

[54] FLAME RETARDANTS FOR BLENDS OF NATURAL AND SYNTHETIC FIBERS

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[58] Field of Search 117/137, 136, 111 F, 121; 106/15 FP; 252/8.1

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[57] ABSTRACT

A process for rendering synthetic materials, of synthetic fibers or mixtures of the same flame resistant which entails employing water insoluble flame retardant agents which are treated as colorless pigments, reduced to extremely finely divided condition, suspended in latex medium and applied as such or as part of a dispersed dye paste to the fabric, dried and set in place.

The active flame retardant agents are brominated organic chemical compounds, and reduced to a fine state of subdivision, preferably under two microns, average particle diameter, which compound is supported in an aqueous suspension with a colloidal protective agent, and thus, is in a form for blending in a binder, plastic resin latex, so that when the composition is dried and cured in place on the fabric, a very useful retardant effect is obtained which is durable to laundering and dry cleaning, and the hand of the fabric is preserved.

9 Claims, No Drawings

FLAME RETARDANTS FOR BLENDS OF NATURAL AND SYNTHETIC FIBERS

RELATED APPLICATION

This application is related to my copending application, Ser. No. 300,732, filed of even date herewith, incorporated herein fully.

BACKGROUND OF THE INVENTION

Purely for safety purposes, flame retardance or flame resistance of a fabric is a highly desirable characteristic. Of many methods available for developing various levels of flame retardancy all possess a variety of disadvantages, the principal ones being the inability of the flame retardant material, or treatment, to last through laundering or dry cleaning operations. Another principal disadvantage of treatments of fabrics to develop this characteristic of flame retardance is the loss of hand in the substrate. The problem is greatly aggravated in some areas of handling, particularly where it is necessary to meet statutory requirements for flame retardance in garments. Their physical condition being in the form of a bundle of fine fibers invites and encourages the sustenance of a flame if one gets started in the fabric. That is, a large area of oxidation is presented to any flame which gets started.

It is accordingly a basic object of this invention to provide a method employing familiar techniques in the textile industry for the application of flame retardant materials to textile fibers, whether the fibers be in the form of woven cloth, knitted cloth or in the form of balls of the thread prior to being woven into cloth.

Other objects and advantages of the invention will be in part be obvious and in part appear hereinafter.

DESCRIPTION OF THE INVENTION

Flame retardants for textiles and related materials of the durable type have been found to possess a multitude of side effects which would either render the flame retarded substrate unusable or reduce its useful life. In addition, most commonly used methods will be effective on one particular substrate while completely ineffective on others or blends of the same.

The present invention relates to a new method of flame retarding textile and related materials using a commonly employed method in pigment printing and dyng, that is, through the use of a primary binder which serves as an adhesive to fasten the flame retardant to a given substrate. In addition this technique can also be employed to flame retard the said binders, which normally are emulsions of synthetic polymeric materials which are highly flammable and contribute to the flammability of flame retarded substrates.

The subject of the present invention consists of two basic elements, the flame retardant element and a binding element.

The flame retarding element is a colorless highly halobrominated, organic compound, solid at room temperature, possessing high melting and decomposition points, which is easily reduced to an extremely small particle size by conventional means of grinding. The solid flame retardant material is reduced to a submicron or micron particle size and suspended in water in a fashion similar to the preparation of pigment dispersions. In some cases, especially when extremely heat stable materials are used, a synergist which will contribute to render the halobrominated solids more heat un-

stable must be employed. This synergist must possess similar characteristics to the halobrominated flame retardant, that is, it is a micropulverized solid possessing good heat stability, finely dispersed in water. In addition it must react with the halobrominated flame retarder at combustion temperatures to form a gaseous non-flammable gas which will prevent oxygen from reaching the flaming substrate, thus impeding the oxidation process.

The second element used in this invention is an emulsion of a high molecular weight polymer, commonly referred to as latex. The polymer employed can be the result of polymerizing acrylic acid, methacrylic acid, acrylamide, methacrylamide, acrylonitrile, esters of acrylic and methacrylic acids, vinyl chloride, vinylidene chloride, styrene, butadiene, maleic or fumaric acids and esters of same and the like. The polymer can be homopolymers or copolymers of the above described monomers. These emulsion polymers are commercially available in differing grades depending on the ultimate properties desired. They have in common the fact that they form films at room or elevated temperatures, alone or in the presence of plasticizers. The properties of the film depend on the chemical composition of the same.

