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Golborn et al.

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[54] **PHOSPHORUS CONTAINING VINYL ETHERS**

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Related U.S. Application Data

[62] Division of Ser. No. 142,075, May 10, 1971, abandoned.

[52] **U.S. Cl.**............... **106/16;** 106/15 FP; 117/140; 204/159.22; 260/80.3 E; 260/80.7; 260/82.1; 260/85.5 ZA; 260/85.7; 260/87.5 G; 260/87.7; 260/88.1 R; 260/88.1 PE; 260/91.1R; 260/968

[51] **Int. Cl.**... **C09k 3/28**

[58] **Field of Search** .... 106/15 FP, 16; 260/45.7 P

[56] **References Cited**

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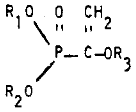
[57] **ABSTRACT**

Compounds of the formula:



in which R_1, R_2 and R_3 are lower alkyl radicals are produced by the dehydroalkoxylation of the corresponding dialkyl 1,1-dialkoxyethyl phosphonates. The vinyl ether phosphonates are useful as flame retarding agents for textile materials and in the production of polymers and copolymers which possess flame retardant properties.

10 Claims, No Drawings

PHOSPHORUS CONTAINING VINYL ETHERS

This is a division of application Ser. No. 142,075, filed May 10, 1971, now abandoned.

BACKGROUND OF THE INVENTION

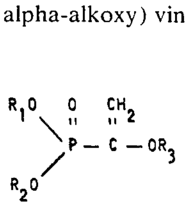
Many flame retarding agents and methods of application have been developed in attempts to obtain flame resistant textile materials. For example, mixtures of ammonium dihydrogen orthophosphate or boric acid with borax have been used to retard flame in cellulosic materials. Wash-proof finishes have been produced by depositing metal oxides within or on the fibers of cellulose by the successive precipitation of ferric oxide and a mixture of tungstic acid and stannic oxide or by successive deposition of antimony trioxide and titanium dioxide. Such processes require plural treatment baths in which strongly acidic solutions are employed. These strongly acidic solutions are both inconvenient to use and pose the problems of possible degradation of the cellulose. Furthermore, the presence of a metal oxide coating on cellulosic textile materials creates difficulties in some subsequent dyeing processes.

One process which involves the use of a single processing bath consists of padding a dispersion of a chlorinated hydrocarbon and finely divided antimony oxide on the cellulosic fabric. The fabric is then heated to render the finish wash-proof. Near the combustion temperature, antimony oxide will react with hydrogen chloride, generated by degradation of the chlorinated hydrocarbon, to form antimony oxychloride which suppresses flame. The combination of a chlorinated hydrocarbon and finely divided antimony oxide are not acceptable finishes for closely woven fabrics because they deleteriously effect the hand of the finished product.

Flame resistance has been imparted to cellulosic materials by esterification of the cellulose with diammonium hydrogen orthophosphate. Products so treated are subject to metathesis reactions with cations in aqueous solution during washing, the ammonium cation being displaced by calcium, sodium or magnesium. The flame resistance properties of the diammonium orthophosphate ester of the cellulosic material is then regenerated by reacting the washed product with an ammonium chloride solution.

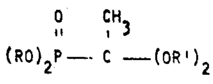
BRIEF DESCRIPTION OF THE INVENTION

In accordance with this invention, there is provided a novel group of flame retardants for textile materials which are dialkyl (alpha-alkoxy) vinyl phosphonates of the formula:



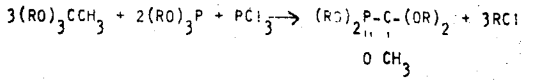
wherein R_1, R_2 and R_3 are lower alkyl radicals independently containing from 1 to 8 carbon atoms.

The compounds of this invention are prepared by dehydroalkoxylation of the dialkyl 1,1-dialkoxyethyl phosphonate of the formula:



$$(RO)_2\overset{\overset{O}{\|}}{P}-\overset{\overset{CH_3}{|}}{C}-(OR')_2$$

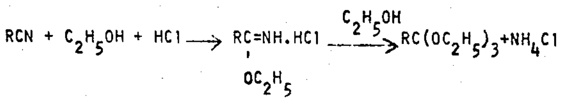
The latter compounds being prepared by the reaction of a trialkyl ortho acetate with a tertiary phosphite and PCl_3 in accordance with known procedures. For example,



$$3(RO)_3CCH_3 + 2(RO)_3P + PCl_3 \rightarrow (RO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{CH_3}{|}}{C}-(OR)_2 + 3RCl$$

in which R is the methyl or ethyl radicals.

