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2,691,566

UNITED STATES PATENT OFFICE

2,691,566

ORGANIC PHOSPHORUS COMPOUNDS FOR INCREASING THE FLAME RESISTANCE OF TEXTILES AND METHOD OF APPLYING THE SAME

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No Drawing. Application October 23, 1951, Serial No. 252,811

6 Claims. (Cl. 8—115.5)

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This invention relates to organic compounds containing phosphorus and particularly to such compounds which also contain a grouping which is an addition product of two isocyanate radicals. It further relates to new organic compounds which are useful in increasing the flame resistance of textiles.

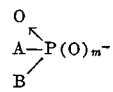
Phosphorus compounds, and particularly organic phosphorus compounds, have been applied to fabrics and films to obtain a variety of useful effects such as flame resistance, anti-static properties and insect-proofing. These effects however have not been permanent, as the treating agents are ordinarily removed by laundering or by dry-cleaning.

Efforts have been made to overcome this fault by applying the phosphorus compounds in company with resins to fasten the compounds to the surface. While this has resulted in some improvement, the durability of the fabric so treated is not great and repeated laundering or dry-cleaning removes the surface treatment. It has been recognized that if the phosphorus compounds could be attached to the surface of the fabric or film by a true chemical union, a permanent effect could be obtained. Heretofore all such attempts have resulted in the severe tendering of the fabric due to the strenuous conditions needed to bring about chemical reaction. Such treatments are obviously not practical.

It is an object of this invention to provide a new series of organic phosphorus compounds which may be applied to textiles and which may be chemically bonded thereto without injury to the textile. A further object is to provide organic phosphorus compounds which are not removed by repeated launderings after bonding to the fabric. A further object is to provide a process of bonding the new phosphorus compounds of this invention to textile materials. Further objects will appear from the detailed description of this invention which follows.

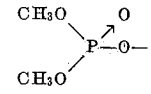
The new compounds of this invention are those in which phosphorus is present in the form of a phosphate, phosphonate, phosphinate or phosphine oxide radical and in which there also occurs the bivalent grouping —R—D—R'—, R and R' representing aryl radicals and D representing an addition product of two isocyanate radicals.

The radical containing phosphorus may be represented generally by the expression:

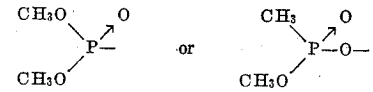


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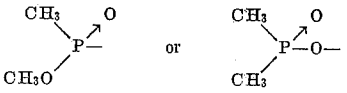
in which A contains from 1 to 12 carbon atoms and is a member of the group consisting of alkyl and alkoxy radicals, B contains from 1 to 12 carbon atoms and is a member of the group consisting of alkyl, aryl, alkoxy and aryloxy radicals, and m is an integer from 0 to 1. The radical may be a phosphate group, for example, using methyl as the hydrocarbon part of the substituents:



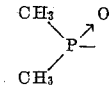
or a phosphonate as



or a phosphinate as

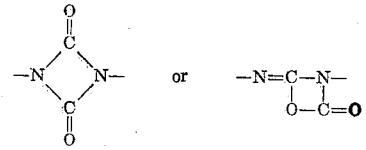


or a phosphine oxide as



The substituents A and B may be alkyl radicals, such as methyl ethyl, propyl, isopropyl, n-butyl, hexyl, octyl, or dodecyl, or the corresponding alkoxy radicals. They may be the same or different. Alternatively, B may be an aryl radical such as phenyl, tolyl, xylyl, naphthyl, biphenyl and the like or the corresponding aryloxy radical.

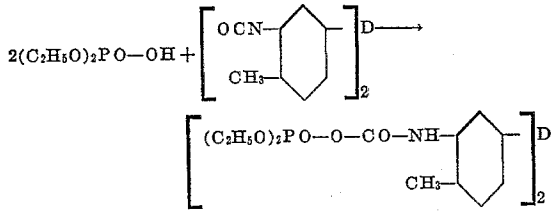
The group —D—, representing an addition product of two isocyanate radicals, probably has one of the following structures:



