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(54) **NOVEL FIRE RETARDANT MATERIALS AND METHOD FOR PRODUCING SAME**

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(57) **ABSTRACT**

An inherently fire retardant material that exhibits endothermic properties when exposed to high temperature and flame. The subject material is prepared by reacting a natural or synthetic polymer containing hydroxyl groups with an inorganic ammonium salt.

NOVEL FIRE RETARDANT MATERIALS AND METHOD FOR PRODUCING SAME

REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent application Nos. 60/376,716 and 60/376,717 filed Apr. 30, 2002 and Continuation application Ser. No. 10/331,562 filed Dec. 30, 2002, which is a Continuation of application Ser. No. 09/702,777, now U.S. Pat. No. 6,524,653.

FIELD OF THE INVENTION

[0002] The present invention is directed to a novel family of materials that is inherently fire retardant, exhibits endothermic properties when exposed to high temperature and flame, and exhibits antifungal, antibacterial, and antimildew properties. The novel compounds can be used in a multitude of applications, including powder, slurry, coating, spray, film, filler, lubricant, adhesive, textile, plastic additive, and fiber.

BACKGROUND OF THE INVENTION

Cellulose Applications

[0003] Cellulose and cellulosic products are considered flammable because they are readily ignited and are rapidly consumed after ignition. This is because cellulose itself is an inherently flammable material. When cellulose is heated to the decomposition temperature, it yields volatile, flammable gases, as well as liquid and tarry products that may also volatize and ignite, leaving a char consisting mainly of carbon. The slow oxidation of this char is responsible for the afterglow.

[0004] The idea of attempting to impart fire retardancy to cellulose is well known in the art. See, for example, M. Lewin and S. Sell, *Technology and Test Methods of Flame Proofing of Cellulosics, Flame-Retardant Polymer Materials,* 19-136 (1975), the entirety of which is incorporated by reference herein. For practical reasons, it is important that any fire retardant effect be durable under all conditions encountered by cellulosic material. For example, textiles must withstand not only water, but also repeated launderings and dry cleanings. Building materials must retain fire retardant properties even in light of being exposed to ordinary weather cycles and precipitation.

[0005] Fire retardant compositions can be classified into three types: (1) non-durable fire retardants that are easily removed by water, humidity, rain, or perspiration; (2) semi-durable treatments that resist leaching, but lose their effectiveness after a limited number of launderings, or exposure to surfactants or the elements; and (3) durable fire-retardant finishes that withstand leaching, laundering and dry-cleaning.

[0006] In the past, interest has been focused upon water-soluble chemicals as non-durable fire-retarding agents. However, such agents can only impart temporary protection, since the effect of the treatment is destroyed not only by laundering, but also by rain and perspiration.

[0007] Cellulosic materials may also be treated with semi-durable fire retardants that are required to withstand not only leaching in water, but also a limited number of launderings. The most obvious means of obtaining semi-durable flame resistance is the application of insoluble salts. However, water-insoluble inorganic salts generally do not easily decompose on heating.

[0008] Polymer-clay, polymer-zeolite and polymer-graphite nanocomposites have also generated a great deal of interest lately due to improved thermal and mechanical properties at the same time, a key advantage over existing condensed phase retardant. However, this type of composite, with well-dispersed intercalated nanocomposite, is very difficult to achieve and only applicable to a very limited number of polymers under very difficult processing conditions.

[0009] Due to environmental and safety concerns, the trend has moved to halogen free, non-toxic and environmentally friendly fire retardants. The present invention describes the ideal fire retardant cellulose, namely a stable and durable cellulosic material suitable for a broad spectrum of uses, with intrinsic, long-lasting, and significant flame retardant properties, which can be manufactured inexpensively and with minimal environmental concerns. The invention disclosed herein is also applicable to molecules related to cellulose, including other polysaccharides such as starch, and petroleum based polymers. The novel chemical processing and cross-linking has broad application to a wide variety of compounds, as disclosed herein.

SUMMARY OF THE INVENTION

[0010] The subject invention achieves an inherently fire retardant material, not through treating it or coating it, but through a chemical reaction and cross-linking mechanism that imparts fire retardancy into the cross-linked materials as a property of the material itself. The family of materials to be reacted and cross-linked includes polysaccharides (such as cellulose, starch), petrochemicals, and novel composites containing those fire retardant materials. The cross-linked materials have a stable shelf-life (i.e., little deterioration of fire resistant properties), are essentially non-toxic when charred, have sufficient adhesiveness, and are malleable. The materials' inherent fire retardancy characteristics do not significantly degrade over time, or exposure to the elements. The cross-linked cellulose, starch and hydrocarbon materials are manufactured with inexpensive base materials, and their manufacture or use do not create environmental problems or concerns. The fire-resistant cellulose molecule is thermally stable and has been shown not to ignite at or higher than 3,500° F.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The subject invention comprises inherently fire retardant natural and synthetic polymers including polysaccharides, such as cellulose or starch, and petrochemicals. Each is discussed separately below.

[0012] The basic reaction involves a polymerization with cross-linking of natural and synthetic polymers containing hydroxyl groups, through use of a cross-linking agent (e.g., a diammonium salt, such as diammonium phosphate (DAP)). In a preferred embodiment, the material to be reacted is treated so that it contains ammonia groups. The sites of the ammonia groups are then linked together with the diammonium salt. Where the salt is DAP, the reaction forms

a cross-linker containing a phosphate group. In yet a further preferred embodiment, water molecules are entrapped in the resulting cross-linked material that contribute to the endothermic characteristics of the material.

[0013] While not wishing to be limited by theory, it is believed that the process of the invention produces a cross-linked fire retardant polymeric product. This product exhibits fire retardant properties that are above and beyond those produced by a simple mixture or blend of the reactants used. Further, there is evidence that the reaction of a natural or synthetic polymer containing hydroxyl groups (e.g. hydroxy ethyl cellulose) with a cross-linking agent (e.g. diammonium phosphate or diammonium sulfate) produces a cellulosic product having a —N—X—N-cross-linking moiety (X═P, S, etc.). Accordingly, preferred cross-linking agents are inorganic ammonium salts containing at least two ammonium groups per molecule. Some examples include diammonium phosphate, diammonium sulfate, diammonium chromate, and diammonium borate of which diammonium phosphate is presently preferred.

[0014] An alternative explanation of the cross-linked results is that the cross-linking moiety consists primarily of phosphorus and oxygen atoms. In the latter case, it would be expected that cross-linking agents containing phosphorus and oxygen (phosphates) other than diammonium phosphate would also produce acceptable fire retardant compositions. Accordingly, the cross-linking agent useful in the present invention in its broadest scope can be an inorganic ammonium salt, a phosphate, or both (e.g. diammonium phosphate). The critical feature of this cross-linking agent is that it is capable of cross-linking or reacting with the natural or synthetic polymer containing branched hydroxyl groups to produce a fire retardant composition that is more fire retardant that a simple mixture or blend of the polymer with the cross-linking agent (an inorganic ammonium salt or a phosphate).

[0015] The preferred phosphate useful as the cross-linking agent or reactant in the invention is diammonium phosphate. However as stated above, any phosphate capable of cross-linking or reacting with a natural or synthetic polymer containing branched hydroxyl groups to produce a fire retardant composition that is more fire retardant that a simple mixture or blend of the polymer with the phosphate is acceptable. Such phosphates are generally selected from inorganic, non-metallic phosphates such as the magnesium phosphates, ammonium phosphates, calcium phosphates, sodium phosphates, potassium phosphates and the like.

Cellulose Starting Materials

[0016] A cross-linked hydroxy ethyl cellulose, or the equivalent (as referenced below), has been discovered in which the cross-linker contains at least two ammonia groups as the reactive sites of the cross-linker (or other cross-linkers as discussed below). In a preferred embodiment of the invention, at least two of the ammonia groups contained in the cross-linker are bound to a phosphate group. The resulting fire retardant cellulosic material has unique characteristics as measured by nuclear magnetic resonance, infrared spectroscopy, and mass spectroscopy. As used herein, the term cellulose refers generally to a polymerized glucose made up of beta glucosidic bonds. The cellulose is preferably hydroxy ethyl cellulose, but may also be hydroxy propyl cellulose, hydroxy isopropyl cellulose, and/or combinations thereof. In addition, cellulose having hydroxy butyl groups, hydroxy pentyl groups and/or longer carbonyl groups may be used and are considered as likely chemical structures to be used in the present invention. In its broadest scope, any cellulosic material capable of cross-linking with the type of cross-linker disclosed herein may be used. As used herein, the term fire resistant is synonymous with flame retardance and flame resistance, and generally refers to a material that self extinguishes when exposed to a source of flame.

[0017] The fire-retardant cellulose polymer, in its solid form, has a varying solubility in water that is related in part to its molecular length and the degree of cross-linking. The degree of cross-linking and average molecular chain length may be varied by the reaction conditions (e.g., the temperature used in the reaction process) as well as by the characteristics of the starting cellulosic material. Centrifuge technology, distillation, and fractionation techniques can be used for separation of the fire retardant cellulosic polymer chain lengths.