The ortho acetate ester is prepared by the alcoholysis of an imino ester hydrochloride which itself is obtained from a nitrile;



$$RCN + C_2H_5OH + HCl \rightarrow R\underset{\underset{OC_2H_5}{|}}{C}{=}NH.HCl \xrightarrow{C_2H_5OH} RC(OC_2H_5)_3 + NH_4Cl$$

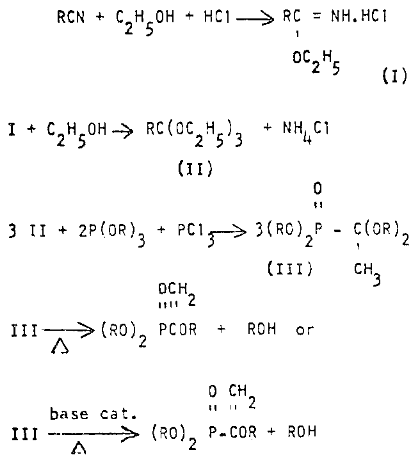
The compounds of this invention may be applied directly to a textile material by conventional finishing techniques such as by thermal or radiation induced pad curing. The finished textile product whether it is subjected to additional finishing treatments or not, exhibits reasonably durable, flame resistant properties. An application of from about 5 to about 40 percent by weight of fire retardant based upon the textile weight is sufficient to provide protection to the treated material.

The flame retarding agents of this invention may be applied to various textiles such as cellulosic materials and proteinaceous materials. By cellulosic materials, applicants intend to embrace cotton, rayon, regenerated cellulose and cellulose derivatives which retain the cellulose backbone and at least one hydroxyl substituent per repeating glucose unit. By proteinaceous material applicants intend to embrace those textile materials which present the functional groups of protein, such as wool, with which the flame retardants are especially durable.

In addition, the compounds of the instant invention may be polymerized to afford relatively low molecular weight polymers which possess flame retardant characteristics and are suitable for use in the treatment of textile materials. Likewise, the monomeric compounds of this invention may be copolymerized with olefinically unsaturated compounds such as ethylene, propylene, styrene, butadiene, acrylic acids, acrylonitriles, acrylates, acrylamides, vinyl acetate, vinyl alcohol, vinyl chloride, vinylidene chloride, etc. and mixtures thereof such as acrylonitrile-butadiene-styrene. The copolymers in themselves possess flame retardant properties rendering them suitable for use by incorporation into other polymer blends as well as for direct treatment of a textile material. The polymerization of the monomers of this invention procedes in the presence of a Lewis acid by a cationic mechanism. The copolymerization of the compounds of this invention are readily conducted by conventional techniques employing free radical initiating reagents such as the organic peroxides, azo compounds, and ionizing irradiation.

DETAILED DESCRIPTION OF THE INVENTION

The compounds of this invention are prepared by the reaction sequence:



$$RCN + C_2H_5OH + HCl \longrightarrow \underset{\substack{|\\ OC_2H_5}}{RC} = NH.HCl \qquad (I)$$

$$I + C_2H_5OH \rightarrow \underset{(II)}{RC(OC_2H_5)_3} + NH_4Cl$$

$$3\ II + 2P(OR)_3 + PCl_3 \longrightarrow \underset{(III)}{3(RO)_2\overset{\substack{O\\ \|}}{P}} - \underset{\substack{|\\ CH_3}}{C}(OR)_2 + 3\ RCl$$

$$III \xrightarrow[\Delta]{} (RO)_2\overset{\substack{O\\ \|}}{P}\overset{\substack{CH_2\\ \|}}{C}OR + ROH \text{ or}$$

$$III \xrightarrow[\Delta]{\text{base cat.}} (RO)_2\overset{\substack{O\\ \|}}{P}-\overset{\substack{CH_2\\ \|}}{C}OR + ROH$$

where R is methyl or ethyl.