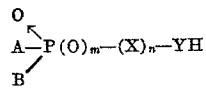
The addition product may be formed by the catalytic dimerization of aromatic isocyanates, preferably in the presence of a catalyst such as phenyldimethylphosphine, as disclosed in copending application Serial No. 248,270 of Otto Stallmann, filed Sept. 25, 1951. Whatever their structure, these dimeric addition products do not share the well-known instability of monomeric isocyanates with respect to water and

other materials containing active hydrogen and they may be stored without special precautions and without deterioration. They may however be ruptured by heating them to a temperature of 125 to 225° C. By this treatment, reactive groups are formed which react readily with compounds containing active hydrogen atoms such as are present in amine, amide, hydroxyl and carboxyl radicals. Phosphorus compounds containing such dimeric isocyanate addition products may therefore be applied to fabrics or films composed of such materials as cotton, wool or nylon, which contain active hydrogens, and may be strongly bonded thereto simply by heating the treated textile.

A particularly important class of compounds are those formed by the reaction between dimeric aromatic diisocyanates and phosphorus-containing compounds which also possess one or more active hydrogen atoms. In the resulting product the aromatic diisocyanate is attached to the phosphorus compound by means of a urethane linkage. A typical example of this reaction is that between diethylphosphoric acid and the dimer of 2,4-tolylene diisocyanate:



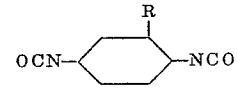
where D is again used to indicate an addition product of two isocyanate radicals. The phosphorus compounds which are useful in this reaction may be represented by the formula

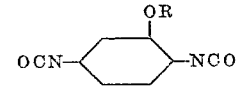


in which A, B and m have the significance described above, X is a bivalent organic radical containing from 1 to 12 carbon atoms, Y is the residue obtained by removing a single hydrogen from a member of the class of functional groups containing active hydrogen consisting of primary amino, secondary amino, primary amido, secondary amido, hydroxyl and carboxyl groups, and n is an integer from 0 to 1, the value of n being at least as great as that of m. Compounds of this sort may be obtained by the action of a substituted phosphoryl chloride on a polymethylene glycol or other compound containing a hydroxyl group and a carboxyl, amino or amido radical. In compounds prepared in this manner, the phosphorus atom will be linked to the radical X through an oxygen atom, i. e., m will be 1. Compounds in which the phosphorus is linked directly to the radical X, i. e., where m is O, may be obtained through a Grignard reaction between a phosphoryl chloride and the Grignard reagent formed from an alkyl halide which also contains a hydroxyl, carboxyl, amino or amido group.

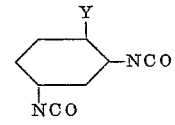
The expression Y includes the following radicals: —O—, —NH—, —COO—, —CONH—, —NR— and —CONR—, where R is an alkyl, aryl or cycloalkyl radical preferably containing no more than 12 carbon atoms. The bivalent organic radical X may be aliphatic, cycloaliphatic, aromatic or a combination thereof. It may contain a carbon chain which is interrupted by hetero atoms or groups such as —O—, —S—, —CO—, —SO_2— and the like. The carbon skeleton of this radical may also be substituted with groups such as ether, ester, halogen or nitro. The radical X need not be present at all in the phosphorus compound, in which case n is zero. In this case m is also zero, since n must be at least as great as m. Examples of such compounds in which m and n are zero are diethylphosphoric acid and dimethylphosphoryl amide.

The aromatic diisocyanate dimers which may be reacted with the phosphorus compound are prepared by known methods from monomeric diisocyanates or mixtures of diisocyanates. At least one of the isocyanate groups present in the monomeric diisocyanate must be attached to an aromatic ring. Compounds of this type include 2,4-tolylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 2-chloro-1,4-phenylene diisocyanate, 2-methoxy-1,4-phenylene diisocyanate and 2-nitro-1,4-phenylene diisocyanate. Other usable diisocyanates include compounds such as

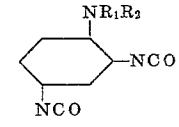




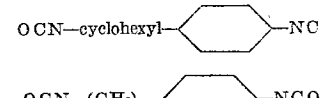
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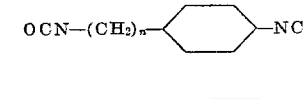


in which Y represents an ester group such as —OOCR or —COOR and in which R represents an alkyl, aryl, aralkyl or cycloalkyl group of from 1 to 10 carbon atoms. The aromatic nucleus may also be substituted with a tertiary amino group as in the compound

