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FLAMEPROOFING METHOD AND PRODUCT

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This invention relates to the impregnation of natural or synthetic cellulosic fibers and fabrics with flameproofing and water-repelling substances and to the flameproofed impregnated cellulosic materials obtained. More particularly, the invention relates to methods of applying impregnating substances to such fibers and fabrics, which methods result in treated materials of tensile strength and storage life comparable to untreated materials.

The invention, in general, contemplates the provision in stable relation upon a fibrous or fabric flammable material of flameproofing and water-repelling substances including both inorganic flame retardant substances, such as antimony oxide, and highly chlorinated organic substances, such as chlorinated paraffin, such substances being maintained in entirely stable relationship on the treated material at ordinary temperatures but being adapted to co-act in flame retarding relationship upon exposure of the treated materials to flame temperatures. In the following specification, the invention is described with relation to its application to woven fabric, such as cotton duck, it being understood, however, that any fibrous or woven material of cellulosic origin may be similarly treated and the advantages of the invention thus obtained.

The flameproofing of fabrics has heretofore been proposed; furthermore, the provision of fabric impregnated with an inorganic flame retardant substance, such as antimony oxide, combined with an organic flame retardant substance, such as highly chlorinated paraffin, is also known. These prior proposals have envisioned the inhibition of flaming at flame temperature both by the individual action of the flame retardant materials and by the combined chemical action of the two substances.

The prior art, however, has not provided an entirely satisfactory solution to the flameproofing of fabrics in that while the action of the materials applied to the fabrics has been satisfactory at flame temperatures, the flameproofing materials on the fabric have resulted in a tendering or weakening of treated fabrics at normal temperatures, especially after relatively extended periods of storage or use and particularly at mildly elevated temperatures or under conditions of exposure to sunlight, such as can be expected to be encountered in ordinary storage and use.

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According to prior practice, inorganic materials, such as antimony oxide, and organic materials, such as chlorinated paraffin, are suspended or dispersed in a liquid medium either alone or with various added materials, such as resinous substances, designed to improve adherence of the flameproofing mixture to the fabric, dyes, fillers or the like, and such suspension is applied to the cloth. Thus, the mixture of inorganic materials, chlorinated material and solvent is in intimate contact with the interstices of the fibers and upon the solvent being removed, the two flame retardant materials remain in such relationship and in contact with each other on the finished fabric.

It is known that highly chlorinated organic materials, such as chlorinated paraffins, are somewhat unstable and tend, especially when heated, to dehydrochlorinate releasing hydrogen chloride; in fact, it is generally believed that at least part of the flameproofing character of the above-mentioned mixture lies in this property and in the subsequent reaction of antimony oxide with hydrogen chloride to form antimony oxychloride, which is characterized by notable inhibition of combustion. Accordingly, at flame temperatures the ready release of hydrogen chloride is desired, for whatever the theory of its action, it is known that flameproofing compositions which do not release hydrogen chloride at such temperatures are relatively inefficient.

The spontaneous release of hydrogen chloride from the chlorinated material on the fabric, which release takes place at an appreciable rate at ordinary temperatures of storage or use, is, however, quite another matter and results in a relatively substantial loss of tensile strength of prior art treated fabrics and in relatively short times. Various neutralizing substances, such as calcium carbonate, have been included in flameproofing materials for the purpose of nullifying the harmful effect of released hydrogen chloride but such modifications have also failed to produce a flameproofed fabric having satisfactory storage life.

As a result of the present invention, however, it is now appreciated that the intimate contact of the highly chlorinated organic substances with the fibers of the fabric is detrimental thereto; the hydrogen chloride released acting to tender or lessen the tensile strength of the cellulosic

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materials. Decomposition of chlorinated materials results presumably in part from spontaneous action and in part from contact with the normal environment of such materials in storage or use, such as light, air and moisture. In addition, the inorganic flame retardant materials or impurities normally present therein, which heretofore have been in intimate contact with the highly chlorinated material, play a substantial role in this undesired production of hydrogen chloride.

