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3,243,391

COMPOSITION AND PROCESS FOR TREATING CELLULOSIC MATERIALS TO MAKE THEM FLAME-RETARDANT

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This application is a continuation-in-part of my co-pending application Serial No. 181,456, filed March 2, 1962, now abandoned.

This invention relates to a composition for imparting flame-retardant characteristics to cellulosic materials and to the resinous precondensate material used in this composition. The invention further relates to a process for the preparation of flame-retardant cellulose, such as paper, as well as to the cellulosic products, e.g. paper products, produced thereby.

In the art of impregnating cellulosic materials, and particularly paper and paper products, it is often desirable that the thus-impregnated products are flame retardant and, additionally, have considerable strength, stiffness, and are capable of being subjected to bending without rupture of the fibers. Exemplary of the uses in which such characteristics of the paper are desired are laminated papers and/or non-woven textiles used as structural members, insulation, etc., paper used for filters in the air cleaners for carburetors in automobiles and the like. Although various flameproofing compositions have heretofore been proposed, containing many and diverse types of ingredients, for the most part, these compositions have not been effective in producing a flame-retardant paper having the desired characteristics of strength and stiffness.

Many of the above disadvantages have been overcome by using an impregnating composition comprising a tetrakis(hydroxymethyl)phosphonium chloride, a vinyl chloride-vinylidene chloride copolymer latex, and a resin precondensate of urea-formaldehyde. Paper and paper products impregnated with this composition have been found to be not only flame-retardant, but, additionally, possess the desired characteristics of stiffness and resistance to bending without fiber rupture. This type of formulation is described in U.S. application Ser. No. 845,596, now U.S. Patent 3,087,836. The use of this type of formulation, although producing a paper product having excellent flame retardancy and finish has been found in some instances to be subject to some drawbacks.

One disadvantage is that of cost. Since, in this formulation, the principle flame-retarding material is tetrakis(hydroxymethyl)phosphonium chloride, in order to impart the desired flame retardancy to the paper product, an amount of this material must be used which may make the cost of this composition somewhat unattractive, in some instances. Additionally, and even more important, the presence of a vinyl chloride latex in the composition, which material is used to give the paper product the desired finish, tends to restrict the solutions from which the composition can be applied to substantially aqueous solutions. This is disadvantageous in that, customarily, the plants processing impregnated paper may not be equipped with sufficient drying capacity to drive out all of the water of solution from the impregnated paper. Moreover, much of the paper used in the impregnating processes has a sufficiently low wet strength that in contacting the paper with an aqueous solution, the paper may become difficult to handle, e.g., be ruptured easily or fall apart.

It is, therefore, desirable to be able to impregnate the paper and paper products from a solution containing a

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non-aqueous solvent, e.g., an alcohol, such as isopropanol. As is well known by those in the art however, vinyl chloride-containing latexes tend to coagulate when they are contacted with many organic solvents, including the common alcohol solvents such as isopropanol. Accordingly, until the present time it was not possible to produce a flame-retardant paper product having desirable stiffness, porosity, and flexibility, using impregnating solution containing a non-aqueous solvent, even as a co-solvent with water.

It is, therefore, an object of the present invention to provide an impregnating composition, which composition may be applied to paper and paper products from a solution which contains a non-aqueous solvent.

A further object of the present invention is to provide a flame-retardant paper or paper product having good stiffness and porosity, while still being capable of bending without rupture of the fibers.

Another object of the present invention is to provide a novel resinous precondensate which acts as a dispersing agent to prevent the coagulation of a vinyl halide-containing latex when it is in contact with an organic solvent material.

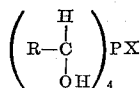
A still further object of the present invention is to provide a flame-retardant impregnating composition for paper, which composition can be applied from a solution containing an organic solvent without effecting coagulation of any vinyl halide-containing latex in the composition.

These and other objects will become apparent from the description of the present invention which follows.

