United States Patent Office 3,054,698 Patented Sept. 18, 1962

3,054,698

FLAME PROOFING OF CELLULOSIC MATERIALS

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No Drawing. Filed Nov. 21, 1960, Ser. No. 70,387
22 Claims. (Cl. 117—136)

This invention relates to a process for the preparation of flame-retardant cellulosic materials and to the compositions produced thereby. More particularly, this invention relates to the treatment of cellulosic textiles with a solution containing a hydroxymethyl phosphonium chloride compound and a high softening point polyvinyl chloride resin to yield flame-retardant cellulosic textiles having markedly improved hand.

Numerous processes have been developed for treating cellulosic materials such as textiles with methylol-phosphorus polymers to render the textile flame-retardant, as exemplified by the disclosure of U.S. Patent No. 2,809,941, issued to Wilson A. Reeves and John D. Guthrie on October 15, 1957. When techniques such as these are employed, the treated fabric is flame-retardant when subjected to the standard char test, but under certain conditions the treated fabric will ignite, particularly after several washings of the treated cloth.

In another process it has been proposed to admix the methylol-phosphorus compounds disclosed by Reeves and Guthrie in the aforesaid patent with plasticized polyvinyl chloride resins having a softening point below about eighty degrees centigrade. Mixed polymers such as these also render the treated textile flame-retardant. However, frequent washings of the treated textile significantly affect the flame retarding properties of the textile. Furthermore, the treated cloth has a relatively poor hand. In addition, cloth which has been treated with the aforesaid mixed polymers, becomes extremely stiff and boardy after repeated ironing. Additionally, when textiles are treated with the aforesaid mixed polymers, the fibers of the textile tend to swell, and remain in a swollen state after treatment, thereby significantly increasing the thickness of the cloth. This increase in thickness appears to adversely affect the hand of the treated cloth.

It is an object of this invention to provide an improved method of preparing flame-retardant cellulosic materials.

A further object of the invention is to provide novel flame-retardant cellulosic materials.

Another object of the invention is to provide a method of improving the flame retardance and hand of cellulosic textiles.

Still another object of the invention is to provide novel cellulosic textiles which retain their flame-retarding properties after frequent washings.

Another object of the invention is to provide flame-retardant cellulosic textiles having an improved hand, even after being subjected to frequent ironing.

These and other objects of the invention, which will be apparent to those skilled the art, can be effected by the instant novel invention, which is described in detail hereinafter.

It has now been discovered that flame-retardant cellulosic materials having improved physical properties may be prepared by impregnating the cellulosic material with an aqueous resin dispersion containing a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is as defined below, a water soluble cyclic nitrogen-containing compound, a water soluble tertiary alkyl amine, urea, and a polyvinyl chloride resin having a high softening point, and then drying and curing the resulting resin impregnated cellulosic material. When a cellulosic textile is treated in accordance with the instant invention, the resin impregnated textile has markedly improved hand, tear strength, tensile strength and flame retarding properties, when compared with textiles treated with resin compounds by techniques of the prior art.

Hydroxymethyl phosphonium chloride compounds suitable for use in the instant invention are those water soluble compounds having the formula $(CH_2OH)_3RPCl$, where R is hydroxymethyl, lower alkyls having between about one and about eight carbon atoms, and chlorinated lower alkyls having between about one and about eight carbon atoms. Typical examples of suitable water soluble hydroxymethyl phosphonium compounds are tetrakis(hydroxymethyl) phosphonium chloride, tris(hydroxymethyl) methyl phosphonium chloride, tris(hydroxymethyl) ethyl phosphonium chloride, tris(hydroxymethyl) butyl phosphonium chloride, tris(hydroxymethyl) octyl phosphonium chloride, tris(hydroxymethyl) chlorooctyl phosphonium chloride, and mixtures thereof. The phosphonium chloride may be used in monomer form or in a partially polymerized form, so long as it is still water soluble. For example, tetrakis(hydroxymethyl) phosphonium chloride may be heated to effect partial polymerization before dissolving in the aqueous solution.

Water soluble cyclic nitrogen-containing compounds suitable for use in the instant invention include triazines and dimethylol cyclic alkylene ureas. Typical examples of suitable triazines include methylol melamine, modified methylol melamine, such as the trimethyl ether of methylol melamine, triazones, and mixtures thereof. Typical examples of suitable cyclic alkylene ureas include dimethylol ethylene urea and dimethylol propylene urea.

