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COMPOSITION FOR WATERPROOFING AND
FIREPROOFING TEXTILE MATERIAL, AND
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shohocken, Pa., a corporation of PennsylvaniaNo Drawing. Application November 24, 1942,
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1

The present invention relates to the art of imparting flame- and water-resistance to combustible materials, and more particularly it relates to a novel composition by which textile fabrics and other combustible sheet material may be simultaneously rendered water-proof and fire-proof, and to a process for water-proofing and fire-proofing fabrics and the like in a single operation.

Previously flame-proofing has been effected by the application to the fabric either of a water solution of any of the large number of non-combustible salts or of a solution of a highly chlorinated material in an organic solvent. Water-proofing of fabrics has been effected by treatment with a solution of a hydrolyzable salt of aluminum (generally aluminum acetate) in which a water repellent organic substance has been emulsified, or by treatment with an organic waxy material dissolved in an organic solvent. In order to obtain the best results, the fabric has been treated with both the hydrolyzable salt and the organic waxy material.

Heretofore, fabrics generally have been water-proofed and fire-proofed by one of two methods. In the first method, a very heavy continuous coating of a highly chlorinated waxy material has been applied to the fabric by treating it with an organic solvent solution of the waxy material. In order that the treatment may be efficacious, it has been necessary to fill the interstices of the cloth with the chlorinated material since a lesser amount will not make the textile material water-proof due to the fact that the water repellency of the oleaginous material has been reduced very materially by its chlorination. This method is expensive because of the relatively high cost of materials involved as well as the large amount of coating necessary. Furthermore, fabrics so treated are stiff and heavy and, therefore, unsuitable for the majority of purposes for which textiles are used.

In the second method, the fabric is treated first with a fire-proofing solution and then in a separate operation with a water-proofing solution. This procedure results in a much lighter weight and, therefore, less costly fire- and water-proofing deposit, with less change in the natural characteristics of the fabric. However, the necessity of employing two separate baths for treatment renders the process cumbersome and inflexible

2

and in numerous textile mills the adoption of the process would necessitate complete re-arrangement of the equipment which is impractical where other materials are manufactured on the same equipment between the runs of water- and fire-proof goods. Suggested procedures to water-proof and fire-proof materials by a combination treatment using in one step the type of materials employed in the two-step process have been highly complex and subject to various kinds of disturbing factors and have not been commercially successful.

One object of the present invention is to provide a composition by which combustible materials such as fabrics and the like may be simultaneously rendered substantially water-proof and fire-proof without deleterious impairment of the desirable mechanical properties of the material.

Still another object of the invention is to provide a composition by which material possessing flame- and water-resistance may be obtained as a result of treatment with the composition in a single solution and in a single step, thus greatly enhancing the practicability and reducing the cost of the treatment.

A further object of the present invention is to provide a process for the treatment of materials such as fabrics by which the material may be easily and economically rendered fire-proof and water-proof in a single operation.

Other objects will be apparent from a consideration of this specification and the claims.

To one who is not familiar with the problems of water-proofing and fire-proofing fabrics, it might appear on first thought that it should not be a difficult matter to mix the water-proofing solution and the fire-proofing solution to obtain a single bath by which both treatments may be accomplished. However, a consideration of the chemical properties of the materials applicable for use for fire-proofing and water-proofing will show that a difficult problem is presented. The water-repellent agent employed is a composition comprising an emulsified water-repellent material combined with a hydrolyzable aluminum salt. For efficient application to a textile fabric, the emulsion must remain stable in water dispersion and the hydrolyzable aluminum salt must remain soluble in water until the composition is dried upon the fabric. The stability of the emulsion is

3

dependent upon the emulsifying agent used in its preparation, and the emulsion must, of course, tolerate the addition of the hydrolyzable aluminum salt, and in the case of the combined reagents the addition of fire-resistant salts as well. But, the hydrolyzable aluminum salts, because of their chemical nature, are stable only in an acid medium of pH about 4 or less, or in any event lower than 4.85. The fire-resistant salt, if included in the composition, must be compatible with the water-repellent agent, and if a fire-resistant salt is chosen which in water solution is compatible with the hydrolyzable aluminum salt, it must necessarily have a pH lower than 4.85 in solution.