Pursuant to the above objects, the impregnating composition of the present invention includes a resinous precondensate of a tetrakis(hydroxyorgano)phosphonium halide, urea, and formaldehyde, in combination with a polyvinyl halide, preferably as a latex, and antimony oxide. This composition may be applied to paper or paper products from a media containing a non-aqueous solvent, as, for example, an alcohol or a mixed alcohol-water media. The fact that this composition can be so applied is deemed to be surprising in that, ordinarily, a latex containing polyvinyl halide is coagulated in the presence of an alcohol solvent. In the present instance, however, this coagulation of the polyvinyl halide-containing latex is prevented by use of the resin precondensate of a tetrakis(hydroxyorgano)phosphonium halide, urea, and formaldehyde.

More specifically, the subject impregnating composition may comprise polyvinyl chloride in an amount of about two to about twenty-five percent by weight, preferably added in the form of a latex, a resin precondensate of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde, in an amount from about ten to about forty percent by weight, preferably added in the form of a dispersion, antimony oxide in an amount from about two to about fifteen percent by weight, with the remainder of the composition to make 100 percent by weight being solvent such as water, a lower aliphatic alcohol, e.g., isopropanol, or the like. In addition to the above constituents, the composition may also contain a suitable catalyst for aiding in curing the resinous precondensate, and/or a protective colloid, and/or a wetting agent. These latter three ingredients, i.e., the wetting agent, the protective colloid and catalyst, are generally present in an amount up to about three percent by weight of the total composition. Generally, the total solids content of the above composition will be within the range of about 10 percent to about 55 percent by weight of the total composition, with a total solids content of about 30 percent by weight of the total composition being typical for many operations.

The tetrakis(α - hydroxyorgano)phosphonium halide compound of the subject composition may be further defined as a compound having the formula:



wherein R is selected from the group consisting of hydrogen, lower alkyls having between about 1 and about 6 carbon atoms, halogenated lower alkyls having between about 1 and about 6 carbon atoms, lower alkenyls having between about 1 and about 6 carbon atoms, halogenated lower alkenyls having between about 1 and about 6 carbon atoms, aryls having between about 5 and about 10 carbon atoms, halogenated aryls having between about 5 and about 10 carbon atoms, cycloalkyls having between about 3 and about 6 carbon atoms, halogenated cycloalkyls having between about 3 and about 6 carbon atoms, and X is a halogen, such as chlorine, bromine, fluorine or iodine. Typical examples of suitable tetrakis(α -hydroxyorgano)phosphonium halide compounds are tetrakis(hydroxymethyl)phosphonium chloride, tetrakis(hydroxychloromethyl)phosphonium chloride, tetrakis(hydroxymethyl)phosphonium bromide, tetrakis(hydroxyethyl)phosphonium chloride, tetrakis(α - hydroxypropyl)phosphonium chloride, tetrakis(α -hydroxyallyl)phosphonium chloride, tetrakis(α - hydroxybenzyl)phosphonium chloride, tetrakis(α - hydroxy - p - chlorobenzyl)phosphonium chloride, tetrakis(α - hydroxymethylcyclohexyl)phosphonium chloride, tetrakis(α - hydroxymethyl - 4 - chlorocyclohexyl)phosphonium chloride, tetrakis(α -hydroxypropionyl)phosphonium chloride, tetrakis(α - hydroxybutanol)phosphonium chloride, tetrakis(α - hydroxy - 4-chlorobutanol)phosphonium chloride and mixtures thereof.

