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[54] **ALLYL
2-CARBAMOYLALKYLPHOSPHONATES
FLAME RETARDANTS**

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Related U.S. Application Data

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No. 3,762,865.

[52] U.S. Cl. **252/8.1, 260/606.5 P, 8/116 P,**
106/15 FP, 117/136

[51] Int. Cl. **B27k 3/00**

[58] Field of Search **8/116 P; 252/8.1;**
106/15 FP; 117/136; 260/606.5 P

[56] **References Cited**

UNITED STATES PATENTS

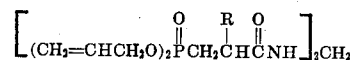
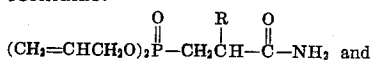
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Primary Examiner—Stephen J. Lechert, Jr.

[57] **ABSTRACT**

The present invention provides a process for flame retarding textiles, paper and other flammable, solid substrates by applying to the substrate at least one allyl 2-carbamoylalkylphosphonate corresponding to the formulae:



where R is a hydrogen or methyl radical, whereupon the phosphonate is cured by free radical initiation so as to form an insoluble, fire retardant resinous finish.

6 Claims, No Drawings

ALLYL 2-CARBAMOYLALKYLPHOSPHONATES FLAME RETARDANTS

This is a division of application Ser. No. 139,222 filed Apr. 30, 1971, now U.S. Pat. No. 3,762,865.

BACKGROUND OF THE INVENTION

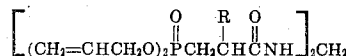
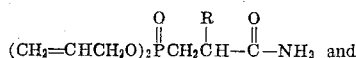
As shown, for example, in U.S. Pat. No. 3,374,292, it is known in the textile and paper finishing art that cellulosic fabrics can be flame retarded by applying compounds such as N-methylol 2-carbamoylethylphosphonates which are then cured on the substrate by means of acid catalysts. However, there are several limitations in this type of process including the fact that the resulting finish is ineffective for flame retarding non-cellulosic fabrics and is also unsatisfactory for blends of cellulosic and synthetic fibers which contain a major proportion of non-cellulosic fibers. In addition, such finishes require the use of acid catalysts at elevated temperatures in the range of about 150°-160°F. which leads to some acid catalyzed or thermal degradation of cellulosic fabrics with a resultant loss of their physical properties such as their tear strength. Moreover, because of the elevated temperatures required for their application, sublimation of these phosphonates, or of their decomposition products, can occur causing sticky deposits as well as drippage in the curing oven which often leads to spotting of the cloth and which may require shutting down in order to permit cleaning of the equipment. And, finally, the evolution of formaldehyde vapors from these phosphonates creates an unpleasant atmospheric pollutant.

As is described in the U.S. Pat. Nos. 2,848,507 and 2,867,548, it has also been known in the textile finishing art to use certain diallyl phosphorus compounds such, for example, as diallyl 2-cyanoethyl phosphonate, in preparing flame retarding textile finishes. However, the successful use of such compounds requires their pre-polymerization which complicates the process and necessitates the use of specific organic solvents with a resultant high cost which is uneconomical for large scale commercial textile finishing. Furthermore, these systems require high add-ons, i.e. the deposition of high concentrations of reagents, with a resultant poor "hand," i.e. unfavorable tactile qualities, stiffness and harsh surface characteristics, in the resulting treated fabrics. Because of these problems, these diallyl phosphonate finishes have only had limited experimental use, particularly with heavy weight military fabrics.

Thus, it is the prime object of this invention to provide a novel flame retardant finishing process which is suitable for use with textiles made from either natural or synthetic fibers as well as with blends of each of the latter fiber types. It is another object of this invention to provide a flame retardant finishing process for various other flammable, solid substrates such, for example as paper, wood, batting and rope, which are capable of being impregnated and/or coated with a flame retardant, resinous finish. It is a further object to provide a flame retardant textile finishing process which is operable at ambient or moderately elevated temperatures and which can employ aqueous systems thereby avoiding fabric degradation and the need for expensive and troublesome organic solvents. Another object is to provide a process for flame retarding textiles which is operable with low add-ons of the flame retardant finish thereby providing a pleasing hand to the finished fabrics.

TECHNICAL DISCLOSURE OF THE INVENTION

This process comprises the application to a textile, or other flammable solid substrate, followed by curing, of an effective amount of at least one flame retarding allyl 2-carbamoylalkylphosphonate corresponding to the formulae:



where R is a hydrogen or methyl radical. Exemplary of those compounds are diallyl 2-carbamoylethylphosphonate, diallyl 2-carbamoylisopropylphosphonate, N,N'-methylenebis(diallyl 2-carbamoylethylphosphonate) and N,N'-methylenebis(diallyl 2-carbamoylisopropylphosphonate). These flame retardants are applied to a fabric or other substrate at a concentration of from about 5 to 40 percent, as calculated on the dry weight of the substrate, and are thereafter cured, i.e. polymerized, so as to form an insoluble, fire retardant resinous finish by free radical initiation using either a chemical initiator or actinic radiation in order to induce the desired reaction.

