

1

3,817,779

PROCESS FOR IMPARTING FLAME RETARDANCY TO A TEXTILE

Peter Golborn, Lewiston, N.Y., assignor to Hooker
Chemical Corporation, Niagara Falls, N.Y.

No Drawing. Continuation-in-part of application Ser. No.
215,192, Jan. 3, 1972. This application Mar. 1, 1972,
Ser. No. 230,951

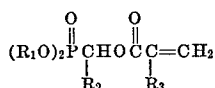
Int. Cl. C09d 1/00

U.S. Cl. 117-136

9 Claims 10

ABSTRACT OF THE DISCLOSURE

Normally flammable textiles are rendered flame retardant by the intimate association therewith of a flame retarding amount of a compound of the formula

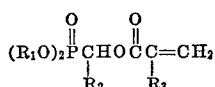


wherein R_1 is lower alkyl of 1 to 4 carbon atoms, R_2 is hydrogen and lower alkyl of 1 to 4 carbon atoms and R_3 is hydrogen and lower alkyl of 1 to 4 carbon atoms.

This is a continuation-in-part of pending application Ser. No. 215,192, filed Jan. 3, 1972.

FIELD OF INVENTION

This invention relates to improvements in rendering flame retardant, normally flammable, fabrics such as cellulosic materials, proteinaceous materials and analogous man-made materials by applying thereto a flame retarding amount of a compound of the formula



wherein R_1 is lower alkyl of 1 to 4 carbon atoms, R_2 is hydrogen and lower alkyl of 1 to 4 carbon atoms and R_3 is hydrogen and lower alkyl of 1 to 4 carbon atoms.

BACKGROUND OF THE INVENTION

Many flame retarding agents and methods of application have been developed in attempts to obtain flame retardant textile materials. For example, mixtures of ammonium dihydrogen orthophosphate or boric acid with borax have been used to retard flame in cellulosic materials. Flame retardant textiles 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 problem 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 as well as deleteriously affecting the hand of the finished product. 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 a cellulosic fabric. The fabric is thereafter 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 affect the hand of the finished product.

2

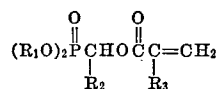
Flame resistance has been imparted to cellulosic materials by esterification of the cellulose with diammonium hydrogen orthophosphate. Products so treated are subjected to metathesis reactions with cations in aqueous solutions during washing, the ammonia cation being displaced by calcium, sodium or magnesium.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

OBJECTS OF THE INVENTION

It is, therefore, a principal object of this invention to provide flame retarding textile fabrics comprising normally flammable cellulosic, proteinaceous or analogous man-made materials.

Another object is to provide a process for treating normally flammable cellulosic, proteinaceous or analogous man-made materials to render them flame retardant.

A particular object is to devise a composition comprising normally flammable cellulosic, proteinaceous or analogous man-made material and an effective flame retarding amount of the compound represented by the formula

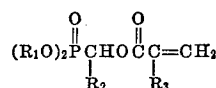


wherein R_1 , R_2 and R_3 are as above described.

These and other objects of the present invention will be obvious from the following description.

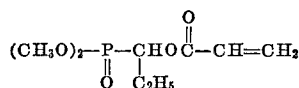
DESCRIPTION OF THE INVENTION

In accordance with this invention, a process is provided for imparting flame retardancy to textile materials by incorporating into or on the textile material a flame retarding amount of one or more novel dialkylphosphonoalkyl acrylates and methacrylates of the formula