[0018] When the fire-retardant product is subjected to an ignition source, the cellulose chars but does not combust. The cross-linked ammonia groups appear to prevent oxygen from igniting the cellulose molecule. In addition, vapor is also generated when the cellulose product is contacted with an ignition source. It is postulated that the disclosed cross-linking mechanism traps water within the cellulose polymer. Finally, a cross-link which includes either phosphates or sulfates may further increase the fire retardancy of the compound.

[0019] As used herein, the term THERMOLOSE™ refers to the novel material made by practicing the invention that is available from Thermolose Technologies, Inc., 1981 Pine Hall Drive, State College, Pa. 16803.

[0020] The following three examples describe the basic synthesis of the fire resistant cellulose.

EXAMPLE 1

[0021] About 19.2 grams of hydroxy ethyl cellulose powder was added to about 1,200 ml water, resulting in a solution containing about 10% hydroxy ethyl cellulose. The solution was then heated to about 60-70° C. Approximately 320 ml of liquid ammonia was mixed into the solution. Approximately 32 grams of solid diammonium phosphate was then added to the solution. The temperature of the solution was increased to approximately 90° C. for about 10 to 15 minutes, resulting in a thick, viscous liquid.

EXAMPLE 2

[0022] About 4.8 grams of hydroxy ethyl cellulose powder was added to about 80 ml of liquid ammonia at approximately room temperature. The resulting solution was stirred for about 30-45 minutes. Eight (8) grams of diammonium phosphate was then added and stirred into the solution until a clear solution was obtained. The solution was allowed to cross-link for about 24 hours, resulting in a more viscous solution than that obtained according to Example 1.

EXAMPLE 3

[0023] Approximately 4.8 grams of hydroxy ethyl cellulose powder was added to approximately 80 ml of liquid

ammonia at approximately room temperature. The solution was then heated to approximately 60-70° C. and was stirred for about 30-45 minutes. Eight (8) grams of diammonium phosphate was then added and stirred into the solution until a clear solution was obtained. The temperature of the solution was increased to approximately 60-70° C. and then to approximately 90° C. for 10-15 minutes. The solution cross-linked, resulting in a viscous solution.

[0024] In the above examples, cross-linking was obtained through introduction of diammonium phosphate. However, the invention is in no way limited to the reaction set forth above. The following examples demonstrate the breadth of methods that may be used to form the novel materials.

[0025] Various other methods and processes may be used to cross-link the cellulose or other starting material. Several preferred methods are discussed below.

EXAMPLE 4

[0026] Three hundred (300) ml of pure water was placed in a suitable reactor vessel. Nine and six tenths (9.6) grams of hydroxyethyl cellulose (HEC) was slowly added to the water. After adding the HEC to the water, the temperature of the solution was raised to approximately 60° C. Seventy-five (75) ml of a 5% Ammonia solution was then added to the HEC solution. The pH of the resultant solution was approximately 10.0. The temperature of the solution was then raised to approximately 73° C. When the solution reached 73° C., approximately 78 ml of diammonium phosphate solution (0.16 g/l) was added. The pH of the solution then dropped to approximately 7.5-8.0. The temperature of the solution was then raised to approximately 93° C. The solution effervesced for several minutes as the reaction occurred. After the effervescing subsided, the solution temperature was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape from the reacted solution. The reacted solution was then allowed to cool to room temperature and was then placed in a suitable container for storage. The resultant solution contained approximately 12 to 15% fire retardant cellulose polymer in water.

[0027] Various types of HEC materials have been utilized in this process. The HEC types are as follows: pharmaceutical grade HEC, HEC treated with glyoxal as a wetting agent, hydrophobically modified HEC, HEC containing biostabilizers and various molecular weights of HEC.

EXAMPLE 5

Pre-Compounding a 1× Concentration

[0028] As used herein, pre-compounding refers to the method of combining all constituents of a solution at the outset of the reaction. Three hundred (300) ml of pure water was placed in a suitable container along with 9.6 grams of hydroxyethyl cellulose (HEC), 75 ml of a 5% ammonia solution, and approximately 78 ml of diammonium phosphate solution (0.16 g/l). This mixture was covered and stored for reaction at a later time. It must be noted that the conversion to a fire retardant cellulose polymer begins to take place, although slowly, as soon as the starting ingredients are brought together as a mixture. At a later time, the pre-compounded mixture was reacted by raising the temperature of the pre-compounded solution to approximately 93° C. The solution then effervesced for several minutes. After the effervescing subsided, the solution temperature was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape from the reacted solution. The reacted solution was then allowed to cool to room temperature and placed in a suitable container for storage. The resultant solution contained approximately 12 to 15% fire retardant cellulose polymer in water.

[0029] After the reaction has taken place (i.e., the effervescing has subsided), the resulting mixture can immediately be stored in a suitable container. It must be noted that the mixture may contain a noticeable amount of ammonia. This residual ammonia can be allowed to outgas naturally by leaving the container uncovered under an exhaust hood or the ammonia can be removed at a later time by heating the mixture to approximately 80° C. until the residual ammonia has been removed. The reacted material should be allowed to cool at a normal rate. Accelerated cooling may cause the reacted polymer solution to separate into multiple phases. Depending on the conditions, these phases may or may not recombine. Boiling the mixture should be avoided. Boiling may break up or fragment the cellulose polymer structure.

EXAMPLE 6

4× Concentration

[0030] Three hundred (300) ml of a 5% ammonia solution was placed in a suitable reactor vessel. Thirty-eight and four tenths (38.4) grams of hydroxyethyl cellulose (HEC) were slowly added into the ammonia solution. The pH of the resulting solution should be equal to or greater than 10.0. One hundred (100) ml of pure water was added to reduce the viscosity of the solution. After adding the water to the solution of HEC and ammonia, the temperature of the solution was raised to approximately 70° C. When the solution reached 73° C., approximately 156 ml of diammonium phosphate solution (0.32 g/l) was added. The pH of the solution immediately dropped to approximately 7.5-8.0. The temperature of the solution was then raised to approximately 93° C. The solution then effervesced for several minutes. After the effervescing subsided, the temperature of the solution was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape. The reacted cellulose polymer solution was then allowed to cool to room temperature and placed in a suitable container for storage.

[0031] Various types of HEC materials have been made utilizing this process. The HEC types are as follows: pharmaceutical grade HEC, HEC treated with glyoxal as a wetting agent, hydrophobically modified HEC, HEC containing biostabilizers, and various molecular weights.

[0032] The reaction time for producing the 4× concentration can be shortened by mixing the HEC and standard ammonia in a suitable container and allowing the mixture to stand covered several hours. This will allow the HEC to dissolve into the ammonia. This pre-staged mixture can then be stored and reacted at a later time. This method significantly reduces processing time over that of previous examples. The water normally added in the standard 4× process can be added to this start solution to reduce viscosity.

EXAMPLE 7

Pre-Compounding a 4× Concentration

[0033] Three hundred (300) ml of a 5% ammonia solution, 38.4 grams of hydroxyethyl cellulose (HEC), and approximately 156 ml of diammonium phosphate solution (0.32 kg/l). This mixture was covered and stored for reaction at a later time. It must be noted that the conversion to a fire retardant cellulose polymer begins to take place, although slowly, as soon as the start ingredients are brought together as a mixture. At a later time, 100 ml of pure water was added to the pre-compounded mixture and the resultant solution was reacted by raising the temperature of the solution to approximately 93° C. The solution then effervesced for several minutes as the reaction occurred. After the effervescing subsided, the solution temperature was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape from the reacted solution. The reacted solution was then allowed to cool to room temperature and placed in a suitable container for storage.

EXAMPLE 8

4× Concentration—Dry Processing

[0034] Thirty-eight and four tenths (38.4) grams of hydroxyethyl cellulose (HEC) were placed in an open mixing vessel under an exhaust hood. Forty-nine and two tenths (49.2) grams of diammonium phosphate were ground into a talc-like consistency. The HEC and the diammonium phosphate were then mixed together to form a well-blended dry mixture. Thirty (30) ml of a 50% ammonia solution was mixed into the dry mixture. A small amount of pure water, approximately 40 ml, was added to allow the mixture to assume a workable paste like consistency. The wetted mixture was mechanically blended to produce a uniform paste like structure. The vessel containing the paste was then placed into a larger vessel containing water heated to approximately 95° C. As the temperature of the paste reached approximately 93-95° C., the paste effervesced, thus out gassing ammonia achieving the desired reaction. The paste mixture was held at this temperature until the outgassing subsided. The resultant cellulose polymer paste was allowed to dry producing a solid form of the fire retardant cellulose polymer.

[0035] After the reaction has taken place (i.e., the effervescing has subsided), the resulting mixture can immediately be stored in a suitable container. It must be noted that the mixture may contain a noticeable amount of ammonia. This residual ammonia can be allowed to outgas naturally by leaving the container uncovered under an exhaust hood or the ammonia can be removed at a later time by heating the mixture to approximately 80° C. until the residual ammonia has been removed.