Due to the fact that the latexes possess extremely good adhesive properties, they are normally used for bonding purposes. They are used for bonding of pigments to hard to dye substrates, to bond fibers with fibers to obtain non woven fabrics, to bond fibers to fabrics to produce flocked fabrics and to bond fabrics to fabrics, fabrics to foams, fabrics to films, to non wovens, etc., to obtain laminated fabrics. They are also used for fabric backcoating to achieve various effects such as dimensional stability, to prevent ravelling, to give fabrics non-slipping characteristics, with a filler, to impart opacity to the same, etc., and for finishing to achieve dimensional stability, to increase strength, decrease air permeability, impart waste repellency, etc.

This invention relates to two uses of these materials:

- a. To bond the flame retardant to non-reactive substrates by the use of latex adhesives; and
- b. To use the flame retardant to make the latex films non-combustible or self extinguishing when they are applied to flame retarded substrates.

In this application the solid flame retardant is the predominant ingredient and the latex is the minor ingredient.

The micropulverized solid flame retardant is first dispersed in water containing a wetting agent by adding it slowly to the aqueous phase under strong agitation, with a high speed, high shear mixer. After addition of the solid has been completed, the resulting dispersion is stabilized by adding small quantities of a protective colloid (commonly called thickener) such as carboxy methyl cellulose, methoxy or ethoxycellulose of selected molecular weight to achieve an optimum viscosity and prevent the particles from settling.

The FR (flame retardant) is now diluted with water to a predetermined strength and sufficient amount of latex to achieve adhesion is added. This solution is now applied to the substrate by dipping it into this solution and removing the excess by squeezing between two rollers. The wet substrate is now air dried at any convenient temperature and baked at 125°C. to 150°C. for 180 to 90 seconds.

The resulting material is flame retardant when tested by commonly used flammability tests and the flame retardant is not lost after multiple launderings and/or dry cleanings. The feel or hand of the flame retarded material is unchanged, but can be made stiff, if desirable, by selecting a harder latex.

The FR dispersion prepared as described above, is diluted in water, the latex is added and the viscosity adjusted by the use of a thickener.

This treating batch is now applied by different techniques depending on the final effect desired. It can be padded, knife coated, roller coated, sprayed, roller printed, screen printed, applied by saturation and the like. The substrates are now air dried at any convenient temperature, and baked as above.

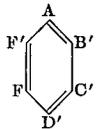
This technique is usually employed when the substrate to which the latex is applied is either intrinsically flame retardant or has been flame proofed in a separate operation. It can be used to flame retard latices, which will be employed as flocking adhesives, for fabric back-coating, pigment dyeing or printing, bonding or non woven fabric lamination and the like.

The process of this invention is applicable to textile materials, in staple, tow, yarn, fiber, woven fabrics, non-woven fabrics, circular and flat knits, carpets and the like, to paper, to films, to foams, etc.

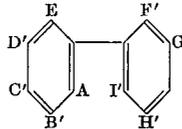
The substrate can be of natural origin such as cotton, linen, jute, coco fiber, wool, silk and the like, man made such as regenerated cellulose, cellulose di- and triacetates, fiberglass and the like or synthetic polymeric materials such as nylon, polyester, acrylics, polypropylene and the like.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

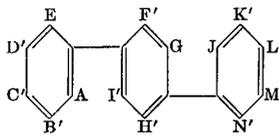
The present invention utilizes brominated aromatic compounds, preferably brominated as flame retarding materials. The preferred aromatic compounds employed are derivatives of