The diallyl compounds used as flame retardants in the process of this invention, i.e. diallyl 2-carbamoylethylphosphonate and diallyl 2-carbamoylisopropylphosphonate, are known and may be readily prepared by the addition of diallyl phosphonate to either acrylamide or methacrylamide as described, for example, in U.S. Pat. No. 2,754,320, or by the addition of diallyl phosphonate to an alkyl ester of acrylic or methacrylic followed by ammonolysis. These diallyl compounds are crystalline, colorless solids of negligible odor which are soluble in many organic solvents as well as in water.

On the other hand, the above listed tetraallyl compounds, i.e. N,N'-methylenebis(diallyl 2-carbamoylethylphosphonate) and N,N'-methylenebis(diallyl 2-carbamoylisopropylphosphonate), are new compositions of matter which are prepared by means of the base catalyzed addition of at least two moles of diallyl phosphonate per mole of either N,N'-methylenebisacrylamide or N,N'-methylenebismethacrylamide. In conducting this reaction, the diallyl phosphonate and the N,N'-methylenebisacrylamide or N,N'-methylenebismethacrylamide may be combined in the absence of a solvent or, if desired, they may be slurried in a suitable non-interfering solvent such, for example, as methylene chloride, chloroform, carbon tetrachloride, benzene, toluene, acetone or dioxane. The selected base catalyst, which can be sodium methylate, an alkali metal hydroxide or any other suitable basic material, is then introduced into the reaction mixture at a concentration of from about 0.001 to 10 percent, as based upon the diallyl phosphonate, resulting in an exothermic reaction which may cause the mixture to boil. Trace solids are removed from the resulting reaction mixture by filtration yielding the tetraallyl compound in the form of a viscous syrup having a substantial degree of solubility in water and organic solvents.

In addition to their use in the flame retardant finishing application described herein, both the tetraallyl and the diallyl 2-carbamoylalkylphosphonates can be employed as monomers in the preparation of flame retardant, thermoset homo- and copolymers which can be used in a variety of applications including, for example,

as flame retardant additives for flammable polymers and also as intermediates for preparing the flame retardant additives and monomers such as those which can be made by the addition of bromine to all or part of the double bonds of these compounds. For purposes of brevity, the novel tetraallyl 2-carbamoylalkylphosphonates as well as the diallyl 2-carbamoylalkylphosphonates of the prior art will, in this disclosure, be collectively referred to as the "allyl phosphonates."

While the use of aqueous solutions comprises the most economical means of application for these allyl phosphonate flame retardants, they may also, if desired, be applied to a normally flammable substrate while dissolved in any of the organic solvents commonly used in the solvent finishing of textiles including, for example, trichloroethylene, dichloroethane, trichloroethane, perchloroethylene, methylene chloride, etc. and mixtures thereof. The solutions, either aqueous or organic solvent, containing one or more of the selected allyl phosphonates may be applied to textiles or other substrates by the use of any desired procedure. It is merely necessary to have the diallyl phosphonate evenly absorbed throughout the mass of the textile, or other substrate, and/or to apply it to at least one surface thereof by means of any convenient procedure. Thus, it may be applied by being sprayed onto one or both surfaces of the substrate or, as is more frequently the case, the substrate may be passed or padded through the solution while the latter is being held in a tank or other suitable container. Such a process is commonly referred to as a "padding technique" with the solution being referred to as a "padding bath" or "padding solution."

The concentration of the allyl phosphonate within the padding bath, or other applicable solution, will be dependent upon a number of factors including, in the case of textile substrates, the nature of the fibers which comprise the textile, the weight and weave of the textile, the degree of flameproofing that is desired in the finished textile, as well as other technical and economic considerations known and understood by those skilled in the art. However, it is generally desirable that the padding bath should contain an amount of the phosphonate such that when the wet uptake is reduced to a dry deposit upon the textile or other substrate, the treated substrate will contain from about 5 to 40 percent of the allyl phosphonate, as based upon the dry weight of the substrate. Again, it is to be stressed that the latter limits are merely illustrative and may be varied so as to provide a finished article having any desired degree of flame retardancy.

The thus applied allyl phosphonate may be cured in the wet state or it may be completely or, most preferably, partially dried before curing. The mode of curing in accordance with the process of the invention involves the use of a free radical initiated reaction in order to induce the double bonds, i.e. the ethylenic unsaturation, of the allyl groups present in these compounds to polymerize intermolecularly so as to form a crosslinked, insoluble resin in and/or on the individual fibers, or other structural elements, which comprise the textile or other substrate.