The polyvinyl halide-containing latex used in the present composition contains a major amount of the polyvinyl halide. By polyvinyl halide, as used hereinafter in the specification and claims, is meant polyvinyl chloride and polyvinyl fluoride. Because of its low cost and ready availability, the preferred polyvinyl halide for use in the present invention is polyvinyl chloride. For this reason, specific reference will be made hereinafter to polyvinyl chloride. This is to be taken merely as being illustrative of the present invention, however, and not as a limitation. Additionally, although primary reference has been made to the use of a polyvinyl halide latex, it is to be understood that other dispersible forms of the polyvinyl halide may also be used, provided the dispersing agents, plasticizers, solvents and the like utilized are not detrimental to either the impregnating composition or the product produced and are either flame-retardant or are removed in either the impregnation or subsequent operation.

Although it is to be understood that latexes formed of polyvinyl chloride copolymers may be used in the present invention, as, for example, copolymers of vinyl chloride and vinylidene chloride, and copolymers of vinyl chloride and vinyl acetate, the preferred latex is one formed of polyvinyl chloride itself. Where, however, copolymers of vinyl chloride and another material are used, the vinyl chloride is desirably present in an amount in excess of about 50 percent by weight of the copolymer. Generally, copolymers containing even greater amounts of polyvinyl chloride are preferred, as, for example, copolymers containing at least 70 percent to 80 percent by weight of polyvinyl chloride. The preferred latex for use in the present invention is one of polyvinyl chloride containing about 50 percent by weight of solids. It is to be appreciated, however, that latexes containing greater and lesser quantities of solids may also be used without detrimentally affecting the present composition.

The resinous precondensate of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde for the present composition may be prepared by charging

formaldehyde, generally as a 37 percent solution to a suitable reactor fitted with an agitator. Thereafter, triethanolamine and urea are added, in that order, to the reactor. After all of the urea is in solution, the tetrakis(hydroxymethyl)phosphonium chloride is then added to the reactor, followed by the addition of a lower alcohol, such as methanol or isopropyl alcohol. During the addition of the urea to the reaction mixture, a temperature drop occurs to about ten to fifteen degrees centigrade. Thereafter, the addition of the tetrakis(hydroxymethyl)phosphonium chloride and the alcohol will raise the temperature to about twenty degrees centigrade, after which, a slow exotherm occurs which, in an insulated vessel, will raise the temperature to about thirty-five degrees centigrade in a period of about four hours. It is to be noted, that it is desirable that this exotherm, since, if the initial temperature is too low and the exotherm does not occur, unreacted formaldehyde may polymerize and precipitate. Accordingly, in some instances, it may be desirable to apply external heat to bring about the reaction. The condensation reaction may be carried out by maintaining the temperature of the reaction mix at about seventy to eighty degrees centigrade for a period of thirty to forty-five minutes. Alternatively, the condensation reaction may be carried out by maintaining the reaction mixture at about thirty-five to forty degrees centigrade, for a period of five to seven days.

With regard to the formaldehyde, it is to be noted that the expression, "total formaldehyde" is intended to refer to the formaldehyde which is actually added as such, generally, as a thirty-seven percent solution, as well as the formaldehyde equivalents which are present in the tetrakis(hydroxymethyl)phosphonium chloride. Accordingly, it is apparent that the amount of formaldehyde that is actually added in forming the resinous precondensate will depend on the amount of the tetrakis(hydroxymethyl)phosphonium chloride used, since this latter amount will determine the formaldehyde equivalents which are present. Generally, the amount of formaldehyde equivalents in the tetrakis(hydroxymethyl)phosphonium chloride will vary within the range from about fifteen to about sixty-five percent of the total formaldehyde which is to be in the composition.

In forming the resinous precondensate composition, the molar ratio of urea to tetrakis(hydroxymethyl)phosphonium chloride should be within the range of about 14:1 to 3:1, with a molar ratio of about 10:1 being preferred. The molar ratio of total formaldehyde to urea, in this composition should be within the range of about 1.5:1 to about 2.5:1, with a molar ratio of about 2:1 being specifically preferred. The triethanolamine in this composition, which acts as a catalyst and a pH control, is preferably present in an amount within the range of about fifteen to about thirty percent by weight, based on the weight of the tetrakis(hydroxymethyl)phosphonium chloride used. A preferred amount of triethanolamine is about twenty percent by weight, based on the weight of the tetrakis(hydroxymethyl)phosphonium chloride. Finally, the amount of lower aliphatic alcohol, as, for example, isopropanol, which is added to the composition will be sufficient to make up one hundred percent by weight. Generally, the amount of alcohol added will be within the range of about fifteen to forty percent by weight of the total composition, with an amount of about twenty percent of the total composition being specifically preferred.