The production of the ortho acetate type compounds is a conventional organic preparation illustrated by S. M. McElvain et al, J.A.C.S. 64, 1942 pp. 1825–1827. The conversion of the ortho acetate to the dialkyl 1,1-dialkoxyethyl phosphonate (III) is a conventional preparation illustrated by H. Gross et al. J. Prakt Chem. 311 (1969) 571.

The dehydroalkoxylation reaction of the instant invention employed in the preparation of the novel compounds of this invention is a beta elimination of an alcohol from an alpha, alpha, dialkoxy dialkyl phosphonate ester performed generally at a temperature from about 90° to 250°C. with removal of the alcohol as it is formed. It is generally desired to remove the alcohol as rapidly as possible and for this reason the temperatures normally employed are those in the upper range of operability between about 150° to 220° centigrade. The beta elimination reaction may be base catalyzed. Among the base catalysts employed are sodium carbonate, sodium bicarbonate, sodium acetate, sodium methoxide, sodium phenoxide, n-butyl lithium, triethylamine, and the like. Therefore, the base catalysts operable in the process of the instant invention may be generally classified as the alkali metal salts of carbonic acid or lower alkanoic acids, the alkali metal lower alkoxides or phenoxides, the tertiary lower alkylamines and the lower alkyl organo metallic derivatives in which the metal is selected from the Group I, II, III and the transition metals of the Periodic Table as presented in the Handbook of Chemistry and Physics, 43rd Edition, 1961–1962, Chemical Rubber Publishing Co.

As monomers for the production of homo- and copolymers, the alpha-alkoxyvinylphosphonate esters of this invention afford flame retardant properties to the polymer which renders it especially useful in castings, moldings, foams and laminates for use in the construction industry in the form of wall coverings and panels or electric system conduits and castings as well as in the textile industry where flame retardance is often of paramount importance.

EXAMPLE I

190 g. (0.75 mole) diethyl-1,1-(diethoxy)-ethyl phosphonate, 2.5 g sodium carbonate and 2.5 g. hydroquinone was placed in a round bottomed flask. The reaction mixture was heated and over the temperature range 190° to 228°C. ethanol was distilled from the reaction flask. A total of 39 g. distillate was collected in 3 hours. The reaction mixture was cooled and vacuum distilled at 69° to 84°C. under 0.3 millimeters mercury pressure to yield 105.3 g. diethyl ethoxyvinyl phosphonate.

Calculated: C, 46.2; H, 8.2; P, 14.9.

Found: C, 45.2; H, 8.8; P, 14.4.

EXAMPLE 2

198 g. (1.0 mole) dimethyl-1,1(dimethoxy)-ethyl phosphonate, 2.5 g. sodium bicarbonate and 2.5 g. hydroquinone were placed in a round bottomed flask. The reaction mixture was heated and over the temperature range 158° to 200°C. methanol was removed from the reaction flask by distillation. 39 g. distillate was collected in 2.5 hours. After cooling, the reaction mixture was distilled to give 126.4 g. dimethyl methoxyvinyl phosphonate, boiling at 75° to 84°C. under a pressure of 0.6 to 0.9 millimeters of mercury.

Calculated C, 36.2; H, 6.7; P, 18.6.

Found C, 34.9; H, 6.8; P, 18.9.

EXAMPLE 3

In a round bottomed flask fitted with a thermometer, mechanical stirrer, distillation head cooled with dry ice and acetone and a heating mantle was placed 198 g. (1.0 mole) dimethyl-1,1-(dimethoxy)-ethyl phosphonate, 2.5 g. anhydrous sodium acetate and 2.5 g. hydroquinone. The reaction mixture was heated and at about 160°C. methanol was formed and was removed from the reaction vessel by distillation. 39.5 g. distillate was collected in 3.5 hours and during the distillation, the temperature of the reaction mixture increased to 185°C. The reaction mixture was cooled and distilled to yield 110.7 g. dimethyl methoxyvinyl phosphonate, boiling at 69° to 75°C. under a pressure of 0.2 to 0.6 millimeters of mercury.

Calculated C, 36.2; H, 6.7; P, 18.6

Found C, 34.9; H, 7.1; P, 18.5.

EXAMPLE 4

In a round bottomed flask equipped with a thermometer, mechanical stirrer, distillation head cooled with dry ice and acetone and a heating mantle, was placed 127 g. (0.5 mole) diethyl-1,1-(diethoxy)-ethyl phosphonate, 2 g. sodium methoxide and 2.5 g. hydroquinone. The reaction mixture was heated under nitrogen and at about 158°C. ethanol was formed and was removed by distillation. 26.5 g. ethanol was collected over 3.25 hours and during the distillation the temperature of the reaction mixture rose to 210°C. Reaction mixture was cooled and distilled to give 78.3 g. diethyl ethoxyvinyl phosphonate, boiling at 60° to 67°C. under a pressure of 0.2 millimeters mercury, n^{25}_D 1.4410.

Calculated C, 46.2; H, 8.2; P, 14.9.

Found C, 46.0; H, 8.6; P, 14.8.

EXAMPLE 5

198 g. (1.0 mole) dimethyl-1,1-(dimethoxy)-ethyl phosphonate, 2.5 g. sodium phenoxide and 2.5 g. hydroquinone were placed in a round bottomed flask. The reaction mixture was heated under nitrogen and over the temperature range 140° to 200°C. methanol was removed from the reaction vessel by distillation. 42 g. distillate was collected over a period of 5.5 hours. Reactive mixture was cooled and vacuum distilled at 80° to 90°C. under 0.4 to 1.0 millimeters mercury pres-

sure to yield 105 g. dimethyl methoxyvinyl phosphonate, n^{25}_D 1.4434.

Calculated C, 36.2; H, 6.7; P, 18.6.

Found C, 34.0; H, 7.1; P, 18.6.

EXAMPLE 6

Dimethyl-1,1-(dimethoxy)-ethyl phosphonate (198 g. 1.0 mole) and hydroquinone (2.5 g.) was placed in a round bottomed flask fitted with a thermometer, dropping funnel, mechanical stirrer, distillation head and a heating mantle. n-butyl lithium (2 g.) in hexane (20 ml.) was added over 5 minutes to the reaction mixture which was then heated and methanol and hexane was removed by distillation. 54 g. distillate was collected over 3.5 hours and the temperature of the reaction mixture increased during this period of time from 92° to 200°C. After cooling, the reaction mixture was vacuum distilled at 95° to 108°C. under 2.8 to 3.8 millimeters mercury pressure to yield 54 g. dimethyl methoxyvinyl phosphonate, n^{22}_D 1.4420.

Calculated C, 36.2; H, 6.7; P, 18.6.

Found C, 34.8; H, 6.7; P. 18.0.

EXAMPLE 7

In a round bottomed flask fitted with a thermometer, mechanical stirrer, distillation head cooled with dry ice and acetone and a heating mantle, was placed 198 g. (1.0 mole) dimethyl-1,1-(dimethoxy)-ethyl phosphonate, 5 ml. triethylamine and 2.5 g. hydroquinone. The reaction mixture was heated under nitrogen and at about 140°C methanol was formed and was removed by distillation. 36 g. methanol was collected over 2.5 hours and during this time the temperature of the reaction mixture rose to 180°C. The reaction mixture was cooled and vacuum distilled at 90° to 100°C under 0.9 to 2.6 millimeters mercury pressure to give 122.5 g. dimethyl methoxyvinyl phosphonate, n^{25}_D 1.4445.

Calculated C, 36.2; H, 6.7; P, 18.6.

Found C, 34.6; H, 6.9; P, 18.6.

EXAMPLE 8

Dimethyl-1,1-(dimethoxy)-ethyl phosphonate (198 g. 1.0 mole) and hydroquinone (2.5 g) was placed in a round bottomed flask, fitted with a thermometer, mechanical stirrer, distillation head cooled with dry ice and acetone and a heating mantle. The reaction mixture was heated under nitrogen and methanol was removed by distillation as it was formed. 64 g. distillate was collected over 5 hours and the temperature of the reaction mixture increased from 197° to 220°C. The reaction mixture was cooled and vacuum distilled at 74° to 80°C under 0.8 to 1.0 millimeters mercury absolute to yield 98.1 g. dimethyl methoxyvinyl phosphonate n^{25}_D 1.4437.