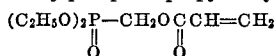


wherein R_1 is lower alkyl of 1 to 4 carbon atoms, R_2 is hydrogen and lower alkyl of 1 to 4 carbon atoms and R_3 is hydrogen and lower alkyl of 1 to 4 carbon atoms. The compounds useful in this invention are prepared by conventional methods for producing dialkylphosphonoalkyl acrylates or methacrylates which generally comprise the steps of (1) adding a dialkylhydrogen phosphite to an aldehyde to form a crude dialkyl-1-hydroxyalkylphosphonate, followed by (2) reacting the latter intermediate with acrylyl or methacryl chloride in the presence of a hydrogen chloride acceptor such as pyridine or sodium carbonate. U.S. Pat. 3,030,347 describes a process, wherein paraformaldehyde, acetaldehyde or propionaldehyde are utilized to form a crude dialkyl (1) hydroxy phosphonate, followed by (2) reacting the latter intermediate with acrylyl or methacryl chloride. Ser. No. 215,192 of which the present application is a continuation-in-part, describes a process for the preparation of diisopropylphosphonomethyl acrylates or methacrylates by reacting the diisopropyl phosphite with aqueous formaldehyde in the presence of a base and thereafter reacting the product of this step with an alkyl acrylate to prepare the diisopropylphosphonomethyl acrylate or methacrylate.

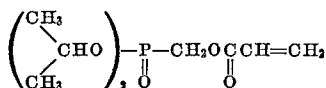
Illustrative examples of compounds useful in the present invention include, but are not limited to, compounds such as:



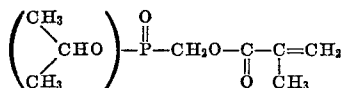
1-dimethylphosphonopropyl acrylate



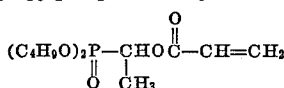
Diethylphosphonomethyl acrylate



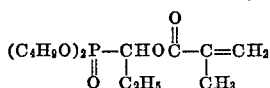
Di-isopropylphosphonomethyl acrylate



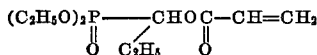
Di-isopropylphosphonomethyl methacrylate



1-dibutylphosphonoethyl acrylate



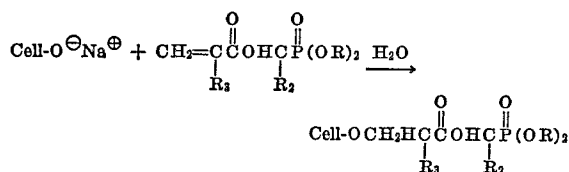
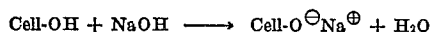
1-dibutylphosphonopropyl methacrylate



1-diethylphosphonopropyl acrylate

The compounds of this invention may be applied to textile materials by conventional finishing techniques such as by thermal or radiation induced pad curing so as to incorporate into the textile a flame retardant amount thereof. The compounds of this invention have advantages over the flame retardant agents of the prior art in that they may be used on a variety of textile materials of different chemical compositions, and they may be applied by a variety of methods. They may be applied to materials in either the fiber or fabric form to give flame retarding materials with minimum detectable physical changes in the quality or hand of the textile material.

Cellulosic textile materials may be made flame retardant by way of a variety of methods. Typically, the cellulose may be treated with aqueous NaOH solutions to produce an anionic cellulosic form which will add to the acrylate of this invention. Theoretically, the reaction is by the addition of the cellulose alkoxide to the unsaturated carbonyl compound of this invention by the following manner.



Applicant however, does not wish to be bound by this theory, intending to protect the claimed invention in whatever form or by whatever mechanism it takes place.

Generally, when treating cellulosic materials with aqueous NaOH, samples of the material are immersed in a 5 to about 30% by weight NaOH solution for about 1 to about 20 minutes and squeezed to a wet pick up of about 60 to about 80%, based upon the weight of cellulosic material, using a two role laboratory padder at about 60 lbs. per square in gauge pressure. The samples

are then dried to about 200 to about 275° Fahrenheit, for about 1 to about 5 minutes in a circulating air oven. The samples are then immersed in an aqueous solution of the flame retardant compound of this invention (20 to 70% by weight) for about 1 to about 20 minutes and squeezed to about 60 to about 120% wet weight pick-up, based upon the weight of textile. The materials are then cured in a circulating air oven at about 150 to about 450° Fahrenheit or preferably from about 275 to about 375° Fahrenheit for about 1 to about 10 minutes to promote reaction. Thereafter the samples are washed in hot water to remove residual unreacted material and dried.