The solids content of the above resinous precondensate is, preferably, about fifty percent by weight of the total precondensate. However, as with the polyvinyl chloride-containing latex, precondensate compositions containing greater and lesser amounts of solids can be used.

The antimony oxide used in the impregnating composition may be one of many types available which are designed for dispersion in flame-retardant applications. As has been set forth hereinabove, the amount of antimony

oxide used is generally within the range of about two to fifteen percent by weight of the total composition. An amount of antimony oxide of about six percent by weight of the total composition has been found to give exceptionally good results and, hence, is typical for many applications.

Exemplary of protective colloids which may be used are polyvinyl alcohol, hydroxyethyl cellulose, hydroxymethyl cellulose and the like. These are generally present in an amount of about 0.05 percent by weight of the total composition. Where the total solids concentration of the composition is twenty percent or less, however, the quantity of hydroxyethyl cellulose, or similar protective colloid used, is preferably increased at least about two or three times. The type and viscosity grade of the protective colloid used will, of course, depend on the final solids content of the impregnating composition, as well as the viscosity, which is desired. It is believed that those skilled in the art will readily be able to determine the type and viscosity grade which will be used in each instance.

Exemplary of catalysts which may be included in the impregnating composition is citric acid, although other equivalent materials which act to catalyze the curing of the resinous precondensate may also be used. These catalysts are preferably present in the composition in amounts of about 0.1 to about 0.2 percent by weight of the total composition and are generally added as an aqueous solution, e.g., a 50 percent solution. Wetting agents which may be used are preferably of the non-ionic type, such as the non-ionic oxyethylated alkyl phenols, and the like. When used, these are preferably present in an amount within the range of about 1 to about 2 percent by weight of the total impregnating composition. If desired, other additives, such as water repelants, e.g., silicones, wax emulsions, and long chain nitrogen complexes, may also be incorporated in the composition, provided they are compatible with the other components, amounts within the range of about 0.1 to about 1 percent by weight being typical.

Depending upon the solids content desired in the impregnating composition, additional solvent may be added, over and above that which is put into the composition with the latex, the resinous precondensate and the like. This solvent may be water or where advantages of impregnating from a composition having a reduced water content are desired, a non-aqueous solvent, such as an alcohol, e.g. isopropyl alcohol, may be used. It will be appreciated that where an impregnating bath having a very high percent of solids is used, e.g., 50-55 percent solids, the addition of solvent, other than that added in the formulation of the latex, etc., may not be required.

In forming the impregnating bath of the present composition, the polyvinyl chloride-containing latex is first charged to the mixing vessel, and, thereafter, the colloid, e.g. hydroxyethyl cellulose is added. The resinous precondensate of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde, is then added slowly with good agitation. Thereafter, the solvent, e.g., alcohol is charged slowly to the stirred dispersion, and the antimony oxide is then dispersed into the composition. Finally, the citric acid catalyst is added, and, preferably, should be admixed just prior to use of the bath.

In impregnating paper or paper products with this composition, it has been found that the best results are obtained if the paper is completely immersed in the bath and then passed through squeeze rolls. However, kiss-rolls or spraying methods may also be used. In using the latter methods for applying the impregnating composition, the absorbent nature of the paper will cause the solution to penetrate the fibers throughout the paper. Generally, it is desirable that the resin add-on on the paper, after impregnation, be at least about 20 percent by weight. Typically, in many instances, higher resin add-ons, e.g., 27-35 percent by weight will be utilized, with

add-ons as high as 45 percent being used in some cases.

After the paper or paper products have been impregnated, they are subjected to drying and curing conditions so as to remove the alcohol or other diluent from the paper and effect a cure of the resinous components of the composition. The drying and curing conditions used may be varied, depending on the type of substrate which is being treated. Generally, air drying in ovens at about two hundred to two hundred and twenty degrees Fahrenheit for from one to five minutes has been found to be satisfactory. These temperatures and time can, of course, be varied, depending on the substrate used and the solids content of the impregnated bath, as will be apparent to those skilled in the art. The thus-dried product is found to be soft and flexible, and can be cured either immediately following the drying operation, or after a time interval up to about six months.

In curing the impregnated paper or paper products, the curing cycles, likewise, can be varied over a range of time and temperature, e.g., 275-400 degrees Fahrenheit for from 1-10 minutes. A curing cycle of about five minutes at three hundred and thirty-five degrees Fahrenheit in a forced air oven has been found to give excellent results, although temperatures as low as two hundred and seventy-five degrees Fahrenheit can be employed for cure times of ten minutes or even more without detrimentally affecting the product. The extent of the cure will, of course, affect such properties of the impregnated paper as stiffness, bursting, and tensile strength, as well as resistance to water. Accordingly, it is believed that variations in the curing cycle can readily be made by those skilled in the art, depending upon the characteristics of the paper products which are desired. It is also to be noted that in some instances, such as for example, where no forming operations for the paper are required, the impregnated paper stock can be dried and cured in a single operation.

The treated and cured paper or paper products produced in accordance with the above process are characterized by durable flame-retardance, high stiffness values without excessive brittleness, excellent tensile and bursting strength, and resistance to leaching by water and most organic solvents. Additionally, there is found to be only a slight loss in these desirable properties when the treated material is exposed to relative humidity as high as one hundred percent. Although, there may be some reduction in the air porosity of the treated substrate as compared to the untreated stock, this difficulty may be easily overcome and a product having any desired air porosity produced by impregnating stock having a more open furnish.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given.

Example 1

A resinous precondensate is prepared using the following components:

	Percent by weight
Tetrakis(hydroxymethyl)phosphonium chloride	5
Triethanolamine	1
Urea	24
Formaldehyde (total)	1.54
Isopropyl alcohol	16

16.6% by weight being added as a 37% formaldehyde solution.

The formaldehyde is charged to a suitable reactor, equipped with an agitator. Thereafter, the triethanolamine and, then, the urea are added to the reactor, while the reaction mixture is subject to continuous agitation. When all of the urea is in solution, the tetrakis(hydroxymethyl)phosphonium chloride is added. Following the addition of the tetrakis(hydroxymethyl)phosphonium chloride, condensation of the reaction mixture is effected by heating at a temperature within the range of seventy

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to eighty degrees centigrade for a period of about thirty to forty-five minutes. Thereafter, the resinous material is diluted by the addition of the isopropyl alcohol to form a solution having a solids content of about fifty percent, by weight. This product is found to be a clear, substantially colorless solution, having a specific gravity within the range of 1.12 to 1.13 at twenty degrees centigrade.

Example 2

The procedure of Example 1 is repeated with the exception that the following components are used:

	Percent by weight
Tetrakis(hydroxymethyl)phosphonium chloride	20
Triethanolamine	4
Urea	19
Formaldehyde (total)	18.9
Isopropyl alcohol	38.1

¹ 6.6% by weight being added as a 37% formaldehyde solution.

The resulting product has a solids content of about fifty percent by weight and is a clear, substantially colorless solution, having a specific gravity between 1.12 and 1.13 at twenty degrees centigrade.

Example 3

The procedure of Example 1 is repeated using the following components:

	Percent by weight
Tetrakis(hydroxymethyl)phosphonium chloride	7.5
Triethanolamine	1.5
Urea	23.0
Formaldehyde (total)	49.0
Isopropyl alcohol	19.1

¹ 39.2% by weight being added as a 37% formaldehyde solution.

