United States

[11] 3,900,327

[45] Aug. 19, 1975

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[54] FLAME RETARDANT CELLULOSIC MATERIALS

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[22] Filed: Oct. 12, 1973

[21] Appl. No.: 405,962

[52] U.S. Cl. ..... 106/15 FP; 117/137; 117/143 R; 117/147; 111/152; 117/154; 162/159

[51] Int. Cl. ..... C09d 5/18

[58] Field of Search ..... 117/136, 137, 152, 154, 117/143 R, 147; 106/15 FP; 252/8.1; 260/953, 944, 948

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[57] ABSTRACT

Cellulosic materials such as paper, wood, cotton, rayon and the like are rendered flame retardant by the intimate association therewith of an effective flame retardant amount of a reaction product of aqueous solution of phosphoric acid or an acid ammonium phosphate and an alkylene oxide e.g., ethylene oxide. Amounts of said reaction product of at least, and preferably in excess of, 0.5 percent by weight are generally effective to render the cellulosic material flame retardant. Preferably the reaction product is rendered neutral before or after application to the cellulosic material in order that the material be rendered non-corrosive and non-irritating in nature.

13 Claims, No Drawings

# FLAME RETARDANT CELLULOSIC MATERIALS

## FIELD OF INVENTION

The invention relates to improvements in the art of rendering cellulosic materials flame retardant. More particularly it relates to the treatment of cellulosic materials such as paper, wood, cotton, rayon and the like, with effective fire retardant amounts of a reaction product of aqueous solutions of phosphoric acid or an acid ammonium salt thereof with an alkylene oxide.

## BACKGROUND OF THE INVENTION

Cellulosic materials such as paper, wood, and cotton textiles, are highly flammable substances and once ignited continue to burn. Methods for the flame proofing of these materials are known but such methods are either too costly for general commercial use, relatively ineffective, or give rise to products having poor surface character.

With particular reference to paper, methods involving the application of salts of phosphoric acid, boric acid and sulfamic acid are, or have been, used. These methods while commercially attractive, costwise, are troublesome due to the crystallization of such salts on the treated material after drying. Further, the salts crystallize on the application equipment necessitating the frequent shut down of such equipment for cleaning.

Organo phosphorus compounds, such as tetrakis-(alpha hydroxyethyl) phosphonium chloride and various derivatives thereof, have also been suggested for the flame proofing of cellulosic materials. Such compounds provide a level of flame retardancy which is at least equivalent to that obtained with the aforementioned phosphate and borate salts. Moreover, the organo phosphorus compounds provide a durable flame retardant character which withstands repeated laundering and dry cleaning. Such compounds, however, because of their relatively high cost, are economically feasible salts only where a durable finish is required.

Accordingly it can be seen that a need exists for a low cost effective method for rendering cellulosic materials fire retardant which methods do not deleteriously affect the surface characteristics of the treated material.

## OBJECTS OF THE INVENTION

It is, therefore, a principal object of this invention to devise improved fire retardant cellulosic materials.

Another object is to provide a process for treating cellulosic materials to render them non-corrosive and non-irritating as well as flame retardant.

A particular object is to devise compositions comprising a cellulosic material and an effective fire retardant amount of a reaction product of aqueous phosphoric acid and an alkylene oxide intimately associated therewith.

These and other objects of the present invention will be obvious from the following description.

## BRIEF SUMMARY OF INVENTION

In accordance with the present invention, cellulosic materials are rendered fire retardant by intimately admixing the material with an effective fire retardant amount of a reaction product of an aqueous phosphoric acid and an alkylene oxide. The resultant product is preferably rendered neutral in character and thereafter dried to yield a product which not only is surprisingly fire retardant, non-corrosive and non-irritating in character but also has a pleasant surface character, i.e., "hand".



By "effective flame retardant amount" is that amount of said reaction product which suffices to impart flame retardant character to the cellulosic material as defined by the American Society of Testing Materials Test Standard D-777-46 and/or TAPPI Standard Test T-461.

The term "Oxygen Index" as used herein below is that value determined in accordance with the testing procedure described in "The Oxygen Flame Flammability Test" J. L. Isaacs, J. Fire and Flammability Vol. 1 (Jan. 1970, page 36 et seq.).

The materials treated in accordance with the present invention may be formed in part or in whole of cellulosic materials such as paper, wood, cotton and rayon and may be in various forms such as wood pulp, textile fibers or sheet goods. The materials can also be in comminuted form e.g., paper pulp, cotton fibers, etc. nonwoven form, e.g. paper sheets, wood boards, woven form, e.g., cotton or rayon textile sheeting, and the like. Accordingly although, hereinafter, primary reference will be made to the treatment of sheets of paper, this is not to be taken as a limitation as other forms of cellulosic material may be utilized as the materials treated in accordance with the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

In accordance with a preferred mode of carrying out the present invention cellulosic materials, as above defined, are intimately associated with an effective flame retardant amount of a reaction product of an aqueous solution of phosphoric acid or an acid ammonium salt thereof and an alkylene oxide. Thereafter the treated material is contacted with an alkaline material, e.g., ammonia, ammonium hydroxide, organic amines such as ethyl amine, ethylene diamine and the like, to render the treated material substantially neutral, i.e., a pH of about 6 to 7.5. Alternatively the reaction product, prior to association with the cellulosic material, may be neutralized and thereafter utilized as a substantially neutral solution.

The fire retardant treatment of the invention can be accomplished by several means. For example, the cellulosic material, in finished or unfinished condition, can be immersed, padded, sprayed, dipped or otherwise admixed with the aqueous reaction product, the thoroughly wetted or intimately associated mixture dried to remove excess moisture and then exposed to gaseous ammonia vapors until the treated material reacts substantially neutral. The treated cellulosic material may be heated to below its decomposition temperature without significant effect on the treatment.

Alternatively the material can be intimately associated with an aqueous solution of the substantially neutral reaction product to thoroughly impregnate the cellulosic material. Thereafter the treated material containing an effective fire retardant amount of the neutralized reaction product can be dried in any convenient manner.

The reaction product used in the process of this invention is a complex mixture of unknown composition and is obtained by reacting an alkylene oxide e.g., ethylene oxide, 1,2-propylene oxide, 2,3-butylene oxide, and the like with an aqueous solution of a phosphoric acid, such as ortho phosphoric acid, meta phosphoric acid, pyrophosphoric acid, and the like, or an acid am-

monium salt thereof such as monoammonium ortho phosphoric acid, diammonium ortho-phosphoric acid, monoammonium meta-phosphoric acid, and the like.

The preferred reactants are ortho phosphoric acid or diammonium acid ortho phosphate, and ethylene oxide because of their overall effectiveness and low cost.

Aqueous solutions of the phosphoric acid or ammonium salts thereof are used. Such solutions may contain from about 5 to about 85 percent by weight of 100% phosphoric acid (or the equivalent amount of the acid ammonium phosphate) although preferably dilute solutions containing from about 7 to about 25 percent of 100% phosphoric acid are used.

To carry out the preparation of the said reaction product, an aqueous solution of the phosphoric acid or acid ammonium salt thereof is placed in a suitable reactor which may be equipped with an agitator and the alkylene oxide is bubbled into the solution. The initial exotherm may be controlled by cooling the mixture and/or by adjusting the rate of addition of the alkylene oxide. The temperature of the reaction is adjusted to from about 0° to about 100° centigrade and preferably from about 10° to about 80° centigrade and an amount of the alkylene oxide which is from about one-half to about one and one half times the weight of 100 percent phosphoric acid, or its equivalent, present. Preferably from about one to about one and one-half the weight of 100% phosphoric acid equivalent is added. The resultant solution can be used directly but preferably it is neutralized to a pH of about 6.0 to about 7.5 or higher, with ammonia or other alkaline reacting substances, as defined above.

The resulting aqueous solution of the reaction product is a rather complex mixture which does not crystallize on standing or on evaporation, or if crystals do form they are rather minimal in amount. Thus the reaction product is a liquid to a fluid slurry even after drying. The reaction product is substantially neutral or can be rendered neutral in situ or after application to the cellulosic material. Such a composition is eminently advantageous since it can be more effectively applied to and distributed throughout the material than a composition which crystallizes on drying and thus deposits isolated crystals on the material thereby affecting the surface character, e.g., hand, of the treated material.

Without being bound by any theory or explanation of the reactions which take place during the formation of the reaction product of the aqueous phosphoric acid or acid ammonium salt thereof and alkylene oxide, it is believed that when reacting, for example, ethylene oxide and aqueous ortho phosphoric acid a major amount of a hydroxy ethyl ester of ortho phosphoric acid is formed together with lesser amounts of ethylene glycol and other phosphorus containing organic compounds. Also there may be more or less amounts of unreacted phosphoric acid ions present which upon neutralization with ammonia or ammonium hydroxide form ammonium phosphates. Such a complex mixture, fortuitously, resists crystallization even when dried to a low water content, and thus provides not only an effective fire retardant agent, but also a non-irritating, i.e., non-acidic, which can be readily applied to cellulosic materials and dried thereon without affecting the surface properties, e.g., hand, of the thus treated material.

The present invention can be most advantageously utilized for imparting flame retardant character to paper and paper products either at the pulp stage or finished stage in such products as crepe or tissue paper used for decorative purposes and the like. The aqueous reaction product can also be used to treat Christmas trees by dipping, spraying and the like, to make the trees fire retardant. Further as has been discovered by another, the aqueous solution is a highly effective flame retardant material which can be used to combat forest fires. In such applications, additives such as jaguar gums to regulate viscosity, wetting agents, iron oxides and other coloring agents, other flame retardant additives such as antimony oxides, can be dissolved or suspended in the aqueous solution. This then can be used to spray the burning area and/or limit the burning area by spraying the area adjacent thereto and thereby to prevent or to limit the fire. On evaporation of the water from the solution a viscous liquid remains which adheres to and coats the trees and effectively renders them flame retardant.

The following examples will illustrate the present invention. Parts and percentages are by weight and temperatures are given in degrees centigrade.

## EXAMPLE 1

Preparation of Reaction Product of Aqueous Phosphoric Acid and Ethylene Oxide

A mixture of 58.5 parts of 85% ortho phosphoric acid was diluted to 500 parts with water. The solution has a specific gravity of 1.055 at 25 degrees. Ethylene oxide was bubbled into the solution for about 10 minutes. The solution gained 75.7 parts in weight and had a specific gravity of 1.073 at 25°. This was a 15% solution of the reaction product.

The above procedure was repeated but ethylene oxide was bubbled into the solution for only about four minutes. The resulting solution gained only 37.0 parts and had a specific gravity, at 25°, of 1.064. This was a 7% solution of the reaction product.

In a similar manner, ethylene oxide was bubbled into a 10% phosphoric acid solution for about three minutes to give a gain in weight of 20.5 parts and a specific gravity (25°) of 1.0595. This was a 4% aqueous solution of the reaction product.

In a similar manner, ethylene oxide was bubbled into a 10% aqueous solution of phosphoric acid for about eight minutes, to give an 11% solution of the reaction product. The gain in weight was 54.9 parts, final temperature 77°, and the specific gravity (25°) was 1.068.

## EXAMPLE 2

A two inch wide strip of tissue paper ("Kim-Wipe") was immersed in an aqueous solution of the reaction product of ortho phosphoric acid and ethylene oxide containing 4% of said reaction product and prepared as described in Example 1 above. The impregnated tissue paper was laid on a metal plate and covered with a piece of filter paper and a paper towel. the "sandwich" was squeezed "dry" by rolling. The tissue paper was then placed in a 70° oven until dry. The tissue paper was tested according to ASTM D-777-46 and found to be fire retardant (char length 4 inches). The hand of the treated tissue paper was excellent and its strength was practically unaffected by the treatment.

## EXAMPLE 3

Swatches of cotton cheese cloth and cotton sheeting were immersed in an aqueous solution of the reaction

product of phosphoric acid and ethylene glycol containing 15% of the reaction product and prepared as described in Example 1 above. The solution was neutralized to a pH of 6.9 with ammonium hdyroxide. The swatches were squeezed out manually and then dried in a 70° oven.

The Oxygen Index of the treated cotton swatches was 35–36 (OI of untreated cotton is 19) and strips of each of the treated cotton swatches exposed to a vertical flame was self extinguishing with a 3–3 ½ inch char length.

## EXAMPLE 4

To a solution of 58.5 parts of 85% ortho phosphoric acid diluted to 500 parts with water, ethylene oxide was added. The latter was bubbled into the acid solution at such a rate that the temperature did not exceed about 50°. After the addition of about 75 parts of ethylene oxide, the addition was completed. The reaction mixture was agitated for about 5 minutes and then rendered neutral (pH of about 7) by the addition of ammonium hydroxide.

Tissue paper was impregnated with this solution by placing a sheet of the paper on a 6 inch metal plate and lowering the plate into a tray containing the solution. The paper swelled and floated in the solution. Thereafter the metal plate was raised with a slight slant to remove the impregnated paper. The tissue paper was covered with a sheet of filter paper and then several paper towels were laid on the filter paper. The resulting sandwich was rolled with a heavy roller to squeeze excess solution out of the tissue paper. The tissue paper was placed in a 40° oven for about 1 hour and then hung in the air at about 23° and 51% R.H. for about one hour. The treated dried and equilibrated tissue paper was then tested for flame retardancy according to TAPPI-T-461 and found to be flame retardant. The tests were made with strips of treated paper cut both parallel and perpendicular to the screen. Single thickness and double thickness tissue papers were tested and found to be flame retardant.

## EXAMPLE 5

A solution of 50 parts of diammonium acid phosphate in 450 parts of water was cooled to about 0° in an ice bath. Ethylene oxide was bubbled into the solution until about 50 parts were added. The ethylene oxide was absorbed rapidly and the temperature of the aqueous reaction mixture rose to about 13°. The solution was placed in a stoppered bottle and permitted to stand for about 24 hours at ambient temperature. The solution remained clear and free of crystals. A small portion of the aged solution was placed on a metal plate and evaporated in an oven. The solution did not crystallize and a thick oily mass remained.

Strips of tissue paper were impregnated with the aged solution by the method described in Example 4 above and then tested for flame retardancy according to TAPPI-T-461. The treated tissue paper was found to be flame retardant by this standard test procedure.

The invention has been described in the above specification and illustrated by reference to specific embodiments in the illustrative examples. However, it is to be understood, that this not be so limited since changes and modifications in the specific details disclosed hereinabove can be made without departing from the scope or spirit of the inventions disclosed herein.

What is claimed is:

**1.** Fire retardant cellulosic containing material which material contains an effective fire retardant amount of a reaction product of aqueous ortho phosphoric acid or an acid ammonium salt thereof and an alkylene oxide wherein said reaction product has been obtained by reacting an aqueous solution of a ortho phosphoric acid or an acid ammonium salt thereof containing from about 1 to about 85 percent by weight of ortho phosphoric acid or the equivalent amount of an acid ammonium salt thereof with an amount of an alkylene oxide which is from about 0.5 to 1.5 times the weight of 100 percent phosphoric acid or equivalent thereof present, intimately associated therewith.

**2.** Fire retardant cellulosic material as claimed in claim **1** wherein the material is paper.

**3.** Fire retardant cellulosic material as claimed in claim **1** wherein the material is cotton.

**4.** Fire retardant cellulosic material as claimed in claim **1** wherein the material comprises at least 0.5 percent by weight of the reaction product of aqueous phosphoric acid and an alkylene oxide.

**5.** Fire retardant cellulosic materials as claimed in claim **1** wherein the alkylene oxide is ethylene oxide.

**6.** The fire retardant material of claim **1** wherein the aqueous phosphoric acid solution contains from about 7 to about 25 percent by weight of phosphoric acid.

**7.** The fire retardant material of claim **1** wherein the solution of the reaction product contains from about 7 to about 11 percent by weight of the reaction product.

**8.** Flame retardant cellulosic material as claimed in claim **4** wherein said reaction product has been neutralized with an alkaline reacting substance of the group consisting of ammonia and organic amines.

**9.** Fire retardant cellulose materials as claimed in claim **4** wherein the alkylene oxide is ethylene oxide.

**10.** Fire retardant cellulosic materials as claimed in claim **4** wherein said material is paper.

**11.** Fire retardant cellulosic materials as claimed in claim **4** wherein said material is cotton.

**12.** The fire retardant material of claim **5** wherein sufficient ethylene oxide is reacted with the phosphoric acid to yield a solution containing from about 4 to about 15% by weight of the reaction product.

**13.** The fire retardant material of claim **8** wherein the aqueous reaction product is rendered neutral with ammonia.

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