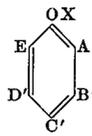
Benzene



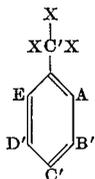
Biphenyl



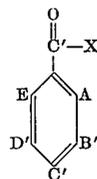
Terphenyl



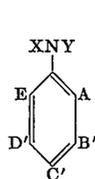
Phenol



Toluene



Benzoic acid

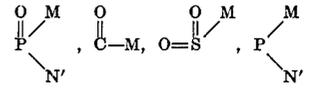


Aniline

Where A through N' are the same or different and can be H, Br, CH₃, C₂H₅, C₃H₇,

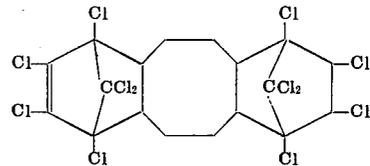
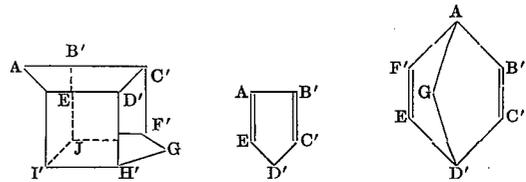


C₄H₉ and the like; and X, Y, Z can be the same or different and can be H, CH₃, C₂H₅, C₃H₇, C₆H₅,

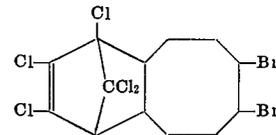


and the like, where N' and M can be the same or different and can be chosen among H, NH₄, NH₂, Na, K, Li, Ca, Mg, Ba, Sb, Ti, I, IV, VI, VII, and the like.

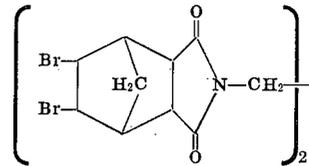
Cyclic compounds of the nature:



Bis(hexachlorocyclopentadieno)-cyclooctane



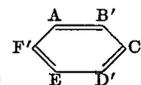
Dibromohexachlorocyclopentadienocyclooctane



N₁N₁-ethylbis(dibromonorbornene)-dicarboxamide

The preferred entities are:

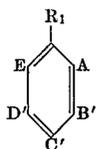
1. Polybrominated benzenes of the general formula:



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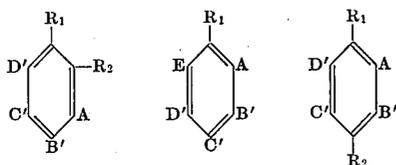
where A to F are the same or different and may be H, Br, with at least one Br present on the benzene ring.

2. Polybromo monoalkyl benzene of the general formula:



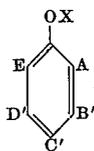
where R₁ may be alkyl, preferably of 1-5 carbons such as methyl, ethyl, propyl, butyl, pentyl, isopropyl, tert-butyl; unsaturated alkyls, haloalkyl or polyhaloalkyl wherein the moiety may include up to four bromine atoms where the halogens are chlorine and/or bromine and A, B', C', D', E, are as above.

3. Polybromo dialkyl benzene of the general formula:

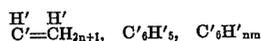
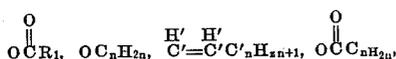


where R₁ and R₂ are the same or different and are similar to R₁ in (2).

4. Polybrominated phenols of the general formula:



where X can be H', R, OR,



where *n* is 1 to 4, X is Cl or Br and *m* varies between 1 to 5,

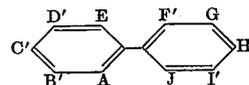


where R₃ and R₄ are the same or different and can be H, alkyl preferably of 1-5 carbon atoms, bromoalkyl, polybromoalkyl and the like; aryl, phenyl, bromoaryl, bromophenyl, polybromoaryl, polybromophenyl, NH₂, NH₂, Na, K, Li, Ca, Ba, Sb, Ti and the like;

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5. Polybrominated biphenyls of the general formula:

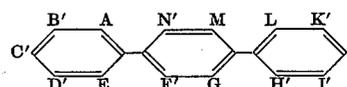


where A to J are the same or different and can be H, Br, lower alkyl C₁ to C₅ aryl,



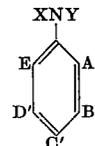
X being OH, NH₂, ONH₄, Na, K and the like.