Calculated C, 36.2; H, 6.7; P, 18.6.

Found C, 34.6; H, 7.0; P, 18.6.

EXAMPLE 9

A sample of rayon staple fiber was immersed in an aqueous solution containing 15 g. sodium hydroxide per 100 g. solution for 10 minutes and then squeezed to about 60% wet pick up and dried at 250°F. for 2 minutes. The sample was then immersed in a solution containing 50 g. diethyl ethoxyvinyl phosphonate and 50 g. methanol for 10 minutes and squeezed to remove excess solution. The sample was then held at 330°F. for 2.5 minutes, then rinsed in hot water and dried. The fiber was twisted tightly and held in a bunsen flame. Upon removal, the material was self-extinguishing. A sample not treated by the procedure described was completely consumed by the bunsen flame.

EXAMPLE 10

A sample of cotton sheeting, 5.0 ounces per square yard was impregnated with an aqueous solution containing 15 g. solium hydroxide per 100 g. of solution and squeezed to about 80% wet pick up. The impregnated fabric was then dried at 250°F for 2 minutes. The resulting fabric was then impregnated with a methanolic solution containing 50 g. diethyl ethoxyvinyl phosphonate per 100 g. of solution and squeezed to about 100% wet weight pick up. This impregnated fabric was cured for 2.5 minutes at 330°F, then washed in hot water and dried. The treated cotton sheeting had a char length of 6.5 inches as measured by AATCC Method 34-1966.

EXAMPLE 11

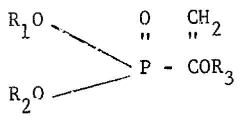
A sample of rayon staple fiber was immersed in a solution of 63 g. dimethyl methoxyvinyl phosphonate, 37 g. maleic anyhydride, 2 g. azo-bis-isobutyronitrile and 100 ml. benzene for 1.5 hours and then squeezed to about 80% wet pick up and held at 75°C for 12 hours. The fiber was twisted tightly and held in a bunsen flame. Upon removal, the material was self-extinguishing. A sample not treated by the procedure described was completely consumed by the bunsen flame.

EXAMPLE 12

A sample of wool bedford cord of approximately 8.0 ounces per square yard was immersed in a solution of 63 g. dimethyl methoxyvinyl phosphonate, 37 g. maleic anhydride, 2 g. azo-bis-isobutyronitrile and 100 ml. benzene for 1.5 hours. After squeezing the fabric to about 80% wet pick up, it was cured at 75°C. for 12 hours. The treated fabric showed an initial char of about 1.0 inches and about 2.0 inches after 5 home washes.

What is claimed is:

1. A process for imparting flame resistance to a textile material comprising combining, from 5 to 40 percent by weight of textile material, a compound of the formula



wherein R_1, R_2 and R_3 are lower alkyl radicals independently containing from 1 to 8 carbon atoms, with a textile material selected from the group consisting of cellulosic material and proteinaceous material.

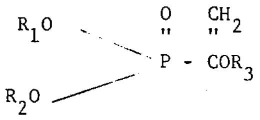
2. The process of claim 1 wherein said compound is diethyl (alpha-ethoxy) vinyl phosphonate.

3. The process of claim 1 wherein said compound is dimethyl (alpha-methoxy) vinyl phosphonate.

4. The process of claim 1 wherein said textile material is selected from the group consisting of rayon, cotton and wool.

5. A composition comprising a textile material selected from the group consisting of a cellulosic material and a proteinaceous material and from 5 to 40 percent,

by weight of textile material, of a compound of the formula



wherein R_1, R_2 and R_3 are lower alkyl radicals independently containing from 1 to 8 carbon atoms.

6. The composition of claim **5** wherein said compound is diethyl (alpha-ethoxy) vinyl phosphonate.

7. The composition of claim **5** wherein said compound is dimethyl (alpha-methoxy) vinyl phosphonate.

8. The composition of claim **5** wherein said textile material is selected from the group consisting of rayon, cotton and wool.

9. The process of claim **1** wherein the textile material is immersed in said compound and thereafter squeezed to about 80% wet pickup.

10. The process of claim **1** wherein the textile is immersed in an aqueous solution of sodium hydroxide, squeezed, dried, and thereafter immersed in said compound.

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