The products may also be grafted to cellulose by way of a free radical source generated on the cellulose backbone by way of electron beam irradiation. Cellulose is known to form stable free radicals under the influence of this type of irradiation.

The materials to be grafted are immersed in a solution of the dialkyl phosphonoalkyl acrylated methylacrylate and squeezed in a two role laboratory padder at about 60 pounds per square inch gauge pressure to a wet weight pickup of about 70 to about 120%. The materials are then passed under an electron beam to give an average dose of 1.66 megarads to induce grafting. The samples are thereafter boiled in water to remove any homopolymer of the acrylate or methacrylate which may have formed and dried. The finished textile product, whether subjected to additional finishing treatments or not, exhibits good flame resistant properties with minimum detectable physical changes in the quality or hand of the textile material.

The flame retardant agents of this invention may be applied to various textiles such as cellulosic materials, proteinaceous materials and blends of cellulosic or proteinaceous materials with polyethylene terephthalate and analogous man made fibers. By cellulosic materials, applicant intends to embrace cotton, rayon, paper, regenerated cellulose and cellulose derivatives which retain a cellulose backbone of at least one hydroxy substituent per repeating glucose unit. By proteinaceous material applicant intends to embrace those textile materials comprising the functional groups of proteins such as the various animal wools, hairs and furs. Of special interest is the applicability of fire retardant agents of the instant invention to analogous man made fibers such as blends of cotton and polyethylene terephthalate, in textile fabrics and fibers to provide a uniform, flame retardant finish.

The following examples are presented for purposes of illustration rather than a limitation of the scope of the invention. In each of the examples the process steps were performed as follows, except where a specific method is otherwise indicated. Padding was done on a standard two role laboratory padder at a gauge pressure sufficient to obtain about 100% wet weight pick-up. Drying was done in a standard home type automatic circulating air tumble dryer. Flammability testing was done in accordance with (American Association of Textile Chemists and Colorists) Test Method 34-1969, the standard vertical char method. Therein 2 3/4 in. x 10 in. fabric test specimens are exposed to a controlled burner flame under controlled conditions for a period of 12.0 seconds and 3.0 seconds. The charred specimens are thereafter subjected to controlled tearing tests, using tabulated weights, and the average tear length is measured as representing the char length of the flame retardant treated fabric.

The finished samples for testing have a flame retardant add on of about 5 to about 40% by weight preferably from about 10 to about 25% by weight of substrate.

In each of the examples the indication of a char distance for the textile indicates self-extinguishment at that point. For comparison purposes the corresponding non-treated textile would be completely consumed.

EXAMPLE I

A sample of 5 oz. per square yard, cotton sheeting, was immersed in a solution containing 25 grams of 1-diethyl-

5

phosphonoethylacrylate and 75 grams of methanol. The sample was padded to about 100% wet pick up, air dried for about 24 hours and thereafter tested by AATCC Method 34-1969 for charring. The treated fabric had a calculated char length of 5.5 inches.

EXAMPLE II

A sample of 5.0 ounces per square yard, cotton sheeting was immersed in a 15% aqueous sodium hydroxide solution for about 10 minutes, padded to about 60% wet pick up then circulating air oven dried at about 250° Fahrenheit. The sample was then immersed for about 10 minutes in an aqueous solution of 1-diethylphosphonoethyl acrylate containing about 40% by weight acrylate, padded to about 75% wet pick up and then cured in a circulating air oven, at about 320° Fahrenheit, for about five minutes. Thereafter, the sample was washed with hot water in a home type automatic washer and tumble dried. The treated sample, when tested by AATCC Method 34-1969 for charring was found to have a char length of 6.5 inches.

EXAMPLE III

A sample of 5.0 ounces per square yard of cotton sheeting was immersed in a 15% aqueous solution of sodium hydroxide for ten minutes, padded to about 60% wet pick up and thereafter dried in a circulating air oven at about 250° Fahrenheit. The sample was then immersed for ten minutes in a solution containing 200 grams of di-isopropylphosphonomethyl acrylate and 200 grams of methanol, cured in a circulating air oven at about 325° Fahrenheit for about 3 minutes, washed with hot water and tumble dried. The sample was then tested by AATCC Method 34-1969 for charring and was found to have a char length of 4.8 inches.