6. Polybrominated terphenyls of the general formula:



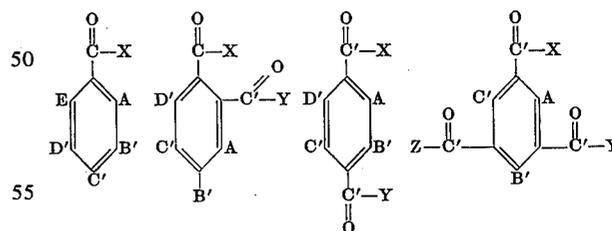
where A to N are the same as in 5.

7. Polybrominated aniline of the general formula:

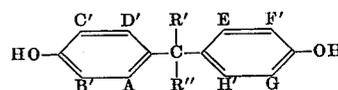


where A to E are the same as in 5, and X and Y are H, lower alkyl C₁ to C₅, aryl, bromoalkyl, polybromoalkyl, bromoaryl, polybromoaryl, phenyl bromophenyl, polybromophenyl and the like.

8. Polybrominated aromatic mono and polyacids, anhydrides or esters of the same or the general formula:



9. Polybrominated bisphenol A of the general formula:



In the process of preparing the flame proofing agent of the present invention, there is also utilized a synergist which reacts with the halobrominated organic material at the flame temperatures inducing its decomposition and liberating a nonflammable gas which forms a blanket around the flaming substrate, displacing the oxygen from the vicinity of the same thus impeding the oxidation process of the combustion.

The synergists are normally metallic oxides of the general formula:

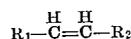


where Me can be Al, Ga, Si, Ge, As, Sb, Bi, Ti, Zr, and the like and n is the valence of the metal in its oxidized state. Especially are the oxides of aluminum, germanium, antimony and titanium useful.

These oxides must also be present in a fine particle state of the same size as the halobrominated compound or smaller.

The synergist is blended with the halobrominated compound during the preparation of the FR dispersion, the ratio of halobrominated compound to synergist depending on the stability of the halobrominated material and the reactivity of the particular metallic oxide employed. It was found that normally 3 to 7 parts halobrominated flame retarder for each part of metallic oxide, preferably 4-6 parts to 1 part, give the best results.

The emulsion polymers, commonly referred to as synthetic latices, are commercially available materials, obtained by emulsion homo- or co-polymerization of monomers of the general class:



where R₁ and R₂ can be the same or different and can be selected among H, Cl, Br, CH₃, C_nH_m, where n is 1 to 5 and m = 2n + 1, COOH, CONH₂, CN, CH = CH₂, C₆H₅ and the like.

The preferred monomers are alkyl esters of acrylic and methacrylic acids, acryl- and methacryl amides, acrylonitrile, acrylic and methacrylic acids, maleic or fumaric acids and alkyl esters of the same vinyl and vinylidene chlorides, styrene and butadiene.

Due to the infinite number of possible combinations we will class the polymers in the following group:

- a. Acrylic latices, mainly homo- or co-polymers of alkyl esters of acrylic or methacrylic acids which can also contain acrylic or methacrylic acid, acrylonitrile, acrylamide, n-methylol acrylamide, vinyl and vinylidene chlorides and the like. The alkyl group of the esters can also contain hydroxyl groups. The presence of reactive groups, such as HO, CONH₂, COOH,



suggests the possibility of further crosslinkage by the effect of heat leading to a higher molecular weight and thus much more stable polymers. These types of polymers are referred to as cross-linking, self-cross linking or thermosetting latices.

- b. Acrylonitrile Latices: where the major ingredient is acrylonitrile which can be found as homo polymers or copolymers as in (a).

- c. Vinylchloride Latices: where the major constituent is this monomer homo-polymerized or copolymerized as in (a).

- d. Vinylidene chloride latices;

- e. ABS (acrylonitrile - butadiene - styrene) latices: where these three monomers are the principal ingredients and can also be copolymerized with other monomers as in (a).

- f. SBR (styrene - butadiene - rubber) latices.

- g. Also there are employed emulsion polymers obtained by the reaction of a polyisocyanate and an aliphatic polyol which can be a polyether, a polyester, or a polycaprolactone, the preferred polyisocyanate being a mixture of isomers of toluene diisocyanate and the preferred polyol being a polyethylene glycol condensate having a molecular weight in excess of 3,000, commonly referred to as a polyurethane latex.