The problem, however, is further complicated by the fact that if a salt with such a pH in solution is applied to a textile fabric, the acidity of that salt will, on aging, injure the fabric, resulting in serious loss of tensile strength. The exact pH value at which the deterioration will become serious is dependent both upon the nature and construction of the fabric and upon the chemical constitution of the applied salt. It has been found that in some cases a pH of 6.5 has caused deterioration of the fabric, in most cases a pH of 6.2 has caused deterioration, and in almost every case a pH of 5.85 has caused progressive destruction of the fabric. On the other hand, if a fire-resistant salt is chosen which has a pH in solution such that on aging the salt will not injure the fabric to which it is applied, the pH of the salt in solution will be so high that it will be incompatible with the hydrolyzable aluminum salt.

In accordance with the present invention, a homogeneous, aqueous, fire-proofing and water-proofing composition is provided containing fire-proofing and water-proofing materials and a volatile acid, the composition having a pH at which the components are mutually compatible, viz., at pH lower than 4.85. The combustible material after application of the composition is dried to form a residue of the water-proofing and fire-proofing substances thereon having a pH substantially non-injurious to combustible material. The fire-proofing and water-proofing substances may be selected from a wide variety of materials, examples of which will hereinafter be given.

The present invention makes possible the utilization of any fire-resistant salt, whatever its pH in water solution, in combination with any water-repellent agent comprising an oil-in-water emulsion of an emulsifiable water-repellent material including an emulsifying agent, and a hydrolyzable metal salt of an organic acid. By this invention, the danger of injury to the fabric because of excessively high or low pH of the fire-resistant salt is eliminated by combining with this salt a buffering agent, an acidic buffer being used with a basic fire-resistant salt and a basic buffer with an acidic fire-resistant salt. In this manner, the solid fire-resistant constituents are converted to materials having a pH substantially non-injurious to fabrics. These materials are then made compatible with the hydrolyzable metal salt by the addition of a volatile acid. In the water dispersion in which the fire-resistant agent and the water-repellent agent are applied to the textile fabric, this volatile acid gives a low pH at which the hydrolyzable aluminum salt is stable. When the combustible material is dried, however, the acid is volatilized, leaving the residue on the material at such a pH that the com-

4

combustible material will not deteriorate. In addition, when the acid is volatilized so that the pH is increased beyond the point where the hydrolyzable metal salt is stable, that salt hydrolyzes or decomposes to form a precipitate. I have found that to insure compatibility of the ingredients in the liquid composition, the pH must not exceed 4.85, and to prevent deterioration of the cloth, if that is the combustible material treated, the pH of the dried composition, after evaporation of the volatile acidic constituents, must not be less than pH 5.85. In actual practice, the shift of pH may be much greater, say from 3.5 to pH 6.5, but in any case, the shift must be at least from pH 4.85 to pH 5.85.

Examples of emulsifiable water-repellent materials which are applicable for use are paraffin wax, carnauba wax, amorphous wax, hydrogenated castor oil, a sorbitol maleate alkyd resin, a polyvinyl acetate resin, a cumarone-indene type resin, ethyl cellulose, and the like.

Examples of the hydrolyzable metal salt of an organic acid which may be used are, normal aluminum acetate, basic aluminum acetate, aluminum formate, a mixture containing equivalent parts of aluminum sulphate and sodium acetate, and mixtures of these and of similar ingredients. While hydrolyzable aluminum salts are now the only salts commercially used in water-proofing compositions, other hydrolyzable metal salts are applicable for use in a similar manner, if desired. Acetates of bismuth and tin, for example, may be made in 10% solution in strong acetic acid, either by dissolving the basic salt in glacial acetic acid or by metathesis of the chloride and silver acetate. These acetates, when employed in quantity equivalent to that of aluminum acetate in a composition give water repellency beyond that accounted for by the emulsifiable water-repellant material alone; tin in particular may even be superior to aluminum. The hydrolyzable salts of other metals may also be used, for example, the hydrolyzable salts of the rare earth metals, such as lanthanum, germanium, yttrium, and ytterbium.

As the emulsifier, any of the customary emulsifying materials well known to the art, may be used, in amounts sufficient to produce a stable emulsion of the water-repellent material in water. As examples of such emulsifiers may be mentioned glues, gelatins, polyvinyl alcohols, sulphated higher fatty alcohols, naphthalene sulphonates, soaps, sulphonated castor oil, alkyl aryl sulphonates, and the like.

Similarly, any volatile acid free from hydroxyl groups may be used. Examples of volatile acids which are effective are formic, acetic, and hydrochloric acids. In place of a volatile acid, and included within that term, an acidic salt or the like from which acid will be volatilized may be used.

As a fire-resistant agent, it is possible to use any salt or combination of salts which when used alone has fire-resistant properties and which is soluble in the aqueous phase of the composition. Of the various fire-proofing salts, zinc chloride, calcium chloride, ammonium sulphate, sodium borofornate, and borax are particularly suitable. Ammonium phosphate, ammonium sulphamate, sulphamic acid, and phosphoric acid also impart excellent fire-resistance, but in conjunction with the other ingredients disclosed in the invention, tend to form emulsions which, although useable, are somewhat less stable than when the preferred fire-resistance ingredients are used. Mag-

5

nesium chloride, ammonium chloride, tin chloride, zinc sulphate, copper sulphate, chrome alum, lead acetate, magnesium acetate, and sodium bisulphate also impart a fair degree of fire-resistance, while, for example, barium chloride, sodium chloride, magnesium sulphate, ammonium alum, ferrous sulphate, sodium bisulphate, cadmium sulphate, zinc acetate, calcium acetate, ammonium acetate, chrome acetate, sodium phosphate, and boric acid, although useful when used in sufficient concentration are less suitable and are generally not preferred. In fact, every non-combustible salt, which does not generate oxygen when heated, possesses fire-resistant properties, and these are particularly effective in those salts which melt at temperatures below 1220° C.

Any buffering material may be used, although the choice of buffering material is necessarily dependent upon the acidity or basicity of the fire-resistant salt with which the buffer is to be used. Examples of applicable buffers are borax, sodium acetate, salts of other organic acids, organic amines such as triethanolamine, etc., ammonium phosphate, alkali phosphates, and zinc chloride. It is advantageous, though not necessary, to use as a buffer, a material which is also a fire-resistant salt.

The composition may be prepared as a concentrated base material comprising the various materials hereinbefore described and containing little or no water in addition to that associated with the acid or other materials. This concentrated base may be marketed and the purchaser of the base at the time of its use may dilute it with the required amount of water and may agitate it sufficiently to emulsify the water repellent material and to form an aqueous homogeneous composition of the materials. Generally, however, the material marketed will contain water in a sufficient amount at least so that the emulsion and a homogeneous aqueous composition are formed and this may be prepared in any suitable manner, the order of combining the ingredients not being particularly important. Since, however, emulsions usually tend to become unstable upon the addition of large quantities of salts in high concentrations, it is advantageous to prepare an emulsion of the water-repellent material and the emulsifying agent containing the hydrolyzable metal salt in solution, and to combine this with a solution containing the fire-resistant salt, the buffer, and the volatile acid. If desired, the composition marketed may contain sufficient water so that it may be employed without dilution to fire-proof and water-proof materials.

In place of marketing a product containing all of the ingredients of the fire-proofing and water-proofing composition, the various ingredients may be associated in two or more products to be mixed by the textile concern. For example, a mixture of the fire-proofing material, buffer, and volatile acid may be sold as a comparatively dry material (the acid being absorbed by the salts) or if water is added thereto, as a paste, heavy or light, or as a solution depending on the water content, and, as the other product, a mixture of the water-repellent material, the hydrolyzable metal salt and the emulsifier, with or without the addition of water may be marketed. If desired, a portion or all of the volatilizable acid may be mixed with the product containing the water repellent and other water-proofing materials. Furthermore, if desired, any of the in-

6

redients may be sold separately, for example, the volatilizable acid; the hydrolyzable metal salt; and the fire-proofing material and the buffer, either mixed or separately. In a typical case, a product may be marketed comprising a mixture of about 10% water, 10% volatilizable acid, and 80% fire-proofing composition and buffer. The second product may comprise 15% water-repellent material, and about 25% of a 30% solution of basic aluminum acetate, the remainder being water and emulsifier. In water-proofing and fire-proofing textile material, 15% of the first product, 8% of the second product, and 77% water are mixed to form a homogeneous emulsion.

In the treatment of fabrics and the like with the fireproofing and water-proofing composition, any of the methods commonly used to give a product which is fire-resistant and water-repellent may be employed. The amount of water associated with the other materials in the composition will depend upon the type of material being treated and upon the equipment employed; for example, if the fabric is to be sprayed, a solution containing a relatively large amount of water and, therefore, of low viscosity will generally be employed, whereas if the composition is to be spread on the fabric by means of calender rolls or other spreading device, the amount of water will be relatively low so that a relatively viscous composition is provided. After the treatment of the fabric or other combustible material with the composition, the material is dried in any convenient manner, for example, by the use of drier rolls. This drying step not only dries the material and the non-volatile residue of the composition deposited within and upon the surface of the material, but also volatilizes the volatile acid so that the pH of the residue remaining on the material is raised to a point where it will not cause deterioration of the material.

Wide variations are permissible in the proportions of the various ingredients and the invention is not limited to any particular proportion or relation between the ingredients, or to any specific amount of water associated with the ingredients in the fire- and water-proofing treatment. Usually, the composition employed in the treatment of fabrics will contain sufficient water so that the various components of the composition will be present within the following ranges: fire-proofing salt, about 6% to about 14%; buffer, about 2% and about 8%; emulsifiable water-repellent material, about .5% and about 5%, more specifically about .5% and about 3%; hydrolyzable metal salt, about ½% to about 6%. The emulsifying agent will be sufficient to emulsify satisfactorily the water-repellent material and the volatile acid will be sufficient to give a pH of the composition in solution of 4.85 or less. In the event the buffer is also a fire-proofing salt, the amount of the combined fire-proofing salt and buffer may be between about 6% and about 20%. While the preferable range of water-repellent material is given above, useful increases in water resistance are obtained by the use of less than about ½% in the case a highly efficient fire-proofing salt is employed and amounts greater than those stated above may be necessary if the percentage of fire-proofing salt is high. In a typical case, the water- and fire-proofing solution with which the textile is treated may contain 10% of the fire-proofing composition (ammonium sulphate), 5% of the buffer (sodium

7

acetate), 2% of the volatile acid (acetic acid), 2% of water-repellent material (wax), 2% of the hydrolyzable aluminum salt (solid aluminum acetate), .14 of emulsifying agent, and the balance water.

The invention is illustrated by the following specific examples, the parts being by weight:

Example I

	Parts by weight
Zinc chloride-----	10
Borax -----	4
Glacial acetic acid-----	2
Water -----	44

are mixed together and heated until a clear solution is obtained at 130°-160° F. As a separate dispersion

	Parts by weight
Water-repellent agent-----	7
Water -----	33

are heated together at 130°-160° F. The water-repellent agent used is an oil-in-water emulsion containing 15% emulsified paraffin wax and 30% of 30% basic aluminum acetate in water, the balance being emulsifying agent, and water. After preparing the two components of the composition, they are mixed by pouring the water-repellent agent dispersion into the fire-resistant agent solution with stirring. This gives a composition with which a fabric may be treated by any of the commonly used methods to give a product which is fire-resistant and water-repellent.

Example II

An oil-in-water emulsion of hydrogenated castor oil is prepared by mixing with high speed stirring thirty parts of the molten wax into sixty-eight parts of water at the same temperature, containing dissolved therein two parts of polyvinyl alcohol. Five parts of this emulsion are added to seventy-eight parts of water containing dissolved therein two parts of 30% basic aluminum acetate, ten parts of calcium chloride, and three parts of sodium acetate and one part glacial acetic acid. Cloth treated with this composition is thoroughly resistant to fire and to impinging water.

Example III

Twelve parts of zinc chloride, five parts of sodium acetate, and four parts of acetic acid are dissolved in fifty parts of water. Fifteen parts of the water-repellent agent employed in Example I are diluted with fourteen parts of water. This gives a solution containing between one and two parts emulsified water-repellant material and between one and two parts hydrolyzable aluminum salt. The second solution is added to the first with stirring. Cloth treated with the final composition is thoroughly fire-resistant and shows a good water-repellency.

Example IV

An oil-in-water emulsion of paraffin wax is prepared from seventy-five parts of paraffin wax, four hundred parts of water, four parts of a salt of triethanolamine and stearic acid, and two parts of glacial acetic acid. This is done by dissolving the salt and acid in water at 80° C., and stirring into this the molten wax at the same temperature, high speed stirring being used. Seven parts of this emulsion are added to seventy-seven parts of water containing dissolved

8

therein ten parts of calcium chloride, three parts of sodium acetate, two parts of 30% basic aluminum acetate in water, and one part acetic acid. Cloth treated with the resulting composition shows a fair degree of fire-resistance and of water-repellency.

Example V

Ten parts of zinc chloride, three parts of borax, and one part of acetic acid are dissolved in forty parts of warm water. Five parts of the water-repellent agent employed in Example I are dissolved in thirty-seven parts of water containing dissolved therein one part of acetic acid. This gives a solution containing between one and two parts each of an emulsified water-repellent material and a hydrolyzable aluminum salt. The second solution is then added to the first with stirring. Cloth treated with the final composition showed excellent fire-resistance and water-repellency.

Example VI

Eight parts of borax, three parts of zinc chloride, and three parts of acetic acid are dissolved in forty parts of warm water. Five parts of the water-repellent agent employed in Example I are dissolved in forty-one parts of water as in Example III. The second solution is added to the first with stirring. Cloth treated with the final composition shows excellent fire-resistance and water-repellency.

Example VII

Ten parts ammonium sulphate, two parts borax, one part acetic acid, five parts of the water-repellent agent used in Example I, and eighty-two parts of water are combined as in Example V. Cloth treated with this composition shows good fire-resistance and water-repellency.

While reference has been made above to fire- and water-proofing compositions, it is fully realized that frequently it is not necessary to apply these compositions in such amounts as to actually obtain a full resistance to fire and/or water. It suffices that the fabrics or the materials impregnated are rendered flame-retardant, or partially water-repellent, since it is obvious that compositions which under optimal circumstances will give effective fire- and water-proofing, when used in smaller amounts, can achieve this effect to a partial extent, and that this partial water- or fire-proofing may be sufficient for many practical purposes; also that ingredients, which even under optimum conditions do not impart complete fire- or water-resistance may have other valuable properties warranting their use in special instances. All such treatments are included within the claims which refer to imparting flame- and water-resistance to combustible material such as textiles.

From the above detailed disclosure, it is evident that the invention is capable of wide variations, and the above description is illustrative and should not be construed as limiting the invention, the scope of which is defined in the following claims, in which it is my intention to cover the novelty inherent therein as broadly as possible, in view of prior art.

I claim:

1. A stable bath for rendering fibrous material fire-retardant and water-repellant, which includes a water solution of alkali borate, a water-soluble aliphatic carboxylic acid free from hydroxyl groups, and an emulsion of a water-repellant composition.

2,424,831

9

2. A composition for imparting flame- and water-resistance to combustible material in a single application of substances imparting said properties, which comprises a homogeneous aqueous composition which upon application to said combustible material and drying deposits a non-injurious residue thereon, said composition comprising fire-resistant material, which is soluble in the aqueous phase of said composition and when dried provides a pH non-injurious to the combustible material, present in an amount effective to impart flame-resistance to the combustible material upon the deposition of said residue, an oil-in-water emulsion of an emulsifiable water-repellent material, a hydrolyzable metal salt of an organic acid, the water-repellent material and the hydrolyzable metal salt being present in the composition in an amount effective to impart water-resistance to the combustible material upon the deposition of said residue, and a volatile acid free from hydroxyl groups to provide a pH at which said hydrolyzable metal salt is stable, said acid being volatilizable to increase the pH to a point whereby the hydrolyzable metal salt hydrolyzes to form a precipitate and a residue having a pH non-injurious to the combustible material is obtained.

3. The composition of claim 2 wherein the pH is not greater than 4.85.

4. The composition of claim 2 wherein the hydrolyzable metal salt is an aluminum salt.

5. A composition for imparting flame- and water-resistance to fabric in a single application of substances imparting said properties, which comprises a homogeneous aqueous composition which upon application to said fabric and drying deposits a non-injurious residue thereon, said composition comprising a fire-resistant combination of materials, which are soluble in the aqueous phase of said composition and which conjointly when dried provide a pH non-injurious to the fabric, present in an amount effective to impart flame-resistance to the fabric upon the deposition of said residue, an oil-in-water emulsion of an emulsifiable water-repellent material, a hydrolyzable metal salt of an organic acid, the water-repellant material and the hydrolyzable metal salt being present in the composition in an amount effective to impart water-resistance to the fabric upon the deposition of said residue, and a volatile acid free from hydroxyl groups to provide a pH at which the said hydrolyzable metal salt is stable, said acid being volatilizable to increase the pH to a point whereby the hydrolyzable metal salt hydrolyzes to form a precipitate and a residue having a pH non-injurious to the fabric is obtained.

6. The composition of claim 5 wherein the hydrolyzable metal salt is an aluminum salt.

7. The composition of claim 5 wherein the hydrolyzable metal salt is an aluminum salt and the materials are present in the composition as follows: the fire-resistant combination of materials about 6% to about 20%; water-repellent material about 0.5% to about 5%; hydrolyzable metal salt of an organic acid about 1/2% to about 6%.

8. A combustible material rendered flame- and water-resistant by a residue deposited thereon by the drying after application thereto of a homogeneous aqueous composition comprising fire-resistant material, which is soluble in the aqueous phase of said composition and when dried provides a pH non-injurious to the combustible material, present in an amount effective to im-

10

part flame-resistance to the combustible material upon the deposition of said residue, an oil-in-water emulsion of an emulsifiable water-repellant material, a hydrolyzable metal salt of an organic acid, the water-repellant material and the hydrolyzable metal salt being present in the composition in an amount effective to impart water-resistance to the combustible material upon the deposition of said residue, and a volatile acid free from hydroxyl groups to provide a pH at which said hydrolyzable metal salt is stable, said acid being volatilizable to increase the pH to a point whereby the hydrolyzable metal salt hydrolyzes to form a precipitate and a residue having a pH non-injurious to the combustible material is obtained.

9. The product of claim 8 wherein the pH of the aqueous composition is not greater than 4.85.

10. The product of claim 8 wherein the hydrolyzable metal salt is an aluminum salt.

11. A combustible fabric rendered flame- and water-resistant by a residue deposited thereon by the drying after application thereto of a homogeneous aqueous composition comprising a fire-resistant combination of materials, which are soluble in the aqueous phase of said composition and which conjointly when dried provide a pH non-injurious to the fabric, present in an amount effective to impart flame-resistance to the fabric upon the deposition of said residue, an oil-in-water emulsion of an emulsifiable water-repellant material, a hydrolyzable metal salt of an organic acid, the water-repellant material and the hydrolyzable metal salt being present in the composition in an amount effective to impart water-resistance to the fabric upon the deposition of said residue, and a volatile acid free from hydroxyl groups to provide a pH at which the said hydrolyzable metal salt is stable, said acid being volatilizable to increase the pH to a point whereby the hydrolyzable metal salt hydrolyzes to form a precipitate and a residue having a pH non-injurious to the fabric is obtained.

12. The product of claim 11 wherein the hydrolyzable metal salt is an aluminum salt.

13. The product of claim 11 wherein the hydrolyzable metal salt is an aluminum salt and the materials are present in the aqueous composition as follows: the fire-resistant combination of materials about 6% to about 20%; water-repellant material about 0.5% to about 3%; hydrolyzable metal salt of an organic acid about 1/2% to about 6%.

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