Water soluble tertiary alkyl amines which are suitable for use in the instant invention include triethylamine, triethanolamine, triisopropanolamine, and the like.

Polyvinyl chloride resin suitable for use a a component of the novel flame-proofing composition are polyvinyl chloride resins having a softening point between about one hundred and seventy and about two hundred degrees centigrade. The polyvinyl chloride resin is preferably unplasticized and substantially pure, but may contain minor proportions of other monomers such as polyvinyl acetate, acrylics and plasticizers, but the proportions of these ingredients in the polyvinyl chloride resin should be less than those proportions that will reduce the softening point of the resulting mixture to below about one hundred and sixty degrees centigrade. The polyvinyl chloride resin is preferably employed as an aqueous dispersion or emulsion containing between about forty-five and about fifty-five percent by weight of polyvinyl chloride resin in the dispersion.

Urea is also employed as a component of the flame-proofing composition in the proportions defined below.

The approximate proportions of the aforesaid components used in preparing the aqueous resin dispersion or emulsion are as follows:

Component:	Proportion, percent by weight
Hydroxymethyl phosphonium chloride compound	6 to 20
Water soluble cyclic nitrogen-containing compound	3 to 12
Water soluble tertiary amine	1 to 4
Urea	3 to 12
High softening point polyvinyl chloride resin (dry basis)	7 to 25
Water	45 to 80

Any cellulosic material such as cotton, rayon, ramie, jute, wool, paper, cardboard and the like may be treated in accordance with the instant invention, but the inven-

tion is particularly effective when applied to the treatment of cellulosic textiles, since the treated textiles have a markedly improved hand as well as flame retarding properties.

In preparing the aqueous dispersion or emulsion, the aforesaid components are admixed with sufficient water to yield an aqueous resin dispersion or emulsion containing between about forty-five and about eighty percent, and preferably between about fifty and about seventy percent total solids by weight. The term "total solids" as used throughout the description and claims, is intended to include both the solids that are dissolved in the aqueous component, as well as those solids which are colloidally dispersed or otherwise dispersed in the aqueous dispersion or emulsion. The word "dispersion," as used throughout the description and claims, is intended to include the dispersion and/or emulsion that results from admixing the above defined hydroxymethyl phosphonium chloride compound, the cyclic nitrogen-containing compound, the water soluble tertiary alkyl amine, urea, polyvinyl chloride resin and water in the proportions defined above. Greater or lesser proportions of the aforesaid components may be employed so long as the concentration of total solids in the aqueous dispersion is sufficient to provide an adequate resin add-on for the cellulosic material being treated.

The cellulosic material is impregnated with the aqueous resin dispersion by padding, by spraying, by rolling, or by other impregnating techniques well known to the art. It is preferred to immerse the cellulosic material in the aqueous dispersion until the cellulosic material is completely saturated, and then pass the cellulosic material through squeeze rolls to remove resin dispersion in excess of that amount necessary to saturate the cellulosic material.

The saturated cellulosic material is then subjected to conditions of temperature and time, sufficient to effect drying of the saturated cellulosic material and curing of the resin. Drying and curing can be effected by any commercially feasible technique. For example, drying of the cellulosic material can be effected in a conventional forced hot air oven wherein the saturated cellulosic material is heated at a temperature between about eighty and about one hundred and twenty degrees centigrade for between about two and about four minutes. Curing of the dried cellulosic material can be effected in the same apparatus by heating the dried cellulosic material to a temperature of between about one hundred and forty and about one hundred and sixty degrees centigrade, for between about two and about four minutes. If desired, curing of the dry, treated cellulosic material can be effected in an infrared oven at a temperature between about five hundred and about seven hundred degrees Fahrenheit, for a period between about five and about twelve seconds.

After curing, the resin impregnated cellulosic material is preferably subjected to a scouring step in order to remove unpolymerized resin. For example, scouring can be effected by immersing the cured cellulosic material in an aqueous solution containing about 0.2 percent by weight of soap and about 0.2 percent by weight of sodium carbonate. After immersing the resin impregnated cellulosic material in the solution, it is then dried as described above.