Free radical initiation of the desired polymerization reaction may be induced either by the use of those chemical catalysts known as free radical initiators or by the use of the actinic radiation. Suitable free radical catalysts encompass peroxygen compounds, which may

be used as part of a so-called redox system which contain a chemical reducing agent in addition to the peroxygen compound, and azo compounds. Examples of suitable peroxygen catalyst are hydrogen peroxide, which is often used in conjunction with ferrous salts; ammonium, sodium or potassium persulfate; t-butyl hydroperoxide; benzoyl peroxide; lauroyl peroxide; dicumyl peroxide; cumene hydroperoxide; t-butyl peroxyphosphate; methyl ethyl ketone peroxide; caprylyl peroxide and acetyl peroxide. Examples of suitable azo catalysts include azobisisobutyronitrile and azobisisovaleronitrile. These catalysts should be used in an effective amount in the range of from about 0.01 to 5 percent, by weight, of the allyl phosphonate flame retardant; the precise amount required being dependent upon the tightness of the cure, i.e. the degree of crosslinking, which is required as well as the extent to which free radical, chain inhibiting substances such as oxygen have been excluded from the system.

Actinic radiation encompasses high energy protons and other particles capable of initiating free radical reactions including ultraviolet light, x-rays, gamma rays, alpha rays, beta rays, i.e. electron beam radiation, and plasma, i.e. highly ionized atoms in the vapor state. A preferred source of actinic radiation involves the use of an electron beam, i.e. beta radiation, since equipment adaptable for textile and paper mill use is readily available and is eminently suited for rapid, continuous processing. In any event, regardless of the type of actinic radiation that is used, it should be applied in an effective dosage in the range of from about 0.1-10 megarads; the exact dosage being dependent on the tightness of cure required, the amount of inhibitors present and the geometry and nature of the substrate.

Where a cure is induced by the use of a free radical catalyst, the selected catalyst is generally activated by heating up to about 200°C. but, preferably, in the range of from about 60° to 165°C. so as to minimize any thermal damage to the substrate. Alternatively, the catalyst can be activated, even at ambient temperatures, by applying a reducing agent to the textile or other substrate either before or after applying the flame retardant reagent and catalyst. Suitable reducing agents include sulfur dioxide, ferrous salts, such as the halides and sulfates, as well as sulfurous, phosphorous, or hypophosphorous acids and their water soluble salts such, for example, as sodium bisulfite, sodium phosphite and sodium hypophosphite. The catalyst may also be activated by actinic radiation.

When actinic radiation is used, either alone or in combination with a free radical catalyst, it is only necessary to expose the substrate to a beam from a radiation source. If desired, this can be done at ambient temperature thus sparing the substrate from thermal damage. The exposure can be conveniently conducted by passing the substrate through the beam which may be produced, for example, by a bank of ultraviolet lamps, corona-discharge points, a cobalt-60 source, an X-ray source or an electron beam source. Reasonably homogeneous radiation flux is desirable where an electron beam is used, thus the beam can be transversely scanned at a rapid rate across the substrate so as to evenly irradiate all points thereon. If desired, a suitable mechanical arrangement of rollers can be employed so that the substrate can be made to repeatedly pass through the radiation field thereby facilitating more

complete use of the available radiation flux while also obtaining more uniform irradiation.

The use of radiation initiation does not generally require the use of a chemical activator. However, the efficiency of the radiation can frequently be improved by use of such an activator. Suitable activators for this purpose include ketones, such as acetone or benzoin; polycyclic hydrocarbons, such as polyphenyl; and, azo compounds such as azobisisobutyronitrile. Where an electron beam is used, the application of about 0.1–10 megarads, at a voltage sufficient to substantially penetrate the substrate to the depth to which the flame retardant polymer is to be formed, generally suffices to effect the desired cure.

The resulting cure, or polymerization, of the allyl phosphonate which is induced by either a catalyst and/or actinic radiation generally takes place on the surface and within the body of the fibers, or other structural elements, which comprise the substrate. Moreover, in some cases the resulting polymer network may be grafted, or chemically bonded, onto the fiber molecules of the textile or other substrate. However, such grafting is not crucial to the attainment of a durable, flame retardant finish.

The irradiation of the substrate is usually carried out subsequent to the application of the allyl phosphonate although, in the case of cellulosic fibers, which can be irradiated so as to form stable, long lived free radical sites, the allyl compound can be applied subsequent to irradiation whereupon it will proceed to cure.