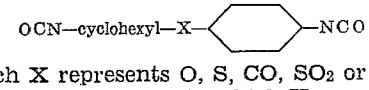


in which R_1 and R_2 represent alkyl, aryl, aralkyl or cycloalkyl groups, the total number of carbon atoms in R_1 and R_2 being from 2 to 12. Other diisocyanates containing a single phenyl group which are useful in the process of this invention are

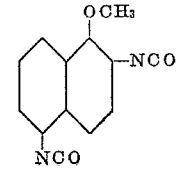




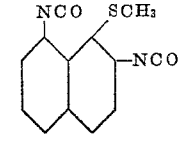
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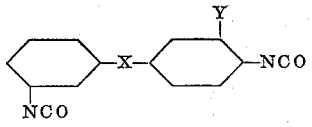
in which X represents O, S, CO, SO_2 or $(CH_2)n$, and similar compounds in which X represents an alkylene group which is interrupted by a hetero atom such as oxygen, sulfur or nitrogen. In these compounds n may be from 1 to 12. The diisocyanates may contain naphthyl groups as in



or

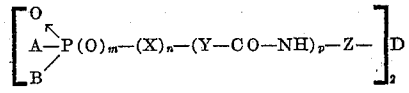


or a plurality of phenyl groups as in



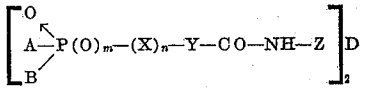
where X is O, S, CO, SO_2, CH=CH, N=N, $(CH_2)n$ or an alkylene group which is interrupted by a hetero atom such as oxygen, sulfur or nitrogen, where Y is a saturated or unsaturated hydrocarbon group, an ether group, an ester group, a tertiary amino group, —NCS, halogen or nitro, and where n is from 1 to 12.

The new compounds of this invention includes those having the general formula

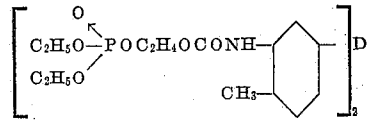


in which A, B, m, n, X, Y and D have the significance described above, Z is an aryl radical and p is an integer from 0 to 1. In this expression, n must be 1 when m and p are both 1.

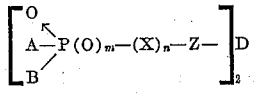
When p is equal to 1, the compounds of this class are derived from diisocyanates and have the general formula



A preferred compound of this type is that obtained from the reaction of ethylene glycol with diethylchlorophosphate and with the dimer of 2,4-tolylene diisocyanate. This compound has the formula



When p equals zero, the compounds of this class are derived from mono-isocyanates and have the general formula



Examples of this type of compound are the dimer of 4 - isocyanatophenyldiethylphosphine oxide, the dimer of 4-isocyanatophenyldiisopropyl phosphate, and the dimer of 4-isocyanatophenylethylenephenylmethylphosphine oxide.

It is obvious that compounds within the scope of this invention which contain more than two phosphate, phosphonate, phosphinate or phosphine oxide groups or more than one isocyanate addition product per molecule will have the same general properties and utility as will compounds having precisely these proportions. Such compounds may be formed for example from the reaction of a tri- or tetrahydroxy compound with a substituted phosphoryl halide and a dimeric diisocyanate.

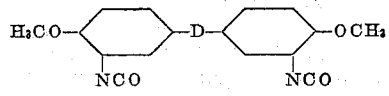
The new compounds of this invention may be prepared by reacting an organic phosphorus compound containing an amino group attached to an aromatic ring with phosgene to convert it to the corresponding isocyanate, and thereafter dimerizing the isocyanate by known methods. Alternatively, an aromatic diisocyanate may be dimerized and may then be reacted with an organic phosphorus compound containing an active hydrogen group. This reaction is best carried out in a solvent which is free from active

hydrogen atoms so as to be non-reactive with the isocyanate group.

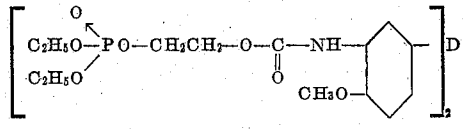
The preparation and use of the compounds of this invention are illustrated by the following examples, in which parts are by weight:

Example 1

To 620 parts of ethylene glycol are slowly added 173 parts of diethylphosphoryl chloride with good agitation. After the evolution of HCl ceases the excess ethylene glycol is distilled off under vacuum at 90–95° C. The syrupy residue is dissolved in 1000 parts of dioxane, 190 parts of the dimer of 2,4-anisylene diisocyanate having the formula



where D is an addition product of two isocyanate radicals, are added, and the mixture is stirred while holding the temperature at 60–65° C. The compound of the following structure is formed

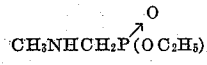


The dioxane is evaporated off on a hot water bath under reduced pressure.