[0036] The reacted material should be allowed to cool at a normal rate. Accelerated cooling may cause the reacted polymer solution to separate into multiple phases. Depending on the conditions, these phases may or may not recombine.

[0037] Boiling the mixture should be avoided. Boiling may break up or fragment the cellulose polymer structure.

EXAMPLE 9

Jet Cooking

[0038] Flowing the un-reacted pre-compounded paste solution through a Jet Cooker where injected steam is the cooking mechanism will also produce the desired cellulose polymer structure. The steam brings the temperature of the paste to the reaction point and also helps to carry away the ammonia released when the reaction takes place and the fire retardant cellulose polymer is produced.

[0039] Although the methods disclosed herein are currently the preferred methods of manufacture for environmental, cost, and efficiency reasons, it is possible for the invention to be produced in a number of different ways. For instance, in the manufacturing process, anhydrous ammonium hydroxide can be substituted for liquid ammonia. Ammonium gas may be sparged through the cellulosic solution. The liquid ammonia could be pre-heated prior to adding with the cellulosic solution or the cellulosic solid material. Cellulose powder can be added to liquid ammonia to form a solution, and thereafter diammonium phosphate can be added to the solution, thereby forming the cross-linked cellulosic material. It is believed that DAP can be added directly to a heated solution or slurry or cellulose material, wherein dissociated ammonia groups from the DAP serve as a source of ammonia for the reaction. This results in a variety of end products including, but not limited to, polymeric salts of cellulose, phosphoric and phosphrous acids, MAP (monoammonium phosphate), and THERMOLOSE™. As an alternative to creating cross-linking with diammonium phosphate, other diammonium salts may be used, including diammonium sulfate, diammonium chromate or diammonium borate. Many sources of energy may be employed to cross-link the material, including radiant, solar, laser, electrical or electromagnetic. The cellulose could be hydroxy butyl cellulose, and/or a combination of its isomers, or hydroxy pentyl cellulose, and/or a combination of its isomers. The cellulose used can be put into solution, or can be put into a partial solution, with particulates included in the solution. The cellulose can also be added to water as a gel-like solution. None of these processing methodologies changes the underlying basis for the invention in question, namely a cross-linked cellulosic material where the cross-linker contains a minimum of two ammonium groups as its active sites. The ammonia that is out gassed at the time of reaction of the material is suitable for recycling and reuse in the production of the fire retardant cellulose polymer.

[0040] The fire retardant cellulose polymer has been made using a wide variety of molecular weights of HEC. As molecular weight increases, so does the viscosity of the solution to be reacted. A mixture of reacted cellulose polymers has been mixed into a single solution. The fire retarding effect remains the same. The solubility, flexibility, and residual water content of the resulting solution changes depending on the molecular weights of HEC used to produce the variations of fire retardant cellulose polymer.

[0041] The inventors are not aware of any published literature or patents which disclose or anticipate a cross-linked cellulosic material as described in this patent application. The novelty of the invention is due in part to the manner in which the cross-linking reaction was designed. In

the present invention, hydroxy ethyl cellulose, or an equivalent, as stated above, is chemically altered by the addition of ammonium groups. It is hypothesized that these reaction mechanisms are based on the concept of "tricking" the base starting material (such as cellulose) into behaving and/or reacting as if it were a different material to achieve a specific cross-linked result. That is the methodology used in the subject invention. By adding the ammonium groups to a starting material with hydroxyl groups, such as hydroxy ethyl cellulose (or the equivalent) the cellulose reacts and behaves as if it is an ammonium compound. In this way, it can be "tricked" into cross-linking in a manner similar to other compounds containing ammonium groups. In this fashion, nitrogen containing compounds, such as ammonium groups, are incorporated into the cross-linked structure. It is well known that such groups impart such flame retardant properties. In a preferred embodiment of the invention, another well known flame retardant chemical, a phosphate group, is incorporated into the cross-linker. This may be done through use of diammonium phosphate. Cross-linkers incorporating sulfur into the cross-link through use of diammonium sulfate have been used; however, the flame retardancy characteristics are not as great. Finally, the specific mechanism of cross-linking starting materials in this fashion is thought to entrap water molecules within the material which further enhances the fire retardancy characteristics of the cross-linked material. The unique method of this cross-linking reaction results in an equally unique material which has significant fire retardancy characteristics.

[**0042**] Through a cross-linking reaction with a compound containing at least two ammonium groups as its active sites, the resultant fire retardant cellulosic polymer also entraps any chemical substitutions of the original phosphate group as described herein, i.e. any other salt, organic and inorganic intermediary group that is attached to the ammonium groups used as the chemical cross-linkers.

[**0043**] As discussed below, numerous inventors and authors have reported cross-linked cellulosic materials, however, none of the prior art teaches or anticipates a cross-linker similar to the subject invention, or a cross-linked material with inherent fire retardant properties.

[**0044**] In U.S. Pat. Nos. 6,309,565 and 6,365,070 a process is disclosed for an aqueous finishing composition for cellulose containing materials that includes a cross-linking agent. However, the cross-linking reaction is entirely different from the process disclosed herein, and the resulting cross-linked compound bears no relation to the compounds in question. For instance, the alpha-hydroxy acids (such as citric acid) that are used as cross-links, involve an entirely different approach to polymerization than does the approach herein, namely the use of salts, including diammonium phosphate, to cause the cellulose to cross-link.

[**0045**] The Block patent, U.S. Pat. No. 4,389,319, discusses an invention of a drilling fluid which comprises a cross-linked cellulose, including hydroxy ethyl cellulose. However, that patent is based primarily upon the use of a hydroxy containing aluminum component which contributes to the pseudo-plasticity and fluid lock control property of the invention. The cross-linking properties of the cellulose materials is not critical to this invention. Most importantly, this invention does not disclose or teach a cross-linking chemistry which includes as a part of the cross-linked cellulose ammonium groups as the active sites, or phosphorus containing groups.

[**0046**] The Acton patent, U.S. Pat. No. 4,225,310, discloses a textile finishing process for textiles containing cellulosic fibers. The process results in a textile which has "crease resistant" properties. The three components which are applied to the cellulose substrate bear no relation to the subject reaction materials, and from the nature of the specifications, it appears that the cross-linking described therein occurs by and between components A, B and C, and not of the cellulose itself. More importantly, the final material described therein does not include a cross-linked cellulose which includes ammonium groups as the active sites, or phosphorus containing groups.

[**0047**] In the Norlander patent, U.S. Pat. No. 5,536,369, the inventors describe a cross-linked cellulose for use in absorbent sanitary products. All of the methods disclosed in that patent involve using a heterocyclic compound as a cross-linking agent. The resultant material after using the described methods is alleged to have increased volume and absorption capacity, which is attributable to the use of the heterocyclic compound as the cross-linking agent. The material described in the invention would not be fire retardant. In any event, the Norlander patent does not teach or anticipate a cross-linked cellulose which would contain ammonium groups as the active sites, or phosphorous containing groups.

[**0048**] The paper entitled "Selected Aspects of Surface Engineering with Cellulose Polymers" by Plagge, et al, published in *Advanced Engineering Materials,* Vol. II, No. 6, pages 376-378, discloses a cross-linked cellulose. However, the cross-linking agent was a UV-sensitive cinnemate group which was used for the purpose of making the cellulose exhibit greater at adhesion properties for surgical implants. This cross-linked cellulose did not include or anticipate a cross-linker with ammonium groups as the active sites, or phosphorus containing groups.

[**0049**] In the patent application filed by Agricultural Research Service, U.S. patent application Ser. No. 07/627,470, an invention is described wherein cellulosic material is "cross-linked" with a methylolamide cross-linking agent, and is further modified by both one or more glycol swelling agents and one or more salts of a hydroxyalkyl amine or a hydroxyalkyl quaternary ammonium compound. It is unlikely that the disclosed invention therein relates to an actual cross-linking reaction, as the invention describes imparting smooth chemical finish to cellulosic fabrics, and not an actual cross-linking of the cellulose itself. In any event, this invention would not operate as a fire retardant, as the "cross-linking" agents described are flammable, and the cross-link in question does not involve ammonium groups or nitrogen containing groups at the active site of the cross-link.

[**0050**] U.S. Pat. No. 5,888,987 describes a method for manufacturing a softer, more comfortable polysaccharized sponge wherein polysaccharides are cross-linked as a result of process where a frozen solution containing the polysaccharides is immersed in a water-miscible organic solvent which contains a cross-linking agent. Although the patent includes hydroxy ethyl cellulose as one of many soluble alginates, the patent does not specifically define any cross-

linking agent when hydroxy ethyl cellulose is used. More importantly, the cross-linking reaction described in the patent is only a standard cross-linking reaction which is not capable of producing a material sharing properties with the present invention. In particular, the patent does not teach nor does it anticipate a cross-link cellulosic material having a nitrogen and phosphorus containing group.