The process of this invention may, if desired, include the use of other free radical curable, i.e. polymerizable, comonomers along with the selected allyl phosphonate as a means of achieving variations in the properties of the resulting treated textiles. Thus, suitable optional comonomers for use in conjunction with the allyl phosphonates include:

1. Monomers containing an amide nitrogen such as acrylamide, methacrylamide, N-methylolacrylamide, diacetonylacrylamide, methylenebisacrylamide, triacryloylhexahydrotriazine, N-vinylpyrrolidone and cellulose-grafted N-methylolacrylamide, the use of the latter monomer being disclosed in U.S. Pat. No. 3,434,161. The use of these amide nitrogen containing comonomers at a concentration of about 0.1–6 moles per mole of the allyl phosphonate, permits a more economical finish, particularly with cellulosic fibers, since less of the more costly phosphonate monomer needs to be used in order to achieve a given level of flame retardancy.

2. Monomers containing more than one polymerizable double bond such, for example, as the polyol polyacrylates or methacrylates, the glycol diacrylates, the glycol dimethacrylates, methylenebisacrylamide, triacryloylhexahydrotriazine, triallylphosphonate, diallyl allylphosphonate and triallyl cyanurate. By using this class of comonomers, the crosslink density of the resulting finish can be increased thereby enhancing its durability with respect to wear and laundering.

3. Monomers contributing to flame retardancy, i.e. monomers having phosphorus, bromine or chlorine atoms in their molecules including, for example, vinyl and vinylidene halides such as vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene bromide and vinylidene chlorobromide; chloroprene; triallyl phosphate; diallyl allylphosphonate; diallyl cyanoethylphosphonate; diallyl carboxyethylphosphonate; dialkyl

vinylphosphonates such as diethyl vinylphosphonate, bis(2-chloroethyl) vinylphosphonate or its polycondensation products; and, in general all of the unsaturated phosphonate monomers disclosed in my copending applications Ser. Nos. 23,493 (now abandoned) and 23,499 (now U.S. Pat. No. 3,695,925, issued Oct. 3, 1973) both filed Mar. 27, 1970. Other suitable flame retardant comonomers are the compounds made by base catalyzed addition of 1 to 2 moles of dialkyl phosphite and/or 1 to 3 moles of diallyl phosphite to the double bonds of triacryloylhexahydrotriazine. When utilized in the process of this invention, these optional comonomers should be present in the system in a concentration of up to about 10 percent, by weight, of the diallyl phosphonate.

It should be noted, at this point, that the use of the term "crosslinked" in describing the cured, fire retardant resins resulting from the polymerization of the selected allyl phosphonate in the finishing process of this invention will indicate to those skilled in the art that these resins possess a highly intermeshed, three-dimensional configuration or network rather than a simple linear or branched structure of the type found in non-crosslinked copolymers. Thus, such crosslinked polymers may be further characterized by the fact that they will not lose more than about 20 percent of their total weight upon being extracted with methanol in a Soxhlet extractor. Moreover, as used in this disclosure, the term "fire retardant" is intended to refer to that particular property of a material which provides it with a degree of resistance to ignition and burning. Thus, a fire or flame retardant textile, paper or other solid substrate is one which has a low level of flammability and flame spread. This property may be conveniently evaluated by means of any of the standard flame retardancy tests.

In contrast to the known diallyl 2-cyanoethyl phosphonate finishes, pre-polymerization of the above described allyl phosphonates is not necessary in the process of this invention. However, it is within the purview of this process to permit such pre-polymerization for the purpose of permitting extremely rapid cures of the flame retardant finish on the textile or other substrate since some of the polymer links will have been formed prior to its application to the cloth. Advantageously, pre-polymers of these allyl phosphonates can be prepared without losing the solubility in water which is displayed by the unpolymerized phosphonates by simply limiting the extent of the pre-polymerization so that it does not exceed the gel point. With any given catalyst system, this can be readily determined by a preliminary experiment to define the required heating time and temperature prior to preparing the treating bath for the full-scale finishing operation. However, in general, in preparing these pre-polyomers it may be noted that the solution of the allyl phosphonate should be heated until its viscosity has increased by about 50–500 percent with heating being halted at the first appearance of cloudiness. Moreover, it is to be noted that the novel tetraallyl phosphonates of this invention have an advantage over the diallyl phosphonates since they act like pre-polymers in the sense of being able to cure extremely rapidly to a thermoset condition using amounts of initiator or of radiation which are only about half (or less) of those required with the diallyl compounds.

The process of this invention is compatible with a wide variety of other textile finishing operations which

can be carried out prior, simultaneous with, or subsequent to the process of the invention. These other operations include application of durable press, softening, antistatic, abrasion resistance, water-repellent, soil-release, and antimicrobial finishes, as well as bleaching, dyeing, printing, flocking, and texturing.

Thus, the finishing formulations of the invention may also optionally contain other types of ingredients known in the textile finishing art. For example, water and soil repellents, optical brighteners and colorants, softening agents such as polyethylene emulsions, hand-modifying agents, buffering agents, pH-controlling agents which may be acidic or basic, emulsified waxes, chlorinated paraffins, polyvinyl chloride, polyvinylidene chloride, homo- and copolymers of the alkyl acrylates and other resinous finishing agents may be added in conjunction with the finishing agents of the invention. And, where an extremely high degree of flame retardance is required, it is also possible to employ systems containing antimony oxide, a resinous binder, particularly one containing chloride such as a chlorinated paraffin of polyvinyl chloride, along with the allyl phosphonates required in the process of this invention. Moreover, in treating wood and paper substrates, the fire retardant finishes of this invention may be applied along with and as part of an aminoplastic binder resin. And, when used for finishing paper, these allyl phosphonates can be used in conjunction with any of the various adhesives, sizes, wet strength additives and other materials which are ordinarily employed in the paper finishing art.

A hitherto unmentioned advantage of the process of this invention over prior art flame retardant finishing process resides in the fact that the application of the finish does not depend upon the presence in the system of compounds containing readily broken $-N-CH_2-$ or $-O-CH_2-$ linkages, thereby permitting high levels of durability to be achieved in the resulting flame retardant finishes, including durability to acidic "laundry sour" which strip the prior art aminoplast finishes from the textile.

All types of textiles may be treated by means of the process of this invention so as to provide them with durable, fire retardant finishes. Thus, one may treat textiles derived from natural fibers such as cotton, wool, silk, sisal, jute, hemp and linen, wood and from synthetic fibers including nylon and other polyamides; polyolefins such as polypropylene; polyesters such as polyethylene terephthalate; cellulose fibers such as rayon, cellulose acetate and triacetate; fiber glass (which is flammable when coated with organic sizing agents); acrylics and modacrylics, i.e. fibers based on acrylonitrile copolymers; saran fibers, i.e. fibers based on vinylidene chloride copolymers; rubber based fibers; spandex fibers, i.e. fibers based on a segmented polyurethane; vinyl fibers, i.e. fibers based on vinyl alcohol copolymers; vinyon fibers, i.e. fibers based on vinyl chloride copolymers and, metallic fibers. Textiles derived from blends of any of the above listed natural and/or synthetic fibers may also be treated by means of the process of this invention.

As used in this disclosure, the term "textile" or "textiles" is meant to encompass woven or knitted fabrics as well as non-woven fabrics which consist of continuous or discontinuous fibers bonded so as to form a fabric by mechanical entanglement, thermal interfiber bonding or by use of adhesive or bonding substances.

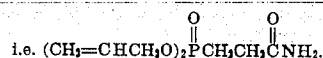
Such non-woven fabrics may contain a certain percentage, up to 100 percent, of wood pulp as well as conventional textile fibers in which case part of the bonding process is achieved by means of hydrogen bonding between the cellulosic pulp fibers. In non-woven fabrics, the finishing agents of this invention can serve not only as flame retardant finishes but can also contribute to the interfiber bonding mechanism by serving as all or part of the adhesive or bonding resin component. This dual role can also be played by the finishing agents of this invention in fabric laminates where the finishing agent can at the same time serve as the interlaminar bonding agent and as the flame retardant. In both of these systems, i.e. non-woven fabrics and laminated fabrics, the finishing agents of this invention can also be blended with the usual bonding agents such, for example, as acrylic emulsion polymers, vinyl acetate homo- and copolymer emulsions, styrenebutadiene rubber emulsions, urethane resin emulsions, polyvinyl chloride emulsions, vinyl chloride-alkyl acrylate copolymer emulsions, polyacrylates modified by vinylcarboxylic acid comonomers and the like.

It should also be noted, at this point, that in addition to being used to provide flame retardant finishes for textiles, the above described allyl phosphonates can also be employed for the flameproofing of a wide variety of polymeric substrates such as cellulose in the form of paper, wood, plywood, chipboard, jute, batting and the like; urethane foams, coatings, and elastomers; aminoplast resins and phenolic resins as well as their composites with paper, wood flour and the like; alkyd coatings and molding resins; and, paints and varnishes derived from natural or synthetic resins.

The following examples will further illustrate the embodiment of this invention. In these examples all parts given are by weight unless otherwise noted.

EXAMPLE I

This example illustrates the preparation of diallyl 2-carbamoylethylphosphonate,



To a stirred mixture of 162 g. of diallyl phosphonate and 71 g. of acrylamide, there is slowly added a 4 percent, by weight, solution of sodium in allyl alcohol. The mixture is cooled during and subsequent to its preparation so as to maintain its temperature below 65°C. When no further temperature rise occurs, the reaction mixture proceeds to form a solid, m.p. 51.2°C., the infra-red spectrum of which shows no P-H band. The nuclear magnetic resonance spectrum shows protons characteristic of $P-CH_2CH_2C(=O)-$ (δ 2.33), CH'_2-O-P (δ 4.5), $CH_2=CH-$ (δ 5.6) and NH_2 (two NH 's) in the correct area ratio of 4:4:6:2.

EXAMPLE 2

This example illustrates the preparation of a flame retardant textile finish by means of the process of this invention.

An aqueous padding bath is prepared which contains 20 percent, by weight, of the diallyl 2-carbamoylethylphosphonate whose preparation is described in Example 1 along with 0.6 percent, by weight, of ammonium persulfate as a catalyst. Cotton and dacron, i.e. polyethylene terephthalate, cloths are padded therein,

dried at room temperature to a slight degree of moisture retention and thereupon cured by pressing for 3 minutes, at 330°F., in a steam heated press. The thus treated cloths are then washed in water, dried and analyzed for phosphorus by means of X-ray fluorescence. They are then subjected to an accelerated laundering procedure by being boiled for 3 hours in a solution containing 0.5 percent, by weight, of soap and 0.2 percent, by weight, of sodium carbonate. The thus treated cloths are then reanalyzed and their flame retardancy evaluated by means of the limiting oxygen index (LOI) method as described in ASTM D-2863. In brief, this procedure directly relates flame retardancy to a measurement of the minimum percentage concentration of oxygen in a oxygen:nitrogen mixture which permits the sample to burn; the LOI being calculated as follows:

$$\text{LOI} = [\text{O}_2]/[\text{O}_2] + [\text{N}_2] \times 100$$

Thus, a higher LOI is indicative of a higher degree of flame retardancy.

The following table presents the results of these evaluations.

Fabric	% P Before Soap-Soda Wash	% P After Soap-Soda Wash	LOI
Cotton	1.1	1.1	24.8
Dacron	0.8	0.7	24.5
Untreated Cotton*	—	—	18.4
Untreated Dacron *	—	—	20.8

* Control

These results show excellent durability to laundering and good flame retardancy on the part of fabrics treated with the flame retardant finish of this invention. Moreover, the thus treated cloths exhibit a good "hand," good tear strength as well as a retention of their original white color.

EXAMPLE 3

This example again illustrates the preparation of a flame retardant textile finish by means of the process of this invention which, in this case, utilizes an actinic radiation induced cure. It also provides a comparison with the use of diallyl 2-cyanoethylphosphonate.

A padding bath is prepared by dissolving 20 parts, by weight, of diallyl 2-carbamoylethylphosphonate in 79 parts of water which also contains 1 part, by weight, of octyl phenoxy polyethoxy ethanol as a wetting agent. For comparative purposes, a padding bath is prepared containing 79 parts of diallyl 2-cyanoethylphosphonate, 1 part of octyl phenoxy polyethylene ethanol and, because of the insolubility of the cyanoethyl phosphonate in water, 15 percent, by weight, of methanol is also included. An 8 ounce cotton cloth is padded in each of these baths to about a 70 percent, by weight, wet add-on. These cloths are then dried to a slightly moist condition and exposed to 4 megarads of electron beam radiation at 1.5 Mev. The flame retardancy of the thus treated cloths is then evaluated by means of the LOI procedure both before and after 5 detergent launderings.

Fire Retardant	% Dry Add-on	LOI Before Washing	LOI After Washing
diallyl 2- carbamoylethyl phosphonate	12.79	25	24
diallyl 2-cyanoethyl phosphonate	11.83	24	19
Control *	—	18	—

* Untreated Cotton

Thus, the above given data reveal that the carbamoyl compound required for use in the process of this invention provides durable, flame retardant properties in the treated fabric whereas the finish derived from the cyanoethyl compound is substantially all removed by laundering.

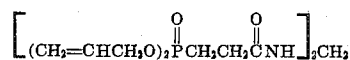
In another comparison of intrinsic flame retardant properties, aside from the question of durability, the carbamoyl and cyano compounds are again compared at varying levels of add-on on 3.2 oz. cotton cloths which are treated in the manner described hereinabove. The following table provides the results of this comparison.

Fire Retardant	% Dry Add-on	LOI Before Washing
diallyl 2-carbamoylethyl phosphonate	10	23.9
Do.	15	26.0
Do.	20	27.5
Do.	25	28.7
diallyl 2-cyanoethylphos- phonate	10	23.5
Do.	15	24.8
Do.	20	25.6
Do.	25	26.2

The above data clearly indicate that at all add-on levels, the finishes of this invention display superior fire retardancy when compared with the finishes derived from the cyanoethyl phosphonate compound.

EXAMPLE 4

This example illustrates the preparation of N,N'-methylenebis(diallyl-2-carbamoylethylphosphonate), i.e.