The reason for blending these various monomers is to achieve polymers with varying film properties, such as:

1. Feel or hand of film. This can vary from soft to hard and from tacky to dry. This parameter is measured by the glass transition temperature (T.G.) or in some cases by T₃₀₀ (temperature at which the torsional modulus of an air dried film is 300 Kg/CM²). Both are measured in °C and can range from -100°C to +100°C. As a general rule, the lower the TG or T₃₀₀ the softer the film, the film becoming harder with increasing temperatures.
2. Solvent swelling resistance. Latices are known to swell when wetted with organic, especially chlorinated solvents, resulting in lack of durability to dry cleaning. This property is improved by introducing cross-linkable sites into the molecule of the polymer.
3. Film strength. The strength of the film is also improved by increasing the molecular weight of the polymer through the introduction of crosslinkable sites which are made to react by heat and/or catalysts.
4. Adhesion of film. This property is very important since the durability of the flame retarder will greatly depend on it.

In the process of preparing the flame retardant dispersion 1 to 4 parts, preferably 2 to 3 parts, of a finely divided powdered halobrominated organic material is dispersed in 1 part of water containing 0.1 to 1% of anionic wetting agent by the use of a high shear mixer. After addition is completed 0.1 to 1 part, preferably 0.2 to 0.4 part, based on the weight of the halobrominated organic compound of a metallic oxide is slowly added. After addition is complete the dispersion is stabilized by adding 0.1 to 0.5%, preferably 0.2 to 0.3%, on the weight of the dispersion of a protective colloid such as ethoxy cellulose.

In the case when it is necessary to flame retard a given substrate 0.5 to 1.5 parts, preferably 0.8 to 1.2 parts, of FR dispersion are dissolved in 1 part of water with mild agitation. To this solution 0.05 to 0.4, preferably 0.1 to 0.3 part of a latex containing 35 to 65%, preferably 45 to 55%, of a polymer is added. In treating hydrophobic substrates, 0.5 to 1.5%, preferably 0.8 to 1.2% of a wetting agent is added.

The substrate to be treated is dipped in this solution and the excess removed by squeezing between two rollers. The wet material is air dried in an oven at 80°C to 130°C, preferably 100°C to 110°C, and baked at 140°C

to 18°C, preferably 150°C to 170°C for ½ to 5 minutes, preferably 1 ½ to 3 minutes.

When the substrate to be treated is either intrinsically flame resistant or has been flamed retarded in a separate operation and must be treated with a flammable latex to achieve some desirable effect on the substrate the treating solution is prepared as follows: To 1 part of water 0.5 to 1.5 parts, preferably 0.8 to 1.2 parts, of latex is added, and the solution is mixed until uniform. 0.05 to 0.2 part, preferably 0.1 to 0.15 part, based on the weight of the latex of FR dispersion is added and mixed to uniformity. At this point any other needed auxiliaries, such as pigments, thickeners, fillers, plasticizers, wetting agents, catalysts, and the like, are incorporated in any required proportion and the solution mixed.

The treating solution is now applied to the flame resistant substrate by any convenient way, such as padding, coating, printing, saturation and the like and the wet goods are dried and baked as above.

EXAMPLE I

70 parts of finely divided decabromo biphenyl possessing an average particle size between 1 and 2 microns was slowly added to 50 parts water containing 0.2% anionic wetting agent of the alkyl-aryl sulfonate type, under strong agitation with a high speed, high shear mixer. After completing the addition of the brominated compound 12 parts of finely divided antimony-trioxide possessing an average particle size between 1 and 2 microns were slowly added while agitation was continued. After all the antimony trioxide was added the resulting milky white dispersion was stabilized by addition of 5 parts of a 4% aqueous solution, having a viscosity of 300,000 centipoise, of ethoxycellulose. This dispersion, thus obtained, remained uniform after prolonged storage at room temperature and was designated dispersion I.

50 parts of dispersion I were now dissolved in 40 parts of water and 10 parts of a 50% aqueous emulsion of a copolymer of ethyl acrylate and acrylamide having a T_{300} of -47°C were added.