Cellulose Material Characteristics

[0051] Another feature of the subject invention is that the material is highly endothermic, wherein heat is absorbed by the reaction process. This characteristic is evident from the manufacturing process, as described below. When the intermediary cellulosic material (e.g., cellulose and ammonium hydroxide) was reacted in solution with diammonium phosphate, thereby commencing the cross-linking process, the temperature of the batch was reduced by approximately 20° F., due in part to the endothermic nature of the cross-linking reaction. More importantly, this same characteristic contributes to the flame retardant properties of the subject invention, and allows the material to continue to char, without igniting, in temperatures well in excess of 3,500° F. Some materials containing THERMOLOSE™ are cool to the touch only seconds after the flame from a propane torch is extinguished.

[0052] The resulting cross-linked cellulosic material has unique characteristics as measured by nuclear magnetic resonance, infrared spectroscopy, and mass spectroscopy. NMR studies were done to characterize the resultant cellulosic material including THERMOLOSE™. Proton and Carbon 13 spectra were obtained using a Brucker AMX-2-500, operating in the quadrature mode at 25° C. The Proton frequency was 500.13 MHz, and the Carbon 13 frequency was 125.76 MHz. Carbon 13 spectra were obtained with proton decoupling. Thirty-two (32) scans were acquired for each Proton spectrum. About 32,000 scans were acquired for each carbon 13 spectrum. The results of the NMR Studies confirmed that the invention in question is a stable compound with well defined spectra, and further confirmed that the compound exhibits long-term stability.

Cellulose Applications

[0053] The material has numerous uses. In addition to the materials' unique flame retardancy, THERMOLOSE™ also exhibits superior antifungal, antimold, antimildew, antibacterial and antiviral properties. During the manufacturing process, borax or a borate can be added to the solution to form an insect repellent, which will contribute to enhanced fire retardancy for both external and internal applications.

[0054] The cross-linked cellulose is extremely versatile. It may be used as a powder, in a slurry, coating, filler, spray, film, lubricant, adhesive, textile, fiber or plastic additive. It may be incorporated into virtually all building materials, including wood, plywood, particle board, duct materials, shingles, ceramics, concrete, gypsum, plastics, grouts, paints, vinyl products, varnishes, insulations and laminates. It can be added as a coating to other building materials, such as glass, fiberglass, plastics, steel, composites and matrix materials. It has broad application to apparel, including children's sleepwear, auto racing clothing, fiberfill, and virtually all fabrics. It may be used in home furnishings, such as curtains, bedding, carpet fibers and furniture.

[0055] The invention may be used for numerous insulation needs, including buildings, wires, cables, foams, Styrofoam, isocyanate foams, polystyrene, polyurethane, and paper products. The invention may be used in adhesive products such as glues, tapes, caulking, cements and epoxys. It may be used in brake pads, tires, lubricants, greases, antifreezes, transmission fluids, gas, water and sewer pipes, gaskets and seals, art canvas and art preservation, paper products, Christmas tree decorations, fertilizers, forest fire prevention and fighting compounds, fire fighting garments, tools and equipment, camping and outdoor gear, including tents, tarps, sleeping bags, paper products, medical equipment, including shielding for cautery treatment, laser surgery, or any thermal treatment requiring tissue shielding, armor products, and military uniforms, protective garments, and equipment.

[0056] The fire retardant cellulose polymer can be utilized in a variety of forms including, but not limited to the following: as a material to coat an object; as a component or filler used in a mixture of various materials; and as a component of a blend of materials. As a coating material, the fire retardant cellulose polymer can be used to coat an object or surface in a variety of ways including, but not limited to, painting onto, spraying onto, foaming onto, or coating by dipping the object or surface to be protected. The polymer can be applied in a pure form or as part of a mixture as in an additive to paint or other coating materials. A variant of use as a coating includes use as a pressure-treating compound to fire retard unsealed wood/wood products. The polymer can also be mixed as a dry form into various materials including, but not limited to, various foam materials—both rigid and flexible, composites such as particleboard and Oriented Strand Board (OSB), plastics and other materials to provide the fire retardant effect.

[0057] Of the three methods described above, the preferred usage is that of a blend. Blending the fire retardant cellulose polymer results in the best overall performance and durability. The optimal use of the fire retardant cellulose polymer is to incorporate it into or blend it into the material to be protected. Having the polymer become an integral part of the material to be protected provides optimal performance. This technique can include, but is not limited to, casting and extruding both films and threads. The following examples demonstrate the broad application of the novel fire retardant cellulosic materials.

EXAMPLE 10

[0058] Four inch (4") wide×24" long×¼" thick bass wood boards were used. They were cut into 8" long samples. The samples were cured under a radiant heat lamp at 150° F. for 48 hours to remove as much moisture as possible. The 8" samples were weighed and the weights were recorded. The samples were pressure treated in a 2-gallon paint pressure pot for 1 hour at 80 pounds per square inch of pressure using THERMOLOSE™ 4× solution. The samples were removed and weighed wet. The samples were cured for 48 hours under a radiant heat lamp at approximately 150° F. and reweighed. All samples were inscribed with a line at the 6" mark, including an untreated control sample. The samples were then suspended in a vertical position for a vertical flame test in a lab hood. At that point, a Bunsen Burner flame was adjusted to approximately 1½" long and the bottom edge of the Bass Wood control sample was exposed ¾" into the Bunsen Burner flame for one minute. The burner flame

was removed and the entire control sample was consumed in flame. The sample was extinguished with a water spray. In addition to the fire damage, the control sample incurred severe smoke damage. Treated sample number 8 was tested in the same manner as described above. When the Bunsen burner was removed a small flame flickered at the very bottom of the sample and self-extinguished in 5 seconds. Flame spread was approximately 4" with very little smoke damage.

[0059] A small ¼" sliver was then cut off the bottom edge of Sample #7. The sample was positioned so the fresh cut edge was exposed to the direct flame as described above. When the flame source was removed a small flame remained at the bottom edge for approximately 1 min 30 seconds before it self extinguished. The flame spread was again approximately 4" with little smoke damage. This example shows that pressure treating wood products greatly reduced both flame spread and smoke damage.

	Cured Dry Weight	Pressure Treated Weight Wet	Cured Weight
1.	57.0 grams*	95.7 grams	59.3 grams
2.	60.3 grams*	92.2 grams	61.3 grams
3.	57.4 grams*	96.5 grams	59.4 grams
4.	58.1 grams*	89.3 grams	58.9 grams
5.	51.1 grams**	97.9 grams	57.3 grams
6.	50.1 grams**	90.4 grams	54.7 grams
7.	60.4 grams**	116.8 grams	67.2 grams
8.	61.4 grams**	136.3 grams	69.2 grams

*Denotes THERMOLOSE ™ 2× concentration treatment
**Denotes THERMOLOSE ™ 4× concentration treatment

EXAMPLE 11

[0060] Fabric samples were used relating to the furniture industry, seeking a solution for new proposed testing guidelines that increase the standard from a one second direct flame test against flashover to a twenty second direct flame test that requires self extinguishing. THERMOLOSE™ was "back coated" to the backside of the fabric and tested for flame resistance. The fabric is currently back coated with a latex coating, at the rate of approximately two ounces to five ounces per square yard.

[0061] The fabric was cut into one square foot pieces, then cut again in half, one half for treatment, the other for an untreated burn sample comparison. The samples were weighed dry. The first sample weighed 24.5 grams dry. THERMOLOSE™ was then applied with a brush to the backside. The rate of application was about 40-50 grams of THERMOLOSE™ 4× solution. The wet weight of the fabric was 74.1 grams or 49.3 grams of THERMOLOSE™. After curing under a radiant heat lamp for 12 hours, the cured weight was 32.1 or 7.3 grams of THERMOLOSE™ solids.

[0062] A vertical burn test was conducted using a butane flame, applied to the bottom edge of the control sample. Within 3-4 seconds, the flame was self-sustaining and traveled up the middle of the fabric. Within one minute the fabric was consumed in flames.

[0063] The THERMOLOSE™ coated sample described above was then hung and the test duplicated. The THERMOLOSE™ sample sustained a flame after six seconds. The flame spread took approximately twice as long to consume the sample.

[0064] A second sample was treated with two coats of THERMOLOSE™ 4× and 12.5 grams of solid back coating resulted. A direct flame test using butane held horizontally to the front of untreated fabric sample was conducted. The fabric would support a flame after 4-5 seconds. The treated sample had two burns self extinguished after holding the flame to the fabric for 20 seconds. Several other burns failed the 20-second test, however, all passed the 17 second mark.

[0065] A third sample was treated with four coats of THERMOLOSE™ 4× solution. The cured weight of the back coating was 22 grams. The horizontal butane burn test was conducted and the sample passed the 20-second test, a 24 second test and a 26 second test. This example shows that THERMOLOSE™ slows and retards flame ignition on these fabrics.

EXAMPLE 12

[0066] Samples of Polyurethane resin and Isocynate used in the production of rigid foam were obtained for testing. Forty-five (45) ml of polyurethane resin was poured into a metal pan 8" long,×3¾" wide,×2⅜" high. Forty-five (45) ml of isocynate was poured into the pan. At that time a glass-stirring rod was used for mixing the two ingredients together for approximately 3 minutes. At that time the reaction started and foam began to form. Measurements were taken of the reacting foam and at the high point a temperature of 190° F. was recorded. After approximately 10 minutes the reacted control sample was removed from the pan. The reacted control sample measured approximately 8"×3¾"×1½" and was rigid.

[0067] Forty-five (45) ml of polyurethane resin was poured into a second metal pan. Forty-five (45) ml of THERMOLOSE™ 4× concentration was added and mixed together for about 2 minutes. No adverse reaction occurred. Forty-five (45) ml of isocynate was poured into the pan and mixed together again for approximately 3 minutes. The reaction commenced and the foam began to rise. The sample's reaction temperature never exceeded 90° F. After 10 minutes the foam was removed from the pan. The foam was spongy compared to the hard rigid control sample. The foam was larger in height. The foam was approximately 2½" high.

[0068] Thin sections of each sample were cut and a vertical burn test was conducted. Each sample was subjected to a vertical burn test using butane and propane direct flame for 5 seconds. The control sample continued to burn after the flame source was removed. The THERMOLOSE™ sample self extinguished when the flame source was removed. Smoke density was greatly reduced in the treated sample. This example shows that THERMOLOSE™ 4× liquid can affect the density and mechanical properties of the rigid foam. It may create new applications for this density of flame retardant foam.

EXAMPLE 13

[0069] Twenty-five (25) grams of powdered THERMOLOSE™ 4× concentration or 45 ml by volume was poured into a metal pan. Forty-five (45) ml of polyurethane resin was poured and mixed for approximately 4 minutes. Forty-five (45) ml of isocynate was poured and mixed for approximately 3 minutes. The foam reacted at a high temperature of 147° F. After 10 minutes, the foam loaf was removed from the pan and the sample was very rigid with a height of 1¾"

to 2". Thin slices were cut for a vertical burn testing using butane and propane direct flame exposure for 5 seconds and the sample self extinguished when the flame source was removed. Additional samples have been reacted using 12.5 grams of powder with a reaction temperature of 154° F. and 6.25 grams of powder with a reaction temperature of 180° F. with similar burn test results. This example shows that not only does THERMOLOSE™ 4× powder improve the flame resistance of the foam, but it also produces a greater volume of foam.

EXAMPLE 14

[0070] Standard 100% acrylic water based gloss paint was tested for flame retardancy when mixed with THERMOLOSE™. One hundred fifty (150) ml of THERMOLOSE™ 4× liquid and 300 ml or 1:2 ratio of the paint were blended together with a glass-stirring rod. Ordinary single ply cardboard samples were prepared by cutting into small strips approximately 1"×3". The cardboard samples were used for applying the blended and control paint on each side. The coatings were cured under a radiant heat lamp for several hours. A direct butane flame was applied for 5 seconds to both the coated and uncoated samples. The object of the burn test was to achieve a self-extinguishing flame after the flame source was removed. The untreated cardboard sample burned and consumed completely. The treated sample burned and consumed at a slower rate.

[0071] The second test was conducted using 150 ml of THERMOLOSE™ 4× liquid blended with 150 ml of the Acrylic paint for a 1:1 ratio. The test was conducted in the same manner as describe above. The treated sample burned at a much slower rate than the untreated sample and almost self-extinguished.

[0072] The third test was conducted using 300 ml of THERMOLOSE™ 4× liquid and 150 ml of Acrylic paint or a 2:1 ratio. The same test was conducted as described above. The flame self extinguished as soon as the flame source was removed. This example shows that THERMOLOSE™ can improve the flame resistance of Acrylic paint.

Composite Formulations

[0073] The present invention also encompasses a novel family of composite materials, which exhibit fire retardant properties, and the methods for producing said composite materials. More particularly, the invention describes ceramic, metal, fiberglass, glass and/or carbon fiber composites made with the proprietary flame retardant base compounds described herein. It further describes a preferred embodiment of the composite materials, which exhibit endothermic properties when exposed to heat or flame.

[0074] Generally, ceramics, metals, and carbon fiber materials exhibit limited heat absorptive and flame retardant characteristics. When exposing such materials to the effects of high heat or extreme flames, the materials will melt, fail, or otherwise break down or denature. The inability to withstand high temperatures or flame limits the application of such materials in key markets, including military, aerospace, and automotive markets. Many currently available composites seeking to address these issues incorporate environmentally hazardous or dangerous chemicals to impart certain heat resistant or flame retardant characteristics. The subject invention achieves inherently flame retardant composites, not through treating it or coating it, but by blending into the composite material a sufficient quantity of proprietary THERMOLOSE™ material. The current invention overcomes the shortcomings and is the only known source of producing fire retardant composites containing the materials disclosed in this application.

EXAMPLE 15

[0075] One hundred twenty-five (125) ml of THERMOLOSE™ 4× was put into a beaker. Seventy-five (75) ml by volume of lightweight ceramics was added obtained from Superior Products International II, Kansas City, Mo. A 3/16" steel plate and aluminum tape was used to build up retaining walls about ½" high on the front side of the plate. The THERMOLOSE™/ceramic mixture was then poured onto the plate and allowed to stand in order to seek its own level. The test plate was then set on a stand with an infrared heat lamp directly under the bottom side of the plate. The sample was exposed to bottom side heat for three hours. It was then removed from heat and let air cure for over 12 hours. The plate was set in a stand in a vertical position. A Wagner heat gun model #HT 3000 rated at 1100° F. top temperature was applied over an area 1/16" thick and the backside temperature was measured. At the 15-minute mark, a reading of 320° F. was obtained and at the 30-minute mark, the same 320° F. reading was recorded.

[0076] The same test plate was placed under the lab hood and set up in a vertical position. A Burns-o-matic propane torch was used at approximately 1500° F. The nozzle was positioned 1¼" away from coated surface of test plate. This resulted in a red-hot center with a diameter of approximately 1". The flame area was approximately 1½". The backside temperature was measured every 5 minutes. Readings were taken on the front, right side, bottom corner 7½" away from flame every 5 minutes. The results were as follows.

	Backside Readings	Frontside Readings
5 Min.	200° F.	77° F.
10 Min.	224° F.	83.1° F.
15 Min.	240° F.	91.7° F.
20 Min.	236° F.	94.2° F.
25 Min.	238° F.	100.1° F.
30 Min.	236° F.	100.9° F.

[0077] This example shows that THERMOLOSE™ and ceramics with good thermal properties blended at approximately a 5:3 ratio by volume and produced a very good heat and fire resistant coating.

EXAMPLE 16

[0078] Three hundred (300) ml of THERMOLOSE™ 4× and 45 grams of light weight ceramics (described above) were mixed approximately 1 to 1 by volume. The sample was poured onto a 3/16" steel plate and cured for 24 hours at room temperature and 48 hours using an infrared heat lamp curing from the bottom up. A burn test was conducted. The plate was placed up against the front opening of a radiant heat oven and a good seal was secured. The temperature was increased to 200° F. and the test began. At each five minute interval, the temperature was raised 200° F. and backside

temperature readings were taken. At the 30-minute mark, the temperature was 1200° F. The readings were as follows.

	Inside Oven Temperature	Backside Temperature Reading
5 Min.	200° F.	91° F.
10 Min.	400° F.	121° F.
15 Min.	600° F.	168° F.
20 Min.	800° F.	228° F.
25 Min.	1000° F.	300° F.
30 Min.	1200° F.	373° F.

[0079] This example shows that the surface coating of the sample cracked and lifted but did not fall from the plate during the burn test. The coating produced a very good result for heat and fire resistance.

EXAMPLE 17

[0080] Four hundred (400) ml of THERMOLOSE™ 4× was blended with 3.8 grams of ¼" cut graphite carbon fibers. The blend was poured onto a 1/16" steel plate. The plate was air cured for 24 hours and then cured using an infrared heat lamp exposing the bottom of the plate for a bottom to top cure an additional 24 hours. The sample test plate was then set up in the lab hood in a vertical position. A Burns-o-matic propane torch was positioned 1" away from the coated surface and brought to approximately 2000° F. The backside temperature reading was recorded every 5 minutes. The results were as follows.

Backside Temperature Readings	
5 Min.	409° F.
10 Min.	458° F.
15 Min.	465° F.
20 Min.	470° F.
25 Min.	473° F.
30 Min.	485° F.
35 Min.	490° F.
40 Min.	492° F.
45 Min.	494° F.
50 Min.	488° F.
55 Min.	494° F.
60 Min.	492° F.

[0081] This example shows good integrity of the cured mixture, with no surface cracks. The char was firm, and did not lift from the plate. Fire retardancy was excellent.

EXAMPLE 18

[0082] Three hundred (300) ml of THERMOLOSE™ 4× concentration was blended with 22.5 grams of light weight ceramics and 10 grams of ¼" cut e-glass fibers. A piece of woven 9-ounce e-glass fabric was cut to approximately 6" by 8" in size. Approximately 150 ml of the THERMOLOSE™/Ceramic/E-glass blend was poured onto a 1/16" plate. The woven e-glass fabric was placed on top of the mixture and approximately 150 ml of the remaining mixture was poured on top of the fabric. The mixture was air cured for 24 hours and then placed onto a stand and the bottom side of the steel plate was exposed to an infrared heat lamp for approximately 72 hours. The test plate was then set up in the lab hood for a burn test. The sample was stood in a vertical position and heated with a Bums-o-matic propane torch for a high temperature burn at approximately 2000° F. Backside temperature readings were taken every 5 minutes for 2 hours. The results were as follows.

Backside Temperature Readings	
5 Min.	266° F.
10 Min.	332° F.
15 Min.	358° F.
20 Min.	373° F.
25 Min.	378° F.
30 Min.	382° F.
35 Min.	382° F.
40 Min.	389° F.
45 Min.	387° F.
50 Min.	385° F.
55 Min.	385° F.
60 Min.	390° F.
65 Min.	395° F.
70 Min.	390° F.
75 Min.	390° F.
80 Min.	389° F.
85 Min.	390° F.
90 Min.	390° F.
95 Min.	389° F.
100 Min.	396° F.
105 Min.	391° F.
110 Min.	394° F.
115 Min.	398° F.
120 Min.	390° F.

[0083] This example shows no surface material lifted from the plate. The char evidenced slight cracking; however, composite resulted in very good heat and fire resistance.

Starch Starting Materials

[0084] In similar fashion to cellulosic materials, starches may also be reacted and cross-linked to impart fire retardant and endothermic properties. Generally, materials, which are starch-based, have little to no fire retardancy, due to the chemical structure of basic starch. As a result, products with starch-based components, including cardboards, textiles, veneer based products, and other similar composite or glued products, have poor fire retardancy. In addition, many currently available adhesives and starch- based industrial products incorporate environmentally hazardous or dangerous chemicals to impart certain characteristics. Any starch material capable of becoming fire-retardant by reacting with cross-linking agents disclosed herein may be used in the invention. This would include ethylated starch, propyl hydroxyl starch, or any starch with hydroxyl groups that are located on a linear carbon chain length of five or fewer carbons.

[0085] The process in question requires no volatile formaldehydes or phenols found in conventional adhesives. When starches covered by the invention are used in an adhesive system, this increases air quality that poses less health risk to workers, and also results in a fire retardant product. Moreover, should the base material itself ignite, the resulting fire will not release the chemicals ordinarily found in currently available adhesive systems. The current invention overcomes the shortcomings and is the only source known to the inventors of producing a fire retardant starch, amylopectin or glycogen.

[0086] A basic starch unit, such as a maltose, is initially reacted with NaOH, sodium hydroxide. The resulting product is then reacted with ethylene oxide. Both of these reactions are conducted using published techniques and conditions well known to one skilled in the art. Similarly, hydroxyethyl starch (e.g, ethylated starch) may be acquired from commercial vendors such as Cargill or Grain Processing Corporation. The resulting completely hydrolyzed compound or a partially hydrolyzed compound is then suspended in water or ammonium hydroxide. Where dissolved in water, ammonium is added, either in its hydrous or anhydrous (or gaseous) form. Finally, this reaction product is reacted with diammonium phosphate to produce a cross-linked base material, which constitutes a fire retardant starch. The synthesis route described above also works when the base starting material is an amylopectin or a glycogen, both of which are structurally related to starch, and the molecular differences will not significantly impact upon the reaction process described above or the fire retardant properties of the resultant compound.

[0087] While not wishing to be bound by theory, it is believed the reaction proceeds as follows:

[0088] By adding the ammonium groups to the base polysaccharide as described herein (or the equivalent) the base polysaccharide reacts and behaves as if it is an ammonium compound. In this way, it can be "tricked" into cross-linking in a manner similar to other compounds containing ammonia groups. In this fashion, nitrogen-containing compounds, such as ammonia groups, are incorporated into the cross-linked structure. It is well known that such groups impart such flame retardant properties. In a preferred embodiment of the invention, another well-known flame retardant chemical, such as a phosphate group, is incorporated into the cross-linker. This may be done through use of diammonium phosphate, diammonium sulfate or other diammonium groups. Finally, the specific mechanism of cross-linking the base polysaccharide in this fashion is thought to entrap water molecules within the material, which yet further enhances the fire retardancy characteristics of the cross-linked material. The unique method of this cross-linking reaction results in an equally unique material which has unparalleled fire retardancy characteristics.

[0089] Through use of a cross-linker with at least two ammonium groups as its active sites, the resultant fire retardant starch, amylopectin or glycogen also entraps any chemical substitutions of the original phosphate group as described in the patent, i.e. any other salt, organic and inorganic intermediary group that is attached to the ammonium groups used as the chemical cross-linkers.

[0090] The novel starch is suitable to be used in all starch based products, including food grade starch powders, pharmacological grade starch powders, paper grade starch powders, and textile based starch powders. In the adhesive field, it may be used in a wide range of industrial adhesives for applications as diverse as industrial packaging, corrugated products, nappies/diapers, food and consumer packaging, woodworking and furniture, electronics and paper. Industrial uses for these novel starches could include thickeners and texturisers. In the medical field, specialty starches manufactured with the instant invention may be used for carriers, binders and disintegrants in tablets and capsules; thickeners for liquid dosage medicines; and pharmaceutical grade dusting powders for surgical gloves. It would also have broad application in papermaking and textile production. It may be used as a coating, an additive, a processing agent, an organic binder, or as a base material in a multitude of specialty starches and related products obvious to one skilled in the art.

[0091] It must be noted that hydroxyl-ethyl starch, or Ethylated Starch (ES), is basically insoluble. In order for the ES to be reacted, the ES should be properly hydrated. This may be accomplished by elevating the temperature of the solution to at or near the boiling point of water. The ES can be hydrated either directly or indirectly. Direct hydration involves briefly heating the ES in solution to the boiling point (approximately 100° C.). The boiled solution is then idled at approximately 95° C., then allowed to cool to approximately 65° C. and reacted as described below. Indirect hydration may be accomplished by heating the composite solution to between 93° to 96° C. through a reaction process such as described below.

[0092] Direct hydration prior to reaction of the ES produces a greater level of incorporation of the ES into the resultant solution. Indirect hydration typically results in some portion of the ES precipitating out of the solution.

EXAMPLE 19

[0093] Three hundred (300) ml of pure water was placed in a suitable reactor vessel. Ten (10.0) grams of Ethylated Starch (ES) were slowly added to the water. After adding the ES to the water, the temperature of the solution was raised to approximately 60° C. Seventy-five (75) ml of a 5% Ammonia solution was then added to the ES solution. The pH of the resultant solution should be approximately 10.0. The temperature of the solution was then raised to approximately 73° C. When the solution reached 73° C., approximately 77 ml of diammonium phosphate solution (0.16 Kg/l) was added. The pH of the solution then dropped to approximately 7.5-8.0. The temperature of the solution was then raised to approximately 95° C. The solution effervesced for several minutes as the reaction occurred. After the effervescing subsided, the solution temperature was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape from the reacted solution. The reacted solution was then allowed to cool to room temperature and was then placed in a suitable container for storage. Some ES solids may precipitate to the bottom of the container. Shaking the container will temporarily re-suspend these solids. Direct hydration of the ES prior to reacting the ES will minimize this effect.

[0094] Various types of ES materials have been utilized with this process to produce the desired fire retarded cross-linked starch polymer. The ES types are as follows:

[0095] 1. Food Grade ES

[0096] 2. Various molecular weights

[0097] 3. Various viscosity grades

EXAMPLE 20

Pre-Compounding a 1× Concentration

[0098] Three hundred (300) ml of pure water was placed in a suitable container along with 10.0 grams of Ethylated

Starch (ES), 75 ml of a 5% Ammonia solution, and approximately 78 ml of diammonium phosphate solution (0.16 Kg/l). This mixture was covered and stored for reaction at a later time. Direct hydration of the ES initially prior to pre-compounding will reduce the likelihood of ES precipitation prior to reaction of the pre-compounded mixture. At a later time, the pre-compounded mixture was reacted by raising the temperature of the pre-compounded solution to approximately 95° C. The solution then effervesced for several minutes as the reaction occurred. After the effervescing subsided, the solution temperature was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape from the reacted solution. The reacted solution was then allowed to cool to room temperature and placed in a suitable container for storage.

[0099] After the reaction has taken place, i.e. the effervescing has subsided; the resulting mixture can immediately be stored in a suitable container. It must be noted that the mixture may contain a noticeable amount of ammonia. This residual ammonia can be allowed to outgas naturally by leaving the container uncovered under an exhaust hood or the ammonia can be removed at a later time by heating the mixture to approximately 80° C. until the residual ammonia has been removed.

[0100] The reacted material should be allowed to cool at a normal rate. Excessive boiling of the mixture should be avoided. Excessive boiling may break up or fragment the starch polymer structure.