The proportion of resin added to the cellulosic material by the aforesaid novel technique is generally between about fifteeen and about thirty-five percent by weight of the cellulosic material. This proportion of resin is referred to throughout the description and claims as "resin add-on." The resin formed on the cellulosic material by the instant novel process is the reaction product of the non-aqueous components of the aqueous resin dispersion, i.e., the hydroxymethyl phosphonium chloride compound, the cyclic nitrogen-containing compound, the water-soluble tertiary alkyl amine, urea, and the high softening point polyvinyl chloride resin. When the aqueous resin

dispersion contains the resin forming ingredients in the proportions defined above, the resulting resin which impregnates the cellulosic material is the reaction product of hydroxymethyl phosphonium chloride compound in a proportion equivalent to between about ten and about sixty percent, the cyclic nitrogen-containing compound in a proportion equivalent to between about five and about forty percent by weight, the water-soluble tertiary alkyl amine in a proportion equivalent to between about one and about twenty percent by weight, urea in a proportion equivalent to between about five and about forty percent by weight, and the high softening point polyvinyl chloride resin in a proportion equivalent to between about ten and about seventy percent by weight of the resin forming ingredients.

Cellulosic materials treated in accordance with the instant invention have improved flame retarding properties, which are retained even after the treated cellulosic material is contacted with water and other solvents. For example, when cellulosic textiles are treated in accordance with the instant invention, the textile is not only flame-retardant, but also has a markedly improved hand, that is, the textile is soft and flexible, and these properties are retained after repeated washings and ironings.

The following examples are presented to define the invention more fully without any intention of being limited thereby. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

An aqueous dispersion was prepared from the following components in the following proportions.

Component:	Parts by weight
Tetrakis (hydroxymethyl) phosphonium chloride	17.7
Triethanolamine	3.5
Trimethylolmelamine	10.4
Urea	10.4
Polyvinylchloride resin (aqueous dispersion containing 50% resin solids) [1]	45.0
Water	53.5

[1] Softening point of polyvinylchloride resin was one hundred and eighty degrees centigrade.

The resulting aqueous dispersion contained forty-six percent solids.

A nine-ounce "battle-ax" fabric of the type conventionally used for work garments, was immersed in the above-described aqueous dispersion, then passed through squeeze rolls to remove excess liquid, and then dried at a temperature of two hundred and fifty degrees Fahrenheit. The dried, treated fabric was then placed in an infrared oven for about ten seconds at a temperature of about seven hundred degrees Fahrenheit to effect curing of the resin. The resin treated fabric was then scoured by immersing it in an aqueous solution containing 0.2 percent non-ionic detergent and 0.2 percent sodium carbonate. After scouring, the fabric was dried. The resin add-on of the resin treated fabric after scouring and drying was 33.6 percent. The tensile strength of the treated fabric, as determined in accordance with Federal Specification CCC–T–191b–#5100, using a Scott tensile tester, was one hundred and thirty-five pounds, as compared to a tensile strength of one hundred and thirty for the untreated fabric.

The resin treated fabric was subjected to the standard char test. The char test was carried out in accordance with the American Association of Textile Chemists and colorists, Test AATC 34–1952. In this test, a strip of cloth to be tested is secured on each of its long sides in a vertical position, leaving an exposed area of approximately ten inches by two and one-quarter inches. A Bunsen burner is positioned below the bottom of the cloth so that the top of the burner is about three-quarters of an inch from the cloth. The burner produces a flame which is about one and one-half inches high. The flame

is produced by burning natural gas in the absence of air. The cloth is exposed to the flame for a period of twelve seconds, and the flame is then turned off. The cloth is then removed from the securing means and a weight is attached to one side of the char, the weight being equivalent to ten percent of the tear strength of the cloth. The opposite side of the cloth is then pulled to produce a tear along the char. The length of the tear is then measured to determine the char in inches.

The resin treated fabric had a very good hand, and had a char of 3.8 inches by the standard char test. After twenty commercial launderings, the treated cloth had a char of 3.3 inches; after thirty commercial launderings, it had a char of 3.0 inches. The treated cloth, after being subjected to these extreme laundering conditions, still retained its very good hand, and was soft, flexible and crease resistant.

EXAMPLES 2–7

The procedure of Example 1 was repeated, employing polyvinylchloride resins of various softening points, as indicated in the table below.