The method of the present invention includes the application of the inorganic flame retardant substance and the chlorinated organic material to fabric in such a manner as normally to maintain said substances out of contact with each other and normally to maintain the chlorinated material out of contact with the fabric, while still permitting intimate contact to be readily established to produce flame inhibiting relationship at flame temperatures.

The present invention, which permits the maintenance of the fibers of the fabric out of contact with the chlorinated material during storage or use may be achieved by separating the fibers of the fabric from the chlorinated material with an auxiliary water-repellent, normally hydrogen chloride inert, film which, in addition to functioning as a screen between the chlorinated material and the fibers, binds the inorganic flame retardant substance within the interstices of the fibers. In addition to enhancing the storage life of the fabric, the auxiliary film, which is preferably water-repellent, improves the moisture-proof character of the treated fabric.

Application of the auxiliary film material may be achieved in a number of ways. If desired, the film forming material may be incorporated into a suspension of inorganic flame retardant material prior to application to the fabric in a manner to coat completely the particles of the inorganic material. This combination of inorganic material and film forming material may then be applied to the fabric to insure the complete coating of the fibers of the fabric. Then upon subsequent application of the chlorinated organic material to the thus initially treated fabric, the chlorinated material being preferably applied in a solvent therefor which is a non-solvent for the film material, a system will be obtained wherein the chlorinated material, though closely associated with the fabric and adapted to co-act with the inorganic flame retardant substance at flame temperatures, is nevertheless normally maintained out of actual contact with the fibers of the fabric and with the inorganic materials whereby decomposition of the chlorinated material and release of HCl at other than flame temperatures cannot deleteriously affect the fibers of the fabric.

It is also within the contemplation of the invention that suspended particles of inorganic flame retardant material may be coated with the film forming material, particles of chlorinated material may be similarly so coated and present in the same suspension, whereby a system is achieved wherein the inorganic and organic materials are maintained in separated relationship in suspension in the same solvent. The fabric is then contacted with a film forming material whereby the fibers of the fabric are essentially completely coated, whereupon the prepared suspension of coated inorganic and organic flame retardant material is applied to the thus treated fabric, achieving a finished material wherein as before, the flame retardant agents are separated

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from each other and particularly the chlorinated organic material is separated from the fibers of the fabric. Upon reaching flame temperatures, however, the flame retardant materials co-act to inhibit flaming as described above.

Still another and the preferred method of achieving the desirable results of this invention contemplates the application to the fabric of the inorganic flame retardant material suspended in a volatile solvent, followed by application of a film forming material thereto, and finally applying a solution of chlorinated material in a non-solvent for the film forming material. It will be seen that under the conditions of this aspect of the invention, the desired normal separation of the flame retardant materials and the separation of chlorinated material from the fibers is again achieved, while also providing an environment for the flame retardant to co-act at flame temperatures.

The inorganic flame retardant substance to be used in the practice of the present invention may comprise salts of antimony, arsenic, and bismuth, or salts of phosphoric, boric or stannic acids or mixtures thereof. In general, compounds of antimony, particularly antimony trioxide (Sb_2O_3), are preferred. The highly chlorinated organic flame retardant substance may be any one of several types of chlorinated organic compounds, such as chlorinated oils of vegetable or animal origin, chlorinated paraffin wax, or wax-like substances. In general, it is preferred that the chlorinated substance be non-toxic to warm-blooded animals, readily soluble in organic solvents, and that such substance possess a low vapor pressure, while releasing substantial amounts of hydrogen chloride at flame temperatures. The preferred highly chlorinated organic substance for the practice of the present invention is a chlorinated paraffin wax containing between 40% and 70% of chemically combined chlorine, it also having been found advantageous to use mixtures of highly chlorinated paraffins, one component of such mixture containing about 40% of chemically combined chlorine and another component containing above 65% of chemically combined chlorine.

The film forming substance to be used in the practice of the present invention as a screen or barrier between the somewhat unstable chlorinated organic material and the fibers of the fabric, as well as the inorganic flameproofing material, may be drawn from a wide variety of film forming resinous materials which are characterized by substantial insolubility in at least one solvent in which the chlorinated material has substantial solubility. In addition, of course, in order to enhance the ultimate water-repellency of the fabric treated, the film forming screen material is preferably itself water-repellent when deposited as a film. Also, the film forming material must be readily decomposable at flame temperatures in order that the inorganic and organic flame retardant materials may co-act at such temperatures to inhibit burning of the fabric. At ordinary service temperatures, however, it is preferred that the film forming material be inert to conditions to which fabric may be exposed as well as to both the inorganic and organic constituents of the flameproofing composition.

In the following table are set forth various examples of resinous film forming substances which meet the above conditions; many other specific examples will occur to those skilled in

the art without departing from the scope of the invention herein.

oxide (Sb_2O_3) 100 parts, urea-formaldehyde condensation product (50% solution) 72 parts, com-

Table "A"

Film Forming Material	Solvent	Chlorinated Material	Solvent
Ethyl Cellulose.....	Acetone.....	Chlorinated Paraffin..	Chain Hydrocarbons. ¹
Polyethylene.....	Hot Xylol.....	do.....	Cold Xylol.
Cellulose Acetate.....	Acetone.....	do.....	Chain Hydrocarbons. ¹
Styrene Resins.....	Esters—Ketones.....	do.....	Do. ¹
Polyvinyl Butyral.....	Aliphatic Alcohols.....	do.....	Do. ¹
Methylmethacrylate.....	Acetone.....	do.....	Cyclohexane.
Ethylmethacrylate.....	do.....	do.....	Do.
Isopropylmethacrylate.....	do.....	do.....	Hexane.
n-Butylmethacrylate.....	do.....	do.....	Do.
n-Propylmethacrylate.....	do.....	do.....	Do.
Isobutylmethacrylate.....	do.....	do.....	Do.

¹ Heptanes to light kerosene (duodecane) substantially no aromatics.

The film forming substance may be applied to the cloth in any of the previously described sequences of steps by any suitable means, such as hot rolling, calendering, flame spraying, solution spraying, brushing, doctoring, or the like.

It will be appreciated that the adoption of different chlorinated materials from chlorinated paraffin in the practice of the present invention may introduce slight variations in the information given in the table above. However, as stated hereinbefore, any film forming resin, especially the water insoluble members of such class of resins which is insoluble in a solvent in which the chlorinated material is soluble, may be employed herein. Also, it will be appreciated from the foregoing that, though there exist a number of variations which may be resorted to in the practice of the present method, it is in general preferred, to obtain the desired protection of the fibers of the fabric, that the film forming material be applied to the fabric prior to application thereto of the chlorinated material.

For a more complete understanding of the present invention and in order to enable those skilled in the art to practice the same, the following specific examples are offered, it being understood that the same are to be taken as illustrative only.

Example I

Bath I: Antimony oxide (Sb_2O_3) 200 parts, urea-formaldehyde condensation product (50% solution) 72 parts, xylol 350 parts. Bath II: A 10% hot xylol solution of polyethylene having an average molecular weight of about 15,000. Bath III: Chlorinated paraffin wax containing 40% of chemically combined chlorine 120 parts, comminuted calcium carbonate 200 parts, urea-formaldehyde condensation product (50% solution) 26 parts, cold xylol 633 parts.

A heavy canvas material (14 ounce duck) is dipped in bath I and removed, dried at 190° F. for 30 minutes, and then dipped in bath II and dried at 190° F. for 30 minutes, and then dipped in bath III and dried at 190° F. for 30 minutes. The material is found to have increased in weight after the third dip by about 60% of the original weight of the untreated cloth. Using the standard fire test, E-11 of the Jeffersonville Quartermaster Depot, Specification No. 242, Section F-3, the following results are obtained as an average from several specimens tested: Duration of the flaming (seconds)—0; Length of char (inches)—2%.

Example II

(Olive drab colored coating) Bath I: Antimony

minuted calcium carbonate 100 parts, xylol 375 parts. Bath II: A 10% solution of polyethylene in hot xylol similar to that used in Example I. Bath III: Chromium oxide (Cr_2O_3) 46 parts, yellow iron oxide 34 parts, red iron oxide 24 parts, Ramapo Blue (dye) 2½ parts, comminuted calcium carbonate 50 parts, copper naphthenate (8% solution in xylol) 45 parts, chlorinated paraffin wax containing 40% of chemically combined chlorine 100 parts, chlorinated paraffin wax containing 70% of chemically combined chlorine (70% solution on xylol) 60 parts, cold xylol 255 parts.

A heavy canvas material (14 ounce duck) is dipped in bath I and dried at 190° F. for 30 minutes and is found to have increased in weight by 25.6% based on the original weight of the cloth. This is followed by dipping in bath II and drying at 190° F. for 30 minutes; after this drying, the weight of the deposited film is 4.6% of the original weight of the untreated cloth. This is followed by dipping in bath III, drying at 190° F. for 30 minutes, following which the material has increased by 35.6% of the original weight of the untreated cloth, giving a total pickup from all three baths of 65.8% based on the weight of the untreated cloth. A fire test made by the same specification as that used in Example I gives the following results: Duration of flaming (seconds) 1; length of char (inches) 3. An examination of the cross-section of this material shows that none of the materials contained in bath III penetrate the material which was applied in bath II and further that no pigmented portion is in contact with the fibers of the canvas duck.

Example III

Using the same parts and proportions as in Example I for bath I, a 10% solution of methyl methacrylate in acetone for bath II, and the same proportions described in Example I for bath III, all dissolved (or in the case of calcium carbonate suspended) in cyclohexane, the procedure of Example I results in a water-repellent material having flame retardant properties similar to that of the product of Example I and having shelf and normal use life equal to untreated cloth.

While we have described in detail certain forms of our invention and certain specific examples of its practice, we do not wish to be understood as limiting ourselves to the use of such examples as we realize that changes within the scope of the invention are possible, and we further intend each step in the following claims to refer

to all equivalent steps for accomplishing the same result in substantially the same or equivalent manner, it being our purpose to cover our invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A fibrous cellulosic material of substantial flame-retardant properties comprising, in combination, a fibrous cellulosic base, a non-halogenated inorganic, flame-retardant substance deposited thereon, a resinous, organic, non-halogenated, heat-decomposable, film-forming substance overlaying said inorganic flame-retardant substance deposited upon said cellulosic base, and a highly chlorinated organic flame-retardant substance having a low vapor pressure, capable of releasing substantial amounts of hydrogen chloride at flame temperatures, deposited upon said film-forming substance so as to be maintained out of contact with said cellulosic base and said inorganic flame-retardant substance by means of said film-forming substance.

2. A fibrous cellulosic material having deposited thereon, a non-halogenated inorganic, flameproofing agent comprising antimony oxide (Sb_2O_3), a heat-decomposable, non-halogenated, film-forming, resinous substance overlaying said inorganic flameproofing composition on said cellulosic material, and a highly chlorinated organic flame-retardant substance having a low vapor pressure, capable of releasing substantial amounts of hydrogen chloride at flame temperatures, deposited upon said film-forming substance, said chlorinated organic flame-retardant substance consisting essentially of chlorinated paraffin wax containing more than 40% of chemically combined chlorine.

3. A fibrous cellulosic material of substantial flame-retardant properties comprising, in combination, a fibrous cellulosic base, a non-halogenated inorganic, flame-retardant substance selected from the group consisting of antimony oxide, salts of antimony, arsenic, and bismuth, salts of phosphoric, boric, and stannic acids, and mixtures of said salts, deposited thereon, a film of a heat-decomposable, non-halogenated, film-forming, resinous solid selected from the group consisting of cellulose ethers, cellulose esters, polyethylene, polystyrene, polyvinyl butyral, and polyacrylic acid esters, overlaying said inorganic flame-retardant substance deposited upon said film, said highly chlorinated organic flame-retardant substance being selected from the group consisting of chlorinated vegetable oils, chlorinated animal oils, and chlorinated paraffin wax.