A woven fabric weighing 4 ozs. per square yard composed of 50% cotton 50% polyester was now treated with this solution by immersing it in the same and removing the excess by squeezing between two rollers. The wet pick-up was 90%. The fabric was now dried at 110°C and baked at 150°C for 3 minutes.

The fabric thus obtained was quite soft to the feel was further softened by padding it through a 10% emulsion of polyethylene softener in water.

The flame resistance of the fabric thus treated was evaluated by testing according to test method given in "Standard for the Flammability of Children's Sleepwear" DOC FF3-71 giving an initial average char length of 1 ½ inches and 2 inches after 50 launderings and tumble dryings.

EXAMPLE II

70 parts of finely divided hexabromo benzene having an average particle size between 1 and 2 microns were dispersed in 50 parts of water in a similar fashion to dispersion I. 15 parts of aluminum oxide were added to the dispersed brominated compound and this dispersion was stabilized as dispersion I. This material was designated dispersion II.

40 parts of dispersion II were dissolved in 52 parts of water and 8 parts of a 50% emulsion of a styrene butadiene copolymer having a glass transition temperature of -80°C were added.

A piece of 100% cotton circular knit weighing 8 ozs./yd² was immersed in this solution and the excess removed by squeezing between two rollers. The wet pick-up was 120% and the fabric was dried at 110°C and baked at 150°C for 3 minutes. The fabric was softened by padding through a 10% emulsion of a polyethylene softener and dried.

The fabric was judged flame retardant by using method outlined in DDC FF3-71, giving an initial average char length of 1 inch and 2 ½ inches after 50 launderings and tumble dryings.

EXAMPLE III

70 parts of finely divided pentabromo toluene and 20 parts of titanium dioxide having an average particle size of between 1 and 2 microns were dispersed in 50 parts of water as in Example I. This dispersion was designated dispersion III.

50 parts of dispersion III were dissolved in 40 parts of water and 10 parts of a 50% acrylonitrile-styrene-butadiene latex having a glass transition temperature of -60°C were added to this solution. The resulting mixture was padded onto a woven fabric composed of 80% rayon and 20% cellulose diacetate in a similar fashion as in Examples I and II. The fabric was dried at 110°C, baked at 150°C, top softened with a 10% emulsion of a polyethylene softener and redried.

The treated fabric gave an average char length of 3 inches initially, when treated according to AATCC Flammability Test 34-1967, an average char length of 4 inches after 5 launderings and tumble dryings and an average char length of 5 inches after 5 commercial dry cleanings.

EXAMPLE IV

70 parts of Tris dibromophenyl phosphate and 10 parts of antimony trioxide having an average particle size between 1 and 2 microns were dispersed in 40 parts of water as in Example I. This dispersion was designated dispersion IV.

50 parts of a 50% emulsion of a butyl acrylate - N-methylol acrylamide - acrylonitrile copolymer latex having a glass transition temperature of 0°C were dispersed in 30 parts of water. To this solution 10 parts of a 50% aqueous dispersion of disperse blue 1 (color index No. 42025) and 10 parts of dispersion IV were added and the resulting mixture agitated until uniform.

A 100% woven fiberglass drapery fabric was immersed in this solution, the excess removed by squeezing between two rollers to obtain a wet pick-up of 50%, dried at 110°C and baked at 150°C for 3 minutes.

This fabric gave an average char length of 3 inches when tested using AATCC flammability test 34-1967 initially, after 5 launderings and tumble drying and 5 commercial dry cleanings.

EXAMPLE V

70 parts of finely divided tribromoaniline and 15 parts of micropulverized aluminum trioxide having a particle size of between 1 and 2 microns were dispersed in 50 parts of water following procedure given in Example I. This dispersion was designated as dispersion V.