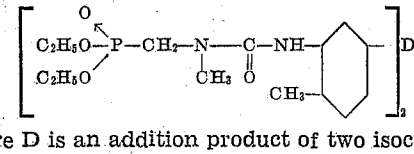
The resulting pasty mass is applied to a fabric by first mixing thoroughly one part with one-half part of a dispersing agent made by condensing isooctylphenol with five molecular parts of ethylene oxide, and then diluting slowly with water with vigorous agitation. The fabric is then padded with this solution, dried and heated to 180–190° C. for 3 minutes. When cotton cloth is so treated the fabric is flame-retardant and the effect persists after washing. When nylon is so treated, the cloth is found to possess a very considerable degree of anti-static property which remains after repeated laundering.

Example 2

Eighteen (18) parts of the diethyl ester of methylamino methylene phosphonic acid,



are dissolved in 175 parts of dioxane. To this solution are added 20 parts of the dimer formed from 2,4-tolylene diisocyanate and the mixture is gently refluxed for one hour while stirring. The free isocyanate radicals react with the imino hydrogen to form a compound of the following structure:

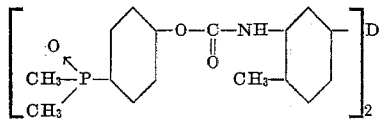


where D is an addition product of two isocyanate radicals. The resulting solution is diluted with an equal amount of water and used as a pad bath for applying the compound to a cotton fabric. After drying and heating to 160° C. for 2–3 minutes the phosphorus compound has reacted with the cloth to give a durable flame-resistant surface.

Example 3

Twenty (20) parts of 4-hydroxyphenyldimethylphosphine oxide are dissolved in 200 parts of dioxane and 23.5 parts of the dimer of 2,4-tolylene diisocyanate are added and the mixture is

stirred at 60–65° C. for 3–4 hours. The reaction product has the following formula:



where D is an addition product of two isocyanate radicals.

This product is recovered by evaporating off the solvent under reduced pressure.

It may be used to produce anti-static and flame resistant effects on fabric by the procedure illustrated in the previous examples.

The phosphorus compounds containing dimeric isocyanate addition products may be applied to fabrics or films from solvents or emulsions, dried and then heated to about 125 to 200° C. to rupture the isocyanate adducts and thus generate reactive groups, which are presumably nascent —NCO groups. These groups will then react with active hydrogens on the surface of the fabric or film to form urethane type linkages, thus chemically binding the molecule to the surface. For example, on cotton, viscose rayon and acetate rayon —OH groups are available and on nylon =NH groups are available and on terephthalic acid polyesters either —OH or —COOH groups are available.

The phosphorus compounds thus linked to the surface are not removed by repeated launderings or dry-cleanings. Ordinary abrasion will not remove them. Removal requires either extreme abrasion or strong hydrolytic conditions, either of which will destroy or practically destroy the surface as well as the chemical bond between the phosphorus containing molecule and the surface.

The compounds of this invention may usually be applied to surfaces as emulsions. The emulsion may be made in known ways by use of emulsifying agents with or without the aid of special machinery. Thus the solid may be ground finely and dispersed in water with the aid of a nonionic emulsifying agent such as the condensation product of oleyl alcohol with 16–18 moles of ethylene oxide. A colloid mill may be used to aid the dispersion. By a different procedure, an emulsifying agent such as diethyl cyclohexylamine hexadecyl sulfate may be added to the solvent solution of the compound and then water may be added slowly with vigorous agitation. At first a water-in-solvent emulsion will form which will then invert to form a phosphate compound/solvent-in-water emulsion. The emulsion may be padded onto the fabric by passing the fabric continuously into the emulsion and then through a nip roll to remove the excess, after which the fabric may be continuously dried at a temperature of not over 100–105° C. This upper temperature limit is essential so that the dimeric compounds are not split prematurely. After drying, the coated fabric is stable under ordinary conditions for at least several days and may be stored and cured when desired. In the curing or fixation step the fabric may be passed continuously through an oven at 125° to 200–225° C. to cause the dimers to split and allow the reactive groups to combine with the active hydrogen atoms on the surface.