In a similar manner a sample of 5.0 ounces per square yard of cotton sheeting was treated with di-isopropylphosphonomethyl methacrylate. After curing, washing and drying, testing by AATCC Method 34-1969 indicated a char length of 6.7 inches.

EXAMPLE IV

A sample, of 3.5 ounces per square yard, of a 75/25 blend of cotton to polyethylene terephthalate fabric was immersed in a 15% aqueous sodium hydroxide solution for about 10 minutes, padded to about 60% wet pick up, then dried in a circulating air oven at about 250° Fahrenheit. The sample was then immersed in a solution containing 200 grams of di-isopropylphosphonomethyl acrylate and 200 grams of methanol for about 10 minutes, and padded to about 75% wet pick up. The fabric was thereafter cured in a circulating air oven at about 325° Fahrenheit for about 3 minutes, washed with hot water and tumble dried. Testing by AATCC Method 34-1969 indicated a char length of 8.0 inches.

EXAMPLE V

A sample of wool bedford cord of approximately 8.0 ounces per square yard was immersed for ten minutes in a solution containing 200 grams of di-isopropylphosphonomethyl acrylate and 200 grams of methanol. The fabric was then padded to about 100% wet pick up and thereafter cured in a circulating air oven at about 325° Fahrenheit for 3 minutes. The so-cured product was then hot water washed and tumble dried. Testing by AATCC Method 34-1969 indicated a char length of 0.7 inch. The fabric sample was then subjected to 5 hot water wash cycles in an automatic home type washer and tumble dried. Testing by AATCC Method 34-1969 indicated a char length of 1.5 inches.

EXAMPLE VI

A sample of wool bedford cord of approximately 8.0 ounces per square yard was immersed for ten minutes in a solution containing 200 grams of 1-di-isopropylphosphonoethyl acrylate and 200 grams of methanol, and thereafter treated in accordance with Example V. Testing under

6

AATCC Method 34-1969, after the first hot water wash and tumble dry indicated char length of 1.0 inches. AATCC Method 34-1969 testing after five automatic home type washing cycles and tumble drying indicated a char length of 2.6 inches.

EXAMPLE VII

A sample of rayon staple fiber was immersed in an aqueous solution containing 15 grams of sodium hydroxide per 100 grams of solution for ten minutes and padded to about 60% wet weight pick up. The sample was then dried in a circulating air oven at 250° Fahrenheit for 3 minutes, and thereafter immersed in a methanolic solution containing 200 grams of di-isopropylphosphonomethyl acrylate per 400 grams of solution for about ten minutes. The treated fiber was then padded to remove excess solution and cured in a circulating air oven at about 325° Fahrenheit for three minutes, rinsed in hot water and tumble dried. The fiber was then twisted tightly and held in a bunsen burner flame. Upon removal, the material was self extinguishing. An untreated sample of the rayon staple fiber, twisted tightly and held in the same bunsen burner flame, was completely consumed thereby.

EXAMPLE VIII

A sample of rayon staple fiber was immersed in an aqueous solution containing 15 grams of sodium hydroxide per 100 grams of solution for ten minutes, thereafter padded to about 60% wet weight pick up and dried in a circulating air oven at about 250° Fahrenheit for about 3 minutes. The sample was then immersed in a methanolic solution containing 50 grams of 1-di-isopropylphosphonomethyl acrylate per 100 grams of solution for about 10 minutes and thereafter treated in accordance with Example VII. After curing washing and drying the fiber was twisted tightly and held in a bunsen burner flame. Upon removal from the flame, the material was self extinguishing. A sample of untreated rayon staple fiber was twisted tightly and held in the bunsen burner flame, was completely consumed by the flame.

