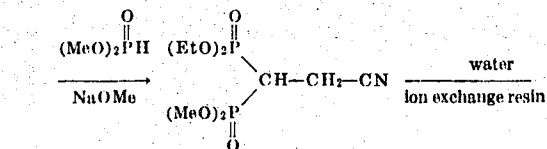
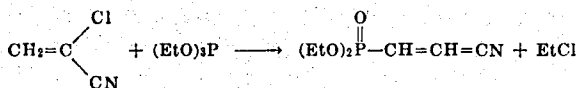


Formula I

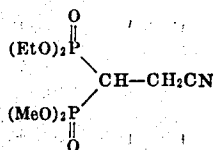


Formula II

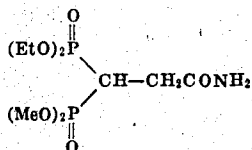
The I and II compounds above were synthesized according to the following equations:



37 ml. of methanolic solution of sodium methoxide (3 ml.) was slowly added to a mixture of β -diethylphosphono acrylonitrile (140 g. made from a known and published reaction set forth in Liebig's Annalen der Chemie, vol. 657, page 19, 1962) and dimethylphosphite (83 g.). An exothermic reaction occurred. After complete addition of the sodium methoxide, the reaction mixture was heated at 90° C. for one hour. Excess methanol and unreacted dimethyl phosphite were stripped off leaving a yellow-colored liquid. IR and NMR showed that the compound of the structure below resulted:



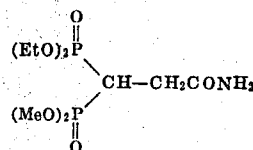
A portion of the above (ca. 100 g.) was converted into its amide



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using water and an ion exchange resin according to the procedure described in Example I for the conversion of the propionitrile derivative into a propionamide compound.

The propionamide compound



was converted into the N-hydroxymethyl compound using 50 g. of the above propionamide and 15 g. of formalin at pH 8 as described in Example I.

The compounds prepared in accordance with the examples set forth hereinabove are soluble in water and are capable of fire-retardant characteristics when chemically combined with cellulosic materials such as cotton, paper and synthetic fabrics from cellulose as illustrated in Examples V and VI.

EXAMPLE V

Cotton fabric was padded with an aqueous solution containing the following ingredients:

	G.
N-hydroxymethyl diethyl phosphonopropionamide	12.0
Aerotex CP Resin (cross-linking agent) ¹	2.5
Cyanlube ²	0.25
Ammonium chloride (catalyst)	0.25
Urea	0.25
Water (solvent)	9.0

¹A melamine-formaldehyde resin marketed by American Cyanamid.
²An American Cyanamid product which is a mixture of lubricants such as fatty acid salts (used to provide "soft hand" of fabric).

The impregnated fabric was dried and was then heated at 165° C. for five minutes. The treated fabric was non-burning to a vertical flame test. A washed sample of this treated fabric was found to be self-extinguishing and no afterglow was observed even after repeated washings.

EXAMPLE VI

Cotton fabric was padded with an aqueous solution containing the following ingredients:

	G.
N-hydroxymethyl derivative of Example IV	12.5
Aerotex Resin (cross-linking agent) ¹	2.5
Cyanalube ²	0.25
Ammonium chloride (catalyst)	0.25
Urea	0.25
Water (solvent)	9.0

¹A melamine-formaldehyde resin marketed by American Cyanamid.
²An American Cyanamid product which is a mixture of lubricants such as fatty acid salts (used to provide "soft hand" of fabric).

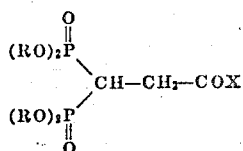
After drying and heating at 165° C. for five minutes, the fabric became non-burning or self-extinguishing.

It will be understood that while the invention has been described in connection with certain specific compounds that are used with certain specific cellulosic compositions, this is by way of illustration and not by way of limitation and that the scope of the invention is defined solely by the appended claims which should be construed as broadly as is consistent with the prior art.

What is claimed is:

1. The flame-retardant composition comprised of a cellulosic composition chemically combined with a bis-

β,β -(dialkylphosphono)propionic acid derivative of the generic formula:



wherein R is a C_1 - C_3 alkyl group and X is selected from the group OR' wherein R' is a C_1 - C_3 alkyl group consisting of NH_2 and NHCH_2OH wherein the bis- β,β -(dialkylphosphono)propionic acid derivative is integrally attached to the cellulosic composition.

2. The flame-retardant composition of claim 1 wherein the cellulosic composition is a fibrous cellulosic material.

3. The flame-retardant composition of claim 1 wherein the flame-retardant component in the cellulosic composition is N-hydroxymethyl-bis- β,β -(diethylphosphono)propionamide.

4. The flame-retardant composition of claim 1 wherein the cellulosic composition is cotton.

5. The flame-retardant composition of claim 1 wherein the cellulosic composition is wood fiber.

6. The flame-retardant composition of claim 1 wherein the cellulosic composition is a cellulosic fabric.

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DONALD E. CZAJA, Primary Examiner

R. W. GRIFFIN, Assistant Examiner

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U.S. Cl. X.R.

8-115.6; 115.7, 116, 116.2, 116.3, 120; 106-15;
260-219, 932

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,560,479 Dated February 2, 1971

Inventor(s) Kailash Chandra Pande

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

Column 7, line 10, before "OR'" should read
-- consisting of --; lines 10 and 11, cancel "consisting o

Signed and sealed this 7th day of November 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Pat