0.5 parts of tetrasodium pyrophosphate were dissolved in 14.5 parts of water. Under strong agitation 10 parts of a finely divided clay and 5 parts of dispersion V were added. Upon completion of the addition 45 parts of a 50% aqueous emulsion of a polymer obtained by the copolymerization of ethyl acrylate, n-methylol acrylamide, acrylonitrile and acrylic acid having a glass transition temperature of -2°C . were mixed in. The viscosity of this dispersion was adjusted to 35,000 centipoises by adding 24 parts of a 4% solution of methoxy cellulose. Finally, 1 part of a 10% solution of oxalic acid (acid catalyst) were mixed into this dispersion. This dispersion was designated V-A.

A piece of the 80% rayon 20% cellulose diacetate fabric treated in Example III was coated on one side with dispersion V-A using a doctor blade to a loading of 70% on the weight of the fiber. The fabric was dried at 125°C and cured at 160°C for 2 minutes.

The fabric thus treated gave a char length of 3 inches when tested according to AATCC method 34-1967, initially after 5 launderings and 5 dry cleanings. The same fabric coated with the same composition, but without dispersion V was consumed entirely when tested by this flammability method.

EXAMPLE VI

70 parts of finely pulverized tetrabromo phthalic anhydride and 10 parts of arsenic trioxide having an average particle size between 1 and 2 microns were dispersed in 40 parts of water similarly to Example I. The resulting dispersion was designated VI.

Using a standard pebble mill a latex exterior paint was prepared using the following formulations:

	Parts By Weight	
	VI-A	VI-B
Water	300	300
Anionic Dispersing Agent	1	1
Hydroxyethyl Cellulose Thickener	5	5
Talc	125	125
Rutile Titanium Dioxide	225	225
50% Solids Vinylacetate-ethylacrylate copolymer	400	400
Dispersion VI	45	

The dispersion were prepared by predissolving the ingredients in the given order in a tank equipped with a high-speed high-shear mixer and then transferring the resulting dispersion into the pebble mill and milling for 5 hours.

Two pieces of plywood were coated on both sides with dispersions VI-A and VI-B using a paint brush and air dried at room temperature.

The flammability of both pieces of plywood was tested by applying to them a flame from a butane blow torch for 15 seconds. The piece of plywood treated with dispersion VI-A immediately extinguished after removal of the blow torch giving a charred surface where the flame was in contact with the coating, whereas the plywood coated with dispersion VI-B continued burning until completely consumed.

EXAMPLE VII

70 parts of finely divided hexachlorocyclopentadienodibromocyclooctane and 10 parts of micropulverized antimony trioxide having a particle size between 1 and 2 microns were dispersed in 40 parts of

water following procedure given in Example I. This dispersion was designated dispersion III.

20 parts of dispersion VII were dispersed in 40 parts of water and 40 parts of a 50% aqueous emulsion of a polymer obtained by reaction of a mixture of isomers of toluene diisocyanate and a condensation product of ethylene glycol having a molecular weight of approximately 4,000.

A piece of 100% nylon upholstery fabric was immersed in this solution and excess removed by squeezing between two rollers to achieve a 70% wet pickup and then dried at 125°C .

The fabric thus treated was judged flame retardant when it gave a 3 inches char length when listed according to AATCC method 34-1969, whereas the untreated fabric burned the entire length when tested according to the same method.

Using and techniques and formulations of any of the examples given, namely, 1 through 7, the following compounds may be used for application to the various bases identified in the several examples:

Polybrominated biphenyl	=	hexabromo
Polybrominated biphenyl oxide	=	decabromo biphenoloxide
Polybrominated benzene	=	hexabromo
Polybrominated toluene	=	pentabromo toluene
Polybrominated chlorotoluene	=	tetrabromo
Polybrominated phenol	=	pentabromo phenol
Polybrominated aniline	=	tribromo aniline
Polybrominated benzoic acid	=	dibromo benzoic acid
Tris phosphates of polybrominated phenols		
Polybrominated cyclopentane	=	tetrabromo cyclo
Polybrominated cyclohexane	=	hexabromo cyclo
Polybrominated cyclooctane	=	hexabromo cyclo
Polybrominated cyclodecane	=	hexabromo cyclo
Polybrominated cyclododecane	=	hexabromo cyclo
Hexachlorocyclopentadienodibromocyclooctane	=	hexabromo cyclo
N,N'-ethyl-bis(dibromonorbornene-dicarboximide)		
Per chloro penta cyclodecane		