Table

Example	2	3	4	5	6	7
Softening point of polyvinyl chloride, ° C	40–50	70–80	110–120	140–150	180–200	190–200
Percent resin add-on after cure and scour	31	30	30	30	31	30
Gurley stiffness, mg	330	620	540	820	540	420
Thickness, mills	34.2	32.5	33.4	31.5	31.9	31.2
Hand rating of treated cloth (1=best, 6=worst):						
Observer A	5	4	6	3	2	1
Observer B	3	4	5	6	2	1
Observer C	3	5	4	6	2	1

Examples 6 and 7 show the improved results that are obtained by the technique of the instant novel invention, while Examples 2, 3, 4 and 5 show the results obtained by procedures of the prior art. The cloths produced in Examples 6 and 7 had a superior hand as compared to the treated cloths produced in Examples 2 to 5, and the cloths of Examples 6 and 7 also were significantly less bulky than the cloths of Examples 2, 3 and 4. Although the stiffness of the cloth produced in Example 2 (where a low softening point polyvinyl chloride resin was employed), was less than that obtained with the high softening point polyvinyl chloride in Examples 6 and 7, nevertheless the thickness or bulkiness of the cloth produced in Example 2 was much greater than that obtained in Examples 6 and 7, and as a result, the hand of the treated material produced in Examples 6 and 7 was markedly superior to that of Example 2.

It will be recognized by those skilled in the art that various modifications within the invention are possible, some of which have been referred to above. Therefore, I do not wish to be limited except as defined by the appended claims.

I claim:

1. A process for preparing a flame-retardant, cellulosic material which comprises impregnating the cellulosic material to be treated with an aqueous dispersion of a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is selected from hydroxymethyl, lower alkyls having between one and about eight carbon atoms, and chlorinated lower alkyls having between one and about eight carbon atoms, a member of the group consisting of triazines and dimethylol cyclic alkylene ureas, a water-soluble tertiary alkyl amine, urea, and a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade, and drying and curing the treated cellulosic material.

2. A process for preparing a flame-retardant, cellulosic material which comprises impregnating the cellulosic material to be treated with an aqueous dispersion containing between about forty-five and about eighty percent by weight of water, between about six and about twenty percent by weight of a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is selected from hydroxymethyl, lower alkyls having between one and about eight carbon atoms, and chlorinated lower alkyls having between one and about eight carbon atoms, between about three and about twelve percent by weight of a member of the group consisting of triazines and dimethylol cyclic alkylene ureas, between about one and about four percent by weight of a water-soluble tertiary alkyl amine, between about three and about twelve percent by weight of urea, and between about seven and about twenty-five percent by weight of a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade, and drying and curing the treated cellulosic material.

3. The process of claim 2 wherein said hydroxymethyl phosphonium chloride is tetrakis(hydroxymethyl) phosphonium chloride.

4. The process of claim 2 wherein said cellulosic material is a cellulosic textile.

5. The process of claim 2 wherein the resin add-on of the treated cellulosic material after curing is between about fifteen and about thirty-five percent by weight of the cellulosic material.

6. The process of claim 2 wherein drying of the cellulosic material impregnated with said aqueous dispersion is effected at a temperature between about eighty and about one hundred and twenty degrees centigrade for a period between about two and about four minutes, and curing of the resulting material is effected at a temperature between about one hundred and forty and about one hundred and sixty degrees centigrade for between about two and about four minutes.

7. A process for preparing a flexible, flame-retardant cellulosic textile which comprises impregnating the cellulosic textile to be treated with an aqueous dispersion containing between about forty-five and about eighty percent by weight of water, between about six and about twenty percent by weight of tetrakis(hydroxymethyl) phosphonium chloride, between about one and about four percent by weight of triethanolamine, between about three and about twelve percent by weight of trimethylolmelamine, between about three and about twelve percent by weight of urea, and between about seven and about twenty-five percent by weight of a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade, and drying and curing the treated cellulosic material.

8. The process of claim 7 wherein the resin add-on of the treated cellulosic material after curing is between about fifteen and about thirty-five percent by weight of the cellulosic textile.

9. The process of claim 7 wherein the cellulosic textile impregnated with said aqueous dispersion is dried at a temperature between about eighty and about one hundred and tweny degrees centigrade, for a period between about two and about four minutes, and curing of the resulting

dried, resin impregnated cellulosic textile is effected at a temperature between about one hundred and forty and about one hundred and sixty degrees centigrade for a period between about two and about four minutes.

10. A flame retardant cellulosic material comprised of a cellulosic material impregnated with a resinous material comprised of the reaction product of a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is selected from hydroxymethyl, lower alkyls having between one and about eight carbon atoms, and chlorinated lower alkyls having between one and about eight carbon atoms, a member of the group consisting of triazines and dimethylol cyclic alkylene ureas, a water-soluble tertiary alkyl amine, urea, and a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade.