To a slurry of 154 gms. of N,N'-methylenebisacrylamide and 324 gms. of diallyl phosphonate in 800 ml. of methylene chloride there is added, with stirring, 2.9 gms. of sodium methylate. The reaction mixture spontaneously boils and methylene chloride is allowed to distill off until the reaction subsides. The resulting reaction mixture is homogeneous

except for trace solids which are removed by filtration. The infrared spectrum of the filtrate shows no remaining P-H compound. The solution is then stripped to 50 °C. under vacuum leaving a substantially quantitative yield of the product as a yellowish syrup, n_D²⁰ 1.4998 which is completely soluble in water.

- Analysis: Calcd. for C₁₉H₃₂O₈P₂N₂: 13.0% P

Found: 12.9% P

The above given structure is confirmed by nmr spectroscopy. When this monomer is directly exposed to the radiation from a mercury vapor lamp for a period of several hours, it cures to form a clear, solid, extremely hard polymer having a Barcol hardness value of 50. This polymer also has good impact strength as demonstrated by the fact that a 1/8" × 2 inch diameter plaque survives several 40 ft. falls without shattering.

In a repetition of the above described procedure, N,N'-methylenebismethacrylamide is, in this instance, substituted for N,N-methylenebisacrylamide thereby yielding N,N'-methylenebis(diallyl 2-carbamoylpropylphosphonate) as the product of the reaction in the form of a viscous syrup.

EXAMPLE 5

This example again illustrates the preparation of a flame retardant textile finish by means of the process of this invention.

Three padding baths are prepared whose respective compositions, in parts by weight, are shown in the following table. Cotton cloth having a weight of 32 oz/yd² is padded in each of these baths, passed through a wringer, dried at room temperature for 15 minutes and then cured between heated rolls at 280°-300° F. for 5 minutes. The LOI of each cloth before and after 5 detergent washes is then determined and these results are also shown in the table.

Padding Bath	A	B	C
N,N'-methylenebis (diallyl 2-carbamoylethylphosphonate)	35	25	15
Acrylamide (comonomer)	—	10	20
Ammonium persulfate (catalyst)	0.5	0.5	0.5
Octyl phenoxypolyethylene ethanol (wetting agent)	0.4	0.4	0.4
Water	64.1	64.1	64.1
Dry add-on (%)	26.3	25.2	23.6
LOI before washing	30.69	30.27	27.38
LOI after 5 detergent washings	24.23	25.74	24.21

Since the untreated cloth has an LOI of only 18, it is seen that the process of this invention imparts a substantial degree of durable flame retardancy.

EXAMPLE 6

This example illustrates the flame retarding of paper by means of the process of this invention.

Weighted pieces of paper are impregnated with each of the below described solutions:

(A₁₀) diallyl 2-carbamoylethylphosphonate 10% by wt. (aqueous)

(A₂₀) diallyl 2-carbamoylethylphosphonate 20% by wt. (aqueous)

(A₄₀) diallyl 2-carbamoylethylphosphonate 40% by wt. (aqueous)

(B₁₀) diallyl 2-cyanoethylphosphonate 10% by wt. (alcoholic)

(B₂₀) diallyl 2-cyanoethylphosphonate 20% by wt. (alcoholic)

(B₄₀) diallyl 2-cyanoethylphosphonate 40% by wt. (alcoholic)

(C₁₀) N,N-methylenebis(diallyl 2-carbamoylethylphosphonate) 10% by wt. (aqueous)

(C₂₀) N,N-methylenebis(diallyl 2-carbamoylethylphosphonate) 20% by wt. (aqueous)

(C₄₀) N,N-methylenebis(diallyl 2-carbamoylethylphosphonate) 40% by wt. (aqueous)

In each case, the paper is saturated to a wet-uptake of approximately 200 percent, by weight. The thus treated papers are dried for 15 minutes in an oven set at 70 °C. and then irradiated by exposure to a 400-watt high pressure mercury arc lamp for a period of 24 hours. The dry add-ons, i.e. the weight of the treated paper less its original weight × 100/original weight, are determined both before and after a 15 minute wash with running water, and the flame retardancy of each sample is evaluated both before and after the water wash. The flame retardancy of these sheets is expressed on the following scale:

+++ (excellent retardancy) self-extinguishing when its lower edge is ignited while the strip is suspended in the vertical position;

++ (good retardancy) self-extinguishing when its lower edge is ignited while suspended at an inclination of 45°;

+ (slight retardancy) self-extinguishing where one end is ignited while the strip is suspended in a horizontal position; and

— (not self-extinguishing in any position).