What is claimed is:

1. A method of rendering flammable textile materials flame retardant which comprises:

treating said materials with a flame retardant composition consisting essentially of a brominated, organic aromatic or cyclic compound and a metallic oxide, in aqueous dispersion, in admixture with an aqueous emulsion of a suitable high molecular weight polymeric adhesive binder, said brominated compound and said metallic oxide being solids at room temperature, substantially totally insoluble in water, having been reduced to an average particle size below 2 microns, and being in weight ratio of 1:4 parts of brominated compound to 0.1:1 part of metallic oxide, said high molecular weight polymeric binder being present in amount sufficient to secure said brominated organic compound and metallic oxide flame retardant composition to said material, and drying and curing said treated material, wherein the total amount of flame retardant deposited on said material is effective to reduce the flammability of the textile and is durable to laundering and dry cleaning.

2. The method in accordance with claim 1 whereby drying is carried out at elevated temperatures of 100° – 175°C .

3. The method in accordance with claim 1 in which the flame retardant is applied by padding.

4. The method in accordance with claim 1 in which the flame retardant is applied by knife coating.

5. The method of claim 1 wherein the brominated solid organic material is selected from the group consisting of:

Polybrominated biphenyl
 Polybrominated biphenyl oxide
 Polybrominated benzene
 Polybrominated toluene
 Polybrominated chlorotoluene
 Polybrominated phenol
 Polybrominated aniline
 Polybrominated benzoic acid
 Tris phosphates of polybrominated phenols
 Polybrominated cyclopentane
 Polybrominated cyclohexane
 Polybrominated cyclooctane
 Polybrominated cyclodecane
 Polybrominated cyclododecane
 Hexachlorocyclopentadieno-dibromocyclooctane
 and
 N,N' -ethyl-bis (dibromo-norbornene-dicarboximide).

6. The method of claim 1 wherein the metallic oxide is selected from the group consisting of: Al, Ga, Si, Ge, As, Sb, Bi, Ti and Zr oxides.

7. The method of claim 1 wherein the latexes are selected from the group consisting of:

Polymers of esters of acrylic acid
 Styrene butadiene copolymers
 Acrylonitrile-styrene-butadiene copolymers
 Copolymers of ethyl acrylic-N-methylol acrylamide-acrylonitrile-acrylic acid
 Vinyl acetate-ethyl acrylate copolymers
 Butyl acrylate-N-methylol acrylamide-acrylonitrile,
 and
 Polyurethane polymers.

8. A textile material inherently flammable, rendered

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flame resistant by the impregnation with a flame retardant composition in accordance with the process of claim 1.

9. The method of claim 1 wherein the brominated compound is selected from the group consisting of:

Polybrominated biphenyl
 Polybrominated biphenyl oxide
 Polybrominated benzene
 Polybrominated toluene
 Polybrominated chlorotoluene
 Polybrominated phenol
 Polybrominated aniline
 Polybrominated benzoic acid
 Tris phosphates of polybrominated phenols
 Polybrominated cyclopentane
 Polybrominated cyclohexane
 Polybrominated cyclooctane
 Polybrominated cyclodecane
 Polybrominated cyclododecane
 Hexachlorocyclopentadieno-dibromocyclooctane,
 and,
 N,N' -ethyl-bis (dibromo-norbornene-dicarboximide),

the metallic oxide is selected from the group consisting of:

Al, Ga, Si, Ge, Sb, Bi, Ti, and Zr oxides,
 and

the latex is selected from the group consisting of:

polymers of esters of acrylic acid
 styrene butadiene copolymers
 acrylonitrile-styrene-butadiene copolymers
 copolymers of ethyl acrylate-N-methylol acrylamide-acrylonitrile-acrylic acid
 vinyl acetate-ethyl acrylate copolymers
 butyl acrylate-N-methylol acrylamide-acrylonitrile
 and
 polyurethane polymers.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,877,974 Dated April 15, 1975

Inventor(s) Vladimir Mischutin

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 Page, "[21] Appl. No.: 330,731"
should read: - - [21] Appl. No.: 300,731 - -

Signed and sealed this 17th day of June 1975.

(JEM)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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