11. A flame retardant cellulosic material comprised of a cellulosic material impregnated with a resinous material, said resinous material being the reaction product formed from resin forming ingredients comprised of a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is selected from hydroxymethyl, lower alkyls having between one and about eight carbon atoms, and chlorinated lower alkyls having between one and about eight carbon atoms, in a proportion equivalent to between about ten and about sixty percent by weight, a member of the group consisting of triazines and dimethylol cyclic alkylene ureas in a proportion equivalent to between about five and about forty percent by weight, a water-soluble tertiary alkyl amine in a proportion equivalent to between about one and about twenty percent by weight, urea in a proportion equivalent to between about five and about forty percent by weight, and a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade in a proportion equivalent to between about ten and about seventy percent by weight of the resin forming ingredients.

12. The flame retardant cellulosic material of claim 11 wherein said hydroxymethyl phosphonium chloride compound is tetrakis(hydroxymethyl) phosphonium chloride.

13. The flame retardant cellulosic material of claim 11 wherein said cellulosic material is a cellulosic textile.

14. The flame retardant cellulosic material of claim 11 wherein the resin add-on is between about fifteen and about thirty-five percent by weight of the cellulosic material.

15. A flame retardant cellulosic material comprised of a cellulosic material impregnated with a resinous material, said resinous material being the reaction product formed from resin forming ingredients comprised of tetrakis(hydroxymethyl) phosphonium chloride in a proportion equivalent to between about ten and about sixty percent by weight, trimethylol melamine in a proportion equivalent to between about five and about forty percent by weight, triethanol amine in a proportion equivalent to between about one and about twenty percent by weight, urea in a proportion equivalent to between about five and about forty percent by weight, and a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade in a proportion equivalent to between about ten and about seventy percent by weight of the resin forming ingredients.

16. The flame retardant cellulosic material of claim 15 wherein said cellulosic material is a cellulosic textile.

17. The flame retardant cellulosic material of claim 15 wherein the resin add-on is between about fifteen and about thirty-five percent by weight of said cellulosic material.

18. The flame retardant cellulosic material of claim 15 wherein said polyvinyl chloride resin has a softening point between about one hundred and seventy and about two hundred degrees centigrade.

19. A flame retardant cellulosic textile comprised of a cellulosic textile impregnated with a resinous material, said resinous material being the reaction product formed from resin forming ingredients comprised of tetrakis(hydroxymethyl) phosphonium chloride in a proportion equivalent to between about ten and about sixty percent by weight, trimethylol melamine in a proportion equivalent to between about five and about forty percent by weight, triethanol amine in a proportion equivalent to between about one and about twenty percent by weight, urea in a proportion equivalent to between about five and about forty percent by weight, and a polyvinyl chloride resin having a softening point in the range between about one hundred and seventy and about two hundred degrees centigrade in a proportion equivalent to between about ten and about seventy percent by weight of said resin forming ingredients, wherein the resin add-on is between about twenty and about thirty-five percent by weight of said flame retardant cellulosic material.

20. A cellulosic material treating composition comprised of a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is selected from hydroxymethyl, lower alkyls having between one and about eight carbon atoms, and chlorinated lower alkyls having between one and about eight carbon atoms, a member of the group consisting of triazines and dimethylol cyclic alkylene ureas, a water-soluble tertiary alkyl amine, urea, a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade, and water.

21. A cellulosic material treating composition comprised of an aqueous dispersion containing between about six and about twenty percent by weight of a hydroxymethyl phosphonium chloride compound having the formula $(CH_2OH)_3RPCl$, where R is selected from hydroxymethyl, lower alkyls having between one and about eight carbon atoms, and chlorinated lower alkyls having between one and about eight carbon atoms, between about three and about twelve percent by weight of a member of the group consisting of triazines and dimethylol cyclic alkylene ureas, between about one and about four percent by weight of a water-soluble tertiary alkyl amine, between about three and about twelve percent by weight of urea, between about seven and about twenty-five percent by weight of a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade, and between about forty-five and about eighty percent by weight of water.

22. A textile treating composition comprised of an aqueous dispersion containing between about six and about twenty percent by weight of tetrakis(hydroxymethyl) phosphonium chloride, between about one and about four percent by weight of triethanol amine, between about three and about twelve percent by weight of trimethylol melamine, between about three and about twelve percent by weight of urea, between about seven and about twenty-five percent by weight of a polyvinyl chloride resin having a softening point between about one hundred and seventy and about two hundred degrees centigrade, and between about forty-five and about eighty percent by weight of water.

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