4. The article of claim 3 in which the inorganic flame-retardant substance is antimony oxide (Sb_2O_3), the heat-decomposable, non-halogenated, film-forming, resinous solid is polyethylene, and the highly chlorinated organic flame-retardant substance is chlorinated paraffin wax containing from 40%-70% of chemically combined chlorine.

5. The method of flameproofing a fibrous cellulosic material, which includes the steps of (1) impregnating said material with a non-halogenated inorganic, flame-retardant substance, (2) depositing upon the thus-impregnated cellulosic material a film of a heat-decomposable, organic, non-halogenated, polymeric, film-forming, resinous substance inert to said inorganic flame-retardant substance and to highly chlorinated organic substances, thereby to form a screen between said inorganic flame-retardant substance and highly chlorinated organic substances sub-

sequently applied thereto, and (3) applying to the composite thus formed, a highly chlorinated organic flame-retardant substance having low vapor pressure, and capable of releasing substantial amounts of hydrogen chloride at flame temperatures.

6. The method of impregnating a fibrous cellulosic material with a flameproofing, water-repellent coating, which includes the steps of (1) impregnating said material with a substance selected from the group consisting of antimony trioxide, salts of antimony, arsenic, and bismuth, salts of phosphoric, boric, and stannic acids, and mixtures of said salts, (2) applying to the thus-impregnated material a solution of a heat-decomposable, organic, non-halogenated, film-forming, resinous solid selected from the group consisting of cellulose ethers, cellulose esters, polyethylene, polystyrene, polyvinyl butyral, and polyacrylic acid esters, (3) evaporating the solvent from the solution deposited upon said impregnated material to leave a film of said resinous solid overlaying said impregnated material, (4) applying to said film upon said impregnated material, a solution of a highly chlorinated organic flame-retardant substance selected from the group consisting of chlorinated vegetable oils, chlorinated animal oils, and chlorinated paraffin wax containing from 40%-70% of chemically combined chlorine, the solvent of said solution of said highly chlorinated organic substance being substantially a non-solvent for said film-forming, resinous solid, and (5) evaporating the solvent from said solution of said highly chlorinated organic substance applied to said film.

7. The method of impregnating a fibrous cellulosic material with a flame-retardant, water-repellent coating, which includes the steps of (1) impregnating said material with antimony trioxide, (2) applying to the thus-impregnated cellulosic material, a solution of a heat-decomposable, organic, non-halogenated, film-forming, resinous substance selected from the group consisting of cellulose ethers, cellulose esters, polyethylene, polystyrene, polyvinyl butyral, and polyacrylic acid esters, (3) evaporating the solvent from the solution applied to said impregnated material to deposit a film of said resinous substance upon said impregnated cellulosic material, (4) applying to said film a solution of chlorinated paraffin wax in a solvent which is substantially a non-solvent for said resinous, film-forming substance, said chlorinated paraffin wax containing from 40%-70% of chemically combined chlorine, and (5) evaporating the solvent from said solution of said chlorinated paraffin wax applied to said film.

8. The method of claim 7 in which said heat-decomposable, organic, non-halogenated, film-forming, resinous substance is polyethylene.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,860,506	Kennedy	May 31, 1932
2,010,015	Fletcher	Aug. 6, 1935
2,178,625	Clayton et al.	Nov. 7, 1939

(Other references on following page)

2,640,000

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UNITED STATES PATENTS

Number	Name	Date
2,380,775	Meyer -----	July 31, 1945
2,416,447	Laughlin et al. -----	Feb. 25, 1947
2,424,386	Czeczowitzka -----	July 22, 1947
2,427,997	White -----	Sept. 23, 1947
2,428,716	McGill et al. -----	Oct. 7, 1947
2,431,001	Sullivan -----	Nov. 18, 1947
2,494,391	Johnson et al. -----	Jan. 10, 1950

10

FOREIGN PATENTS

Number	Country	Date
552,909	Great Britain -----	Apr. 29, 1943

OTHER REFERENCES

Little, "Flameproofing Textile Fabrics," A. C. S., Monograph Series No. 104, published 1947, pages 240, 241, 249.