EXAMPLE 21

4× Concentration

[0101] Three hundred (300) ml of a 5% ammonia solution was placed in a suitable reactor vessel. Forty (40.0) grams of Ethylated Starch (ES) were slowly added into the ammonia solution. The pH of the resulting solution should be equal to or greater than 10.0. One hundred (100) ml of pure water was added to control the viscosity of the solution. After adding the water to the solution of ES and ammonia, the temperature of the solution was raised to approximately 70° C. When the solution reached 73° C., approximately 154 ml of diammonium phosphate solution (0.K32 g/l) was added. The pH of the solution immediately dropped to approximately 7.5-8.0. The temperature of the solution was then raised to approximately 93° C. The solution then effervesced for several minutes. After the effervescing subsided, the temperature of the solution was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape. The reacted starch polymer solution was then allowed to cool to room temperature and placed in a suitable container for storage. Some ES solids may precipitate to the bottom of the container. Direct hydration of the ES prior to reaction of the ES will minimize this effect.

[0102] Various types of ES materials have been utilized with this process to produce the desired fire retarded cross-linked starch polymer. The ES types are as follows:

[0103] 1. Food Grade ES

[0104] 2. Various molecular weights

[0105] 3. Various viscosity grades

EXAMPLE 22

Pre-staging the ES

[0106] The reaction time for producing the 4× concentration can be shortened by mixing the ES and standard ammonia in a suitable container and allowing the mixture to stand covered several hours. This pre-staged mixture can then be stored and reacted at a later time. This method significantly reduces processing time. The water normally added in the standard 4× process can be added to this start solution to reduce viscosity. Some ES solids may precipitate to the bottom of the container. Direct hydration of the ES prior to reaction of the ES should minimize this effect.

EXAMPLE 23

Pre-Compounding a 4× Concentration

[0107] Three hundred (300) ml of a 5% Ammonia solution, 40.0 grams of Ethylated Starch (ES), and approximately 156 ml of diammonium phosphate solution (0.32 Kg/l) were combined and placed in a suitable reactor vessel. This mixture was covered and stored for reaction at a later time. At a later time, 100 ml of pure water was added to the pre-compounded mixture and the resultant solution was reacted by raising the temperature of the solution to approximately 93° C. The solution then effervesced for several minutes as the reaction occurred. After the effervescing subsided, the solution temperature was reduced to approximately 85° C. and held at that temperature to allow free ammonia to escape from the reacted solution. The reacted solution was then allowed to cool to room temperature and placed in a suitable container for storage. Some ES solids may precipitate to the bottom of the container. Direct hydration of the ES prior to reaction of the ES should minimize this effect.

EXAMPLE 24

4× Concentration—Dry Processing

[0108] Forty (40.0) grams of Ethylated Starch (ES) were placed in an open mixing vessel under an exhaust hood. Fifty (50.0) grams of diammonium phosphate were ground into a talc-like consistency. The ES and the diammonium phosphate were then mixed together to form a well-blended dry mixture. Thirty (30) ml of a 50% Ammonia solution was mixed into the dry mixture. A small amount of pure water, approximately 40 ml, was added to allow the mixture to assume a workable paste like consistency. The wetted mixture was mechanically blended to produce a uniform paste like structure. The vessel containing the paste was then placed into a larger vessel containing water heated to approximately 95° C. As the temperature of the paste reached approximately 93-95° C., the paste hydrated and effervesced, thus out gassing ammonia achieving the desired reaction. The paste mixture was held at this temperature until the outgassing subsided. The resultant starch polymer paste was allowed to dry producing a solid form of the fire retardant starch polymer.

[0109] After the reaction has taken place, i.e. the effervescing has subsided; the resulting mixture can immediately be stored in a suitable container. It must be noted that the mixture may contain a noticeable amount of ammonia. This residual ammonia can be allowed to outgas naturally by

leaving the container uncovered under an exhaust hood or the ammonia can be removed at a later time by heating the mixture to approximately 80° C. until the residual ammonia has been removed.

[0110] The reacted material should be allowed to cool at a normal rate.

[0111] Excessive boiling of the mixture should be avoided. Boiling may break up or fragment the starch polymer structure.

EXAMPLE 25

Jet Cooking

[0112] Flowing the un-reacted paste through a Jet Cooker where injected steam is the cooking mechanism will also produce the desired starch polymer structure. Proper hydration of the ES is essential. The steam brings the temperature of the pre-compounded starch paste described above to the reaction point and also helps to carry away the ammonia released when the reaction takes place and the fire retardant starch polymer is produced.

[0113] The fire retardant starch polymer has been made using a wide variety of molecular weights of ES. As molecular weight increases, so does the viscosity of the solution to be reacted.

[0114] A mixture of reacted Starch polymers has been mixed into a single solution. The fire retarding effect remains the same. The solubility, flexibility, and residual water content of the resulting solution changes depending on the molecular weights of ES used to produce the variations of fire retardant starch polymer.

Petrochemical Starting Materials

[0115] The invention may also be used to cross-link and fire retard petrochemicals, such as polyethylene glycol and other similar poly glycols. Useful petrochemical polymers are those that are capable of reacting with the cross-linking agents disclosed herein. Typically, these will be polymers containing hydroxyl groups that are located on a linear carbon chain length of five or fewer carbons.

EXAMPLE 26

[0116] Thirty-eight and four tenths (38.4) grams of PEG 400 was added as a liquid into a flask to approximately 300 ml of standard ammonia. One hundred (100) ml of RO/H_2O was reserved. The resulting solution was placed in a reactor with mechanical stirring. Once in solution, the solution was heated slowly to 70° C. As it was heated, the pH of the solution decreased slightly as indicated in the following table.

T° C.	pH
27	11.45
30	11.43
40	11.32
50	11.15
60	11.05
70	11.00

[0117] Once the solution reached 70° C., 156 ml of standard diammonium phosphate solution was added and heated until approximately 95° C. The solution was maintained at 95° for approximately 4 minutes and then cooled to 70° over a period of approximately 30 minutes. A test strip coated with the cooled solution passed a flame test. The resulting reactant solution separated into two phases. Although the first phase showed negligible flame retardant properties, the second phase exhibited flame retardancy.

EXAMPLE 27

[0118] Thirty-eight and four tenths (38.4) grams of PEG 6000 was added as a liquid into a flask to approximately 300 ml of standard ammonia. One hundred (100) ml of Reverse Osmosis Water (RO/H_2O) was reserved. The resulting solution was placed in a reactor with mechanical stirring. Once in solution, the solution was heated slowly to 70° C. As it was heated, the pH of the solution decreased slightly as indicated in the following table.

T° C.	pH	
30	>11	
40	>11	
50	—	←Added 100 ml
60	—	RO/H_2O to make sure
70	10.8	pH meter probe tip is covered

[0119] Once the solution reached 70° C., 156 ml of standard diammonium phosphate solution was added and heated until approximately 95° C. The solution was maintained at 95° for approximately 4 minutes and then cooled to 70° over a period of approximately 30 minutes. A test strip coated with the cooled solution passed a flame test. The resulting reactant solution separated into two phases. Although the first phase showed negligible flame retardant properties, the second phase exhibited flame retardancy.

EXAMPLE 28

[0120] Seventy-six and eight tenths (76.8) grams of PEG 400 was added as a liquid into a flask to approximately 300 ml of standard ammonia. One hundred (100) ml of RO/H_2O was added. The resulting solution was placed in a reactor with mechanical stirring. Once in solution, the solution was heated slowly to 70° C. As it was heated, the pH of the solution decreased slightly as indicated in the following table.

T° C.	pH
25	10.92–11.15 (-settling-)
30	—
40	11.00
50	10.85
60	10.70
70	10.63

[0121] Once the solution reached 70° C., 312 ml of standard diammonium phosphate solution was added and heated until approximately 97° C. At approximately 70° C.,

the cross-linking reaction began to occur with significant amount of cross-linking occurring between 95° and 97°. The solution was then cooled to room temperature. The resulting reactant solution separated into two phases. Although the first phase showed negligible flame retardant properties, the second phase exhibited flame retardancy, and a test strip coated with the second phase of the material self extinguished and passed a flame test.

EXAMPLE 29

[0122] Seventy-six and eight tenths (76.8) grams of PEG 6000 was added as a liquid into a flask to approximately 300 ml of standard ammonia. One hundred (100) ml of RO/H_2O was added. The resulting solution was placed in a reactor with mechanical stirring. Once in solution, the solution was heated slowly to 70° C. As it was heated, the pH of the solution decreased slightly as indicated in the following table.

T° C.	pH	
22	11.14	Ammonia is still
30	11.08	saturated at the 4×
40	10.97	quantity (300 ml)
50	10.82	
60	—	
70	10.54	

[0123] Once the solution reached 70° C., 312 ml of standard diammonium phosphate solution was added and heated until approximately 96° C. A significant amount of cross-linking occurred between 93° and 95°. The solution was then cooled to room temperature. The resulting reactant solution separated into two phases. Although the first phase showed negligible flame retardant properties, the second phase exhibited partial flame retardancy exceeding that of the separate constituent materials used.