The resulting composition is condensed after the addition of the isopropyl alcohol, by maintaining the composition at a temperature within the range of thirty-five to forty degrees centigrade, for a period of five to seven days. The resulting product has a solids content of about fifty percent by weight, and is a clear, substantially colorless solution, having a specific gravity between 1.12 and 1.13 at twenty degrees centigrade.

Example 4

The impregnating bath is made using the following components:

	Percent by weight
Polyvinyl chloride latex (50%-55% solids)	15.0
Hydroxyethyl cellulose (5% solution)	1.0
Resinous precondensate (as prepared in Example 3)	30.0
Isopropyl alcohol	47.8
Antimony oxide	6.2
Citric acid (50% solution)	0.21

The above components are mixed in the order shown. The polyvinyl chloride latex is first charged to the mixing vessel, followed by the addition of the hydroxyethyl cellulose. Thereafter, the tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde resin is added slowly with good agitation. The isopropyl alcohol is then added slowly to the stirred dispersion, and following the addition of the alcohol, the antimony oxide is added. Finally, the citric acid catalyst is added to the impregnating solution.

Sheets of carburetor air cleaner paper are immersed in the above-impregnating solution. The sheets are squeezed by means of a heavy roller until the wet pick-up is between one hundred and eighty and two hundred and twenty percent. Thereafter, the paper is dried for one minute at two hundred degrees Fahrenheit and cured for a period of three to ten minutes at a temperature of two hundred and seventy-five to three hundred and fifty degrees Fahrenheit. The thus-cured sheets contain from thirty to thirty-two percent by weight of resin, and show a bursting strength of fifteen pounds per square inch as measured

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on the Mullin paper tester. By comparison, untreated paper shows a bursting strength of six pounds per square inch. The treated paper was completely flame resistant and could be fluted through a one hundred and eighty degree angle without breaking.

Example 5

The procedure of Example 4 was repeated using the following components:

	Percent by weight
Polyvinyl chloride latex (50-55% solids)	5
Hydroxyethyl cellulose (5% solution)	1.0
Resinous precondensate (as prepared in Example 3)	40
Isopropyl alcohol	51.8
Antimony oxide	2
Citric acid (50% solution)	0.2

The carburetor air cleaner paper impregnated with the above formulation, dried and cured, was found to have a bursting strength, flame resistance, and resistance to bending without breaking comparable to that produced in the preceding example.

Example 6

The procedure of Example 4 is repeated using the following components:

	Percent by weight
Polyvinyl chloride latex (50-55% solids)	25
Hydroxyethyl cellulose (5% solution)	1.0
Resinous precondensate (as prepared in Example 3)	20
Isopropyl alcohol	43.8
Antimony oxide	10
Citric acid (50% solution)	0.2

The carburetor air cleaner paper impregnated with the above composition, dried and cured, was found to have a bursting strength, flame resistance, and resistance to bending without breaking comparable to that produced in Example 4.

Example 7

The impregnated paper as produced in accordance with Example 4 is subjected to additional testing to show various other properties of the paper. In making these determinations, the Gurley stiffness was taken in two directions: Machine Direction (MD), and Cross Machine Direction (CD). Similarly, the tensile strength determination was also taken in two directions: Machine Direction and Cross Machine Direction. The water resistance determination was a determination of the resistance of the paper to absorption of a drop of water at room temperature (cold) and at two hundred degrees Fahrenheit (hot). The determination of air permeability involved an indication of the pressure increase in inches of water at an air flow of 2.4 cubic feet per minute. Using these procedures, the following results were obtained:

Gurley stiffness (mg.):

Uncured:	
CD after one minute drying at 200° F.	1135
CD after two minutes drying at 200° F.	1755
MD after one minute drying at 200° F.	2260
MD after two minutes drying at 200° F.	2875
Cured, dry:	
CD	2460
MD	3735
Cured, wet ¹ :	
CD	500
MD	650
Tensile strength (lbs./in.):	
CD	11.4
MD	17.0
Water resistance:	
Cold	Good
Hot	Good
Air permeability:	
Untreated paper	0.18
Treated paper	0.19

¹ After 10 minutes in H₂O at 200-212° F., determined while still hot and wet.