The impregnation of the fabric may be carried out in various other ways. The emulsion may be sprayed onto the surface or if it is thick it may be spread on with a blade such as a doctor knife.

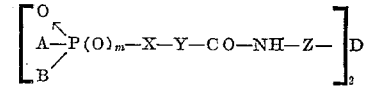
A solution of the compound in a solvent may be employed but generally an emulsion is preferable since special solvent recovery equipment may thereby be dispensed with.

The extent of the effect which is produced on the fabric by the treating agents of this invention will be in rough proportion to the amount of agent applied and to the phosphorus content of the agent. The phosphorus compounds of this invention ordinarily contain from about 2 to 16% by weight phosphorus. Loadings which result in as much as 1.5% phosphorus by weight on the textile usually produce self-extinguishing properties in the treated material, while loadings which give from 2.5 to 3% phosphorus on the textile result in excellent flame resistance. Still larger amounts may in some cases be applied, up to about 5%. On the other hand, applications of as little as 0.05% by weight of treating agent produce some anti-static effect and when this is the principal objective sought, considerably smaller applications of the phosphorus compounds will be made than when flame resistance is desired.

Polymeric compounds in which both phosphorus-containing radicals and dimeric isocyanate addition products are attached to hydroxyl-containing polymers such as cellulose, polyvinyl alcohol and the like are disclosed and claimed in our co-pending application Serial No. 252,812, filed October 23, 1951.

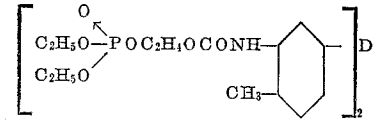
We claim:

1. A compound having the formula



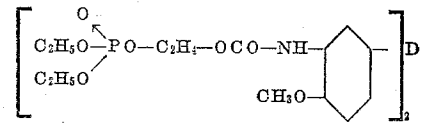
in which A and B contain from 1 to 12 carbon atoms and are members of the group consisting of alkyl and alkoxy radicals, m is an integer from 0 to 1, X is a bivalent hydrocarbon radical containing from 1 to 12 carbon atoms, Y is the residue obtained by removing a single hydrogen from a member of the class of functional groups consisting of amino and hydroxyl groups, Z is an aryl radical containing no more than two aromatic rings and D is an addition product of two isocyanate radicals.

2. The compound having the formula



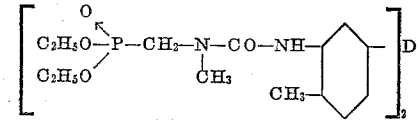
in which D is an addition product of two isocyanate radicals.

3. The compound having the formula:



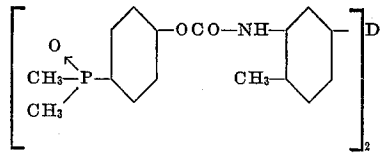
in which D is an addition product of two isocyanate radicals.

4. The compound having the formula:



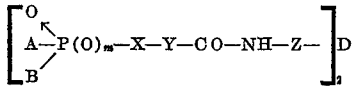
in which D is an addition product of two isocyanate radicals.

5. The compound having the formula:



in which D is an addition product of two isocyanate radicals.

6. A method of increasing the flame resistance of textile materials in which the fiber molecules contain active hydrogen atoms which comprises applying to the surface of the said textile a compound having the formula



in which A and B contain from 1 to 12 carbon atoms and are members of the group consisting of alkyl and alkoxy radicals, *m* is an integer from

0 to 1, X is a bivalent hydrocarbon radical containing from 1 to 12 carbon atoms, Y is the residue obtained by removing a single hydrogen from a member of the class of functional groups consisting of amino and hydroxyl groups, Z is an aryl radical containing no more than two aromatic rings and D is an addition product of two isocyanate radicals, said compound being dispersed in a liquid, and thereafter heating the treated textile to a temperature from 125° to 225° C.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,625,531	Seeger	Jan. 13, 1953
2,636,889	Jones et al.	Apr. 28, 1953

OTHER REFERENCES

Blair et al., J. Am. Chem. Soc., vol. 56, pp. 907 to 910 (1934).