[0124] While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various alterations in form and detail may be made therein without departing from the spirit and scope of the invention.

What is claimed:

1. A fire retardant composition prepared by reacting a natural or synthetic polymer containing hydroxyl groups with an inorganic ammonium salt containing at least two ammonium groups per molecule.

2. The fire retardant composition according to claim 1 prepared by reacting a solution containing ammonium hydroxide and the natural or synthetic polymer containing hydroxyl groups with an inorganic ammonium salt containing at least two ammonium groups per molecule.

3. The fire retardant composition according to claim 1 wherein the salt is a diammonium salt selected from the group consisting of diammonium phosphate, diammonium sulfate, diammonium chromate, and diammonium borate.

4. The fire retardant composition according to claim 3 wherein the diammonium salt is diammonium phosphate.

5. The fire retardant composition according to claim 1 wherein the composition comprises cross-linked natural or synthetic polymer wherein the linking group contains nitrogen.

6. The fire retardant composition according to claim 1 which additionally contains an antisolubility agent.

7. The fire retardant composition according to claim 1 which is in liquid form.

8. The fire retardant composition according to claim 1 which has been dried to a powder or a coating.

9. The fire retardant composition according to claim 1 which does not ignite at temperatures less than or equal to 3,500° F.

10. The fire retardant composition according to claim 1 wherein the polymer is a hydroxyl group containing polysaccharide.

11. The fire retardant composition according to claim 10 wherein the polysaccharide is a hydroxyl group containing cellulose.

12. The fire retardant composition according to claim 10 wherein the polysaccharide is a hydroxyl group containing starch.

13. The fire retardant composition according to claim 1 wherein the polymer is a hydroxyl group containing petroleum.

14. The fire retardant composition according to claim 1 which additionally contains borax.

15. A fire retardant composition prepared by reacting a natural or synthetic polymer containing hydroxyl groups with a phosphate compound capable of cross-linking the natural or synthetic polymer containing hydroxyl groups.

16. The fire retardant composition according to claim 15 wherein the phosphate is selected from the group consisting of magnesium phosphates, ammonium phosphates, calcium phosphates, sodium phosphates, potassium phosphates, and mixtures thereof.

17. The fire retardant composition according to claim 15 wherein the polymer is a hydroxyl group containing polysaccharide.

18. The fire retardant composition according to claim 17 wherein the polysaccharide is a hydroxyl group containing cellulose.

19. The fire retardant composition according to claim 17 wherein the polysaccharide is a hydroxyl group containing starch.

20. The fire retardant composition according to claim 15 wherein the polymer is a hydroxyl group containing hydrocarbon.

21. A cross-linked polysaccharide fire retardant composition prepared by reacting a polysaccharide containing hydroxyl groups with a cross-linking agent that is an inorganic ammonium salt, a phosphate or both.

22. A cross-linked cellulose fire retardant composition prepared by reacting a cellulose containing hydroxyl groups with a cross-linking agent that is an inorganic ammonium salt, a phosphate or both.

23. A cross-linked starch fire retardant composition prepared by reacting a starch containing hydroxyl groups with a cross-linking agent that is an inorganic ammonium salt, a phosphate or both.

24. A cross-linked synthetic polymer fire retardant composition prepared by reacting a synthetic polymer containing hydroxyl groups with a cross-linking agent that is an inorganic ammonium salt, a phosphate or both.

25. A method of preparing an inherently fire retardant natural or synthetic polymer wherein said method comprises reacting a hydroxyl group containing natural or synthetic

polymer with an inorganic ammonium salt containing at least two ammonium groups per molecule.

26. The method according to claim 25 wherein the reaction is done in solution.

27. The method according to claim 25 comprising reacting a solution containing ammonium hydroxide and the natural or synthetic polymer containing hydroxyl groups with an inorganic ammonium salt containing at least two ammonium groups per molecule

28. The method according to claim 25 wherein the inorganic ammonium salt is a diammonium salt selected from the group consisting of diammonium phosphate, diammonium sulfate, diammonium chromate, and diammonium borate.

29. The method according to claim 28 wherein the diammonium salt is diammonium phosphate.

30. The method according to claim 25 wherein the polymer is a hydroxyl group containing polysaccharide.

31. The method according to claim 30 wherein the polysaccharide is a hydroxyl group containing cellulose.

32. The method according to claim 30 wherein the polysaccharide is a hydroxyl group containing starch.

33. The method according to claim 25 wherein the polymer is a hydroxyl group containing petrochemical.

34. A method of preparing an inherently fire retardant natural or synthetic polymer wherein said method comprises reacting a hydroxyl group containing natural or synthetic polymer with a phosphate capable of cross-linking the polymer.

35. The method according to claim 34 wherein the phosphate is selected from the group consisting of magnesium phosphates, ammonium phosphates, calcium phosphates, sodium phosphates, potassium phosphates, and mixtures thereof.

36. A method of preparing a cellulose-based fire retardant composition, comprising:

a. adding cellulose having a hydroxyl group to water, thereby forming a solution;

b. adding ammonium hydroxide to the solution;

c. subsequently adding a diammonium salt to the solution and binding diammonium groups to the cellulose; and

d. crosslinking the cellulose, thereby forming a cellulose-based fire retardant composition.

37. The method according to claim 36, further comprising heating the solution prior to adding the cellulose or after at least one of adding the cellulose, adding the ammonium hydroxide, or adding the diammonium salt.

38. The method according to claim 36, wherein said cellulose is selected from the group consisting of hydroxy ethyl cellulose, hydroxy propyl cellulose, hydroxy isopropyl cellulose, hydroxy butyl cellulose, hydroxy pentyl cellulose and a combination thereof.

39. The method according to claim 36, wherein said cellulose is hydroxy ethyl cellulose.

40. The method according to claim 36, wherein the diammonium salt is selected from the group consisting of diammonium phosphate, diammonium sulfate, diammonium chromate, diammonium borate, and combinations thereof.

41. The method according to claim 40 wherein the diammonium salt is diammonium phosphate.

42. The method according to claim 36 wherein the solution is a saturated cellulose solution.

43. The method according to claim 36, wherein a ratio of diammonium salt to cellulose is about 1.6:1.

44. The method according to claim 36, further comprising heating the cellulose and water solution to a temperature of about 60-70.degree. C.

45. The method according to claim 36, further comprising, after adding the diammonium salt, heating the solution to about 90.degree. C.

46. A method of preparing a cellulose-based fire retardant composition, comprising:

a. adding cellulose powder having a hydroxyl group to liquid ammonia to form a solution;

b. subsequently adding diammonium phosphate to the solution and binding diammonium phosphate groups to the cellulose; and

c. crosslinking the cellulose, thereby forming a cellulose-based fire-retardant composition.

47. A method of preparing a cellulose-based fire retardant composition, comprising:

a. adding one or more cellulose polymers having a hydroxy group to water, thereby forming a solution;

b. catalytically binding a diammonium group to the one or more cellulose polymers in solution; and

c. crosslinking the one or more cellulose polymers, thereby forming a cellulose-based fire retardant composition.

48. A fire retardant composite material comprising:

a. an inherently fire retardant natural or synthetic polymer composition; and

b. a non-water soluble material

wherein the inherently fire retardant natural or synthetic polymer composition was prepared by reacting a solution of a hydroxyl group containing natural or synthetic polymer with an inorganic ammonium salt having at least two ammonium groups per molecule.

49. The fire retardant composite according to claim 48 wherein the polymer is a hydroxyl group containing cellulose.

50. The fire retardant composite according to claim 48 wherein the polymer is a hydroxyl group containing starch.

51. The fire retardant composite according to claim 48 wherein the polymer is a hydroxyl group containing petrochemical.

52. The fire retardant composite according to claim 48 wherein the non-water soluble material is selected from the group consisting of glass, metal, wood, paper, furniture, insulation, plywood, carpet, linen, clothing, thread, rubber, mortar, concrete, ceramic, fiberglass, polymers, carbonaceous materials, and mixtures thereof.

53. The fire retardant composite according to claim 48 wherein the composite has been formed by blending.

54. The fire retardant composite according to claim 48 which is a fiber impregnated with the inherently fire retardant composition.

55. The fire retardant composite according to claim 48 which is a wooden material pressure treated with the inherently fire retardant composition.

56. The fire retardant composite according to claim 48 in the form of a laminate or sheet.

57. The fire retardant composite according to claim 48 which is in the form of an insulating material for use in construction applications.

58. The fire retardant composite according to claim 48 which is essentially magnesium, bromine, antimony and ATH free.

59. The fire retardant composite according to claim 48 which is a molded article.

60. The fire retardant composite according to claim 48 produced in the form of a powder, foam, slurry, or coating

61. The fire retardant composite according to claim 48 which is an open or closed cell foamed polyurethane composite.

62. A fire retardant composition comprising a cross-linked natural or synthetic polymer wherein the cross-linking moiety comprises —N—P—N—.

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