The results of this evaluation are presented in the following table:

Treating Solution	Dry Add-on (%)		Flame Retardance	
	Before Washing	After Washing	Before Washing	After Washing
A ₁₀	16.2	2.1	++	—
A ₂₀	30.3	14.1	+++	—
A ₄₀	62.5	42.4	+++	+
B ₁₀	3.5	0.9	—	—
B ₂₀	7.4	1.0	+	—
B ₄₀	10.5	1.9	++	—
C ₁₀	16.1	9.6	++	+
C ₂₀	37.1	22.1	+++	++
C ₄₀	72.2	70.5	+++	+++

These results reveal that the finish derived from diallyl cyanoethylphosphonate is substantially lost during the curing whereas the finishes of this invention are retained. It is also seen that the novel tetraallyl compound provides a finish which is exceedingly durable to water washing.

EXAMPLE 7

This example illustrates the preparation of a thermoset polymer composition from the diallyl 2-carbamoylethylphosphonate whose preparation is described in Example 1.

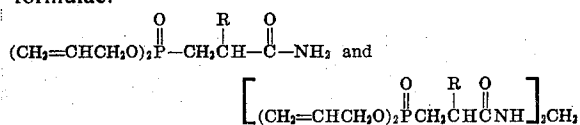
An aqueous solution containing 30 percent, by weight, of diallyl 2-carbamoylethylphosphonate and 2 percent, by weight, of ammonium persulfate is gradu-

ally warmed to within the range of 60°-80°C. During this warming period, the solution forms a viscous pre-polymer. A portion of this pre-polymer is removed and is used as a textile finishing agent which, after being applied to the surface of a fabric, is cured by heating the thus treated fabric so as to yield a water insoluble, flame retardant finish. Prolonged heating of the balance of the pre-polymer solution causes it to gel and thereafter a white, odorless water insoluble polymer is precipitated. This polymeric product is then dried and used as a flame retardant additive for flammable polymers.

Variations may be made in proportions, procedures and materials without departing from the scope of this invention as defined in the following claims.

What is claimed is:

1. A flame retardant polymer of an allyl 2-carbamoylalkylphosphonate corresponding to the formulae:

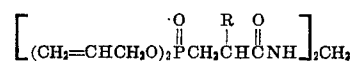


where R is selected from the group consisting of hydrogen and methyl radicals.

2. The polymer of claim 20, wherein said allyl 2-carbamoylalkylphosphonate is selected from the group consisting of diallyl 2-carbamoylethylphosphonate, diallyl 2-carbamoylisopropylphosphonate, N,N'-methylenebis(diallyl 2-carbamoylethylphosphonate) and N,N'-methylenebis(diallyl 2-carbamoylisopropylphosphonate).

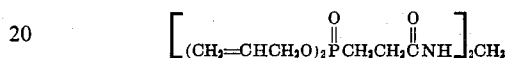
3. The polymer of claim 1 wherein at least one other comonomer is present in the polymer, said comonomer being selected from the group consisting of amide nitrogen-containing monomers, monomers containing more than one polymerizable double bond, and monomers which contribute to flame retardancy and which have phosphorus, bromine or chlorine atoms in their molecules.

4. The allyl 2-carbamoylalkylphosphonates corresponding to the formula:



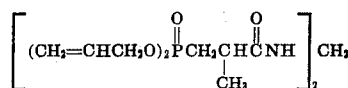
where R is selected from the group consisting of hydrogen and methyl radicals.

5. The compound



according to claim 4.

6. The compound



according to claim 4.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,839,207 Dated October 1, 1974

Inventor(s) Edward D. Weil

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

In the Title, change "ALLYL 2-CARBAMOYLALKYLPHOSPHONATES
FLAME RETARDANTS" to -- ALLYL 2-CARBAMOYLALKYLPHOSPHONATE
FLAME RETARDANTS --.

Signed and Sealed this

ninth Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,839,207 Dated June 27, 1973

Inventor(s) Edward D. Weil

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

Col. 2, line 14, change "those" to -- these --;
Col. 3, line 16, change "dischlorethane" to dichloroethane--;
Col. 3, line 36, change "member" to --number--;
Col. 7, line 22, change "of" to --or--;
Col. 8, line 51, change "51.2" to -- 51-2--;
Col. 8, line 56, change "CH'-O-P" to --CH₂-O-P-- and change
"CH₁=CH-" to --CH₂=CH- --;
Col. 11, line 5, change "n" to -- n₂₃^D --;
Col. 12, line 10, change "(diallyl)" in the formula to --(diallyl--;
Col. 12, lines 28, 31 and 34, insert -- = -- before self-
extinguishing";
Col. 12, line 33, change "45" to -- 45° --;
Col. 12, line 55, change "cyanoethylphosphonate" to -- 2-
cyanoethylphosponate--;
Col. 13, line 27, change "claim 20" to --claim 1--;

Signed and sealed this 11th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks