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PROCESS FOR FLAMEPROOFING CELLULOSIC TEXTILE FABRICS AND PRODUCT OBTAINED THEREBY

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U.S. Cl. 8—116.2 6 Claims

ABSTRACT OF THE DISCLOSURE

The present invention relates to a composition of matter, suitable for flameproofing textile fabrics, consisting of an aziridinyl phosphine oxide or sulfide and a halogen substituted alcohol or phenol which, when heated, will copolymerize and react with the hydroxyl or nitrogen hydrogen of the natural or synthetic fiber of a textile material. The invention also relates to the method for applying the composition to the textile material to impart said flameproofing characteristics to the so-treated textile material.

BACKGROUND OF THE INVENTION

Flameproofing of textile materials has been a goal of the industry for many years. Originally, inorganic chemicals were employed to impregnate the textile materials. The major drawbacks of the use of these chemicals was that large quantities were required to obtain even limited success and the textile material was substantially unwashable because the inorganic chemical was soluble in the wash water. Further, the large quantities of chemicals necessarily employed imparted a harshness to the fabric. The Southern Regional Research Laboratory of the United States Department of Agriculture has disclosed a new family of organic nitrogen and phosphorus containing compounds, aziridinyl phosphine oxides and sulfides, which are employed to impart a degree of flameproofing to textile fabrics. The compounds, compositions and techniques employed are fully disclosed in U.S. patents, representative of which are numbers 2,870,042; 2,886,539; 2,912,412 and 2,915,480. The principal problem encountered in employing the compounds of these patents is the necessity to use large quantities of the chemicals which imparts a harsh hand to the textile. Another disadvantage of their use is that the process results in a product not as durable as is desired and the chemicals can be washed out of the garment after several launderings in harsh soaps. A further disadvantage of the known art is that these compounds, which are ordinarily applied from aqueous systems, are unstable in water such that polymerization reactions between the aziridinyl groups and the active hydrogens of the co-reactants, e.g. alcohols, amides, acids, etc. are enhanced.

It is therefore an object of the present invention to provide a composition of matter which can be employed in smaller quantities than heretofore employed to obtain initial flameproofing properties and which resultant chemical polymer will remain in and attached to the textile for longer periods of time than those previously employed.

Another object of the present invention is to provide a more stable system from which to apply the flameproofing chemicals by the use of non-flammable, halogenated solvents.

A further object of the present invention is to provide a process for applying the chemical reactants to the textile in a manner such that during the polymerization the polymer will become intimately associated with the fiber of the textile material.

These and other objects will become apparent to those skilled in the art from the following description and claims.

BRIEF DESCRIPTION OF THE INVENTION

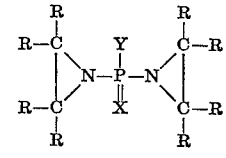
In accordance with the present invention an aziridinyl phosphine oxide or sulfide is copolymerized with a halogen substituted hydroxyl compound while each reactant is intimately in contact with the other and with the fibers of an organic textile material. The resulting product, which is a copolymer of the aziridinyl compound and the halogen substituted hydroxyl compound combined with the textile fibers, is a flameproof textile material. The reactants are applied to the textile material from a halogenated hydrocarbon solvent to ensure proper distribution into the fiber structure of the textile material. After removal of the solvent, the reactants and textile material are heated to between about 120° and 200° C. for up to about five minutes to cause polymerization of the reactants and reaction between the aziridinyl reactant and/or polymer with the fiber of the textile material.

According to the present invention satisfactory flame retardant properties can be achieved with textile fabrics by impregnating the textile fabric with an aziridinyl phosphine oxide or sulfide and a halogenated alcohol or phenol dissolved or suspended in a chlorinated solvent, removing the chlorinated solvent and polymerizing by heating the aziridinyl phosphine compound and halogen substituted hydroxyl compound in the presence of the textile fibers which simultaneously binds the polymer directly to the fiber. In practice the application to the fibers can be made from a single solution of both reactants, or alternatively the aziridinyl and halogen containing compounds can be applied consecutively as, for example, by spraying on separate solutions. Applying both reactants from the same solution can be accomplished by spraying or dipping.

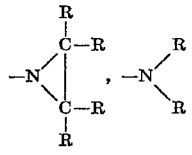
Good results are obtained when the ratio of aziridinyl compound to the halogenated compound is between about 0.5 to 1 and 10 to 1. Suitable chlorinated solvents are those boiling between about 40° and 125° C. The solvent can be removed by air drying, by applying heat or vacuum or by other means known to those skilled in the art. A particularly good method of removing solvent is to vaporize it within a closed chamber where it can be condensed and recovered. After the solvent is removed, the textile fabric containing the reactants is cured at between about 120° C. and 200° C. for from about 0.5 to about 5 minutes. An especially desirable range for conducting the cure is from about 140° C. to 170° C. for a time of about 2–3 minutes. The amount of reactants in the solvent should be sufficient to permit a weight add-on of at least 5 percent in the finished textile fiber.

Thus, a method for imparting flame retardance to textiles comprises (1) impregnating by contacting a textile fabric with (a) an aziridinyl phosphine oxide or sulfide compound and (b) a hydroxyl-containing halogenated hydrocarbon compound, wherein these compounds are dissolved in a halogenated hydrocarbon solvent, (2) removing the solvent, and (3) curing by copolymerizing compounds (a) and (b) above onto the fabric by heating at a temperature above 120° C.

Aziridinyl compounds which have proven satisfactory when used in accordance with the present invention are those having the general formula



wherein X represents the element oxygen or sulfur and each R represents hydrogen or a lower alkyl radical having from 1 to 4 carbon atoms, and Y represents the group



(wherein R is as previously defined), an alkoxy group of from 1 to 13 carbon atoms or an aryloxy group of from 6 to 10 carbon atoms.

Thus, one can employ tris(1-aziridinyl)phosphine oxide, tris(1 - aziridinyl)phosphine sulfide, tris[1 - (2 - methyl) aziridinyl] phosphine oxide, tris[1-(2-ethyl) aziridinyl] phosphine sulfide, and the like.

Halogenated hydroxyl compounds which have been found to be satisfactory co-reactants with the aforedescribed aziridinyl compounds are the brominated, chlorinated and fluorinated aliphatic and aromatic alcohols and phenols such as for example,

1,3-dibromo-2-propanol,
2,3-dibromo-1-propanol,
2,2-bis(bromomethyl)-1,3-propanediol,
3-bromo-2,2-bis(bromomethyl)-1-propanol,
3-chloro-2,2-bis(bromomethyl)-1-propanol,
4,4'-isopropylidene bis(2,6-dibromophenol),
2,4,6-tribromophenol,
2,3,4,6-tetrachlorophenol,
pentachlorophenol,
4,4'-isopropylidene bis(2,6-dichlorophenol),
2,4,6-trichlorophenol,

and their fluorinated analogs.

The halogenated solvents which can be employed in accordance with the present invention are the fluorinated, chlorinated, brominated or mixed halogen hydrocarbons which have boiling points between about 20° C. and 160° C. although those having boiling points between about 40° C. and 125° C. are preferred. Some of such solvents are: methylene chloride, carbon tetrachloride, chloroform, perchloroethylene, trichloroethylene, dichloroethylene, 1,1- and 1,2-dichloroethane, 1,1,1- and 1,1,2-trichloroethane, trichlorobromomethane, trichlorofluoromethane, mono-, di- and tri-chloropropanes and propenes, and tetrachloroethanes. Advantageously, curing can be conducted simultaneously with removal of the solvent when removing solvents at temperatures above 120° C.

DETAILED DESCRIPTION OF INVENTION

Example 1

A sample of 5.8 oz./sq. yd. cotton sateen cloth was conditioned at 75° F. and 65% relative humidity, weighed, and then soaked for five minutes in a solution of 1,1,1-trichloroethane containing 22% by weight, based on the total weight of the solution, of tris(1-aziridinyl) phosphine oxide and 5.5% by weight of 3-bromo-2,2-bis (bromomethyl)-1- propanol. The sample was removed from the solution and passed through squeeze rollers to remove excess solution. Thereafter the sample was air dried for 10 minutes and then cured in an oven maintained at 160° C. for 2 minutes. The sample after curing was conditioned for 16 hours at 75° F. and 65% relative humidity and weighed. The weight add-on of chemicals was 12.9%. The sample was then washed for 2 minutes in a warm solution of TIDE brand of detergent, rinsed in warm water and dried in an electric home drier.

The vertical flame retardance test AATCC Method 34–1966, "Fire Resistance of Textile Fabrics," was conducted using the sample prepared above. The average char length of the sample treated as set forth above according to the present invention was 4½ inches.

After twenty washings, each done in accordance with AATCC Method 88A–1961T, "III" wash, "C" dry, the sample had an average char length of 5 inches.

In a series of similar tests different reactants, employed at various ratios and weight add-ons, were used. The results are set forth in Table I.

TABLE I

Brominated reactant	Wt. ratio APO [1] to coreactant	Percent total add-on	Launderings 0 (Ave. vertical char lengths (inches))	10	20
2,2-bis(bromomethyl) 1,3-propanediol	1.0:1.5	26.8	4	BE [2]	------
	1.0:1.0	27.3	3⅝	BE	------
	1.0:0.5	18.1	4½	BE	------
	1.0:0.25	15.4	3⅜	4¾	BE
3-bromo-2-2,bis(bromomethyl)-1-propanol	----------	11.3	3¾	BE	------
	----------	8.9	4⅜	BE	------
	1.0:0.5	12.3	3½	BE	------
	1.0:0.25	12.9	4½	4¾	5
	----------	10.9	3⅞	6½	BE
	----------	9.3	5¼	BE	------
1,3-dibromopropanol	1.0:0.5	22.6	4⅜	BE	------
	----------	16.8	7½	BE	------
	1.0:0.25	16.5	3⅞	BE	------
	----------	14.5	9¼	BE	------
4,4'-isopropylidene-bis (2,6-dibromophenol)	1.0:1.5	35.7	5⅛	4⅛	4½
	----------	31.4	4⅞	4¼	6
	----------	16.0	4⅝	3½	------
	1.0:1.0	16.9	4½	4⅜	5⅜
	----------	12.5	5⅛	5¼	7⅜
	1.0:0.5	18.1	4½	3⅞	------
	----------	14.0	5	7⅝	------
	----------	12.2	6¼	BE	------
	1.0:0.25	12.0	5	4	6½
	----------	10.3	4⅞	BE	------
	1.0:0.125	10.6	4¼	4	4¼
2,4,6-tribromophenol	1.0:1.5	26.3	3¾	5	5
	----------	13.9	4¾	BE	------
	1.0:1.0	31.1	3⅜	3⅝	5⅛
	----------	20.2	3⅞	4¼	BE
	----------	15.5	3¾	BE	------
	1.0:0.5	19.8	4	3½	3⅞
	----------	16.4	4⅛	4⅛	7⅜
	----------	9.9	4¾	BE	------
	1.0:0.25	13.4	3¾	4½	------
	----------	10.9	3⅞	BE	------

[1] APO=Tris(1-aziridinyl)phosphine oxide.
[2] BE=Burned entirely.

EXAMPLE 2

In another series of experiments cotton sateen (5.8 oz./sq. yd.) was padded 2 dips and 2 nips through a solution consisting of 1,1,1-trichloroethane solvent, 10% by weight propylene glycol, 17% by weight tris(1-aziridinyl) phosphine oxide and 17% by weight pentachlorophenol (86% pentachlorophenol, 10% other chlorophenols and 4% inert material, a technical grade of pentachlorophenol). The wet pickup was 64%. The weight add-on was 21.5%. The sample was dried in an oven for 2½ minutes at 100° C., cured at 165° C. for 2½ minutes and washed, rinsed, dried, conditioned and tested as in Example 1. The vertical char length of the conditioned sample was 3½ inches. After five washings the sample had a 5½ inch char length. Other samples treated with different chloro aromatic compounds in the above manner, washed, etc. gave the results shown in Table II.

TABLE II

Chlorinated reactant	Wt. ratio, APO [1] to coreactant	Percent total add-on	Launderings 0 (Avg. vertical char lengths (inches))	1	5
2,4,6-trichlorophenol	1.0:0.50	18.6	5⅝	[2] BE	------
	1.0:1.0	23.2	4⅝	BE	------
2,3,4,6-tetrachlorophenol	1.0:0.50	18.3	4¼	8⅛	------
	1.0:1.0	21.4	3¾	4¾	6⅛
Pentachlorophenol	1.0:0.50	18.0	4⅛	4⅞	BE
	1.0:1.0	21.6	3½	4½	5½

[1] APO=Tris(1-aziridinyl)phosphine oxide.
[2] BE=Burned entirely.

I claim:

1. A method for imparting flame retardance to cellulose textile fabrics which comprises (1) impregnating

by contacting said fabric with an aziridinyl phosphine oxide compound and a halogenated lower alkanol wherein said halogenated lower alkanol contains at least two halogen atoms and wherein said impregnating compounds are applied from a halogenated hydrocarbon solvent solution and at a weight ratio of 0.5 to 10 aziridinyl phosphine oxide to 1 of halogenated alkanol (2) removing said solvent and (3) curing by copolymerizing said compounds onto said fabric by heating at a temperature of from about 120°–200° C.

2. The method of claim 1 wherein the halogenated lower alkanol is a brominated lower alkanol.

3. The method of claim 2 wherein the brominated lower alkanol is 2,2-bis(bromomethyl)-1,3-propane diol, 3 - bromo - 2,2 - bis(bromomethyl) - 1 - propanol or 1,3-dibromo-2-propanol.

4. The method of claim 1 wherein the impregnating compounds are applied from a single solution.

5. The method of claim 1 wherein the impregnating compounds are applied consecutively from separate solutions.

6. A flame retardant cellulose textile fabric composition made by the process of claim 1.

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