Example 8

An impregnating bath was made using the following components in the amounts indicated:

	Percent by weight
Polyvinyl chloride latex (50-55% solids) -----	28.8
Resinous precondensate (as prepared in Example 3) (50% solids) -----	57.5
Wetting agent (non-ionic oxyethylated alkyl phenol) -----	1.0
Antimony oxide -----	12.0
Citric acid (50% solution) -----	0.3
Silicone (water repellent) -----	0.4

These components are combined in the order shown and in the manner set forth in Example 4 to give a pad bath having a solids content of 55.5%. 99 pound kraft paper was padded through the bath at the rate of about 55-60 feet per minute, a contact or wetting out period of 15 seconds being provided. The thus-impregnated paper was dried on stream heated cans and after curing was found to have a resin add-on of about 27%. The thus-treated paper was tested for flame retardancy and was found to have a char length of about 5.25 inches when subjected to the AATCC Standard Test Method #34 and good flame retardance to propane torch blast. Additionally, the treated paper showed excellent mildew and rot resistance, being substantially unchanged in appearance after being buried for two weeks in bacteria-rich soil, as compared to similar untreated paper which was completely disintegrated after burial for the same period. Similar results were obtained on treated paper which had been formed into a honeycomb structure prior to testing.

The procedure of the above examples is repeated using latexes of polyvinyl fluoride, polyvinyl chloride and polyvinylidene chloride, and polyvinyl chloride and polyvinyl acetate, in place of the polyvinyl chloride latex; precondensates containing tetrakis(hydroxymethyl)phosphonium bromide, tetrakis(hydroxyethyl)phosphonium chloride, tetrakis(α -hydroxy-p-chlorobenzyl)phosphonium chloride and tetrakis(α -hydroxybutanol)phosphonium chloride, in place of the tetrakis(hydroxymethyl)phosphonium chloride; and water in place of the isopropyl alcohol, as solvent, to obtain similar results.

While there have been described various embodiments of the invention, the methods and compositions described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible, and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A flameproofing composition comprising a resinous precondensate of a tetrakis(hydroxyorgano)phosphonium halide, urea and formaldehyde in combination with a polyvinyl halide selected from the group consisting of polyvinyl chloride and polyvinyl fluoride and antimony oxide, the molar ratio of urea to tetrakis(hydroxyorgano)phosphonium halide in the precondensate being within the range of about 14:1 to about 3:1 and the molar ratio of total formaldehyde to urea in the precondensate being within the range of about 1.5:1 to about 2.5:1.

2. A flameproofing composition comprising a polyvinyl halide-containing latex the polyvinyl halide being selected from the group consisting of polyvinyl chloride and polyvinyl fluoride, a resinous precondensate formed by the reaction of a tetrakis(hydroxyorgano)phosphonium halide, urea, and formaldehyde, an antimony oxide the molar ratio of urea to tetrakis(hydroxyorgano)phosphonium halide in the precondensate being within the

range of about 14:1 to about 3:1 and the molar ratio of total formaldehyde to urea in the precondensate being within the range of about 1.5:1 to about 2.5:1.

3. A flameproofing composition comprising a polyvinyl chloride-containing latex, a resinous precondensate formed by the reaction of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde and antimony oxide the molar ratio of urea to tetrakis(hydroxymethyl)phosphonium chloride in the precondensate being within the range of about 14:1 to about 3:1 and the molar ratio of total formaldehyde to urea in the precondensate being within the range of about 1.5:1 to about 2.5:1.