EXAMPLE IX

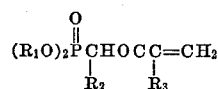
A sample of 5.0 ounces per square yard of cotton sheeting was immersed in a solution containing 60 grams of di-isopropylphosphonomethyl acrylate per 100 grams of methanol for 10 minutes, then padded to about 70% wet pick up. The thus treated sheeting was then exposed to ionizing radiation to an irradiation level of 1.66 megarads. The sample was thereafter boiled for about 0.5 hours in water, then about 0.5 hours in hexane and thereafter tumble dried to about 22.5% weight add on. The sample was then tested by AATCC Method 34-1969 and found to have a char length of 6.5 inches.

EXAMPLE X

A sample of 5.0 ounces per square yard of cotton sheeting was immersed in a solution containing 40 grams of di-isopropylphosphonomethyl acrylate, 60 grams of N-methylolacrylamide and 100 grams of methanol. The sample was padded to about 70% wet weight pick up and irradiated as in Example IX to a level of 1.66 megarads. The sample was then boiled for about 0.5 hours in water, about 0.5 hours in hexane and thereafter tumble dried. Testing by AATCC Method 34-1969 indicated a char length of 5.5 hours.

I claim:

1. A process for imparting flame retardancy to a textile selected from the group consisting of cellulosic material, proteinaceous material and blends thereof with polyethylene terephthalate which comprises treating said textile with an aqueous alkali metal hydroxide solution, contacting the thus treated textile with a compound of the formula:



7

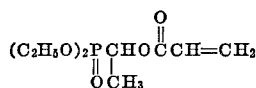
wherein R₁ is lower alkyl of 1 to 4 carbon atoms, R₂ is hydrogen and lower alkyl of 1 to 4 carbon atoms and R₃ is hydrogen and lower alkyl of 1 to 4 carbon atoms, and thereafter drying and curing the thus treated textile.

2. The process of claim 1 in which the amount of flame retardant compound add on is from about 5 to about 40% by weight of textile material.

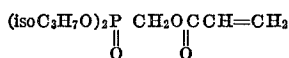
3. The process of claim 1 in which the amount of flame retardant compound is from about 10 to about 25 percent by weight of textile material.

4. The process of claim 1 in which said textile material is a blend of cotton and polyethylene terephthalate.

5. The process of claim 2 wherein the flame retardant compound is of the formula



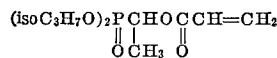
6. The process of claim 2 wherein the flame retardant compound is of the formula



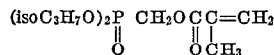
7. The process of claim 2 wherein the flame retardant

8

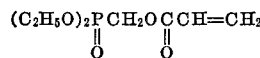
compound is of the formula



8. The process of claim 2 wherein the flame retardant compound is of the formula



9. The process of claim 2 wherein the flame retardant compound is of the formula



References Cited

UNITED STATES PATENTS

2,867,597	1/1959	Costello et al.	117—136 X
2,934,554	4/1960	Lane	117—136 X
2,934,555	4/1960	O'Brien et al.	117—136 X

MICHAEL SOFOCLEOUS, Primary Examiner

T. G. DAVIS, Assistant Examiner

U.S. Cl. X.R.

117—93.31, 118, 138.8 F, 141, 143 R

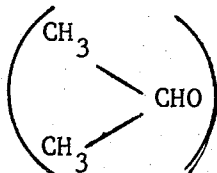
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,817,779 Dated June 18, 1974

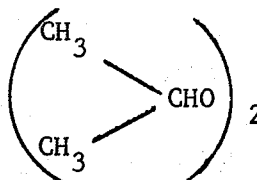
Inventor(s) Peter Golborn

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

Column 1, line 27, after filed Jan. 3, 1972 insert --now U. S. Patent 3,780,146. Column 3, line 19, that portion of the formula reading



should read



Column 3, line 74, "two role" should read --two roll--. Column 4, line 6, "120/" should read --120%--; line 20, "role" should read --roll--; line 51, "preformed" should read --performed--; line 52, "role" should read --roll--; line 63, "representaing" should read --representing--.

Signed and sealed this 8th day of October 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents