FIRE-RESISTANT FINISH FOR TEXTILES COMPRISING ZINC FLUOROBORATE

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4 Claims

ABSTRACT OF THE DISCLOSURE

Fire retardant finishing compositions, especially useful for synthetic fibers, incorporating zinc fluoroborate and emulsification and other additives to maintain the desirable hand and feel of the textile material.

This application is a continuation-in-part of the previously filed application Ser. No. 647,603, filed June 21, 1967 and now abandoned, which was a continuation-in-part of previously filed application Ser. No. 457,209, filed May 19, 1965, and now abandoned.

This invention relates to a novel fire retardant finishing composition for imparting fire retardancy to various textile materials, such as cellulosic materials and synthetic materials, and combinations thereof. More particularly, the fire retardant composition has a high degree of utility in the treatment of synthetic textile materials which are particularly highly inflammable in the final commercially available products. It is frequently desirable to flameproof synthetic textile fabrics and the like and other materials made of or containing cellulose acetate and other organic acid esters of cellulose. The flameproofing, to be satisfactory, should impart to the treated materials a high resistance to burning and/or retard the propagation of a flame when lit, should be inexpensive and easily applied, and should be relatively permanent to laundering, dry cleaning and the like to which the treated materials are normally subjected. In addition, the flameproofing should not alter the hand or other physical properties of the treated materials in an objectionable manner, and should not appreciably affect the dyeing of the said materials.

In recent years, the substantial increase in the use of synthetic materials in the form of textile fibers, yarns and fabrics has been accompanied by the serious problem of the inflammable nature of these materials. Some such materials are not readily inflammable prior to treatment, such as the polyamides or super polyamides which have a tendency to ignite, melt, and drip away when fire is applied. However, when these less inflammable materials are treated with binders, stiffening agents, and the like, they become highly inflammable. Polymers similarly fall into this category. There are other materials which do not have especially low temperatures of ignition, but which when once ignited, become highly inflammable. Typical of these materials are the acrylics. There are in fact, very few synthetic fibers which will resist fire and which are not highly inflammable either before or after treatment with various treating agents conventionally employed.

Prior to this invention, no fully acceptable fire retardant compositions were available. Various prior fire retardant compositions were successful to different degrees in imparting fire retardancy, but the prior fire retardant compositions seriously affect the normal properties of the fibers, yarns or fabrics, properties, such as hand, color, etc. Although there are many substantially satisfactory retardant compositions for use on cellulosic and cellulosic-containing textile materials, such finishes have failed to prove satisfactory for synthetic materials for the reasons stated above.

The need for efficient fire retardant finish which simultaneously, either does not alter hand or improves the hand of the synthetic material being treated is becoming increasingly more important to industries, such as those involved in clothing, draperies, upholstery, carpets, rugs and the like, in order to provide the public with high quality products and to concurrently remove the substantial hazard of inflammability.

Typical of an acceptable fire retardant composition for the treatment of textile substrates, particularly synthetic textile substrates, are: (1) a composition which is easily applied from an aqueous diluent, (2) a non-toxic composition, and (3) a composition which does not adversely affect the color or hand of the treated substrate, such as, causing discoloration, and/or giving the treated substrate an undesirable harshness.

It is therefore an object of this invention to obtain a composition which imparts a high degree of fire retardancy to an inflammable substrate being treated.

Another object is to provide a composition which imparts a high degree of fire retardancy to synthetic material being treated.

Another object is to provide a composition which, when applied to an inflammable substrate textile material, obtains a high grade of hand.

Another object of this invention is to obtain a process for applying a novel fire retardant composition to an inflammable substrate.

Another object of this invention is to obtain a fire retardant synthetic substrate.

Another object is to obtain a process for producing a composition capable of imparting fire retardancy and a high grade of hand to inflammable substrates treated with the composition.

Other objects of this invention become apparent from the above and following disclosures.

The objects of this invention are obtained by applying to an inflammable substrate a composition which includes (1) a cationic surfactant-emulsifier together with a cationic organic substance; or (b) a non-ionic surfactant-emulsifier together with a chlorinated paraffin.

A third ingredient necessary to be added, at least prior to the application of the above composition to an inflammable substrate, is an aqueous diluent in an amount sufficient to form an aqueous dilution of the water-soluble emulsion.

The composition is thereafter applied by any conventional method of application, such as by spraying, dipping, padding and the like. However, incorporation of the material into the fiber dope is also contemplated. The treated
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Substrate is subsequently dried at conventional drying temperatures, preferably at a temperature of about 250° F. In no event would the drying temperature be above the ignition temperature of the fabric.

In the composition of this invention, zinc fluoroborate has no known equivalent. By the application of zinc fluoroborate solely to an inflammable substrate, fire retardancy may be obtained, but only at the sacrifice of acceptable properties of hand. When the zinc fluoroborate is used alone in aqueous dilutions and applied to textile materials upon drying of the treated textile substrate, the zinc fluoroborate acquires a crystalline acicular characteristic, thereby leaving the substrate with a harsh hand and with a fire retardancy which is less durable than when applied with the other components of the composition of this invention.

Therefore, the problem is not solely to obtain fire retardancy. The typical problems solved are (1) the obtaining of a fire retardant without ruination of the commercial acceptability of the hand of the substrate being treated, and (2) the obtaining of a durable fire retardant finish.

In the above composition of this invention, a cationic emulsifier is employed, such as a quaternary amine, for example polyethoxylated quaternary ammonium salts, and the like, which are formed by reacting from about 2 to 20 mols of ethylene oxide with one mol of an additive of a higher fatty acid amine and methyl chloride, said fatty acid moieties having from about 12 to 20 carbon atoms. This includes fatty acid amines derived from such fatty acids as stearic, coconut and oleic acids. Whenever a cationic emulsifier is employed, a cationic organic substance is employed therewith for purposes of the composition of this invention. The cationic organic materials are tertiary amines, such as ethylene oxide condensation products of primary fatty amines and the like, formed by the reaction of an amine of a higher fatty acid with from 2 to 50 mols of ethylene oxide. The higher fatty acid moiety is similar to that of the cationic organic emulsifier.

In the composition of this invention, the non-ionic surfactant-emulsifier are formed by reaction of from 5 to 25 mols of ethylene oxide with an additive of a higher fatty acid and a monocyclic aryl compound. The fatty acid moieties are as described above for the cationic emulsifiers. The non-ionic emulsifiers include for example isooctylphenyl polyethoxylehthanol, nonylphenol poly-(ethylenoxy)ethanol, and the like. In the embodiment in which a non-ionic surfactant-emulsifier is employed with the zinc fluoroborate, for the composition of this invention, a chlorinated paraffin is also included. Any typical chlorinated paraffin having a relatively high degree of chlorination is suitable. For example, long chain paraffins having about 20 to 60, or 50 chlorine substituents are suitable.

Although an acceptable fire retardancy and hand may be obtained by the random admixing of the essential components of the composition of this invention, prior to the application to the treated substrate, in order to obtain a preferred high degree of flame retardancy and concurrently obtain a high quality hand characteristically desired for textile substrates, it is advantageous that a specific method be employed to obtain the fire-retardant composition of this invention.

In the embodiment which employs the non-ionic surfactant-emulsifier and chlorinated paraffin, the emulsion is prepared by first blending the emulsifier with the wax (chlorinated paraffin) and thereafter adding thereto a sufficient amount of water to form a thin paste. Preferably while agitating the thin paste, zinc fluoroborate in a diluted form is admixed with the thin paste, followed by adding the remainder of the aqueous diluent with the agitation preferably continuing until a fine, stable emulsion is obtained.

In the embodiment employing a cationic emulsifier and a cationic organic substance, the cationic emulsifier and the cationic organic substance are each separately blended with an aqueous diluent, and thereafter the aqueous cationic organic substance is added to the aqueous cationic emulsifier, and substantially thereafter the zinc fluoroborate is added to the mixture of the cationic organic substance and cationic emulsifier. During each addition, agitation preferably is employed.

In preparing the composition of this invention, zinc fluoroborate is normally employed in an amount ranging from about 10% to about 30%, and preferably from about 5% to about 20% based on the weight of the final composition following the addition of water. The chlorinated paraffin is normally employed in a range of from about 0.25% to about 2.0%, preferably at about 0.5% to about 1.5%. The non-ionic emulsifier is normally employed in a range from about 0.1% to about 1.5%, preferably 0.5% to about 1.0%. The cationic emulsifier is normally employed in a range of from about 1% to about 1.5%. The cationic organic substance is employed in a range of about 0.5% to about 3%, preferably from about 1% to about 1.5%.

The amount of aqueous diluent added will depend upon the substrate being treated and the amount of wet pickup of the substrate to be employed.

The following examples are for purposes of illustrating the invention and are not intended to limit the scope thereof, except as limited in the appended claims.

In the following examples the following test method was employed to determine the fire retardancy of the treated substrates.

Methenamine pill test for fire-retardancy of textile material

A methenamine pill weighing 0.33 gram (5 grains) is placed on the surface of the carpet or fabric. Using a match, the pill is ignited and remains so until completely consumed (2 1/2 minutes).

The flammability or combustion of the surface fibers is observed and recorded as is the effect of the burning pill on the backing fabric of the substrate being tested.

EXAMPLE I

A wax-fluoroborate emulsion was prepared using the following formula:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc fluoroborate (40% sol'n)</td>
<td>50.0</td>
</tr>
<tr>
<td>Chlorinated paraffin 1</td>
<td>1.0</td>
</tr>
<tr>
<td>Emulsifier 2 (non-ionic)</td>
<td>0.5</td>
</tr>
<tr>
<td>Water</td>
<td>48.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

1 Chlorofix 50, Hercules Powder, Inc.
2 Condensation product of novolac xylene phenol plus 0.5 moles ethylene oxide. (Deerosol 99, American Cyanamid Co.)

