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(54) **Title**: FIBROUS SUBSTRATES ADHERED WITH SUBSTITUTED CELLULOSE ESTER ADHESIVES AND METHODS RELATING THERETO

(57) **Abstract**: Fibrous substrates may be adhered to other substrates utilizing substituted cellulose ester adhesives that comprises a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent that comprises an inorganic, non-metal atom selected from the group consisting of sulfur, phosphorus, boron, and chlorine.

FIBROUS SUBSTRATES ADHERED WITH SUBSTITUTED CELLULOSE ESTER ADHESIVES AND METHODS RELATING THERETO

BACKGROUND

[0001] The present invention relates to fibrous substrates adhered to other substrates utilizing substituted cellulose ester adhesives, and articles and methods related thereto.

[0002] One of the most common adhesives for use in conjunction with fibrous substrates (*e.g.*, carpet backings) is a urea and melamine formaldehyde resin because they strongly bind to many fibrous substrates. However, it is believed that these adhesives may release formaldehyde into the surrounding environment over time, which is undesirable because formaldehyde is a known carcinogen, has a pungent odor, and has been shown to induce asthma attacks in relatively low doses.

[0003] Accordingly, formaldehyde-free adhesives are of much interest. However, alternatives, like polyurethane-based adhesives, often have less than satisfactory adhesive properties, which produce, for example, low-quality carpets. Therefore, formaldehyde-free adhesives that exhibit adhesive properties comparable to or better than urea and melamine formaldehyde resins would be of value.

SUMMARY OF THE INVENTION

[0004] The present invention relates to fibrous substrates adhered to other substrates utilizing substituted cellulose ester adhesives, and articles and methods related thereto.

[0005] In one embodiment of the present invention, an article may comprise a fibrous substrate that comprises a first surface, wherein at least a portion of the first surface is adhered to a second surface with an adhesive that comprises a substituted cellulose ester that comprises a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent that comprises an inorganic, nonmetal atom selected from the group consisting of sulfur, phosphorus, boron, and chlorine.

[0006] In another embodiment of the present invention, a method may comprise providing an adhesive comprising: a solvent and a substituted cellulose ester that comprises a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent that comprises an inorganic,

nonmetal atom select
and chlorine; applying the adhesive to at least a portion of a first surface of a fibrous substrate; placing a second surface in contact with the portion of the surface of the first surface; and drying the adhesive.

[0007] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The following figures are included to illustrate certain aspects of the present invention, and should not be viewed as exclusive embodiments. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

[0009] **Figures 1A-E** provide illustrations of nonlimiting examples of article configurations according to at least some embodiments of the present invention.

[0010] **Figure 2** provides a nonlimiting example of a substituted cellulose ester synthesis route according to at least some embodiments of the present invention.

[0011] **Figure 3** provides a nonlimiting example of a substituted cellulose ester synthesis route according to at least some embodiments of the present invention.

[0012] **Figure 4** provides a nonlimiting example of a substituted cellulose ester synthesis route according to at least some embodiments of the present invention.

DETAILED DESCRIPTION

[0013] The present invention relates to fibrous substrates adhered to other substrates utilizing substituted cellulose ester adhesives, and articles and methods related thereto.

[0014] The present invention provides for, in some embodiments, articles that comprise substituted cellulose ester adhesives that may, in some embodiments, advantageously be at least substantially formaldehyde-free. As used herein, the term "substantially formaldehyde-free" refers to the adhesive comprising less than 0.01% formaldehyde by weight of the adhesive.

[0015] In ac
formaldehyde-based adhesives such as those discussed above, the adhesives described herein are advantageously derived from renewable cellulosic sources. Consequently, the adhesive compositions are, to some degree, degradable in addition to being less noxious. That is, over the long-term the adhesive compositions described herein, under the proper conditions (*e.g.,* in a landfill), may be degradable and enhance the degradation of articles produced therewith. Accordingly, the adhesive compositions described herein provide for articles that are thought to be both more health-friendly and environmentally-friendly.

[0016] It should be noted that when "about" is used in reference to a number in a numerical list, the term "about" modifies each number of the numerical list. It should be noted that in some numerical listings of ranges, some lower limits listed may be greater than some upper limits listed. One skilled in the art will recognize that the selected subset will require the selection of an upper limit in excess of the selected lower limit.

[0017] In some embodiments, an article of the present invention may comprise a fibrous substrate comprising a first surface, the first surface is adhered to a second surface with a substituted cellulose ester adhesive ("SCE-adhesive"). In some embodiments, the fibrous substrate comprises the first surface and the second surface. In some embodiments, the fibrous substrate may comprise the first surface, and an additional substrate may comprise the second surface. In some embodiments, the additional substrate may be a second fibrous substrate. In some embodiments, articles of the present invention may comprise a plurality of substrates, at least one being a fibrous substrate, with multiple surfaces adhered together with SCE-adhesives described herein.

[0018] In some embodiments, articles of the present invention may be designed with the first surface and the second surface adhered in any suitable configuration. Examples of suitable configurations may include, but are not limited to, those illustrated in **Figure 1**. **Figure 1A** illustrates a fibrous substrate **101** and an additional substrate **102** in a stacked configuration. **Figure 1B** illustrates a fibrous substrate **103** and an additional substrate **104** in a side-by-side configuration. **Figure 1C** illustrates fibrous substrates **105** and **106** and additional substrate **107** in a stacked configuration where the fibrous substrate **106** is disposed between the additional substrate **107** and a top fibrous
: **1D** illustrates a plurality of substrates in a hybrid

configuration, wherei

configuration that mate at an angle, a fibrous substrate **110** is shown disposed on top of the additional substrates **108** and **109**, and a fibrous substrate **111** is shown disposed below the additional substrates **108** and **109**. **Figure 1E** illustrates a fibrous substrate **112** rolled and adhered to itself at seam **113**. One skilled in the art with the benefit of this disclosure should recognize that **Figures 1A-1E** are merely examples of possible configurations of articles described herein and that a multitude of other configurations are possible and within the bounds of this disclosure.

[0019] As used herein, the terms "substituted cellulose ester adhesive" and "SCE-adhesive" refer to an adhesive composition that comprises a substituted cellulose ester. As used herein, the term "substituted cellulose ester" refers to a polymeric compound having a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent. As used herein, the term "inorganic ester substituent" refers to an ester that comprises an oxygen bound to an R group and an inorganic, nonmetal atom (*e.g.*, sulfur, phosphorus, boron, and chlorine). It should be noted that inorganic esters encompass esters derived from oxoacids that comprise both inorganic, nonmetal atoms and carbon atoms, *e.g.*, alkyl sulfonic acids like methane sulfonic acid. Details of SCE-adhesives suitable for use in conjunction with articles and methods described herein are described further herein.

[0020] Fibrous substrates suitable for use in conjunction with the articles of the present invention may, in some embodiments, comprise natural fibers, synthetic fibers, any hybrid thereof, and any combination thereof. In some embodiments, natural fibers may be plant-derived and/or animal-derived, including, but not limited to, comprising at least one of cellulose, regenerated cellulose (*e.g.*, viscose rayon), wood pulp, cotton, jute, flax, ramie, hemp, sisal, bind, rattan, agave, coir, bamboo, grass, wheat stalk, rice stalk, barley stalk, tree wood, collagen, silk, angora, mohair, wool, alpaca, byssus, cashmere, catgut, llama, spider silk, yak, and the like any derivative thereof, and any combination thereof. In some embodiments, synthetic fibers may comprise at least one of cellulose acetate, cellulose triacetate, synthetic bamboo, glass, carbon, basalt, metal, ceramic, rayon, acrylic, aramid, nylon, polyolefins, polyethylene, polypropylene, polyesters, polyamides, zylon, and the like, any

any combination thereof.

[0021] Exem

conjunction with articles of the present invention may, in some embodiments, include, but are not limited to, paper, cardboard, corrugated cardboard, card stock, sand paper, bond paper, wallpaper, wrapping paper, cotton paper, tipping paper, bleached paper, colored paper, construction paper, sisal paper, coated paper, wax paper, woven fabrics, continuous filament nonwoven fabrics, carded nonwoven fabrics, tow, fiber bundles, twill, twine, rope, carpet, carpet backing, leather, animal hide, insulation, and the like, and any combination thereof.

[0022] Exemplary examples of additional substrates suitable for use in conjunction with articles of the present invention may, in some embodiments, include, but are not limited to, wood and/or grass derived substrates (*e.g.*, wood veneers, particle board, fiberboard, medium-density fiberboard, high-density fiberboard, oriented strand board, cork, hardwoods (*e.g.*, balsa wood, beech, ash, birch, Brazil wood, cherry, chestnut, elm, hickory, mahogany, maple, oak, rosewood, teak, walnut, locust, mango, alder, and the like), softwoods (*e.g.*, pine, fir, spruce, cedar, hemlock, and the like), rough lumber, finished lumber, natural fibrous material, and bamboo), foam substrates (*e.g.*, memory foams, polymer foams, polystyrene foam, polyurethane foam, frothed polyurethane, and soy-based foams), fibrous substrates described herein, and the like, and any combination thereof. As used herein, the term "wood veneer" refers to a thin slice of wood, typically thinner than about 4 mm. In some embodiments, a wood veneer may be a hard, high quality wood such as cherry.

[0023] Exemplary examples of articles of the present invention comprising SCE-adhesives and at least one fibrous substrate as described herein may, in some embodiments, include, but are not limited to, smoking articles (*e.g.*, cigarettes), envelopes, tape, cardboard packaging (*e.g.*, mailing packages and food containers like cereal boxes and frozen dinner containers), books, notebooks, magazines, corrugated boxes, decorative boxes, paper bags, grocery bags, wrapping paper, wallpaper, paper honeycomb, emery boards, electric insulation paper, air filters, paper-mache articles, carpets, dartboards, furniture or components thereof (*e.g.*, carpet and/or fabric coated headboards, chairs, and stools), picture frames, medical garments (*e.g.*, disposable gowns and surgical masks), and the like.

[0024] By way of nonlimiting example, an article of the present

:tte, a paper grocery bag, or a cereal box) may comprise

a fibrous substrate (e
or an overlap) and/or a second fibrous substrate.

[0025] By way of another nonlimiting example, an article of the present invention (*e.g.*, a book or a magazine) may, in some embodiments, comprise fibrous substrates (*e.g.*, paper and cardboard) bound together with SCE-adhesives described herein.

[0026] By way of yet another nonlimiting example, an article of the present invention (*e.g.*, a picture frame) may comprise a fibrous substrate (*e.g.*, a woven textile) adhered to an additional substrate (*e.g.*, a wooden frame) with SCE-adhesives described herein.

[0027] By way of another nonlimiting example, the article of the present invention (*e.g.*, carpet) may comprise a first fibrous substrate (*e.g.*, a primary carpet backing) and a second fibrous substrate (*e.g.*, a secondary carpet backing) adhered together with SCE-adhesives of the present invention. In some embodiments, the carpet may further comprise a foamed substrate (*e.g.*, a polyurethane foam) adhered between the first and second fibrous substrates with SCE-adhesives described herein. In some embodiments, the carpet may further comprise a foamed substrate (*e.g.*, a polyurethane foam) such that the second fibrous substrate is adhered between the foamed substrate and the first fibrous substrate with SCE-adhesives described herein.

[0028] By way of yet another nonlimiting example, an article (*e.g.*, flooring or a floor) may comprise a fibrous substrate (*e.g.*, carpet) adhered to wood substrates (*e.g.*, plywood or hardwoods) with SCE-adhesives described herein.

[0029] By way of another nonlimiting example, an article of the present invention (*e.g.*, paper) may comprise a fibrous substrate (*e.g.*, wood pulp) adhered to an additional substrate (*e.g.*, wood pulp) with SCE-adhesives described herein (*e.g.*, similar to a paper binder).

Substituted Cellulose Ester Adhesive Compositions

[0030] As described above, the terms "substituted cellulose ester adhesive" and "SCE-adhesive" refer to an adhesive composition that comprises a substituted cellulose ester, where the term "substituted cellulose ester" refers to a polymeric compound having a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent. Further, the term "inorganic
-s to an ester wherein the ether linkage of the ester

comprises an oxyger

(*e.g.*, sulfur, phosphorus, boron, and chlorine). It should be noted that inorganic esters encompass esters derived from oxoacids that comprise both inorganic, nonmetal atoms and carbon atoms, *e.g.*, alkyl sulfonic acids like methane sulfonic acid.

[0031] Organic ester substituents of a substituted cellulose ester described herein may include, but are not limited to, C_1-C_{20} aliphatic esters (*e.g.*, acetate, propionate, or butyrate), aromatic esters (*e.g.*, benzoate or phthalate), substituted aromatic esters, and the like, any derivative thereof, and any combination thereof.

[0032] In some embodiments, the degree of substitution of the organic ester substituents of a substituted cellulose ester described herein may range from a lower limit of about 0.2, 0.5, or 1 to an upper limit of less than about 3, about 2.9, 2.5, 2, or 1.5, and wherein the degree of substitution may range from any lower limit to any upper limit and encompass any subset therebetween.

[0033] Inorganic ester substituents of a substituted cellulose ester described herein may include, but are not limited to, hypochlorite, chlorite, chlorate, perchlorate, sulfite, sulfate, sulfonates (*e.g.*, taurine, toluenesulfonate, C_1-C_{10} alkyl sulfonate, and aryl sulfonate), fluorosulfate, nitrite, nitrate, phosphite, phosphate, phosphonates, borate, and the like, any derivative thereof, and any combination thereof.

[0034] In some embodiments, the weight percent of the inorganic, nonmetal atom of the inorganic ester substituent of a substituted cellulose ester described herein may range from a lower limit of about 0.01%, 0.05%, or 0.1% to an upper limit of about 8%, 5%, 3%, 1%, 0.5%, 0.25%, 0.2%, or 0.15%, and wherein the weight percent may range from any lower limit to any upper limit and encompass any subset therebetween.

[0035] Substituted cellulose esters for use in conjunction with an SCE-adhesive described herein may be derived from any suitable cellulosic source. Suitable cellulosic sources may include, but are not limited to, softwoods, hardwoods, cotton linters, switchgrass, bamboo, bagasse, industrial hemp, willow, poplar, perennial grasses (*e.g.*, grasses of the *Miscanthus* family), bacterial cellulose, seed hulls (*e.g.*, soy beans), recycled cellulose, and the like, and any combination thereof. Unexpectedly, it has been discovered, and is

n, that the adhesive properties of SCE-adhesives may

have a relationship tc
cellulose esters are derived. Without being limited by theory, it is believed that other components, *e.g.*, lignin and hemicelluloses, and concentrations thereof in the various cellulosic sources contribute to the differences in adhesive properties of the substituted cellulose esters derived therefrom. By way of nonlimiting example, a softwood may yield an SCE-adhesive with higher binding strength as compared to an SCE-adhesive derived from a hardwood.

[0036] In some embodiments, substituted cellulose esters described herein, and consequently SCE-adhesives and articles produced therewith, may be degradable, including biodegradable and/or chemically degradable. Without being limited by theory, it is believed that at least some inorganic ester substituents may be more susceptible to hydrolysis than a corresponding cellulose ester that does not comprise (or minimally comprises) inorganic ester substituents. Further, after some inorganic ester substituents undergo hydrolysis, a strong acid may be produced, which may further speed degradation.

[0037] In some embodiments, an SCE-adhesive suitable for use in conjunction with articles of the present invention may comprise at least one substituted cellulose ester and a solvent. Suitable solvents for use in conjunction with an SCE-adhesive described herein may include, but are not limited to, water, acetone, methanol, ethanol, methylethyl ketone, methylene chloride, dioxane, dimethyl formamide, tetrahydrofuran, acetic acid, dimethyl sulfoxide, N-methyl pyrrolidinone, dimethyl carbonate, diethyl carbonate, ethylene carbonate, propylene carbonate, and the like, any derivative thereof, and any combination thereof. The choice of solvent may, in some embodiments, depend on, *inter alia*, the degree of substitution and the amount of inorganic, nonmetal atom of the substituted cellulose ester. By way of nonlimiting example, an SCE-adhesive described herein may comprise at least one substituted cellulose ester having an organic ester substituent degree of substitution of greater than about 0 to about 1, an aqueous solvent, and optionally an organic solvent. By way of another nonlimiting example, an SCE-adhesive described herein may comprise at least one substituted cellulose ester having an organic ester substituent degree of substitution of about 0.7 to about 2.7 and a mixed solvent that comprises an aqueous solvent and an organic solvent (*e.g.*, acetone). By way of example SCE-adhesives of the present invention may, in

some embodiments,
organic ester substituent degree of substitution of about 2.4 to less than about 3, an organic solvent (*e.g.*, acetone), and optionally an aqueous solvent at about 15% or less by weight of the organic solvent.

[0038] In some embodiments, an SCE-adhesive suitable for use in conjunction with articles of the present invention may be formaldehyde-free, which may also be described as "an adhesive with no added formaldehyde." In some embodiments, an SCE-adhesive for use in conjunction with a article of the present invention may be substantially formaldehyde-free, *i.e.*, comprise less than 0.01% formaldehyde by weight of the substituted cellulose acetate of the SCE-adhesive composition.

[0039] In some embodiments, SCE-adhesives suitable for use in conjunction with articles of the present invention may further comprise an additive. Additives suitable for use in conjunction with SCE-adhesives described herein may include, but are not limited to, plasticizers, crosslinkers, insolubilizers, starches, fillers, thickeners, rigid compounds, water resistance additives, flame retardants, lubricants, softening agents, antibacterial agents, antifungal agents, pigments, dyes, and any combination thereof.

[0040] Plasticizers may, in some embodiments, allow for tailoring the viscosity and/or affecting adhesive properties of SCE-adhesives described herein. Examples of plasticizers suitable for use in conjunction with SCE-adhesives described herein may include, but are not limited to, glycerin, glycerin esters, polyethylene glycol, diethylene glycol, polypropylene glycol, alkylglycols (*e.g.*, polyethylene oxide ("PEO"), polypropylene oxide ("PPO"), and PEO-PPO block copolymers), polyglycoldiglycidyl ethers (*e.g.*, PEO-diglycidyl ether, PPO-diglycidyl ether, and PEO-PPO-diglycidyl ether), dimethyl sulfoxide, alkylphosphate esters, polycaprolactone, triethyl citrate, acetyl trimethyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate, di-2-methoxyethyl phthalate, dibutyl tartrate, ethyl o-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, n-ethyltoluenesulfonamide, triacetin, triacetin, o-cresyl p-toluenesulfonate, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, tripropionin, polycaprolactone, and the like, any derivative thereof, and any combination thereof.

[0041] Cross

properties and/or increase water resistance of SCE-adhesives described herein. Examples of crosslinkers suitable for use in conjunction with an SCE-adhesive described herein may, in some embodiments, include, but are not limited to, Lewis-acidic salts (*e.g.*, magnesium salts, aluminum salts, and zirconium salts, and in particular chloride and nitrate salts thereof), boric acid, borate salts, phosphate salts, ammonium zirconium carbonate, potassium zirconium carbonate, metal chelates (*e.g.*, zirconium chelates, titanium chelates, and aluminum chelates), formaldehyde crosslinkers, polyamide epichlorohydrin resin, crosslinkers like urea glyoxal adducts and alkylates thereof (*e.g.*, methylated glyoxal adducts and N-methylolated glyoxal adduct derivatives), crosslinkers containing N-methylol groups, crosslinkers containing etherified N-methylol groups, and the like, any derivative thereof, and any combination thereof. Additional crosslinker examples may include N-hydroxymethyl-reactive resins like 1,3-dimethylol-4,5-dihydroxyimidazolidinone (4,5-dihydroxy-N,N'-dimethylolethyleneurea) or their at least partly etherified derivatives (*e.g.*, derivatives with hydroxymethylated cyclic ethyleneureas, hydroxymethylated cyclic propyleneureas, hydroxymethylated bicyclic glyoxal diureas, and hydroxymethylated bicyclic malonaldehyde diureas). Examples of at least partly etherified derivatives of hydroxymethylated cyclic ethyleneureas may include, but are not limited to, ARKOFIX® products (*e.g.*, for example ARKOFIX® NEC plus or ARKOFIX® NES (ultra-low formaldehyde crosslinking agents, available from Clariant SE Switzerland), glyoxal, urea formaldehyde adducts, melamine formaldehyde adducts, phenol formaldehyde adducts, hydroxymethylated cyclic ethyleneureas, hydroxymethylated cyclic thioethyleneureas, hydroxymethylated cyclic propyleneureas, hydroxymethylated bicyclic glyoxal diurea, hydroxymethylated bicyclic malonaldehyde diureas, polyaldehydes (*e.g.*, dialdehydes), protected polyaldehydes (*e.g.*, protected dialdehydes), bisulfite protected polyaldehydes (*e.g.*, bisulfite protected dialdehydes), isocyanates, blocked isocyanates, dimethyoxytetrahydrafuran, dicarboxylic acids, epoxides, diglycidyl ether, hydroxymethyl-substituted imidazolidinone, hydroxymethyl-substituted pyrimidinones, hydroxymethyl-substituted triazinones, oxidized starch, oxidized polysaccharides, oxidized hemicellulose, and the like, any derivative thereof, and any combination thereof. Combinations of any of the

ay also be suitable. For example, hydroxymethylated

compounds, at lea
compounds, dialdehyde-based compounds, and/or capped dialdehyde compounds may be useful in combination with Lewis-acidic salts. One skilled in the art with the benefit of this disclosure should understand that formaldehyde crosslinkers should be excluded from use in conjunction with formaldehyde-free SCE-adhesives, and limited in substantially formaldehyde-free SCE-adhesives.

[0042] Insolubilizer additives may, in some embodiments, increase the hydrophobic nature of the adhesive. Examples of insolubilizer additives for use in conjunction with SCE-adhesives described herein may, in some embodiments, include, but are not limited to, copolymers of polyvinyl alcohol and polyvinyl acetate, glyoxal, glycerin, sorbitol, dextrine, alpha-methylglucoside, and the like, and any combination thereof.

[0043] Water resistance additives may, in some embodiments, increase the water resistance properties of SCE-adhesives described herein, which may consequently yield articles capable of maintaining their mechanical properties in environments with higher water concentrations, *e.g.*, humid environments. Examples of water resistance additives for use in conjunction with SCE-adhesives described herein may include, but are not limited to, waxes, polyolefins, insolubilizers, or combinations thereof.

[0044] Fillers may, in some embodiments, increase the rigidity of SCE-adhesives described herein, which may consequently increase the mechanical rigidity of a article produced therewith. Fillers suitable for use in conjunction with SCE-additives described herein may include, but are not limited to, coconut shell flour, walnut shell flour, wood flour, wheat flour, soybean flour, gums, starches, protein materials, calcium carbonate, zeolite, clay, rigid compounds (*e.g.* lignin), thickeners, and the like, and any combination thereof.

[0045] Flame retardants suitable for use in conjunction with SCE-additives described herein may include, but are not limited to, silica, organophosphates, polyhalides, and the like, and any combination thereof.

[0046] In some embodiments, SCE-adhesives described herein may be characterized as having a solids content (contributed to, at least in part, by some additives) ranging from a lower limit of about 4%, 8%, 10%, 12%, or 15%, to an upper limit of about 75%, 50%, 45%, 35%, or 25%, and wherein the solids content may range from any lower limit to any upper limit and herebetween.

[0047] In so

comprise a plurality of wood substrates (*e.g.*, any wood substrate disclosed herein including combinations thereof) and SCE-adhesives, according to any embodiments disclosed herein, disposed between at least a portion of at least two of the wood substrates. SCE-adhesives may, in some embodiments, comprise substituted cellulose esters according to any embodiment disclosed herein, optionally solvent, and optionally any additives. Substituted cellulose esters may, in some embodiments, comprise a polymeric compound having a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent and have at least one characteristic selected from the group consisting of at least one organic ester substituent according to those described herein, an organic ester substituent degree of substitution from about 0.2 to less than about 3, at least one inorganic ester substituent according to those described herein, a weight percent of the inorganic, nonmetal atom of the inorganic ester substituent between about 0.01% and about 1%, being derived from a cellulose material described herein, and any combination thereof.

[0048] Substituted cellulose esters described herein may be produced utilizing one of several synthesis routes that, in some embodiments, comprise a hydrolysis reaction where water and inorganic ester oxoacid catalysts are added to a cellulose ester mixture so as to yield the substituted cellulose esters. The synthesis of substituted cellulose esters described herein is described in further detail in copending International Patent Application No. PCT/US12/56802 entitled "Substituted Cellulose Ester Adhesives and Methods and Articles Relating Thereto" filed on the same day as the present application, the entire disclosure of which is incorporated herein by reference. Three nonlimiting examples of synthesis routes are illustrated in Figures 2-4.

[0049] Referring now to Figure 2, in some embodiments, a cellulosic material may undergo (2.1) an activation reaction that swells the cellulosic material in the presence of an activating agent so as to make internal surfaces accessible for subsequent reactions, (2.2) an esterification reaction in the presence of an inorganic ester oxoacid catalyst and an organic esterification reactant so as to yield a cellulose ester mixture, and (2.3) a hydrolysis reaction in the presence of water and additional inorganic ester oxoacid catalyst so as to yield substituted cellulose esters. In some embodiments, the substituted

en optionally be further processed, *e.g.*, to yield purified

substituted cellulose
catalyst of the (2.2) esterification reaction and the (2.3) hydrolysis reaction may be the same or different inorganic ester oxoacid catalysts.

[0050] Referring now to Figure 3, in some embodiments, synthesis of substituted cellulose esters may begin with the cellulose ester starting material, *e.g.*, cellulose acetate. As shown in Figure 3, a cellulose ester mixture (*e.g.*, a swollen cellulose acetate in acetic acid) may undergo (3.1) a hydrolysis reaction in the presence of water, an inorganic ester oxoacid catalyst, and an organic esterification reactant, so as to yield substituted cellulose esters that may optionally be further processed.

[0051] Referring now to Figure 4, in some embodiments, synthesis of substituted cellulose esters may begin with a cellulose sulfate, cellulose phosphate, and/or cellulose nitrate starting material. As shown in Figure 4, the cellulose sulfate, cellulose phosphate, and/or cellulose nitrate starting material may undergo (4.1) an esterification reaction in the presence of an inorganic ester oxoacid catalyst and an organic esterification reactant so as to yield a cellulose ester mixture, and optionally (4.2) a hydrolysis reaction in the presence of additional inorganic ester oxoacid catalyst so as to yield substituted cellulose esters that may optionally be further processed. In some embodiments, the (4.2) hydrolysis reaction may optionally further utilize water, as illustrated in Figure 4. In some embodiments, the inorganic ester oxoacid catalyst of (4.1) an esterification reaction and optionally (4.2) a hydrolysis reaction may be the same or different inorganic ester oxoacid catalysts. One skilled in the art, with the benefit of this disclosure, should recognized that (4.2) the hydrolysis reaction is optional in this synthesis scheme as the starting material has inorganic ester substituents, some of which may be converted to organic ester substituents in (4.1) the esterification reaction, thereby yielding a substituted cellulose ester described herein.

[0052] As illustrated in the nonlimiting examples above, in some embodiments, the synthesis of substituted cellulose esters described herein may involve, *inter alia*, a hydrolysis reaction where inorganic ester oxoacid catalysts, water, and optionally other reactants are added to a cellulose ester mixture so as to yield the substituted cellulose esters. Further, it should be noted that in the nonlimiting examples above, the various chemical components may be mixed

orresponding material and/or mixture in a plurality of

sequences that may

some preferred embodiments, hydrolysis reactions that include organic esterification reactants may be carried with adding the water after the inorganic ester oxoacid catalyst and the organic esterification reactant, so as to minimize potentially deactivating reactions between the water and the other reactants or intermediates thereof. In some preferred embodiments, hydrolysis reactions that do not include organic esterification reactants may be carried with concurrent addition of the water and the inorganic ester oxoacid catalyst, so as to minimize any potential degradation of the cellulose ester mixture by the inorganic ester oxoacid catalyst.

Methods of Articles Described Herein

[0053] In some embodiments, producing articles of the present invention may involve applying an SCE-adhesive described herein to at least a portion of a first surface of a fibrous substrate; placing a second surface in contact with the portion of the first surface; and drying the SCE-adhesive. In some embodiments, producing the article may further comprise applying an SCE-adhesive to at least a portion of the second surface that contacts the portion of the first surface.

[0054] In some embodiments, applying an SCE-adhesive described herein to a substrate (fibrous or otherwise) may involve: painting, rolling, smearing, spreading, squeezing, spraying, atomizing, dotting, any hybrid thereof, and any combination thereof, either continuously or intermittently.

[0055] In some embodiments, drying an SCE-adhesive described herein may involve: allowing time to pass, pulling vacuum, applying an air force, applying heat, applying pressure, and any combination thereof. In some embodiments, applying pressure may be static (*e.g.*, using a c-clamp), moving (*e.g.*, between rollers), any hybrid thereof, and any combination thereof, either continuously or intermittently.

EXAMPLES

[0056] *Example 1*. Three substituted cellulose esters and two cellulose esters were produced and analyzed. Cellulose was treated with acetic acid and then mixed with a cooled solution of acetic acid, acetic anhydride, and sulfuric acid. The temperature of the resultant mixture was increased and allowed to react for about 20 minutes. At this point, cellulose ester compositions were substituted cellulose esters, the mixture was hydrolyzed

in the presence of ad

for the production of the five samples.

Table 1

	Time	Temp (°C)	Acetyl Value (% as acetic acid)	Sulfur Content (ppm)	SO_4 Content (ppm)
CA-1	6	73.0	39.03	105	314
CA-2	4.5	75.0	40.15	160	481
SCA-1	6	65.0	41.43	807	2419
SCA-2	4.5	70.0	38.02	268	805
SCA-3	4.5	68.5	39.08	429	1286

[0057] This example is thought to demonstrate that substituted cellulose esters (specifically, substituted cellulose acetates) can be produced with high sulfur contents at relatively low temperatures and short hydrolysis times that are comparable to standard cellulose acetate hydrolysis times, which is advantageous in the commercial-scale production of substituted cellulose esters.

[0058] *Example 2*. Several adhesive compositions (Adhesives 1-5) having varied solvents and substituted cellulose acetate compositions were tested for their adhesive properties in a variety of wood laminates. Further, two wood laminates were produced and analyzed with commercially available ELMER'S GLUE ALL® (a poly(vinyl acetate)-based adhesive, available from Elmer's Products, Inc.). **Table 2** provides the wood laminate compositions, and **Table 3** provides the results of Lap Shear tests conducted using INSTRON® (Model 3366) as a measure of the adhesive properties of the various adhesive compositions.

[0059] Upon visual inspection, the substituted cellulose acetate adhesives of this example were optically clear and had a high gloss, which may be desirable in some commercial applications.

[0060] To form the laminates, two small wooden blocks or two cardboard pieces were glued together using a 10% aqueous solution of the Adhesives 1-5 (**Table 2**) or ELMER'S GLUE ALL® (as noted) and allowed to dry. The resulting laminates were difficult to separate (*i.e.*, none of the blocks broke in the tensile testing setup used or the cardboard failed before the adhesive bond). When enough force was applied to separate the blocks, the wood fibers

broke which suggests
as strong as the wood fibers.

Table 2

Sample	Adhesive	Solvent System	Solids (wt%)	Sulfur (mg/kg)	Substrate	Drying
1	ELMER'S GLUE ALL®	emulsion	54	---	cardboard	1 hr (ambient)
2	Adhesive 1	aqueous	10	not measured	cardboard	1 hr (ambient)
3	Adhesive 2	aqueous	20	4940	wood	2.25 hr (ambient)
4	Adhesive 3	aqueous	15	4530	wood	2.25 hr (ambient)
5	Adhesive 4	mixed organic/ aqueous	10	4940	wood	2.25 hr (ambient)
6	Adhesive 2	aqueous	15	4940	wood	2.25 hr (ambient)
7	ELMER'S GLUE ALL®	emulsion	27	---	wood	overnight (ambient)
8	Adhesive 5	aqueous	10	5570	wood	1 hr (120 °C)
9	Adhesive 5	aqueous	10	5570	wood	1 hr (120 °C)
10	Adhesive 5	aqueous	10	5570	wood	1 hr (120 °C)

Sample	Adhesive	Substrate	Additional Treatment	Break Point (kgf)	Comments
1	ELMER'S GLUE ALL®	cardboard		58.94	paper failure
2	Adhesive 1	cardboard		43.86	paper failure
3	Adhesive 2	wood		>107	exceeded load cell capacity
4	Adhesive 3	wood		>107	exceeded load cell capacity
5	Adhesive 4	wood		>107	exceeded load cell capacity
6	Adhesive 2	wood		>107	exceeded load cell capacity
7	ELMER'S GLUE ALL®	wood		>107	exceeded load cell capacity
8	Adhesive 5	wood		>107	exceeded load cell capacity
9	Adhesive 5	wood	1 hr (4 °C)	>107	exceeded load cell capacity
10	Adhesive 5	wood	1 hr (4 °C)	>107	exceeded load cell capacity

[0061] It is believed that this example demonstrates, among many things, that substituted cellulose acetates with high sulfur content are effective as an adhesive on a variety of substrates.

[0062] *Example 3.* Various additives were added to three adhesive compositions that comprise substituted cellulose acetate according to at least some embodiments described herein. The resulting compositions were tested for their adhesive properties on wood substrates (1/4" pine strips 1.5" in width) using INSTRON® (Model 3366) Lap Shear test. Summaries of the results are shown below in **Tables 4** and **Table 5**.

[0063] Adhesive 6 comprises substituted cellulose acetate having about 620 mg/kg of sulfur. To the Adhesive 6, varying amounts of ammonium zirconium carbonate were added. **Table 4** provides the results of the Lap Shear test for the various compositions.

%Zr by wt of total solution (%Zr by wt of solids)	Average Break (kgf)*	Average Break (psi)**	Stnd. Dev.
0 (0)	179	263	32
0.04% (0.2%)	271	398	110
0.08% (0.4%)	280	411	35
0.16% (0.9%)	300	441	71
0.32% (1.8%)	362	532	45

* average of 6 replicates

** lap shear of 1.5" x 1" adhered area

[0064] Adhesives 7 and 8 comprise substituted cellulose acetates having about 520 mg/kg of sulfur and about 557 mg/kg of sulfur, respectively. To the Adhesives 7 and 8, varying amounts of additives were added. **Table 5** provides the results of the Lap Shear test for the various compositions.

Table 5

Additive	Adhesive 7 Break Point (kgf)	Adhesive 8 Break Point (kgf)
no additive	225	349
ammonium zirconium carbonate (14% by wt of solids)	348	245
polyvinyl acetate (MW ~ 140,000) (14% by wt of solids)	271	210
polyvinyl alcohol (MW ~ 150,000) (14% by wt of solids)	not tested	154

[0065] As shown in **Table 4**, the addition of zirconium can increase the strength required to break the bond formed by substituted cellulose ester adhesives. Further, **Table 5** demonstrates the use of other polymer as plasticizer in substituted cellulose ester adhesives, which may advantageously allow for tailoring the adhesive strength of such compositions.

[0066] *Example 4*. A plurality of adhesives samples were prepared by adding 8% by weight of a substituted cellulose acetate having about 1286 mg/kg sulfur to the desired solvent system as outlined in **Table 6**. The adhesive samples were mixed overnight. The crosslinkers (if applicable) were added in amounts outlined in **Table 6**, and the adhesive samples were mixed for about 2

minutes. The adhesi\
together and allowed to dry for 15 minutes at 120°C. The Lap Shear test for was tested as described in *Example 2*.

Table 6

Adhesive	Solvent	Crosslinker	Break Point (kgf)
9	6 parts ethanol 4 parts water	none	182.68
10		NES* (1%**)	227.88
11		ZA* (0.5%)	242.38
12	7 parts water 2 parts ethanol 1 part acetone	none	161.45
13		NES (1%)	310.38
14		ZA (0.5%)	145.10
15	4 parts water 1 part ethanol 5 parts acetone	none	109.60
16		NES (1%)	202.96
17		ZA (0.5%)	134.14
18	8 parts water 1.5 parts dimethyl carbonate 0.5 parts acetone	none	138.89
19		NES (1%)	189.30
20		NES (4%)	379.44
21		ZA (0.5%)	285.12
22		ZA (1%)	349.53
23	7 parts water 2 parts dimethyl carbonate 1 part acetone	none	175.99
24		NES (1%)	167.71
25		AZC* (1%)	294.87

* NES is modified dimethylol dihydroxy ethylene urea (available as ARKOFIX® NES from Clariant), ZA is zirconium acetate, and AZC is ammonium zirconium carbonate.

** Crosslinker concentrations are by weight of the solids content of the sample.

[0067] This example demonstrates that both the crosslinker and the solvent system may affect the adhesive properties of substituted cellulose ester adhesives, which may allow for two additional handles that can be utilized in tailoring the adhesive properties for substituted cellulose ester adhesives for the desired application.

[0068] *Example 5.* A plurality of adhesives samples were prepared by adding 12% by weight of a substituted cellulose acetate having about 997 mg/kg sulfur to the desired solvent system as outlined in **Table 7**. The adhesive samples were mixed overnight. The adhesive samples were used to adhere two

blocks of pine wood

Lap Shear test for was tested as described in *Example 2*.

Table 7

Solvent System				Break Point (kgf)
dimethyl carbonate	acetone	water	ethanol	
0	80	20	0	284.10
15	15	70	0	293.38
10	10	80	0	302.17
20	5	75	0	302.63
0	0	40	60	318.97
20	10	70	0	334.33
5	15	80	0	358.10
15	5	80	0	359.00
0	10	40	50	360.06
5	15	80	0	366.00
0	20	80	0	382.43
10	0	70	20	404.86

[0069] This example demonstrates that solvent system may affect the adhesive properties of substituted cellulose ester adhesives, which may allow for an additional handle that can be utilized in tailoring the adhesive properties for substituted cellulose ester adhesives for the desired application.

[0070] *Example 6*. A plurality of adhesives samples were prepared by adding 8% by weight of a substituted cellulose acetate having about 1286 mg/kg sulfur to the desired solvent system as outlined in **Table 8**. The adhesive samples were mixed overnight. A crosslinker of NES at 1% by weight of the solids content of the sample and a crosslinker catalyst ad outlined in **Table 8** (if applicable) at 1.5% by weight of the solids content of the sample were added to the adhesives samples, and the adhesive samples were mixed for about 2 minutes. The adhesive samples were used to adhere two blocks of pine wood together and allowed to dry for 15 minutes at 120°C. The Lap Shear test for was tested as described in *Example 2*.

Adhesive	Solvent	Crosslinker	Break Point (kgf)
26	6 parts ethanol 4 parts water	None	227.88
27		$MgCl_2$	165.69
28		$AlCl_3$	174.59
29	7 parts water 2 parts ethanol 1 part acetone	None	310.38
30		$MgCl_2$	271.45
31		$AlCl_3$	175.57
32	4 parts water 1 part ethanol 5 parts acetone	None	202.96
33		$MgCl_2$	144.42
34		$AlCl_3$	140.17

[0071] This example demonstrates that a crosslinker catalyst is not required to initiate crosslinking with the NES crosslinker, which typically does require such a crosslinker catalyst. Further, such crosslinker catalysts may reduce the adhesive properties of substituted cellulose ester adhesives.

[0072] *Example 7.* Two samples of substituted cellulose acetates were derived from hardwood or softwood having about 1290 mg/kg sulfur or about 1000 mg/kg sulfur, respectively. Each substituted cellulose ester sample was used in producing an SCE-adhesive having 12% solids and no crosslinkers in a solvent system of 60% ethanol and 40% water. The adhesive samples were used to adhere two blocks of either pine or birch wood together and allowed to dry for 15 minutes at 120°C. The Lap Shear test for was tested as described in *Example 2*.

[0073] As reported in **Table 9**, the use of the softwood-derived cellulose acetate yielded a stronger adhesive, *e.g.*, about 60% higher lap strength when adhering pine and about 20% higher lap strength when adhering birch, which demonstrates that the cellulosic source from which a substituted cellulose ester is derived may affect the adhesive properties of the resultant SCE-adhesive.

Pulp	Substrate	Average Break (kgf)*	Stnd. Dev.
hardwood	pine	280	10
hardwood	birch	452	8
softwood	pine	445	17
softwood	birch	549	9

* average of 2 replicates

[0074] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be

incorporated herein l
specification should be adopted.

CLAIMS

The invention claimed is:

1. An article comprising:

a fibrous substrate that comprises a first surface, wherein at least a portion of the first surface is adhered to a second surface with an adhesive that comprises a substituted cellulose ester that comprises a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent that comprises an inorganic, nonmetal atom selected from the group consisting of sulfur, phosphorus, boron, and chlorine.

2. The article of claim 1, wherein the substituted cellulose ester is derived from at least one selected from the group consisting of a softwood, a hardwood, a cotton linter, switchgrass, bamboo, bagasse, industrial hemp, willow, poplar, a perennial grass, bacterial cellulose, a seed hull, recycled cellulose, and any combination thereof.

3. The article of claim 1, wherein the organic ester substituent comprises at least one selected from the group consisting of a C_1-C_{20} aliphatic ester, an aromatic ester, any derivative thereof, and any combination thereof.

4. The article of claim 1, wherein the inorganic ester substituent is selected from the group consisting of hypochlorite, chlorite, chlorate, perchlorate, sulfite, sulfate, a sulfonate, fluorosulfate, nitrite, nitrate, phosphite, phosphate, a phosphonate, a phosphinate, an alkyl phosphonate, borate, any derivative thereof, and any combination thereof.

5. The article of claim 1, wherein the inorganic, nonmetal atom is present in an amount of about 0.01% or greater by weight of the substituted cellulose ester.

6. The article of claim 1, wherein the substituted cellulose ester has a degree of substitution ranging from about 0.2 to less than about 3.

7. The article of claim 1, wherein the adhesive further comprises a solvent comprising at least one selected from the group consisting of water, ethanol, acetone, methylethyl ketone, methylene chloride, dioxane, dimethyl formamide, methanol, tetrahydrofuran, acetic acid, dimethyl sulfoxide, N-methyl

pyrrolidinone, dimethyl carbonate, diethyl carbonate, ethylene carbonate, propylene carbonate, and any combination thereof.

8. The article of claim 1, wherein the adhesive further comprises an additive comprising at least one selected from the group consisting of a plasticizer, a crosslinker, an insolubilizer, a starch, a filler, a thickener, a rigid compound, a water resistance additive, a flame retardant, a lubricant, a softening agent, an antibacterial agent, an antifungal agent, a pigment, a dye, and any combination thereof.

9. The article of claim 1, wherein the adhesive is at least substantially formaldehyde-free.

10. The article of claim 1, wherein the fibrous substrate comprise fibers that comprise at least one selected from the group consisting of cellulose, cotton, regenerated cellulose, jute, flax, ramie, hemp, sisal, bind, rattan, agave, coir, bamboo, grass, wheat stalk, rice stalk, barley stalk, tree wood, collagen, silk, angora, mohair, wool, alpaca, byssus, cashmere, catgut, llama, spider silk, yak, cellulose acetate, cellulose triacetate, synthetic bamboo, glass, carbon, basalt, metal, ceramic, rayon, acrylic, aramid, nylon, polyolefins, polyethylene, polypropylene, polyesters, polyamides, zylon, any derivative thereof, and any combination thereof.

11. The article of claim 1, wherein the fibrous substrate comprises at least one selected from the group consisting of paper, cardboard, corrugated cardboard, card stock, sand paper, bond paper, wallpaper, wrapping paper, cotton paper, tipping paper, bleached paper, colored paper, construction paper, sisal paper, coated paper, wax paper, woven fabrics, continuous filament nonwoven fabrics, carded nonwoven fabrics, tow, fiber bundles, twill, twine, rope, carpet, carpet backing, leather, animal hide, insulation, and any combination thereof.

12. The article of claim 1, wherein the fibrous substrate comprises the second surface.

13. The article of claim 1, wherein an additional substrate comprises the second surface.

14. The article of claim 13, wherein the second substrate comprises at least one selected from the group consisting of a wood-derived substrate, a grass-derived substrate, and a foam substrate.

15. The article of claim 1 being at least one selected from the group consisting of a smoking article, a cigarette, an envelope, tape, cardboard packaging, a mailing package, a food container, a book, a notebook, a magazine, a corrugated box, a decorative box, a paper bag, a grocery bag, a wrapping paper, wallpaper, paper honeycomb, emery board, a electric insulation paper, air filter, a paper-mache article, a carpet, a dartboard, furniture or a component thereof, a carpet and/or fabric coated headboard, a chair, a stool, a picture frame, a medical garment, a disposable gown, and a surgical mask.

16. A method comprising:

providing an adhesive comprising:

a substituted cellulose ester that comprises a cellulose polymer backbone having an organic ester substituent and an inorganic ester substituent that comprises an inorganic, nonmetal atom selected from the group consisting of sulfur, phosphorus, boron, and chlorine; and

a solvent;

applying the adhesive to at least a portion of a first surface of a fibrous substrate;

placing a second surface in contact with the portion of the surface of the first surface; and

drying the adhesive.

17. The method of claim 16, wherein the solvent comprises about 85% or greater of an organic solvent and about 0% to about 15% of an aqueous solvent; and wherein the substituted cellulose ester has a degree of substitution of about 2.4 to less than about 3.

18. The method of claim 16, wherein the solvent comprises an aqueous solvent; and wherein the substituted cellulose ester has a degree of substitution of about 1 or less.

19. The method of claim 16, wherein the solvent comprises an organic solvent and an aqueous solvent; and wherein the substituted cellulose ester has a degree of substitution of about 0.7 to about 2.7.

20. The method of claim 16, wherein the inorganic, nonmetal atom is present in an amount of about 0.01% to about 8% by weight of the substituted cellulose ester.

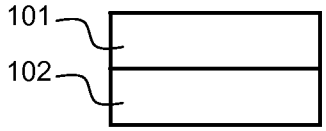

Figure 1A

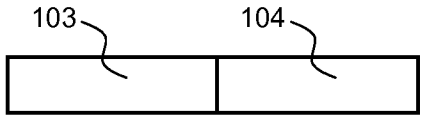

Figure 1B

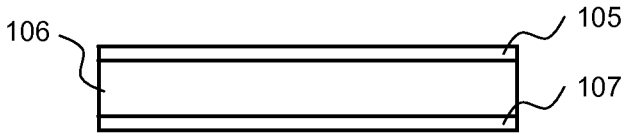

Figure 1C

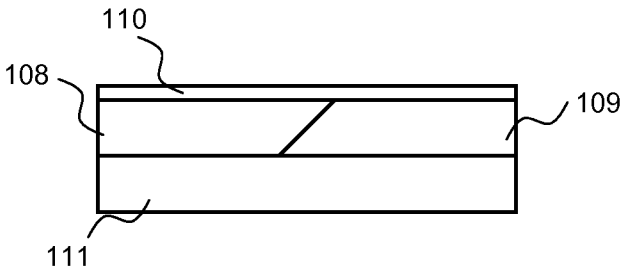

Figure 1D

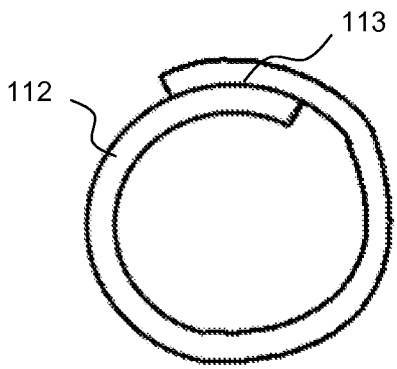

Figure 1E

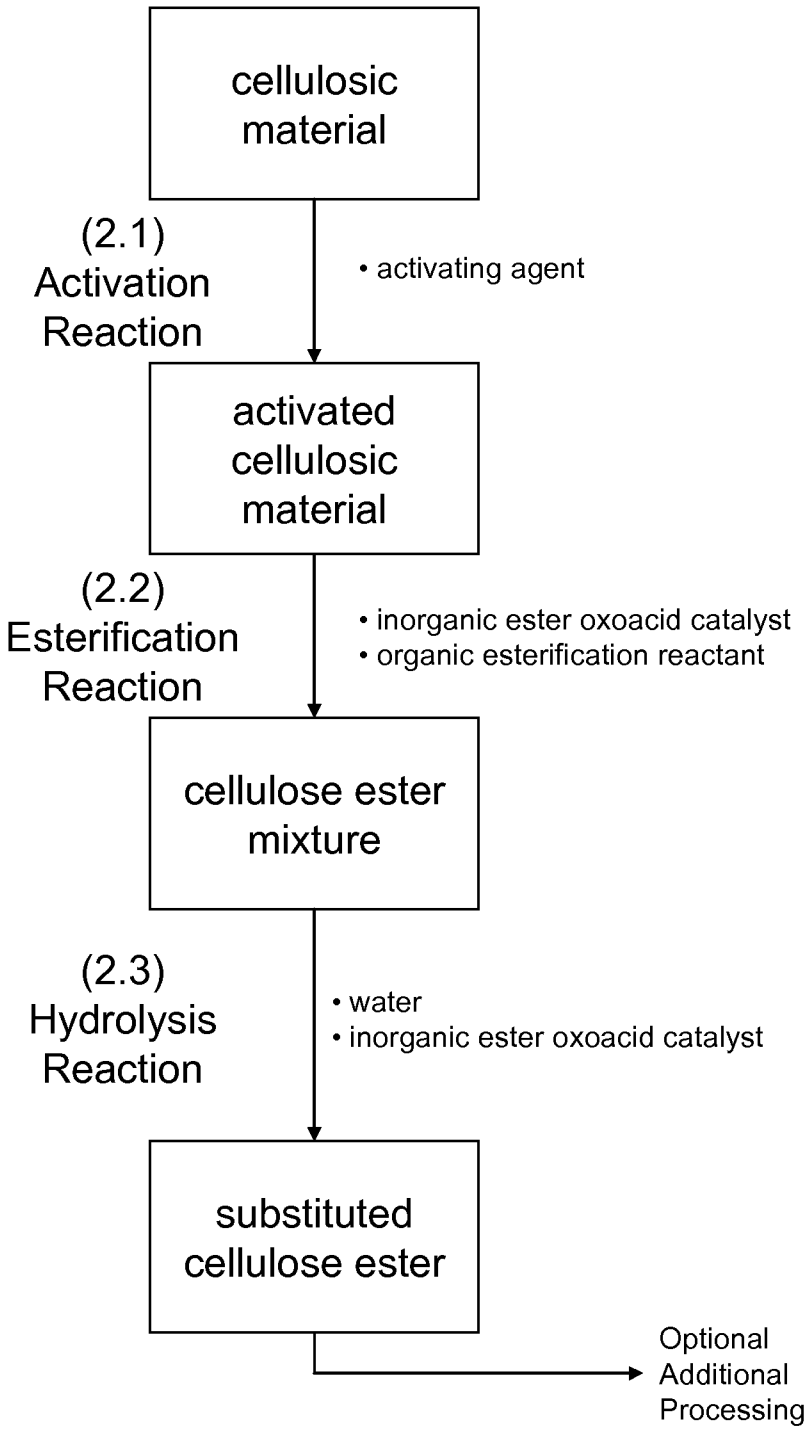
cellulosic material
(2.1) Activation Reaction
• activating agent
activated cellulosic material
(2.2) Esterification Reaction
• inorganic ester oxoacid catalyst
• organic esterification reactant
cellulose ester mixture
(2.3) Hydrolysis Reaction
• water
• inorganic ester oxoacid catalyst
substituted cellulose ester
Optional Additional Processing

Figure 2

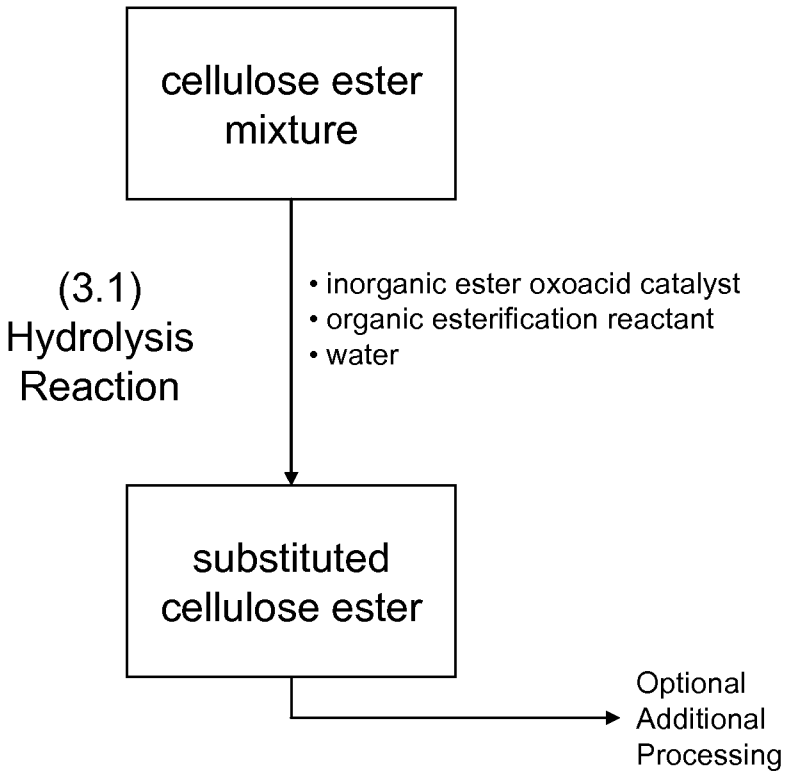
cellulose ester mixture
(3.1) Hydrolysis Reaction
• inorganic ester oxoacid catalyst
• organic esterification reactant
• water
substituted cellulose ester
Optional Additional Processing

Figure 3

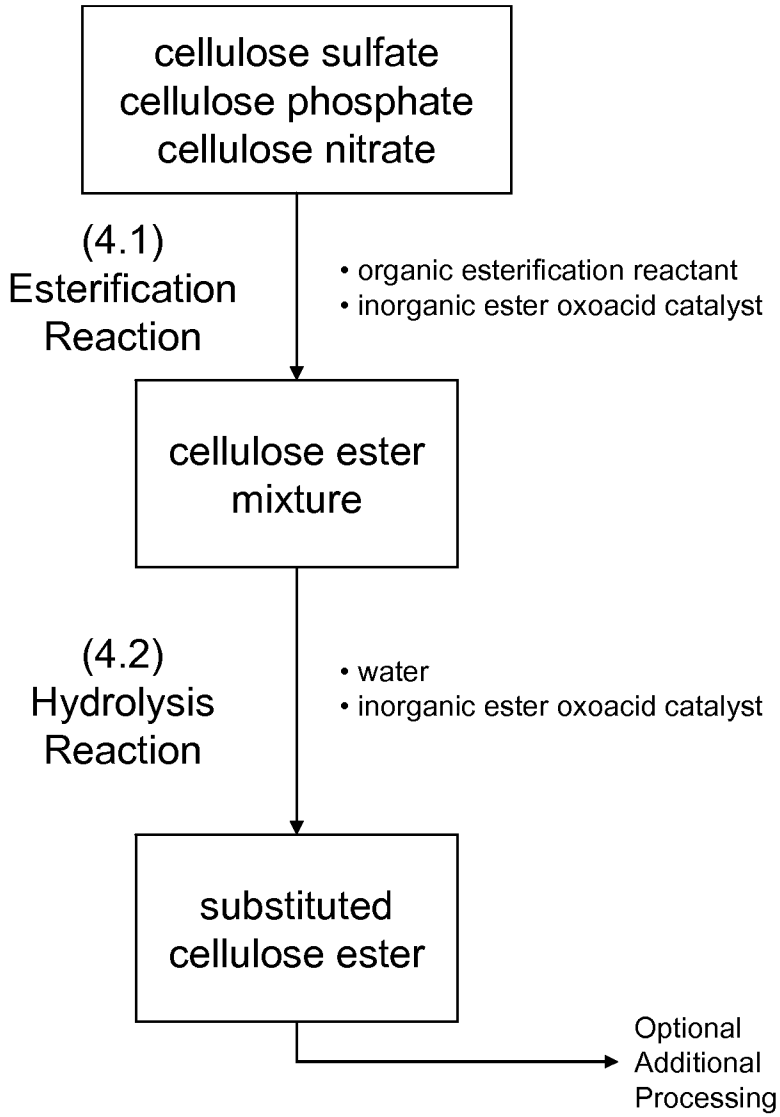
cellulose sulfate
cellulose phosphate
cellulose nitrate
(4.1)
Esterification
Reaction
• organic esterification reactant
• inorganic ester oxoacid catalyst
cellulose ester
mixture
(4.2)
Hydrolysis
Reaction
• water
• inorganic ester oxoacid catalyst
substituted
cellulose ester
Optional
Additional
Processing

Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/056819

A. CLASSIFICATION OF SUBJECT MATTER

B32B 23/10(2006.01)i, B32B 23/14(2006.01)i, B32B 23/20(2006.01)i, B32B 7/12(2006.01)i, C08L 1/10(2006.01)i, C08J 7/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B32B 23/10; B29C 65/54; A61F 13/00; C09J 101/02; B32B 27/14; B32B 23/02; B32B 9/04; B32B 31/06; D02G 3/00; B32B 15/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: adhesive, fibrous substrate, laminate, article

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0311833 A1 (PARKER et al.) 22 December 2011 See abstract; paragraphs [0047]-[0053],[0182]-[0192],[0202]-[0203],[0267]-[02	1-4,8,10-14,16
A	87]; claims 1-71	5-7,9,15,17-20
A	US 2009-0075107 A1 (HEDRICK et al.) 19 March 2009 See abstract; paragraphs [0009]-[0015]; claims 1-10; figure 1	1-20
A	US 6500539 B1 (CHEN et al.) 31 December 2002 See abstract; columns 2-4; claims 1-13	1-20
A	JP 06-079827 A (NISSHIN STEEL CO., LTD.) 22 March 1994 See abstract; paragraphs [0001]-[0011]	1-20
A	US 05681646 A (OFOSU et al.) 28 October 1997 See abstract; columns 1-4; claims 1-13	1-20

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 April 2013 (05.04.2013)	**08 April 2013 (08.04.2013)**

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