4. A flameproofing composition comprising a polyvinyl chloride-containing latex, a resinous precondensate formed by the reaction of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde, and antimony oxide the molar ratio of urea to tetrakis(hydroxymethyl)phosphonium chloride in the precondensate being within the range of about 14:1 to about 3:1 and the molar ratio of total formaldehyde to urea in the precondensate being within the range of about 1.5:1 to about 2.5:1, the above component being dispersed in a solvent so as to form a composition containing from about ten percent to about fifty-five percent by weight solids.

5. The composition as claimed in claim 4 wherein the solvent is water.

6. The composition as claimed in claim 4 wherein the solvent is a lower aliphatic alcohol.

7. A flameproofing composition comprising a polyvinyl chloride latex, in an amount sufficient to provide from about two to about twenty-five percent by weight of polyvinyl chloride in the composition, a resinous precondensate formed by the reaction of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde in an amount within the range of about ten to about forty percent by weight of the total composition, the molar ratio of the urea to tetrakis(hydroxymethyl)phosphonium chloride in the precondensate being within the range of about 14:1 to about 3:1 and the molar ratio of total formaldehyde to urea in the precondensate being within the range of about 1.5:1 to about 2.5:1, antimony oxide in an amount within the range of about two to about fifteen percent by weight of the total composition, and a lower aliphatic alcohol in an amount sufficient to make up the balance of the composition to one hundred percent by weight.

8. The composition as claimed in claim 7 wherein there is also contained a protective colloid and a catalyst, each of these being present in amounts up to about three percent by weight of the total composition.

9. The composition as claimed in claim 8 wherein the protective colloid is hydroxyethyl cellulose and the catalyst is citric acid.

10. A method of forming a flame-retardant paper which comprises impregnating said paper with the composition as claimed in claim 1, and drying the thus-impregnated paper so as to provide a resin add-on in said paper of from about twenty to about forty-five percent by weight.

11. A method of forming a flame-retardant paper which comprises impregnating said paper with the composition as claimed in claim 3, and drying the thus-impregnated paper so as to provide a resin-add-on in said paper of from about twenty to about forty-five percent by weight.

12. A method of forming a flame-retardant paper which comprises impregnating said paper with the composition as claimed in claim 4, and drying the thus-impregnated paper so as to provide a resin-add-on in said paper of from about twenty to about forty-five percent by weight.

13. A method of forming a flame-retardant paper which comprises impregnating said paper with the composition as claimed in claim 7, and drying the thus-impregnated paper so as to provide a resin add-on in said paper of from about twenty to about forty-five percent by weight.

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14. The flame-retardant paper as produced by the method of claim 10.

15. A method of preventing the coagulation of a vinyl halide-containing latex in a solution containing a lower aliphatic alcohol, the vinyl halide being selected from the group consisting of vinyl chloride and vinyl fluoride, which comprises adding to the said alcohol-containing solution from about 10 to 40 percent by weight of said solution of a resinous precondensate comprising the reaction product of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde, the molar ratio of urea to tetrakis-(hydroxymethyl)phosphonium chloride being within the range of about 14:1 to about 3:1 and the molar ratio of total formaldehyde to urea being within the range of about 1.5:1 to about 2.5:1.

16. A method of preventing the coagulation of a vinyl halide-containing latex in a solution containing a lower aliphatic alcohol, the vinyl halide being selected from the group consisting of vinyl chloride and vinyl fluoride, which comprises adding to the said alcohol-containing solution from about 10 to 40 percent by weight of said

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solution of a resinous precondensate comprising the reaction product of tetrakis(hydroxymethyl)phosphonium chloride, urea, and formaldehyde, the molar ratio of urea to tetrakis(hydroxymethyl)phosphonium chloride being about 10:1 and the molar ratio of total formaldehyde to urea being about 2:1.

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