The above emulsion is prepared by blending the emulsifier with the wax and adding thereto enough water to form a thin paste. To this is added slowly (with agitation) diluted zinc fluoroborate. The remainder of the water required is further added and agitation continued until a fine stable emulsion is the resultant product.
Aqueous dilutions of the product of Example I are applied to 3/4" in pile tufted acrylic carpeting containing a cotton back by spraying, whereupon amounts of either 7.5, 5.5, or 3.5 percent total solids were applied. The treated carpets were dried at 250°F. Methenamine pill tests for combustion and flammability were made in accordance to the aforementioned test procedure. Results are shown in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Acrylic pile</th>
<th>Cotton backing</th>
<th>Hand of treated carpet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent total solids applied:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5........</td>
<td>Melted, noncombustible.</td>
<td>Charred</td>
</tr>
<tr>
<td>7.0........</td>
<td>Melted, noncombustible.</td>
<td>Charred</td>
</tr>
</tbody>
</table>

Results show good resistance to fire as obtained on both the pile acrylic fiber and the cotton backing of the treated rug sample.

**EXAMPLES III AND IV**

Additional formulations were made according to Example I, substituting as follows:

<table>
<thead>
<tr>
<th>Example</th>
<th>Chlorinated paraffin</th>
<th>Non-ionic emulsifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.</td>
<td>Chloron 26 (Hercules Powder Co.).</td>
<td>Ethylenediamine polyethoxy ethanol (Triton X-100, Rohm &amp; Haas).</td>
</tr>
<tr>
<td>IV.</td>
<td>Chloron 40 (Hercules Powder Co.).</td>
<td>Nonylphenol poly(ethyleneoxy)ethanol (Gepol OA-715, Antarla Chemical Co.).</td>
</tr>
</tbody>
</table>

Note: In Examples I to IV the numbers on the chlorinated paraffins represent numbers of chlorine substituents on long chain alkanes or paraffin hydrocarbons.

The compositions of Examples III and IV gave similar fire retardant properties to that of Example I.

**EXAMPLE V**

An emulsion was prepared in the following manner:

(A) Parts by wt.

Zinc fluoroborates 5.0

Water 15.0

The zinc fluoroborate is dissolved in the water with stirring.

(B) Parts by wt.

Cationic organic substance: Ethomeen 18/60 1.0

Water 10.0

(C) Parts by wt.

Cationic Emulsifier 1.0

Water 10.0

1 A tertiary amine which is an ethylene oxide condensation product of stearylamine and 50 mols ethylene oxide (Armour Co.).

2 Retarder 880, a quaternary amine (Proctor Chemical Co.).

Products (B) and (C) are each blended with water and then (B) added to (C). Product (A) is then added to this mixture with stirring.

**EXAMPLE VI**

15 milliliters of the formula of Example III is sprayed onto 30 inch square portions of acrylic or acrylic face cotton back fabric. After air drying and conditioning the treated pile fabric is tested by the Methenamine Pill Test Method. Results shown in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Methenamine pill test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic treated</td>
<td>Melted, did not burn.</td>
</tr>
<tr>
<td>Untreated</td>
<td>Fuses and supports flame.</td>
</tr>
<tr>
<td>Acrylic/cotton treated</td>
<td>Melted, did not burn.</td>
</tr>
</tbody>
</table>

The compositions of Examples VII, VIII, and IX gave similar fire retardant properties to that of Example V. It is within the scope of this invention to make such modifications of the compositions and processes disclosed herein as would be obvious to a person of ordinary skill in this art, and it is to be understood that the examples illustrating this invention are intended to limit the scope only insofar as is stated in the specification and as the following claims are limited.

I claim:

1. A fire retardant composition consisting essentially of zinc fluoroborate and a material selected from the group consisting of (a) from about 0.5 to 3% of a cationic emulsifier formed by reacting from 2 to 20 mols of ethylene oxide with one mol of an adduct of a higher fatty acid amine and methyl chloride and from about 0.5% to about 3% of a cationic polyethylene oxide tertiary amine formed by the reaction of the amine of a higher fatty acid with from 2 to 50 mols of ethylene oxide; and (b) from about 0.1 to 1.5% of a non-ionic surfactant emulsifier, formed from 5 to 25 mols of ethylene oxide and an adduct of a higher fatty acid and a monocyclic aryl compound, and from about 0.25 to 2% of a chlorinated paraffin having from 20 to 60 chlorine groups; and water, said zinc fluoroborate being present in the amount ranging from about 5% to about 30%, said percentages being based on total weight of the composition after addition of said water.

2. A fire retardant textile material including the fire retardant composition of claim 1 in an amount sufficient to impart fire retardancy.

3. The textile material of claim 2 wherein said textile material is an acrylic fiber.

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