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(71) Applicant: CELANESE ACETATE LLC [US/US]; 222 West Las Colinas Blvd., Suite 900N, Irving, Texas 75039 (US).

(72) Inventors: COMBS, Michael; P.O. Box 794, Pembroke, Virginia 24136 (US). BISSET, Wendy; 391 Briar Patch Trail, Eggleston, Virginia 24086 (US). MILWARD, Lizbeth; 3000 Richmond Lane Apt. B, Blacksburg, Virginia 24060 (US).

(74) Agents: KAISER, Iona N. et al.; McDermott Will & Emery LLP, The McDermott Building, 500 North Capital Street, N.W., Washington, District of Columbia 20001 (US).

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(54) Title: HOT MELT AND PRESSURE-SENSITIVE ADHESIVES THAT INCLUDE HIGHLY-PLASTICIZED CELLULOSE ESTERS AND METHODS AND ARTICLES RELATING THERETO

(57) Abstract: Highly-plasticized cellulose esters may be useful as adhesives, including for use in producing laminates. For example, producing a laminate may include providing an adhesive melt that comprises an adhesive that comprises a cellulose ester and a plasticizer, the plasticizer included in an amount of about 30% to about 75% by weight of the adhesive; applying the adhesive melt to a substrate; and allowing the adhesive melt to cool so as to yield a laminate on the substrate.



**HOT MELT AND PRESSURE-SENSITIVE ADHESIVES THAT  
INCLUDE HIGHLY-PLASTICIZED CELLULOSE ESTERS AND  
METHODS AND ARTICLES RELATING THERETO**

5                   **CROSS-REFERENCE TO RELATED APPLICATIONS**

**[0001]** The present application claims priority to U.S. Patent Application  
Number 13/796,234 filed on March 12, 2013, entitled "Hot Melt and Pressure-  
Sensitive Adhesives That Include Highly-Plasticized Cellulose Esters and Methods  
and Articles Relating Thereto;" U.S. Patent Application Number 13/796,005 filed  
10 on March 12, 2013, entitled "Hot Melt and Pressure-Sensitive Adhesives That  
Include Highly-Plasticized Cellulose Esters and Methods and Articles Relating  
Thereto;" U.S. Patent Application Number 13/795,779 filed on March 12, 2013,  
entitled "Hot Melt and Pressure-Sensitive Adhesives That Include Highly-  
Plasticized Cellulose Esters and Methods and Articles Relating Thereto;" and U.S.  
15 Patent Application Number 13/930,117 filed on June 28, 2013, entitled "Hot Melt  
and Pressure-Sensitive Adhesives That Include Highly-Plasticized Cellulose Esters  
and Methods and Articles Relating Thereto," the entire disclosures of which is  
incorporated herein by reference.

20                   **BACKGROUND**

**[0002]** The exemplary embodiments described herein relate to hot melt  
and pressure-sensitive adhesives that comprise highly-plasticized cellulose  
esters, and methods and articles relating thereto.

**[0003]** As used herein, the term "hot melt adhesive" refers to an  
25 adhesive composition that is melted by heat, which at room temperature may be  
a solid, self-adhering solid, or a viscous liquid. Hot melt adhesives are useful in  
several applications from arts and crafts (*e.g.*, hot glue sticks) to consumer  
products (*e.g.*, cigarette seam line adhesives) to packaging (*e.g.*, shipping box  
and cereal box adhesives). Some of the desired properties of hot melt adhesives  
30 include low-temperature flexibility, high adhesion strength, wettability, water-  
resistance, optical clarity, and the ability to accept a wide variety of  
modifications and additives. Further, the ability to tailor these and other  
properties of the hot melt adhesive would enhance the applicability of the hot  
melt adhesive across the plurality of applications thereof.

**[0004]** One of the most common hot melt adhesives is an ethylene vinyl acetate copolymer-based adhesive ("EVA-based adhesive"), which is often a mixture of an ethylene vinyl acetate copolymer ("EVA"), a wax, and optionally a tackifier. EVA-based adhesives provide many of the desirable properties described above, including tailorability based on the vinyl acetate content of the EVA. However, because the components of EVA-based adhesives are derived from petroleum precursors, a recent push has been made to develop environmentally-friendly hot melt adhesives derived from renewable resources.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0005]** The following figures are included to illustrate certain aspects of the embodiments presented herein, 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.

**[0006] Figures 1A-E** provide illustrations of nonlimiting examples of article configurations according to at least some embodiments described herein.

**[0007] Figure 2** provides the melt temperature as a function of intrinsic viscosity for highly-plasticized cellulose ester hot melt adhesives according to at least some embodiments described herein.

### **DETAILED DESCRIPTION**

**[0008]** The exemplary embodiments described herein relate to hot melt and pressure-sensitive adhesives that comprise highly-plasticized cellulose esters, and methods and articles relating thereto.

**[0009]** In some embodiments, highly-plasticized cellulose ester adhesives ("HPCE-adhesives") include plasticizers and cellulose esters.

**[0010]** Further, it has been discovered that HPCE-adhesives may be hot melt adhesives, pressure sensitive hot melt adhesives, and pressure sensitive adhesives, which expands the applicability of these bio-derived and degradable adhesive compositions. As used herein, the term "bio-derived" refers to a compound or portion thereof originating from a biological source or produced via a biological reaction. The bio-derived portion of the adhesive compositions described herein refers to the mass percent that is bio-derived. For example, a cellulose acetate produced from cellulose and a petroleum-derived acetic acid

would be less than 100% bio-derived. Whereas a 100% bio-derived cellulose acetate may be produced, for example, from acylation of cellulose with a bio-derived acid chloride (*e.g.*, produced by reacting thionyl chloride with bio-derived acetic acid, which may be produced via a number of methods including those involving microbial fermentation). In some instances, the HPCE-adhesives described herein may be 100% bio-derived with the use of bio-derived plasticizers and cellulose derivatives that utilize bio-derived acids in the derivatization process.

**[0011]** The HPCE-adhesives described herein may, in some embodiments, have several advantageous properties like optical clarity, pressure-sensitive adhesive properties, high adhesion strength, and any combination thereof. For example, the adhesive strength of at least some embodiments of the HPCE-adhesives being comparable to that of EVA-based adhesives was unexpected. The HPCE-adhesives described herein have a plurality of avenues through which the properties of the adhesive compositions (*e.g.*, tackiness, clarity, melt flow index, adhesive shear strength, degradability, and the like) can be tailored. Examples of avenues for manipulating adhesive properties may include cellulose derivative composition, cellulose derivative molecular weight, cellulose derivative degree of substitution, plasticizer composition, plasticizer concentration, and the composition and concentrations of optional additives like tackifiers, fillers, antioxidants, and aromas. For example, the HPCE-adhesives described herein may be designed to be degradable over relatively short periods of time (*e.g.*, weeks) to longer periods of time (*e.g.*, months to years) by manipulating the cellulose derivative composition, cellulose derivative molecular weight, plasticizer composition (*e.g.*, the volatility of the plasticizer), and the like. This may advantageously allow for articles and products that as a whole are more biodegradable than such articles and products utilizing other adhesives like urethanes and EVA-based adhesives.

**[0012]** In addition to being derived from renewable sources, the HPCE-adhesives described herein may be designed to be degradable over relatively short periods of time (*e.g.*, weeks) to longer periods of time (*e.g.*, months to years). Further, the HPCE-adhesives described herein may, in some instances, be recyclable via repulping. This may advantageously enable articles and products that as a whole are more biodegradable and recyclable than such

articles and products utilizing other hot melt adhesives like EVA-based adhesives.

**[0013]** Further, the HPCE-adhesives described herein may be food-grade and utilize cellulose esters and plasticizers (*e.g.*, cellulose diacetate and triacetin) that are approved for use in conjunction with food applications (*e.g.*, food packaging) and other applications with an increased risk for oral ingestion by consumer (*e.g.*, cigarette adhesives). As used herein, the term "food-grade" refers to a material that has been approved for contacting (directly or indirectly) food, which may be classified as based on the material's conformity to the requirements of the United States Pharmacopeia ("USP-grade"), the National Formulary ("NF-grade"), and/or the Food Chemicals Codex ("FCC-grade").

**[0014]** Additionally, in some embodiments, the HPCE-adhesives described herein may be suitable for high-speed coating/adhering methods because there is little to no dry time associated with their application and the melt flow properties of the adhesive composition can be tailored for fast coating processes. This is especially advantageous for laminate coatings and label application. By contrast, emulsion formulations that are used for adhesives and laminate coatings require drying through hundreds of feet of ovens to achieve the desired final product. At least some of the HPCE-adhesives described herein suitable for similar applications, on the other hand, need only cool to achieve a comparable final product. In some instances, a brief heating may be performed to drive off plasticizer, but because the HPCE-adhesives described herein may include volatile to semi-volatile plasticizers, the time and distance associated with heating would be significantly less. Reducing the time and distance associated with heating would advantageously reduce energy costs and machinery footprint.

**[0015]** Further, relative to recycling, the components of at least some of the the HPCE-adhesives described herein are compatible with the current plastic recycling technologies (which allows for a 100% recyclable bottle) and glass bottle washing technologies (which allows for labels to be removed without additional steps and cost). Other technologies that provide this benefit includes some emulsion adhesives, however, as described above, their application when producing labeled bottles is more energy and labor intensive. Therefore, the adhesive compositions described herein provide for a more environmentally

friendly adhesive from production (*i.e.*, from natural products) to application to recycling.

**[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.

#### **I. HPCE-Adhesives and Methods Relating Thereto**

**[0017]** In some embodiments, the HPCE-adhesives described herein may comprise cellulose esters and plasticizers, wherein the plasticizers are present in an amount of about 15% or greater by weight of the HPCE-adhesive. In some embodiments, the plasticizers may be present in HPCE-adhesives described herein in an amount ranging from a lower limit of about 15%, 30%, 40%, 50%, or 60% by weight of the HPCE-adhesive to an upper limit of about 80%, 70%, 60%, or 50% by weight of the HPCE-adhesive, wherein the amount may range from any lower limit to any upper limit and encompass any subset therebetween, *e.g.*, about 20% to about 65%.

**[0018]** Cellulose esters suitable for use in conjunction with HPCE-adhesives described herein may, in some embodiments, have ester substituents that include, but are not limited to, C<sub>1</sub>-C<sub>20</sub> aliphatic esters (*e.g.*, acetate, propionate, or butyrate), functional C<sub>1</sub>-C<sub>20</sub> aliphatic esters (*e.g.*, succinate, glutarate, maleate) aromatic esters (*e.g.*, benzoate or phthalate), substituted aromatic esters, and the like, any derivative thereof, and any combination thereof.

**[0019]** Cellulose esters suitable for use in conjunction with HPCE-adhesives described herein may, in some embodiments, have a degree of substitution of the ester substituent ranging from a lower limit of about 0.5, 1.2, or 2 to an upper limit of less than about 3, about 2.9, 2.7, or 2.5, and wherein the degree of substitution may range from any lower limit to any upper limit and encompass any subset therebetween.

**[0020]** Cellulose esters suitable for use in conjunction with HPCE-adhesives described herein may, in some embodiments, have a molecular weight ranging from a lower limit of about 10,000, 15,000, 25,000, 50,000, or 85,000 to an upper limit of about 125,000, 100,000, or 85,000, and wherein the

molecular weight may range from any lower limit to any upper limit and encompass any subset therebetween. As used herein, the term "molecular weight" refers to a polystyrene equivalent number average molecular weight ( $M_n$ ).

5           **[0021]** Cellulose esters suitable for use in conjunction with HPCE-adhesives described herein may be derived from any suitable cellulosic source. Suitable cellulosic sources may, in some embodiments, include, but are not limited to, softwoods, hardwoods, cotton linters, switchgrass, bamboo, bagasse, industrial hemp, willow, poplar, perennial grasses (e.g., grasses of the  
10 *Miscanthus* family), bacterial cellulose, seed hulls (e.g., soy beans), and the like, and any combination thereof. Further, it has been discovered that the clarity of HPCE-adhesives described herein may be minimally to not impacted by the cellulosic source from which the cellulose esters are derived, which is unexpected because some existing cellulose ester products that do not have  
15 adhesive properties require high quality, expensive cellulosic sources (e.g., hardwoods with low hemicellulose content) to achieve high clarity.

**[0022]** Plasticizers suitable for use in conjunction with the embodiments described herein may, in some embodiments, include, but are not limited to, triacetin, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl  
20 phosphate, triethyl citrate, acetyl trimethyl citrate, acetyl triethyl citrate, acetyl tributyl citrate, tributyl-o-acetyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate, di-2-methoxyethyl phthalate, di-octyl phthalate (and isomers), dibutyl tartrate, ethyl o-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, n-  
25 ethyltoluenesulfonamide, o-cresyl p-toluenesulfonate, aromatic diol, substituted aromatic diols, aromatic ethers, tripropionin, polycaprolactone, glycerin, glycerin esters, diacetin, polyethylene glycol, polyethylene glycol esters, polyethylene glycol diesters, di-2-ethylhexyl polyethylene glycol ester, glycerol esters, diethylene glycol, polypropylene glycol, polyglycoldiglycidyl ethers, dimethyl  
30 sulfoxide, *N*-methyl pyrrolidinone, propylene carbonate,  $C_1$ - $C_{20}$  dicarboxylic acid esters, dimethyl adipate (and other dialkyl esters), di-butyl maleate, di-octyl maleate, resorcinol monoacetate, catechol, catechol esters, phenols, epoxidized soy bean oil, castor oil, linseed oil, epoxidized linseed oil, other vegetable oils, other seed oils, difunctional glycidyl ether based on polyethylene glycol, alkyl  
35 lactones (e.g.,  $\gamma$ -valerolactone), alkylphosphate esters, aryl phosphate esters,

phospholipids, aromas (including some described herein, *e.g.*, eugenol, cinnamyl alcohol, camphor, methoxy hydroxy acetophenone (acetovanillone), vanillin, and ethylvanillin), 2-phenoxyethanol, glycol ethers, glycol esters, polyglycol ethers, polyglycol esters, ethylene glycol ethers, propylene glycol ethers, ethylene glycol esters (e.g. ethylene glycol diacetate), propylene glycol esters, polyethylene glycol esters, polypropylene glycol esters, and the like, any derivative thereof, and any combination thereof.

**[0023]** In some embodiments, plasticizers may be food-grade plasticizers. Examples of food-grade plasticizers may, in some embodiments, include, but are not limited to, triacetin, diacetin, tripropionin, trimethyl citrate, triethyl citrate, tributyl citrate, eugenol, cinnamyl alcohol, alkyl lactones (*e.g.*,  $\gamma$ -valerolactone), methoxy hydroxy acetophenone (acetovanillone), vanillin, ethylvanillin, polyethylene glycols, 2-phenoxyethanol, glycol ethers, ethylene glycol ethers, propylene glycol ethers, and the like, and any combination thereof.

**[0024]** In some embodiments, the HPCE-adhesives described herein may further comprise additives. Additives suitable for use in conjunction with the HPCE-adhesives described herein may include, but are not limited to, tackifiers, crosslinkers, insolubilizers, starches, fillers, thickeners, rigid compounds, water-resistance additives, flame retardants, lubricants, softening agents, antibacterial agents, antifungal and/or antimicrobial agents, pigments, dyes, antioxidants, UV-stabilizers, resins, rosins, waxes, flowing agents, viscosity modifiers, aromas, and the like, and any combination thereof.

**[0025]** In some embodiments, the additives may be present in HPCE-adhesives described herein in an amount ranging from a lower limit of about 0.1%, 1%, 5%, or 10% by weight of the HPCE-adhesive to an upper limit of about 75%, 60%, 45%, or 40% by weight of the HPCE-adhesive, wherein the amount may range from any lower limit to any upper limit and encompass any subset therebetween.

**[0026]** Tackifiers may, in some embodiments, increase the adhesive properties of the HPCE-adhesives described herein. Tackifiers suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, methylcellulose, ethylcellulose, hydroxyethylcellulose, carboxy methylcellulose, carboxy ethylcellulose, amides, diamines, polyesters, polycarbonates, silyl-modified polyamide compounds,

polycarbamates, urethanes, natural resins, natural rosins, shellacs, acrylic acid polymers, 2-ethylhexylacrylate, acrylic acid ester polymers, acrylic acid derivative polymers, acrylic acid homopolymers, an acrylic acid ester homopolymers, poly(methyl acrylate), poly(butyl acrylate), poly(2-ethylhexyl acrylate), acrylic acid ester co-polymers, methacrylic acid derivative polymers, methacrylic acid homopolymers, methacrylic acid ester homopolymers, poly(methyl methacrylate), poly(butyl methacrylate), poly(2-ethylhexyl methacrylate), acrylamido-methyl-propane sulfonate polymers, acrylamido-methyl-propane sulfonate derivative polymers, acrylamido-methyl-propane sulfonate co-polymers, acrylic acid/acrylamido-methyl-propane sulfonate co-polymers, benzyl coco di-(hydroxyethyl) quaternary amines, p-T-amyl-phenols condensed with formaldehyde, dialkyl amino alkyl (meth)acrylates, acrylamides, N-(dialkyl amino alkyl) acrylamide, methacrylamides, hydroxy alkyl (meth)acrylates, methacrylic acids, acrylic acids, hydroxyethyl acrylates, ethylene vinyl acetate, vinyl acetate ethylene polymers, and the like, any derivative thereof, and any combination thereof.

**[0027]** In some embodiments, tackifiers suitable for use in conjunction with the HPCE-adhesives described herein may be food-grade tackifiers. Examples of food-grade tackifiers may, in some embodiments, include, but are not limited to, methylcellulose, ethylcellulose, hydroxyethylcellulose, carboxy methylcellulose, carboxy ethylcellulose, natural resins, natural rosins, and the like, and any combination thereof.

**[0028]** Crosslinkers may, in some embodiments, increase the adhesive properties and/or increase water-resistance of the HPCE-adhesives described herein. Crosslinkers suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, zirconium salts, boric acid, borate salts, ammonium zirconium carbonate, potassium zirconium carbonate, metal chelates (e.g., zirconium chelates, titanium chelates, or aluminum chelates), formaldehyde crosslinkers, polyamide epichlorohydrin resin, crosslinkers containing N-methylol groups and/or etherified N-methylol groups (e.g., ARKOFIX® (an ultra-low formaldehyde crosslinking agent, available from Clariant)), glyoxal, urea glyoxal adduct crosslinkers, urea formaldehyde adduct crosslinkers, melamine formaldehyde, 4,5-dihydroxy-N,N'-dimethylolethyleneurea, hydroxymethylated cyclic ethyleneureas, hydroxymethylated cyclic propyleneureas, hydroxymethylated

bicyclic glyoxal diurea, hydroxymethylated bicyclic malonaldehyde diureas, dialdehydes, protected dialdehydes, bisulfite protected aldehydes, isocyanates, blocked isocyanates, dimethoxytetrahydrofuran, dicarboxylic acids, epoxides, diglycidyl ether, hydroxymethyl-substituted imidazolidinone, 1,3-dimethylol-4,5-  
5 dihydroxyimidazolidinone, hydroxymethyl-substituted pyrimidinones, hydroxymethyl-substituted triazinones, epoxides, epoxidized natural oils (*e.g.*, epoxidized soy oil or epoxidized linseed oil), oxidized starch, oxidized polysaccharides, oxidized hemicellulose, and the like, any derivative thereof, and any combination thereof. One skilled in the art with the benefit of this disclosure  
10 should understand that formaldehyde crosslinkers should be excluded from use in conjunction with formaldehyde-free HPCE-adhesives, and limited in substantially formaldehyde-free HPCE-adhesives (*i.e.*, the adhesive comprising less than 0.01% formaldehyde by weight of the adhesive). In some  
15 embodiments, crosslinkers suitable for use in conjunction with the HPCE-adhesives described herein may be food-grade crosslinkers.

**[0029]** Water-resistance additives may, in some embodiments, increase the water-resistance properties of the HPCE-adhesives described herein, which may consequently yield articles capable of maintaining their mechanical properties in environments with higher water concentrations, *e.g.*, humid  
20 environments. Water-resistance additives suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, waxes, polyolefins, insolublizers, ethylene vinyl acetate, vinyl acetate ethylene polymers, octenyl succinyls, alkenyl succinyls, and the like, and any combination thereof.

**[0030]** In some embodiments, water-resistance additives suitable for use in conjunction with the HPCE-adhesives described herein may be food-grade water-resistance additives. Examples of food-grade water-resistance additives may, in some embodiments, include, but are not limited to, waxes, polyolefins, ethylene vinyl acetate, vinyl acetate ethylene polymers, and the like, and any  
30 combination thereof.

**[0031]** Fillers may, in some embodiments, increase the rigidity of the HPCE-adhesives described herein, which may consequently increase the mechanical rigidity of an article produced therewith. Fillers suitable for use in conjunction with the HPCE-adhesives described herein may, in some  
35 embodiments, include, but are not limited to, coconut shell flour, walnut shell

flour, wood flour, wheat flour, soybean flour, gums, starches, protein materials, calcium carbonate, talc, zeolite, clay, rigid compounds (e.g. lignin), thickeners, and the like, and any combination thereof.

5       **[0032]** In some embodiments, fillers suitable for use in conjunction with the HPCE-adhesives described herein may be food-grade fillers. Examples of food-grade fillers may, in some embodiments, include, but are not limited to, coconut shell flour, walnut shell flour, wood flour, wheat flour, soybean flour, gums, starches, protein materials, calcium carbonate, and the like, and any combination thereof.

10       **[0033]** Flame retardants suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, silica, metal oxides, phosphates, catechol phosphates, resorcinol phosphates, aromatic polyhalides, borates, inorganic hydrates, and the like, and any combination thereof.

15       **[0034]** Antifungal and/or antimicrobial agents suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, polyene antifungals (e.g., natamycin, rimocidin, filipin, nystatin, amphotericin B, candicin, and hamycin), imidazole antifungals such as miconazole (available as MICATIN® from  
20 WellSpring Pharmaceutical Corporation), ketoconazole (commercially available as NIZORAL® from McNeil consumer Healthcare), clotrimazole (commercially available as LOTRAMIN® and LOTRAMIN AF® available from Merck and CANESTEN® available from Bayer), econazole, omoconazole, bifonazole, butoconazole, fenticonazole, isoconazole, oxiconazole, sertaconazole  
25 (commercially available as ERTACZO® from OrthoDermatologics), sulconazole, and tioconazole; triazole antifungals such as fluconazole, itraconazole, isavuconazole, ravuconazole, posaconazole, voriconazole, terconazole, and albaconazole), thiazole antifungals (e.g., abafungin), allylamine antifungals (e.g., terbinafine (commercially available as LAMISIL® from Novartis Consumer  
30 Health, Inc.), naftifine (commercially available as NAFTIN® available from Merz Pharmaceuticals), and butenafine (commercially available as LOTRAMIN ULTRA® from Merck), echinocandin antifungals (e.g., anidulafungin, caspofungin, and micafungin), polygodial, benzoic acid, ciclopirox, tolnaftate (e.g., commercially available as TINACTIN® from MDS Consumer Care, Inc.), undecylenic acid,

flucytosine, 5-fluorocytosine, griseofulvin, haloprogin, octynoic acid, and any combination thereof.

**[0035]** Pigments and dyes suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, plant dyes, vegetable dyes, titanium dioxide, silicon dioxide, tartrazine, E102, phthalocyanine blue, phthalocyanine green, quinacridones, perylene tetracarboxylic acid di-imides, dioxazines, perinones disazo pigments, anthraquinone pigments, carbon black, metal powders, iron oxide, ultramarine, calcium carbonate, kaolin clay, aluminum hydroxide, barium sulfate, zinc oxide, aluminum oxide, CARTASOL<sup>®</sup> dyes (cationic dyes, available from Clariant Services) in liquid and/or granular form (*e.g.*, CARTASOL<sup>®</sup> Brilliant Yellow K-6G liquid, CARTASOL<sup>®</sup> Yellow K-4GL liquid, CARTASOL<sup>®</sup> Yellow K-GL liquid, CARTASOL<sup>®</sup> Orange K-3GL liquid, CARTASOL<sup>®</sup> Scarlet K-2GL liquid, CARTASOL<sup>®</sup> Red K-3BN liquid, CARTASOL<sup>®</sup> Blue K-5R liquid, CARTASOL<sup>®</sup> Blue K-RL liquid, CARTASOL<sup>®</sup> Turquoise K-RL liquid/granules, CARTASOL<sup>®</sup> Brown K-BL liquid), FASTUSOL<sup>®</sup> dyes (an auxochrome, available from BASF) (*e.g.*, Yellow 3GL, Fastusol C Blue 74L), and the like, any derivative thereof, and any combination thereof.

**[0036]** In some embodiments, pigments and dyes suitable for use in conjunction with the HPCE-adhesives described herein may be food-grade pigments and dyes. Examples of food-grade pigments and dyes may, in some embodiments, include, but are not limited to, plant dyes, vegetable dyes, titanium dioxide, and the like, and any combination thereof.

**[0037]** Antioxidants may, in some embodiments, mitigate oxidation and/or chemical degradation of the HPCE-adhesives described herein during storage, transportation, and/or implementation. Antioxidants suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, anthocyanin, ascorbic acid, glutathione, lipoic acid, uric acid, resveratrol, flavonoids, carotenes (*e.g.*, beta-carotene), carotenoids, tocopherols (*e.g.*, alpha-tocopherol, beta-tocopherol, gamma-tocopherol, and delta-tocopherol), tocotrienols, tocopherol esters (*e.g.*, tocopherol acetate), ubiquinol, gallic acids, melatonin, secondary aromatic amines, benzofuranones, hindered phenols, polyphenols, hindered amines, organophosphorus compounds, thioesters, benzoates, lactones, hydroxylamines, and the like, and any combination thereof.

**[0038]** In some embodiments, antioxidants suitable for use in conjunction with the HPCE-adhesives described herein may be food-grade antioxidants. Examples of food-grade antioxidants may, in some embodiments, include, but are not limited to, ascorbic acid, vitamin A, tocopherols, tocopherol esters, beta-carotene, flavonoids, and the like, and any combination thereof.

**[0039]** Viscosity modifiers may, in some embodiments, be advantageous in modifying the melt flow index of the HPCE-adhesives described herein and/or modify the viscosity of HPCE-adhesives described herein that are in a paste or putty form. Viscosity modifiers suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, polyethylene glycols, polypropylene glycols, and the like, and any combination thereof, which, in some embodiments, may be a food-grade viscosity modifier.

**[0040]** Aromas suitable for use in conjunction with the HPCE-adhesives described herein may, in some embodiments, include, but are not limited to, spices, spice extracts, herb extracts, essential oils, smelling salts, volatile organic compounds, volatile small molecules, methyl formate, methyl acetate, methyl butyrate, ethyl acetate, ethyl butyrate, isoamyl acetate, pentyl butyrate, pentyl pentanoate, octyl acetate, myrcene, geraniol, nerol, citral, citronellal, citronellol, linalool, nerolidol, limonene, camphor, terpineol, alpha-ionone, thujone, benzaldehyde, eugenol, isoeugenol, cinnamaldehyde, ethyl maltol, vanilla, vanillin, cinnamyl alcohol, anisole, anethole, estragole, thymol, furaneol, methanol, rosemary, lavender, citrus, freesia, apricot blossoms, greens, peach, jasmine, rosewood, pine, thyme, oakmoss, musk, vetiver, myrrh, blackcurrant, bergamot, grapefruit, acacia, passiflora, sandalwood, tonka bean, mandarin, neroli, violet leaves, gardenia, red fruits, ylang-ylang, acacia farnesiana, mimosa, tonka bean, woods, ambergris, daffodil, hyacinth, narcissus, black currant bud, iris, raspberry, lily of the valley, sandalwood, vetiver, cedarwood, neroli, bergamot, strawberry, carnation, oregano, honey, civet, heliotrope, caramel, coumarin, patchouli, dewberry, helonial, bergamot, hyacinth, coriander, pimento berry, labdanum, cassie, bergamot, aldehydes, orchid, amber, benzoin, orris, tuberose, palmarosa, cinnamon, nutmeg, moss, styrax, pineapple, bergamot, foxglove, tulip, wisteria, clematis, ambergris, gums, resins, civet, peach, plum, castoreum, civet, myrrh, geranium, rose violet, jonquil, spicy carnation, galbanum, hyacinth, petitgrain, iris, hyacinth,

honeysuckle, pepper, raspberry, benzoin, mango, coconut, hesperides, castoreum, osmanthus, mousse de chene, nectarine, mint, anise, cinnamon, orris, apricot, plumeria, marigold, rose otto, narcissus, tolu balsam, frankincense, amber, orange blossom, bourbon vetiver, opopanax, white musk, papaya, sugar candy, jackfruit, honeydew, lotus blossom, muguet, mulberry, absinthe, ginger, juniper berries, spicebush, peony, violet, lemon, lime, hibiscus, white rum, basil, lavender, balsamics, fo-ti-tieng, osmanthus, karo karunde, white orchid, calla lilies, white rose, rhubrum lily, tagetes, ambergris, ivy, grass, seringa, spearmint, clary sage, cottonwood, grapes, brimbelle, lotus, cyclamen, orchid, glycine, tiare flower, ginger lily, green osmanthus, passion flower, blue rose, bay rum, cassie, African tagetes, Anatolian rose, Auvergne narcissus, British broom, British broom chocolate, Bulgarian rose, Chinese patchouli, Chinese gardenia, Calabrian mandarin, Comoros Island tuberose, Ceylonese cardamom, Caribbean passion fruit, Damascena rose, Georgia peach, white Madonna lily, Egyptian jasmine, Egyptian marigold, Ethiopian civet, Farnesian cassie, Florentine iris, French jasmine, French jonquil, French hyacinth, Guinea oranges, Guyana wacapua, Grasse petitgrain, Grasse rose, Grasse tuberose, Haitian vetiver, Hawaiian pineapple, Israeli basil, Indian sandalwood, Indian Ocean vanilla, Italian bergamot, Italian iris, Jamaican pepper, May rose, Madagascar ylang-ylang, Madagascar vanilla, Moroccan jasmine, Moroccan rose, Moroccan oakmoss, Moroccan orange blossom, Mysore sandalwood, Oriental rose, Russian leather, Russian coriander, Sicilian mandarin, South African marigold, South American tonka bean, Singapore patchouli, Spanish orange blossom, Sicilian lime, Reunion Island vetiver, Turkish rose, Thai benzoin, Tunisian orange blossom, Yugoslavian oakmoss, Virginian cedarwood, Utah yarrow, West Indian rosewood, and the like, and any combination thereof.

**[0041]** In some embodiments, HPCE-adhesives described herein may be food-grade HPCE-adhesives that comprise food-grade cellulose esters and food-grade plasticizers and optionally further comprise food-grade additives.

**[0042]** In some embodiments, the HPCE-adhesives described herein may comprise cellulose esters (*e.g.*, having an ester substituent described herein, a degree of substitution described herein, a molecular weight described herein, from a cellulosic source described herein, and a combination thereof), plasticizers (*e.g.*, one or more specific plasticizers describe herein, food-grade plasticizers described herein, aroma plasticizers described herein, and a

combination thereof), and optionally additives described herein (e.g., one or more specific additives describe herein, at amounts described herein, and a combination thereof), wherein the plasticizers are present in an amount of about 15% or greater by weight of the HPCE-adhesive (including specific ranges described herein or subsets thereof).

**[0043]** The physical and chemical properties of cellulose esters and plasticizers described herein may be tailored to achieve the desired characteristics of the HPCE-adhesives. Examples of such properties may include, but are not limited to, the composition of the ester substituents of the cellulose esters, the degree of substitution of the ester substituent of the cellulose esters, the molecular weight of the cellulose esters, the composition of the plasticizers, and the like, and any combination thereof. Further, the amount of plasticizer in the HPCE-adhesives described herein may be tailored to achieve the desired characteristics of the HPCE-adhesives.

**[0044]** The characteristics of the HPCE-adhesives described herein that can be tailored may include, but are not limited to, flow onset point, glass transition temperature, melt flow index, adhesive strength, degradability, clarity, and the like, and any combination thereof.

**[0045]** Tailoring the flow onset of the HPCE-adhesives described herein may enable use of the HPCE-adhesives over a wide variety of applications. For example, lower flow onset points may be useful in pressure-sensitive HPCE-adhesives, while higher flow onset points may be useful in thermal laminating sheets, each application of which is discussed in more detail herein. In some embodiments, tailoring the flow onset point of the HPCE-adhesives described herein may be achieved by, *inter alia*, changing the plasticizer concentration (e.g., decreasing the concentration to increase the flow onset point), changing plasticizer composition, changing the degree of substitution or composition of the cellulose ester, and changing the molecular weight of the cellulose ester (e.g., decreasing molecular weight to decrease the flow onset point).

**[0046]** In some embodiments, the HPCE-adhesives described herein may have a flow onset point of about 220°C or less. In some embodiments, the HPCE-adhesives described herein may have a flow onset point ranging from a lower limit of about 50°C, 70°C, 80°C, 100°C, 110°C, 130°C, or 150°C to an upper limit of about 220°C, 200°C, 170°C, 150°C, 130°C, or 110°C, and wherein the flow onset point may range from any lower limit to any upper limit

and encompass any subset therebetween. In some embodiments, the HPCE-adhesives described herein may have no flow onset point.

**[0047]** In some embodiments, the HPCE-adhesives described herein may exhibit visual flow under a gravitation load (*i.e.*, no additional load) at a temperature ranging from a lower limit of about 75°C, 100°C, 125°C, or 150°C to an upper limit of about 220°C, 200°C, 175°C, or 150°C, and wherein the flow onset point may range from any lower limit to any upper limit and encompass any subset therebetween.

**[0048]** Tailoring the glass transition temperature of the HPCE-adhesives described herein may alter the physical characteristics of the HPCE-adhesive at ambient conditions, *e.g.*, stiff or flexible, brittle or pliable, smooth or tacky, and the like, and any combination thereof. As used herein, the term "tacky" refers to a composition that is at least sticky to the touch at room temperature. For example, HPCE-adhesives having no detectable glass transition temperature may be more tacky and flexible than those having a glass transition temperature. As used herein, the term "no detectable glass transition temperature" and derivatives thereof refers to material having no detectable heat flow event (as measured by DSC), which may be caused by the plasticized material having no glass transition temperature or the heat flow broadening to an extent that the glass transition temperature is not detectable.

**[0049]** In another example, HPCE-adhesives having higher glass transition temperatures may be more stiff and/or brittle than those having moderate to low glass transition temperatures. In some embodiments, tailoring the glass transition temperature of the HPCE-adhesives described herein may be achieved by, *inter alia*, changing the plasticizer concentration (*e.g.*, increasing the concentration to decrease the glass transition temperature), changing the composition of the plasticizer, changing the molecular weight, and changing the degree of substitution of the cellulose ester (*e.g.*, in some instances, increasing the degree of substitution to decrease the glass transition temperature).

**[0050]** In some embodiments, the HPCE-adhesives described herein may have a glass transition temperature of about 190°C or less. In some embodiments, the HPCE-adhesives described herein may have a glass transition temperature ranging from a lower limit of not measurable, about -61°C, -55°C, 10°C, 75°C, 120°C, 130°C, or 150°C to an upper limit of about 190°C, 175°C, or 150°C, and wherein the glass transition temperature may range from any

lower limit to any upper limit and encompass any subset therebetween. The glass transition temperature of an HPCE-adhesive can be measured by either differential scanning calorimetry or rheology. One skilled in the art with the benefit of this disclosure would understand that the glass transition temperature value may fall outside the preferred range described herein for different plasticizers used to produce HPCE-adhesive samples. Accordingly, within the scope of the embodiments described herein, the glass transition can be manipulated based on the composition and concentration of additives included in the HPCE-adhesives.

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10       **[0051]** Tailoring the melt flow index of HPCE-adhesives described herein may enable the use of the HPCE-adhesives over a wide variety of applications. For example, lower melt flow index HPCE-adhesives may be useful in applications where shape is retained until heating (*e.g.*, window films, glue sticks, and pelletized HPCE-adhesives), while higher melt flow index HPCE-  
15 adhesives may be useful in applications where pliable or even spreadable HPCE-adhesives are desired (*e.g.*, for creating thin films for self-adhesive stamps and envelopes). In some embodiments, tailoring the melt flow index of the HPCE-adhesives described herein may be achieved by, *inter alia*, changing the plasticizer composition, changing the plasticizer concentration (*e.g.*, increasing the concentration to decrease the melt flow index), changing the molecular  
20 weight of the cellulose ester (*e.g.*, decreasing molecular weight to decrease the melt flow index), and changing the composition and/or concentration of additives (*e.g.*, increasing crosslinker concentration to increase the melt flow index).

25       **[0052]** In some embodiments, the HPCE-adhesives described herein may have a melt flow index ranging from a lower limit of about 25 g/10 min, 29 g/10 min, 35 g/10 min, or 40 g/10 min (at 130°C/2.16 kg) to an upper limit of about 86 g/10 min, 80 g/10 min, 70 g/10 min, 60 g/10 min, 50 g/10 min, or 40 g/10 min (at 125°C/500 g), and wherein the melt flow index may range from  
30 any lower limit to any upper limit and encompass any subset therebetween. It should be noted that the melt flow index of the HPCE-adhesives described herein may fall outside the ranges described herein depending on, *inter alia*, the additive (*e.g.*, fillers, tackifiers, and the like), included in the adhesive. In some embodiments, the HPCE-adhesives described herein may have a melt flow index

that is higher than can be measured at 125°C/500 g (*e.g.*, greater than about 86 g/10 min at 125°C/500 g kg).

**[0053]** Tailoring the adhesive strength of HPCE-adhesives described herein may enable the use of the HPCE-adhesives over a wide variety of applications. For example, a lower adhesive strength may be useful in semi-permanent adhesive applications (*e.g.*, between substrates with lower mechanical properties as in sticky-notes or peelable protective coatings), while higher adhesive strength may be useful in permanent to semi-permanent applications between substrates with higher mechanical properties (*e.g.*, adhering the cardboard packaging of mailing boxes or laminating applications). Further, in some instances, higher adhesive strength may be useful in forming a film (or coating) on a substrate (*e.g.*, laminating paper, glass, metal, and the like such that the HPCE-adhesive forms a protective coating/laminate on the substrate). In some embodiments, tailoring the adhesive strength of the HPCE-adhesives described herein may be achieved by, *inter alia*, changing the plasticizer composition, changing the plasticizer concentration (*e.g.*, increasing the concentration to decrease the adhesive strength), changing the molecular weight of the cellulose ester (*e.g.*, decreasing molecular weight to decrease the adhesive strength), and changing the composition and/or concentration of additives (*e.g.*, increasing crosslinker and/or tackifier concentration to increase the adhesive strength).

**[0054]** In some embodiments, the HPCE-adhesives described herein may have an adhesive shear strength ranging from a lower limit of about 0.2 kgf, 0.5 kgf, 1 kgf, 2 kgf, or 4 kgf to an upper value limited by the force required to tear the substrate, and wherein the adhesive shear strength may range from any lower limit to any upper limit and encompass any subset therebetween. In some embodiments, the HPCE-adhesives described herein may have an adhesive shear strength ranging from a lower limit of about 0.2 kgf, 0.5 kgf, 1 kgf, 2 kgf, or 4 kgf to an upper limit of about 10 kgf, 8 kgf, 8 kgf, 6 kgf, or 4 kgf, and wherein the adhesive shear strength may range from any lower limit to any upper limit and encompass any subset therebetween. The adhesive shear strength of an HPCE-adhesive can be measured by testing lap shears by tension loading with a 1 kN load cell by a method that includes placing a specimen in the grips of the testing machine so that each end is in contact with the grip assemble, applying the loading immediately to the specimen at the rate of 800

lb force of shear per min, and continuing the load to failure. Substrate failure was observed above the strength of 8 kgf for paper substrates and a glue line less than 3 mm thick. This value may change depending on the substrate and size of the glue line.

5           **[0055]** Tailoring the degradability of HPCE-adhesives described herein may contribute to the overall degradability of products and articles comprising the HPCE-adhesives. In some embodiments, tailoring the degradability of the HPCE-adhesives described herein may be achieved by, *inter alia*, changing the plasticizer composition (*e.g.*, utilizing a plasticizer that biodegrades or dissipates  
10 into the environment at a higher rate to increase the degradability), changing the plasticizer concentration (*e.g.*, increasing the concentration to increase the degradability), changing the degree of substitution of the cellulose ester (*e.g.*, decreasing the degree of substitution to increase the degradability), and changing the composition and/or concentration of additives (*e.g.*, increasing  
15 antioxidant and/or stabilizer concentration to decrease the degradability).

**[0056]** In some embodiments, the HPCE-adhesives described herein may degrade to a greater extent than a cellulose diacetate material plasticized with 20% triacetin. In some embodiments, the HPCE-adhesives may degrade by about 5% or greater by weight than a cellulose diacetate material plasticized  
20 with 20% triacetin in a procedure performed according to EN13432 "Requirements for Packaging Recoverable through Composting and Biodegradation – Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging." In some embodiments, the HPCE-adhesives may degrade by an amount ranging from a lower limit of about 5%, 10%, or 15% to an upper limit  
25 of about 300%, 200%, 100%, 50%, 40%, or 30% by weight than a cellulose diacetate material plasticized with 20% triacetin in a procedure performed according to EN13432 "Requirements for Packaging Recoverable through Composting and Biodegradation – Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging," and wherein the degradation may range from  
30 any lower limit to any upper limit and encompass any subset therebetween. In some instances, the comparative rate of degradation may be outside the ranges described herein depending on the concentration of the plasticizer, the composition of the plasticizer, and the composition of the cellulose ester.

**[0057]** The clarity of the HPCE-adhesives described herein may be  
35 important in some applications, *e.g.*, high clarity (or low haze) may be necessary

when the HPCE-adhesives are used in conjunction with high clarity (or low haze) films (e.g., window tints or CLARIFOIL® packaging) or high clarity laminate films (e.g., laminate or protective coatings on substrates like paper, glass, metal, polymer films). In some embodiments, tailoring the clarity of the HPCE-adhesives described herein may be achieved by, *inter alia*, changing the plasticizer concentration (e.g., increasing the concentration to decrease the clarity/increasing the haze) and changing the composition and/or concentration of additives (e.g., increasing the filler concentration to decrease the clarity/increase the haze).

10           **[0058]** In some embodiments, the HPCE-adhesives described herein may have a haze ranging from a lower limit of about 2, 5, 7, 10, 15, 20, or 25 to an upper limit of about 45, 40, 35, 30, or 25, and wherein the haze may range from any lower limit to any upper limit and encompass any subset therebetween. The haze of an HPCE-adhesive can be measured with properly sized specimens having substantially plane-parallel surfaces (e.g., flat without wrinkling) free of dust, scratches, particles and a thickness of about 0.85mm using an UltraScan Pro from Hunter Lab with D65 Illuminant/10° observer. One skilled in the art with the benefit of this disclosure would understand that the haze value may fall outside the preferred ranges described herein for different thickness of an HPCE-adhesive sample. In some instances, the haze value may be significantly larger than the preferred ranges above (e.g., about 100) when additives like titanium dioxide are used in significant quantities to produce an opaque HPCE-adhesive. Additionally, pigments and dyes may affect the haze of the HPCE-adhesive. Accordingly, within the scope of the embodiments described herein, the haze may range from about 2 to about 100, including subsets therebetween, depending on the composition and concentration of additives included in the HPCE-adhesives.

20           **[0059]** Some embodiments described herein may involve producing HPCE-adhesives described herein, which may involve compounding cellulose esters described herein and plasticizers described herein at a suitable concentration, which may optionally involve heating (e.g., forming an HPCE-adhesive melt). Some embodiments may involve using the HPCE-adhesives immediately for an application (e.g., applying an HPCE-adhesive melt to a substrate so as to form a laminate surface on the substrate), while other  
35           embodiments may involve forming the HPCE-adhesives into a desired form.

Depending on their characteristics, the HPCE-adhesives described herein may be in a desired form, *e.g.*, a paste, a putty, pellets, or a molded shape (*e.g.*, a glue stick or an adhesive sheet). It should be noted that the term "sheet" should not be interpreted to be limited in thickness and encompasses films, layers, and the like.

**[0060]** In some embodiments, HPCE-adhesives in sheet form may comprise plasticizers in an amount ranging from a lower limit of about 30%, 35%, or 40% to an upper limit of about 70%, 55%, or 40% by weight of the HPCE-adhesive, and wherein the amount may range from any lower limit to any upper limit and encompasses any subset therebetween. In some embodiments, the HPCE-adhesives in sheet form may be smooth and substantially non-tacky at room temperature. In some embodiments, the HPCE-adhesives in sheet form may be heated to initiate adhesion to a surface(s) (*e.g.*, iron-on designs or laminating sheets disposed between one or two substrates). In some embodiments, the sheet may be disposed on one or between two release liners that are easily removed and serves to protect the sheet from adhering to another surface. For example, a release liner may be useful to mitigate an HPCE-adhesive in sheet form from adhering to itself when in a roll, especially an HPCE-adhesive in sheet form with higher plasticizer concentrations.

**[0061]** In some embodiments, HPCE-adhesives in sheet form may have a thickness ranging from a lower limit of about 15 microns, 20 microns, 30 microns, 50 microns, or 100 microns to an upper limit of about 1200 microns, 800 microns, 400 microns, 200 microns, or 100 microns, and wherein the thickness may range from any lower limit to any upper limit and encompasses any subset therebetween. While these thicknesses may be preferred, one skilled in the art, with the benefit of this disclosure, should understand that the thicknesses described are not limiting to the structure of a sheet described herein and thicknesses outside these ranges may be achieved.

**[0062]** HPCE-adhesives may be particularly advantageous as a laminate on a substrate in that the HPCE-adhesive may function as both the adhesive and the film (*i.e.*, not requiring a second adhesive to adhere to a surface and cooling to a laminate form). In some embodiments, HPCE-adhesives in laminate form on a substrate may be produced from an HPCE-adhesive melt comprising plasticizers in an amount ranging from a lower limit of about 30%, 35%, or 40% to an upper limit of about 75%, 60%, 50%, or 45% by weight of the HPCE-

adhesive melt, and wherein the amount may range from any lower limit to any upper limit and encompasses any subset therebetween. The plasticizer concentration in the melt and subsequent heating to drive off additional plasticizer may each be tuned to provide a HPCE-adhesive in laminate form with varying properties (*e.g.*, flexibility and rigidity).

**[0063]** In some embodiments, the HPCE-adhesives in laminate form on a substrate may be produced by applying an HPCE-adhesive melt to the substrate (*e.g.*, via melt casting); and allowing the HPCE-adhesive melt to cool, thereby yielding the laminate on the substrate. In some embodiments, the HPCE-adhesives in laminate form on a substrate may be smooth and substantially non-tacky at room temperature. In some embodiments, the HPCE-adhesive melt may comprise HPCE-adhesive that is tacky at room temperature and melted to increase the flow of the HPCE-adhesive. In some embodiments, the HPCE-adhesive melt may comprise HPCE-adhesive that is non-tacky at room temperature and melted to allow for the flow of the HPCE-adhesive.

**[0064]** In some instances, a higher plasticizer concentration may be preferred to increase the flow of the HPCE-adhesive melt at lower temperatures. A HPCE-adhesive melt with increased flow may yield laminates with more uniform thickness and allow for thinner laminates, which tend to be more flexible. More uniform thicknesses provide for higher quality articles and, in some instances, higher clarity laminates.

**[0065]** Some embodiments may further involve treating the laminate to reduce the concentration of plasticizer in the laminate. Treating may involve drying, heating, applying vacuum, and the like, and any combination thereof. Reducing the concentration of the plasticizer may increase the stiffness, clarity, and chemical resistance of the laminate.

**[0066]** Some embodiments may further involve treating the laminate to change surface chemistry of the laminate. For example, a caustic bath may be utilized to produce a laminate with a superhydrophilic surface.

**[0067]** In some embodiments, HPCE-adhesives in laminate form on a substrate may have a thickness ranging from a lower limit of about 15 microns, 20 microns, 30 microns, 50 microns, or 100 microns to an upper limit of about 500 microns, 400 microns, 300 microns, 200 microns, or 100 microns, and wherein the thickness may range from any lower limit to any upper limit and encompasses any subset therebetween. While these thicknesses may be

preferred, one skilled in the art, with the benefit of this disclosure, should understand that the thicknesses described are not limiting to the structure of a laminate described herein and thicknesses outside these ranges may be achieved.

5           **[0068]** In some embodiments, HPCE-adhesives in pellet form or molded shapes may comprise plasticizers in an amount ranging from a lower limit of about 30%, 35%, or 40% to an upper limit of about 65%, 55%, or 45% by weight of the HPCE-adhesive, and wherein the amount may range from any lower limit to any upper limit and encompasses any subset therebetween. In  
10 some embodiments, HPCE-adhesives in pellet form or molded shapes may be tacky. In some embodiments, the HPCE-adhesives in pellet form or molded shapes may be smooth and substantially non-tacky at room temperature. The suitable amount of plasticizer in the HPCE-adhesives to achieve pellet form or molded shapes may depend on, *inter alia*, the degree of substitution of the  
15 cellulose esters, the composition of the cellulose esters, the molecular weight of the cellulose esters, and the composition of the plasticizers.

**[0069]** In some embodiments, HPCE-adhesives in a paste or putty form may comprise plasticizers in an amount of about 40% or greater by weight of the HPCE-adhesive. In some embodiments, HPCE-adhesives in a paste or putty  
20 form may comprise plasticizers in an amount of about 40%, 45%, 50%, or 60% to an upper limit of about 80%, 75%, 70%, 65%, or 60% by weight of the HPCE-adhesive, and wherein the amount may range from any lower limit to any upper limit and encompasses any subset therebetween. In some embodiments, HPCE-adhesives in a paste or putty form may be tacky. In some embodiments,  
25 HPCE-adhesives in a paste or putty form may be smooth and substantially non-tacky. The suitable amount of plasticizer in the HPCE-adhesives to achieve a paste or putty form may depend on, *inter alia*, the degree of substitution of the cellulose esters, the composition of the cellulose esters, the molecular weight of the cellulose esters, and the composition of the plasticizers.

30           **[0070]** Forming the HPCE-adhesives into a desired form may, in some embodiments, be a consequence of compounding, *e.g.*, a paste or a putty. Forming the HPCE-adhesives into a desired form may, in some embodiments, involve methods like extruding, injection molding, blow molding, over molding, compression molding, casting, calendaring, near net shape molding, melt  
35 casting, and the like, any hybrid thereof, and any combination thereof.

[0071] In some embodiments, additives may be incorporated into HPCE-adhesives by inclusion in the compounding step. In some embodiments, additives may be incorporated into HPCE-adhesives after the compounding step by, for example, absorption. Absorption may, in some embodiments, be advantageous for the incorporation of volatile additives and/or small molecule additives, *e.g.*, some fragrances, aromas, dyes, and pigments.

## II. Articles Comprising HPCE-Adhesives and Methods Relating Thereto

[0072] In some embodiments, an article may comprise a first surface having an HPCE-adhesive described herein disposed thereon such that the HPCE-adhesive is exposed to the local environment (*e.g.*, a window tint, window film, light films, light filters, iron-on designs, laminates, substrate coatings, peelable layers or films, and the like).

[0073] In some embodiments, an article may comprise a first surface adhered to a second surface with an HPCE-adhesive described herein. In some embodiments, at least one of the surfaces may be chosen so as to be releasable (*e.g.*, a peelable layer) from the HPCE-adhesive, *e.g.*, an envelope with an adhesive between the paper and a release strip. In some embodiments, the first surface and the second surface may correspond to a first substrate and a second substrate, respectively. In some embodiments, the first surface and the second surface may correspond to a single substrate, *e.g.*, a single piece of paper rolled into a cylinder and adhered to itself. In some embodiments, articles described herein may be extended to three or more surfaces, including hundreds or thousands of surfaces (*e.g.*, adhesive book bindings), without departing from the spirit of this disclosure.

[0074] In some embodiments, the articles described herein may be designed with the first surface and the second surface adhered in any suitable configuration. Examples of suitable configurations may, in some embodiments, include, but are not limited to, those illustrated in **Figure 1**. **Figure 1A** illustrates a first substrate **101** and a second substrate **102** adhered together with an HPCE-adhesive **100a** in a stacked configuration. **Figure 1B** illustrates a first substrate **103** and a second substrate **104** adhered together with an HPCE-adhesive **100b** in a side-by-side configuration. **Figure 1C** illustrates a first substrate **105**, a second substrate **106**, and a third substrate **107** adhered together with an HPCE-adhesive **100c,100d** in a stacked configuration where

each substrate **105,106,107** has different sizes. **Figure 1D** illustrates a plurality of substrates in a hybrid configuration, wherein substrates **109,110,111** are each embedded at one end in an HPCE-adhesive **100e** which further adheres substrates **109,110,111** to substrate **108**. **Figure 1E** illustrates a substrate **112** rolled and adhered to itself at a seam with an HPCE-adhesive **100f**. 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.

10       **[0075]** Exemplary examples of articles described herein comprising HPCE-adhesives and at least one fibrous substrate (or surface) 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), 15 books, notebooks, magazines, sticky-notes, corrugated boxes, decorative boxes, paper bags, grocery bags, wrapping paper, wallpaper, paper honeycomb, emery boards, electric insulation paper, air filters, papier-mâché articles, carpets, dartboards, furniture or components thereof (*e.g.*, carpet and/or fabric coated headboards, chairs, and stools), picture frames, medical garments (*e.g.*, 20 disposable gowns and surgical masks), self-adhesive labels, self-adhesive stamps, self-adhesive window covering films (*e.g.*, protective films for glass or other substrates), self-adhesive window coverings (*e.g.*, decorative window stickers, window films, and window tinting), heat activated films, light films, light filters, iron-on designs, substrates with laminated surfaces (*e.g.*, laminated 25 paper, laminated business cards, a laminated paper board, or a protective covering directly laminated onto a surface like glass), a coated substrate, and the like.

30       **[0076]** Substrates or surfaces suitable for use in conjunction with articles described herein may, in some embodiments, include, but are not limited to, fibers, woven fiber substrates, nonwoven fiber substrates, foamed substrates, solid substrates, and the like, any hybrid thereof, and any combination thereof.

35       **[0077]** Substrates or surfaces suitable for use in conjunction with articles described herein may, in some embodiments, comprise materials that include, but are not limited to, ceramics, natural polymers, synthetic polymers,

metals, natural materials, carbons, and the like, and any combination thereof. Examples of ceramics may, in some embodiments, include, but are not limited to, glass, quartz, silica, alumina, zirconia, carbide ceramics, boride ceramics, nitride ceramics, and the like, and any combination thereof. Examples of natural  
5 polymers may, in some embodiments, include, but are not limited to, cellulose, and the like, any derivative thereof, and any combination thereof. Examples of synthetic polymers may, in some embodiments, include, but are not limited to, cellulose diacetate, cellulose triacetate, synthetic bamboo, rayon, acrylic, aramid, nylon, polyolefins, polyethylene, polypropylene (including biaxially  
10 oriented polypropylene substrates), polyethylene terephthalate, polyesters, polyamides, zylon, and the like, any derivative thereof, and any combination thereof. Examples of metals may, in some embodiments, include, but are not limited to, steel, stainless steel, aluminum, copper, and the like, any alloy thereof, and any combination thereof. Examples of natural materials may, in  
15 some embodiments, include, but are not limited to, wood, grass, animal hide, and the like, and any combination thereof. Examples of carbons may, in some embodiments, include, but are not limited to, carbon fibers, and the like, any derivative thereof, and any combination thereof.

**[0078]** Exemplary examples of substrates suitable for use in conjunction  
20 with the articles described herein may, in some embodiments, include, but are not limited to, paper, 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, CLARIFOIL® (cellulose diacetate film, available from Celanese Corporation), woven fabrics, continuous  
25 filament nonwoven fabrics, carded nonwoven fabrics, tow, fiber bundles, twill, twine, rope, carpet, carpet backing, leather, animal hide, insulation, 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,  
30 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), and the like,  
35 and any combination thereof.

**[0079]** By way of nonlimiting example, an article (*e.g.*, a cigarette paper or a paper towel roll) may comprise two surfaces of a single substrate (*e.g.*, a tipping paper or a cardboard) adhered together (*e.g.*, at a seam line) with HPCE-adhesives described herein.

5 **[0080]** By way of another nonlimiting example, an article (*e.g.*, a cardboard container for shipping or containing food) may comprise two surfaces adhered together with HPCE-adhesives described herein.

10 **[0081]** By way of yet another nonlimiting example, an article (*e.g.*, a food container) may comprise two surfaces (*e.g.*, a cardboard container and a cellulose diacetate film (like CLARIFOIL®)) adhered together with HPCE-adhesives described herein.

15 **[0082]** By way of another nonlimiting example, an article (*e.g.*, window tints or window coverings) may comprise a first surface (*e.g.*, a polyester film) with HPCE-adhesives described herein disposed thereon so as to allow for adherence to a second surface (*e.g.*, a glass surface or other similar transparent surface). In some embodiments, the article may comprise, in order, the first surface, the HPCE-adhesives, and a peelable layer that can be removed before adherence to the second surface. In some embodiments, the article may comprise HPCE-adhesives that are smooth and substantially non-tacky at room  
20 temperature such that a peelable layer is not required and the HPCE-adhesives may be exposed to air. In such embodiments, heat may be utilized in adhering the first surface to the second surface.

25 **[0083]** By way of yet another nonlimiting example, an article (*e.g.*, an iron-on design, heat activated film or laminated card) may comprise a surface or substrate (*e.g.*, paper, a fabric, or a polymer film) with HPCE-adhesives disposed thereon. In some instances, the article may then be adhered to another surface (*e.g.*, applying heat so as to adhere an iron-on design or heat activated film to another surface like a piece of clothing or other fabric). In some embodiments, the article may be formed by applying an HPCE-adhesive melt to the surface or  
30 substrate and allowing the HPCE-adhesive melt to cool so as to form a laminate on the surface or substrate.

35 **[0084]** Some embodiments described herein may involve adhering two or more surfaces together using HPCE-adhesives described herein. In some embodiments, adhering may involve heating the HPCE-adhesives and/or applying pressure to the HPCE-adhesives.

**[0085]** In some embodiments, adhering surfaces together may involve heating an HPCE-adhesive described herein to yield an adhesive melt; applying the adhesive melt to a first surface; and adhering a second surface to the first surface with the adhesive. While any of the HPCE-adhesives described herein  
5 may be suitable for producing adhesive melts, in some preferred embodiments, HPCE-adhesives used for producing adhesive melts may comprise plasticizers in an amount of about 15% to about 70% by weight of the adhesive composition.

**[0086]** In some embodiments wherein an HPCE-adhesive described herein is tacky, adhering surfaces together may involve applying the HPCE-  
10 adhesive to a first surface; and adhering a second surface to the first surface with the HPCE-adhesive.

**[0087]** In some embodiments, adhering surfaces together may involve disposing an adhesive sheet between a first surface and a second surface; and heating the adhesive sheet so as to adhere the first surface and the second  
15 surface together.

**[0088]** Embodiments disclosed herein include:

A. a method that includes providing an adhesive melt that comprises an adhesive that comprises a cellulose ester and a plasticizer, the plasticizer included in an amount of about 30% to about 75% by weight of the  
20 adhesive; applying the adhesive melt to a substrate; and allowing the adhesive melt to cool so as to yield a laminate on the substrate; and

B. a method that includes compounding at least a cellulose ester and a plasticizer to yield an adhesive melt, the plasticizer included in an amount of about 30% to about 75% by weight of the adhesive melt; applying the  
25 adhesive melt to a substrate; allowing the adhesive melt to cool so as to yield a laminate on the substrate; and treating the laminate with at least one selected from the group consisting of heat, vacuum, a caustic bath, and any combination thereof.

**[0089]** Each of embodiments A and B may have one or more of the  
30 following additional elements in any combination: Element 1: the cellulose ester having a degree of substitution between about 0.5 and less than about 3; Element 2: the adhesive having a flow onset point between about 70°C and about 220°C; Element 3: the adhesive having a glass transition temperature between about -61°C and about 190°C; Element 4: the adhesive having no  
35 detectable glass transition temperature; Element 5: the substrate comprising at

least one selected from the group consisting of a ceramic, a natural polymer, a synthetic polymer, a metal, a natural material, carbon, and any combination thereof; Element 6: the cellulose ester comprising at least one organic ester substituent selected from the group consisting of a C<sub>1</sub>-C<sub>20</sub> aliphatic ester, a functional C<sub>1</sub>-C<sub>20</sub> aliphatic ester, acetate, propionate, butyrate, succinate, glutarate, maleate, an aromatic ester, a substituted aromatic ester, any derivative thereof, and any combination thereof; Element 7: the cellulose ester having a molecular weight between about 10,000 and about 125,000; Element 8: the plasticizer comprising a food-grade plasticizer; Element 9: the plasticizer comprising at least one selected from the group consisting of triacetin, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, triethyl citrate, acetyl trimethyl citrate, acetyl triethyl citrate, acetyl tributyl citrate, tributyl-*o*-acetyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate, di-2-methoxyethyl phthalate, di-octyl phthalate (and isomers), dibutyl tartrate, ethyl *o*-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, *n*-ethyltoluenesulfonamide, *o*-cresyl *p*-toluenesulfonate, aromatic diol, substituted aromatic diols, aromatic ethers, tripropionin, polycaprolactone, glycerin, glycerin esters, diacetin, polyethylene glycol, polyethylene glycol esters, polyethylene glycol diesters, di-2-ethylhexyl polyethylene glycol ester, glycerol esters, diethylene glycol, polypropylene glycol, polyglycoldiglycidyl ethers, dimethyl sulfoxide, *N*-methyl pyrrolidinone, propylene carbonate, C<sub>1</sub>-C<sub>20</sub> dicarboxylic acid esters, dimethyl adipate (and other dialkyl esters), di-butyl maleate, di-octyl maleate, resorcinol monoacetate, catechol, catechol esters, phenols, epoxidized soy bean oil, castor oil, linseed oil, epoxidized linseed oil, other vegetable oils, other seed oils, difunctional glycidyl ether based on polyethylene glycol, alkyl lactones (*e.g.*,  $\gamma$ -valerolactone), alkylphosphate esters, aryl phosphate esters, phospholipids, aromas (including some described herein, *e.g.*, eugenol, cinnamyl alcohol, camphor, methoxy hydroxy acetophenone (acetovanillone), vanillin, and ethylvanillin), 2-phenoxyethanol, glycol ethers, glycol esters, polyglycol ethers, polyglycol esters, ethylene glycol ethers, propylene glycol ethers, ethylene glycol esters (*e.g.* ethylene glycol diacetate), propylene glycol esters, polyethylene glycol esters, polypropylene glycol esters, any derivative thereof, and any combination thereof; Element 10: the method further comprising producing an article selected from the group consisting of a laminated card, a laminated paper, a

laminated business card, a laminated paper board, a heat activated film, a coated substrate, an iron-on design, and a substrate with a laminated surface; Element 11: the adhesive further comprising at least one additive selected from the group consisting of crosslinkers, insolubilizers, starches, fillers, thickeners, rigid compounds, water-resistance additives, flame retardants, lubricants, softening agents, antibacterial agents, antifungal and/or antimicrobial agents, pigments, dyes, antioxidants, UV-stabilizers, resins, rosins, waxes, flowing agents, viscosity modifiers, aromas, and any combination thereof; Element 12: Element 12 wherein the additive is a food-grade additive; and Element 13: wherein the adhesive is food-grade (*i.e.*, the components of the adhesive are food-grade).

**[0090]** By way of non-limiting example, exemplary combinations applicable to A and B include: Element 1 in combination with Element 2; Element 1 in combination with Element 3; Element 1 in combination with Element 4; Element 1 in combination with Element 8; Element 2 in combination with Element 3; Element 2 in combination with Element 4; Element 2 in combination with Element 8; Element 3 in combination with Element 8; Element 4 in combination with Element 8; Element 1 in combination with at least two of Elements 2, 3, 5, 6, 7, and 8; Element 2 in combination with at least two of Elements 3, 5, 6, 7, and 8; Element 3 in combination with at least two of Elements 5, 6, 7, and 8; Element 1 in combination with at least two of Elements 2, 4, 5, 6, 7, and 8; Element 2 in combination with at least two of Elements 4, 5, 6, 7, and 8; Element 4 in combination with at least two of Elements 5, 6, 7, and 8; Element 9 in combination with any of the foregoing; Element 10 in combination with any of the foregoing; Element 11 in combination with any of the foregoing; Element 12 in combination with any of the foregoing; Element 13 in combination with any of the foregoing; and so on.

**[0091]** Embodiments disclosed herein also include:

C. an article that includes a substrate with a laminate disposed on at least a portion of a surface of the substrate, wherein the laminate comprises a cellulose ester and a plasticizer in the amount of about 30% to about 75% by weight of the laminate.

**[0092]** Embodiment C may have one or more of the Elements 1 and 5-9 disclosed above. By way of non-limiting example, exemplary combinations applicable to C include: Element 1 in combination with Element 5; Element 1 in

combination with Element 6; Element 1 in combination with Element 7; Element 1 in combination with Element 8; Element 8 in combination with Element 5; Element 8 in combination with Element 6; Element 8 in combination with Element 7; Element 1 in combination with at least two of Elements 5-9; Element 8 in combination with at least two of Elements 5-7 and 9; and so on.

**[0093]** Additional embodiments disclosed herein include:

D. a method that includes heating an adhesive to yield an adhesive melt, the adhesive comprising a cellulose ester and a plasticizer, the plasticizer included in an amount of about 15% to about 60% by weight of the adhesive; applying the adhesive melt to a first surface; and adhering a second surface to the first surface with the adhesive;

E. a method that includes compounding at least a cellulose ester and a plasticizer to yield an adhesive, the plasticizer included in an amount of about 15% to about 60% by weight of the adhesive; and forming the adhesive into a plurality of pellets or a molded shape; and

F. an adhesive that includes a cellulose ester; and a plasticizer in an amount of about 15% to about 60% by weight of the adhesive.

**[0094]** Each of embodiments D, E, and F may have one or more of the following additional elements in any combination: Element 101: the adhesive having a visual flow with a gravitational load at a temperature of about 75°C and about 220°C; Element 102: the adhesive has a glass transition temperature between about 10°C and about 190°C or the adhesive having the adhesive having no detectable glass transition temperature; Element 103: the cellulose ester having a degree of substitution between about 0.5 and about 2.9; Element 104: the cellulose ester comprising at least one organic ester substituent selected from the group consisting of a C<sub>1</sub>-C<sub>20</sub> aliphatic ester, a functional C<sub>1</sub>-C<sub>20</sub> aliphatic ester, acetate, propionate, butyrate, succinate, glutarate, maleate, an aromatic ester, a substituted aromatic ester, any derivative thereof, and any combination thereof; Element 105: the cellulose ester having a molecular weight between about 10,000 and about 125,000; Element 106: the plasticizer being a food-grade plasticizer; and Element 107: the plasticizer comprising at least one selected from the group consisting of triacetin, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, triethyl citrate, acetyl trimethyl citrate, acetyl triethyl citrate, acetyl tributyl citrate, tributyl-o-acetyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate,

di-2-methoxyethyl phthalate, di-octyl phthalate (and isomers), dibutyl tartrate, ethyl o-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, n-ethyltoluenesulfonamide, o-cresyl p-toluenesulfonate, aromatic diol, substituted aromatic diols, aromatic ethers, tripropionin, polycaprolactone, glycerin, glycerin esters, diacetin, polyethylene glycol, polyethylene glycol esters, polyethylene glycol diesters, di-2-ethylhexyl polyethylene glycol ester, glycerol esters, diethylene glycol, polypropylene glycol, polyglycoldiglycidyl ethers, dimethyl sulfoxide, *N*-methyl pyrrolidinone, propylene carbonate, C<sub>1</sub>-C<sub>20</sub> dicarboxylic acid esters, dimethyl adipate (and other dialkyl esters), di-butyl maleate, di-octyl maleate, resorcinol monoacetate, catechol, catechol esters, phenols, epoxidized soy bean oil, castor oil, linseed oil, epoxidized linseed oil, other vegetable oils, other seed oils, difunctional glycidyl ether based on polyethylene glycol, alkyl lactones (e.g.,  $\gamma$ -valerolactone), alkylphosphate esters, aryl phosphate esters, phospholipids, aromas (including some described herein, e.g., eugenol, cinnamyl alcohol, camphor, methoxy hydroxy acetophenone (acetovanillone), vanillin, and ethylvanillin), 2-phenoxyethanol, glycol ethers, glycol esters, polyglycol ethers, polyglycol esters, ethylene glycol ethers, propylene glycol ethers, ethylene glycol esters (e.g. ethylene glycol diacetate), propylene glycol esters, polyethylene glycol esters, polypropylene glycol esters, any derivative thereof, and any combination thereof.

**[0095]** Each of embodiments D and E may have one or more of the following additional elements in any combination: Element 108: the first surface and/or the second surface comprising at least one selected from the group consisting of a ceramic, a natural polymer, a synthetic polymer, a metal, a natural material, carbon, and any combination thereof; Element 109: producing an article selected from the group consisting of a smoking article, a cigarette, tape, cardboard packaging, a mailing package, a food container, a cereal box, a frozen dinner container, a book, a notebook, a magazine, a corrugated box, a decorative box, a paper bag, a grocery bag, paper honeycomb, an emery board, electric insulation paper, an air filter, a carpet, a dartboard, furniture or a component thereof, carpet or fabric coated headboard, a chair, a stool, a picture frame, a medical garment, a disposable gown, a surgical mask, a window film, window tinting, a light film, and a light filter; and Element 110: absorbing an additive into the plurality of pellets or the molded shape, wherein the additive comprise at least one selected from the group consisting of a tackifier, 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, an antioxidant, a UV-stabilizer, a resin, a wax, a flowing agent, a viscosity modifier, an aroma, and any combination thereof.

**[0096]** By way of non-limiting examples, exemplary combinations applicable to D, E, and F include: Elements 101 and 102 in combination; Elements 102 and 103 in combination; Elements 101 and 103 in combination; Elements 101, 102, and 103 in combination; Element 106 in combination with any one or more of Elements 101-105, 107; and so on. By way of additional non-limiting examples, exemplary combinations applicable to D and E include: Elements 101 and 102 in combination; Elements 102 and 103 in combination; Elements 101 and 103 in combination; Elements 101, 102, and 103 in combination; Element 106 in combination with any one or more of Elements 101-105, 107; any of the foregoing in combination with Element 108; any of the foregoing in combination with Element 109; and so on.

**[0097]** Additional embodiments disclosed herein include:

G. a method that includes applying an adhesive that is tacky at an ambient temperature to a first surface, the adhesive comprising a cellulose ester and a plasticizer, the plasticizer included in an amount of about 40% or greater by weight of the adhesive; and adhering a second surface to the first surface with the adhesive;

H. a method that includes compounding at least a cellulose ester and a plasticizer to yield an adhesive that is tacky, the plasticizer included in an amount of about 40% or greater by weight of the cellulose ester; and

I. an adhesive that includes a cellulose ester; and a plasticizer in an amount of about 40% or greater by weight of the cellulose ester, wherein the adhesive is tacky.

**[0098]** Each of embodiments G, H, and I may have one or more of the following additional elements in any combination: Element 201: the adhesive has a flow onset point of about 110°C or less; Element 202: the adhesive has a glass transition temperature about 130°C or less or the adhesive having the adhesive having no detectable glass transition temperature; Element 203: the cellulose ester has a degree of substitution between about 1.5 and about 2.8; Element 204: the cellulose ester comprising at least one organic ester

substituent selected from the group consisting of a C<sub>1</sub>-C<sub>20</sub> aliphatic ester, a functional C<sub>1</sub>-C<sub>20</sub> aliphatic ester, acetate, propionate, butyrate, succinate, glutarate, maleate, an aromatic ester, a substituted aromatic ester, any derivative thereof, and any combination thereof; Element 205: the cellulose ester having a molecular weight between about 10,000 and about 125,000; 5 Element 206: the plasticizer being a food-grade plasticizer; and Element 207: the plasticizer comprising at least one selected from the group consisting of triacetin, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, triethyl citrate, acetyl trimethyl citrate, acetyl triethyl citrate, acetyl 10 tributyl citrate, tributyl-*o*-acetyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate, di-2-methoxyethyl phthalate, di-octyl phthalate (and isomers), dibutyl tartrate, ethyl *o*-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, *n*-ethyltoluenesulfonamide, *o*-cresyl *p*-toluenesulfonate, aromatic diol, substituted 15 aromatic diols, aromatic ethers, tripropionin, polycaprolactone, glycerin, glycerin esters, diacetin, polyethylene glycol, polyethylene glycol esters, polyethylene glycol diesters, di-2-ethylhexyl polyethylene glycol ester, glycerol esters, diethylene glycol, polypropylene glycol, polyglycoldiglycidyl ethers, dimethyl sulfoxide, *N*-methyl pyrrolidinone, propylene carbonate, C<sub>1</sub>-C<sub>20</sub> dicarboxylic acid 20 esters, dimethyl adipate (and other dialkyl esters), di-butyl maleate, di-octyl maleate, resorcinol monoacetate, catechol, catechol esters, phenols, epoxidized soy bean oil, castor oil, linseed oil, epoxidized linseed oil, other vegetable oils, other seed oils, difunctional glycidyl ether based on polyethylene glycol, alkyl lactones (e.g.,  $\gamma$ -valerolactone), alkylphosphate esters, aryl phosphate esters, 25 phospholipids, aromas (including some described herein, e.g., eugenol, cinnamyl alcohol, camphor, methoxy hydroxy acetophenone (acetovanillone), vanillin, and ethylvanillin), 2-phenoxyethanol, glycol ethers, glycol esters, polyglycol ethers, polyglycol esters, ethylene glycol ethers, propylene glycol ethers, ethylene glycol esters (e.g. ethylene glycol diacetate), propylene glycol esters, polyethylene 30 glycol esters, polypropylene glycol esters, any derivative thereof, and any combination thereof.

**[0099]** Each of embodiments G and H may have one or more of the following additional elements in any combination: Element 208: applying the adhesive includes heating the adhesive; Element 209: compounding the 35 cellulose ester and the plasticizer so as to produce the adhesive; Element 210:

the first surface and/or the second surface comprising at least one selected from the group consisting of a ceramic, a natural polymer, a synthetic polymer, a metal, a natural material, carbon, and any combination thereof; Element 211: producing an article selected from the group consisting of a smoking article, a cigarette, an envelope, tape, cardboard packaging, a mailing package, a food container, a cereal box, a frozen dinner container, a book, a notebook, a magazine, a sticky-note, a corrugated box, a decorative box, a paper bag, a grocery bag, wrapping paper, wallpaper, paper honeycomb, an emery board, electric insulation paper, an air filter, a papier-mâché article, a carpet, a dartboard, furniture or a component thereof, carpet or fabric coated headboard, a chair, a stool, a picture frame, a medical garment, a disposable gown, a surgical mask, a self-adhesive label, a self-adhesive stamp, a self-adhesive window covering, a decorative window sticker, a window film, window tinting, a light film, and a light filter; and Element 212: compounding further including an additive into the plurality of pellets or the molded shape, wherein the additive comprise at least one selected from the group consisting of a tackifier, 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, an antioxidant, a UV-stabilizer, a resin, a wax, a flowing agent, a viscosity modifier, an aroma, and any combination thereof.

**[00100]** By way of non-limiting examples, exemplary combinations applicable to G, H, and I include: Elements 201 and 202 in combination; Elements 202 and 203 in combination; Elements 201 and 203 in combination; Elements 201, 202, and 203 in combination; Element 206 in combination with any one or more of Elements 201-205, 207; and so on. By way of additional non-limiting examples, exemplary combinations applicable to G and H include: Elements 201 and 202 in combination; Elements 202 and 203 in combination; Elements 201 and 203 in combination; Elements 201, 202, and 203 in combination; Element 206 in combination with any one or more of Elements 201-205, 207; any of the foregoing in combination with Element 210; any of the foregoing in combination with Element 211; and so on.

**[0100]** Additional embodiments disclosed herein include:

J. a method that includes disposing an adhesive sheet between a first surface and a second surface, the adhesive sheet comprising an adhesive

that comprises a cellulose ester and a plasticizer, the plasticizer included in an amount of about 30% to about 60% by weight of the adhesive; and heating the adhesive sheet so as to adhere the first surface to the second surface;

5 K. a method that includes compounding at least a cellulose ester and a plasticizer to yield an adhesive, the plasticizer included in an amount of about 30% to about 60% by weight of the adhesive; and forming the adhesive into an adhesive sheet; and

L. an adhesive sheet that includes a cellulose ester; and a plasticizer in an amount of about 30% to about 60% by weight of the adhesive.

10 **[0101]** Each of embodiments J, K, and L may have one or more of the following additional elements in any combination: Element 301: the adhesive having a flow onset point between about 75°C and about 180°C; Element 302: the adhesive having a glass transition temperature between about 10°C and about 190°C or the adhesive having the adhesive having no detectable glass  
15 transition temperature; Element 303: the cellulose ester having a degree of substitution between about 1.5 and about 2.7; Element 304: the cellulose ester comprising at least one organic ester substituent selected from the group consisting of a C<sub>1</sub>-C<sub>20</sub> aliphatic ester, a functional C<sub>1</sub>-C<sub>20</sub> aliphatic ester, acetate, propionate, butyrate, succinate, glutarate, maleate, an aromatic ester, a  
20 substituted aromatic ester, any derivative thereof, and any combination thereof; Element 305: the cellulose ester having a molecular weight between about 10,000 and about 125,000; Element 306: the plasticizer being a food-grade plasticizer; and Element 307: the plasticizer comprising at least one selected from the group consisting of triacetin, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, triethyl citrate, acetyl trimethyl citrate, acetyl triethyl citrate, acetyl tributyl citrate, tributyl-o-acetyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate, di-2-methoxyethyl phthalate, di-octyl phthalate (and isomers), dibutyl tartrate, ethyl o-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl  
30 glycolate, n-ethyltoluenesulfonamide, o-cresyl p-toluenesulfonate, aromatic diol, substituted aromatic diols, aromatic ethers, tripropionin, polycaprolactone, glycerin, glycerin esters, diacetin, polyethylene glycol, polyethylene glycol esters, polyethylene glycol diesters, di-2-ethylhexyl polyethylene glycol ester, glycerol esters, diethylene glycol, polypropylene glycol, polyglycoldiglycidyl  
35 ethers, dimethyl sulfoxide, N-methyl pyrrolidinone, propylene carbonate, C<sub>1</sub>-C<sub>20</sub>

dicarboxylic acid esters, dimethyl adipate (and other dialkyl esters), di-butyl maleate, di-octyl maleate, resorcinol monoacetate, catechol, catechol esters, phenols, epoxidized soy bean oil, castor oil, linseed oil, epoxidized linseed oil, other vegetable oils, other seed oils, difunctional glycidyl ether based on polyethylene glycol, alkyl lactones (e.g.,  $\gamma$ -valerolactone), alkylphosphate esters, aryl phosphate esters, phospholipids, aromas (including some described herein, e.g., eugenol, cinnamyl alcohol, camphor, methoxy hydroxy acetophenone (acetovanillone), vanillin, and ethylvanillin), 2-phenoxyethanol, glycol ethers, glycol esters, polyglycol ethers, polyglycol esters, ethylene glycol ethers, propylene glycol ethers, ethylene glycol esters (e.g. ethylene glycol diacetate), propylene glycol esters, polyethylene glycol esters, polypropylene glycol esters, any derivative thereof, and any combination thereof.

**[0102]** Each of embodiments J and K may have one or more of the following additional elements in any combination: Element 308: the first surface and/or the second surface comprising at least one selected from the group consisting of a ceramic, a natural polymer, a synthetic polymer, a metal, a natural material, carbon, and any combination thereof; Element 309: producing an article selected from the group consisting of an envelope, tape, cardboard packaging, a mailing package, a food container, a cereal box, a frozen dinner container, a book, a notebook, a magazine, a corrugated box, a decorative box, a paper bag, a grocery bag, electric insulation paper, an air filter, furniture or a component thereof, carpet or fabric coated headboard, a chair, a stool, and a picture frame; and Element 310: absorbing an additive into the adhesive sheet, wherein the additive comprises at least one selected from the group consisting of a crosslinker, a lubricant, a softening agent, an antibacterial agent, an antifungal agent, a pigment, a dye, a flavorant, an aroma, and any combination thereof.

**[0103]** By way of non-limiting examples, exemplary combinations applicable to J, K, and L include: Elements 301 and 302 in combination; Elements 302 and 303 in combination; Elements 301 and 303 in combination; Elements 301, 302, and 303 in combination; Element 306 in combination with any one or more of Elements 301-305, 307; and so on. By way of additional non-limiting examples, exemplary combinations applicable to J and K include: Elements 301 and 302 in combination; Elements 302 and 303 in combination; Elements 301 and 303 in combination; Elements 301, 302, and 303 in

combination; Element 306 in combination with any one or more of Elements 301-305, 307; any of the foregoing in combination with Element 308; any of the foregoing in combination with Element 309; and so on.

5       **[0104]** To facilitate a better understanding of the embodiments described herein, the following examples of preferred or representative embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the disclosure.

### EXAMPLES

10       **[0105]** *Example 1.* A plurality of HPCE-adhesive samples were prepared by compounding cellulose acetate and a plasticizer in the amounts and compositions detailed in Table 1. The cellulose acetates tested were CA-1 having a degree of substitution of about 2.5 and a molecular weight ( $M_n$ ) of about 78,000, CA-2 having a degree of substitution of about 2.4 and a  $M_n$  of about  
15       44,000, and CA-3 having a degree of substitution of about 2.4 and a  $M_n$  of about 62,000. The characteristics of the HPCE-adhesive samples and control cellulose acetate samples without plasticizer were measured and are reported in Table 2.

**Table 1**

<b>Sample</b>	<b>Cellulose Acetate Composition</b>	<b>Plasticizer Composition</b>	<b>Wt% Plasticizer</b>
CA-1	CA-1		0
HPCE-1	CA-1	triacetin	20
HPCE-2	CA-1	triacetin	40
HPCE-3	CA-1	triacetin	60
HPCE-4	CA-1	tributyl phosphate	20
HPCE-5	CA-1	tributyl phosphate	40
HPCE-6	CA-1	tributyl phosphate	60
CA-2	CA-2		0
HPCE-7	CA-2	triacetin	60
HPCE-8	CA-2	triacetin	70
HPCE-9	CA-2	tributyl phosphate	60
CA-3	CA-3		0
HPCE-10	CA-3	triacetin	60
HPCE-11	CA-2	eugenol	50
HPCE-12	CA-2	ethylvanillin	50
HPCE-13	CA-2	triacetin and ethylvanillin	62 (92:8 triacetin: ethylvanillin)
HPCE-14	CA-2	triacetin and ethylvanillin	64 (84:16)
HPCE-15	CA-2	acetovanillone	50
HPCE-16	CA-2	triacetin and acetovanillone	62 (92:8)

Table 2

Sample	Description	MP <sup>1</sup> (°C)	T <sub>g</sub> <sup>2</sup> (°C)	Complex Viscosity <sup>3</sup> (Pa*s)
CA-1	white flake		167-207 <sup>4</sup>	
HPCE-1	clear; stiff; brittle		80	93,777
HPCE-2	clear; flexible; tacky		-55	7,187
HPCE-3	clear; flexible; stretchy; very tacky	150 <sup>1</sup>	-53	2,417
HPCE-4	clear; stiff; brittle	166 <sup>2</sup>	Non detect	122,456
HPCE-5	clear; stiff with some flexibility	180 <sup>2</sup>	14	56,004
HPCE-6	clear; flexible; tacky	180 <sup>1</sup>	12	13,661
CA-2	white flake		167-207 <sup>4</sup>	
HPCE-7	clear; flexible; stretchy; tacky		-44	4,037
HPCE-8	gel-like		-61	4,037
HPCE-9	clear; flexible		15	23,230
CA-3	white flake		167-207 <sup>4</sup>	
HPCE-10	clear; flexible; stretchy; tacky		-57	
HPCE-11	clear; coloured; tacky; flexible		-43	
HPCE-12	hard; glass-like; clear-yellow		-35	
HPCE-13	clear; flexible		-53	
HPCE-14	clear; flexible		-51	
HPCE-15	hard; glass-like; clear yellow		-34	
HPCE-16	clear; flexible		-52	

<sup>1</sup> Flow onset point as measured by visual inspection upon heating.

<sup>2</sup> Glass transition temperature/melt as measured by TA Instruments DSC Q2000.

<sup>3</sup> Complex viscosity at 140°C by TA Instruments Rheometer Discovery HR-2.

5 <sup>4</sup> Literature values for cellulose acetate.

10 **[0106]** *Example 2.* Samples HPCE-3, HPCE-6, HPCE-7, and HPCE-9 were tested for adherence between a glass surface and a cardboard surface. A portion of the sample was added to a glass slide and heated to between 60°C and 100°C. Then a piece of cardboard was applied to the adhesive, which was then allowed to cool. The cardboard piece was then peeled from the glass slide.

**[0107]** Adhesion was achieved in all samples. Upon trying to separate the two substrates, the cardboard pieces adhered with samples HPCE-3, HPCE-6, and HPCE-7 were unable to be peeled without rupturing the cardboard. The

cardboard piece adhered with sample HPCE-9 was able to be cleanly peeled from the glass slide.

**[0108]** *Example 3.* HPCE-7 was tested for thermal stability by storing in a freezer for over 24 hours two paper surfaces glued together. Once warmed to room temperature, the paper surfaces were manually pulled and remained adhered together. Further, the seam where the HPCE-7 adhered to the two paper surfaces remained flexible after the temperature cycling. This example demonstrates, to at least some extent, the temperature stability of HPCE-adhesives.

**[0109]** *Example 4.* Mixes of CA with intrinsic viscosities from 0.8 to 1.6 and triacetin content to CA ratio of 1:1 and 0.8:1 were prepared. The mixes were analyzed for the changes in melt temperature as a function of intrinsic viscosity. As shown in Figure 2, a substantially linear relationship was observed where increased intrinsic viscosity yields a linear increase in melt temperature. Further, a higher plasticizer concentration yields a lower melt temperature at the same intrinsic viscosity. This example demonstrates the ability to tailor the flow onset temperature response by controlling intrinsic viscosity or plasticizer concentration of HPCE-adhesives.

**[0110]** *Example 5.* An adhesive melt was prepared by compounding cellulose diacetate (40% by weight of the adhesive melt) with triacetin plasticizer (60% by weight of the adhesive melt) and placing the compounded mixture in an oven for about 5 min at 140°C. The adhesive melt was then coated to one surface/side of a card-stock paper substrate and allowed to cool so as to yield a laminate film on the paper surface. The coated substrate was subjected to an additional heating step at 140°C for 2-3 minutes. The laminate film was glossy, flexible, and well adhered to the surface precluding the need for both film and laminating adhesive.

**[0111]** Therefore, this disclosure 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 embodiments described herein 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 disclosure. The embodiments 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  
5 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  
10 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  
15 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  
20 incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

**CLAIMS**

The invention claimed is:

1. A method comprising:
  - providing an adhesive melt that comprises an adhesive that comprises a cellulose ester and a plasticizer, the plasticizer included in an amount of about 30% to about 75% by weight of the adhesive;
  - applying the adhesive melt to a substrate; and
  - allowing the adhesive melt to cool so as to yield a laminate on the substrate.
2. The method of claim 1, wherein the cellulose ester has a degree of substitution between about 0.5 and less than about 3.
3. The method of claim 1, wherein the adhesive has a flow onset point between about 50°C and about 220°C.
4. The method of claim 1, wherein the adhesive has a glass transition temperature between about -61°C and about 190°C.
5. The method of claim 1, wherein the adhesive has no detectable glass transition temperature.
6. The method of claim 1, wherein the substrate comprises at least one selected from the group consisting of a ceramic, a natural polymer, a synthetic polymer, a metal, a natural material, carbon, and any combination thereof.
7. The method of claim 1, wherein the cellulose ester comprises at least one organic ester substituent selected from the group consisting of a C<sub>1</sub>-C<sub>20</sub> aliphatic ester, a functional C<sub>1</sub>-C<sub>20</sub> aliphatic ester, acetate, propionate, butyrate, succinate, glutarate, maleate, an aromatic ester, a substituted aromatic ester, any derivative thereof, and any combination thereof.
8. The method of claim 1, wherein the cellulose ester has a molecular weight between about 10,000 and about 125,000.
9. The method of claim 1, wherein the plasticizer comprises a food-grade plasticizer.
10. The method of claim 1, wherein the plasticizer comprises at least one selected from the group consisting of triacetin, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, triethyl citrate, acetyl trimethyl citrate, acetyl triethyl citrate, acetyl tributyl citrate, tributyl-o-acetyl citrate, dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate,

di-2-methoxyethyl phthalate, di-octyl phthalate, dibutyl tartrate, ethyl o-benzoylbenzoate, ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate, n-ethyltoluenesulfonamide, o-cresyl p-toluenesulfonate, aromatic diol, a substituted aromatic diol, an aromatic ether, tripropionin, polycaprolactone, glycerin, a glycerin ester, diacetin, polyethylene glycol, a polyethylene glycol ester, a polyethylene glycol diester, di-2-ethylhexyl polyethylene glycol ester, a glycerol ester, diethylene glycol, polypropylene glycol, a polyglycoldiglycidyl ether, dimethyl sulfoxide, *N*-methyl pyrrolidinone, propylene carbonate, a C<sub>1</sub>-C<sub>20</sub> dicarboxylic acid ester, dimethyl adipate, a dialkyl ester, di-butyl maleate, di-octyl maleate, resorcinol monoacetate, catechol, a catechol ester, a phenol, epoxidized soy bean oil, castor oil, linseed oil, epoxidized linseed oil, a vegetable oil, a seed oil, difunctional glycidyl ether based on polyethylene glycol, an alkyl lactone, an alkylphosphate ester, an aryl phosphate ester, a phospholipid, an aroma, 2-phenoxyethanol, a glycol ether, a glycol ester, a polyglycol ether, a polyglycol ester, an ethylene glycol ether, a propylene glycol ether, an ethylene glycol ester, a propylene glycol ester, a polyethylene glycol ester, a polypropylene glycol ester, any derivative thereof, and any combination thereof.

11. The method of claim 1 further comprising:

producing an article selected from the group consisting of a laminated card, a laminated paper, a laminated business card, a laminated paper board, a heat activated film, a coated substrate, an iron-on design, and a substrate with a laminated surface.

12. A method comprising:

compounding at least a cellulose ester and a plasticizer to yield an adhesive melt, the plasticizer included in an amount of about 30% to about 75% by weight of the adhesive melt;

applying the adhesive melt to a substrate;

allowing the adhesive melt to cool so as to yield a laminate on the substrate; and

treating the laminate with at least one selected from the group consisting of heat, vacuum, a caustic bath, and any combination thereof.

13. The method of claim 12, wherein the cellulose ester has a degree of substitution between about 0.5 and less than about 3.

14. The method of claim 12, wherein the adhesive has a flow onset point between about 50°C and about 220°C.

15. The method of claim 12, wherein the adhesive has a glass transition temperature between about -61°C and about 190°C.

16. The method of claim 12, wherein the adhesive has no detectable glass transition temperature.

17. The method of claim 12, wherein the cellulose ester comprises at least one organic ester substituent selected from the group consisting of a C<sub>1</sub>-C<sub>20</sub> aliphatic ester, a functional C<sub>1</sub>-C<sub>20</sub> aliphatic ester, acetate, propionate, butyrate, succinate, glutarate, maleate, an aromatic ester, a substituted aromatic ester, any derivative thereof, and any combination thereof.

18. The method of claim 12, wherein the cellulose ester has a molecular weight between about 10,000 and about 125,000.

19. The method of claim 12, wherein the plasticizer comprises a food-grade plasticizer.

20. A method comprising:

heating an adhesive to yield an adhesive melt, the adhesive comprising a cellulose ester and a plasticizer, the plasticizer included in an amount of about 15% to about 60% by weight of the adhesive;

applying the adhesive melt to a first surface; and

adhering a second surface to the first surface with the adhesive.

21. A method comprising:

compounding at least a cellulose ester and a plasticizer to yield an adhesive, the plasticizer included in an amount of about 15% to about 60% by weight of the adhesive; and

forming the adhesive into a plurality of pellets or a molded shape.

22. An adhesive comprising:

a cellulose ester; and

a plasticizer in an amount of about 15% to about 60% by weight of the adhesive.

23. The adhesive of claim 22, wherein the cellulose ester has a degree of substitution between about 0.5 and about 2.9.

24. A method comprising:

applying an adhesive that is tacky at an ambient temperature to a first surface, the adhesive comprising a cellulose ester and a plasticizer, the plasticizer included in an amount of about 40% or greater by weight of the adhesive; and

adhering a second surface to the first surface with the adhesive.

25. A method comprising:
  - compounding at least a cellulose ester and a plasticizer to yield an adhesive that is tacky, the plasticizer included in an amount of about 40% or greater by weight of the cellulose ester.
26. An adhesive comprising:
  - a cellulose ester; and
  - a plasticizer in an amount of about 40% or greater by weight of the cellulose ester,wherein the adhesive is tacky.
27. The adhesive of claim 26, wherein the cellulose ester has a degree of substitution between about 1.5 and about 2.8.
28. A method comprising:
  - disposing an adhesive sheet between a first surface and a second surface, the adhesive sheet comprising an adhesive that comprises a cellulose ester and a plasticizer, the plasticizer included in an amount of about 30% to about 60% by weight of the adhesive; and
  - heating the adhesive sheet so as to adhere the first surface to the second surface.
29. A method comprising:
  - compounding at least a cellulose ester and a plasticizer to yield an adhesive, the plasticizer included in an amount of about 30% to about 60% by weight of the adhesive; and
  - forming the adhesive into an adhesive sheet.
30. An adhesive sheet comprising:
  - a cellulose ester; and
  - a plasticizer in an amount of about 30% to about 60% by weight of the adhesive.
31. The adhesive sheet of claim 30, wherein the cellulose ester has a degree of substitution between about 1.5 and about 2.7.

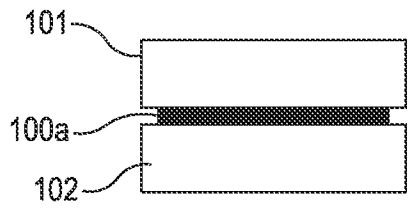


FIG. 1A

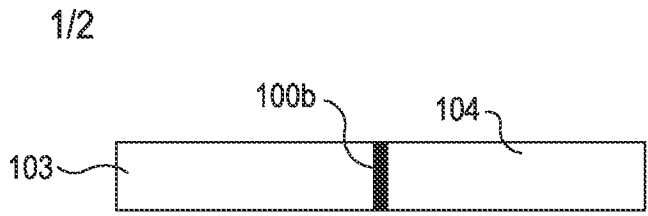


FIG. 1B

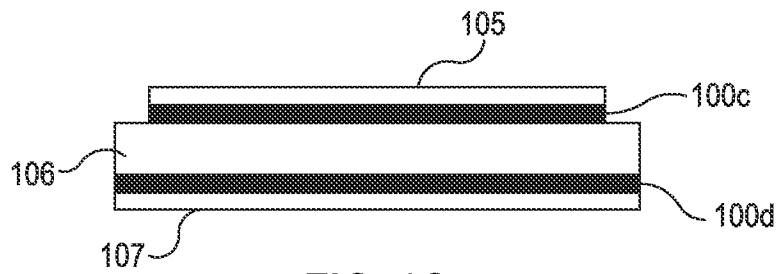


FIG. 1C

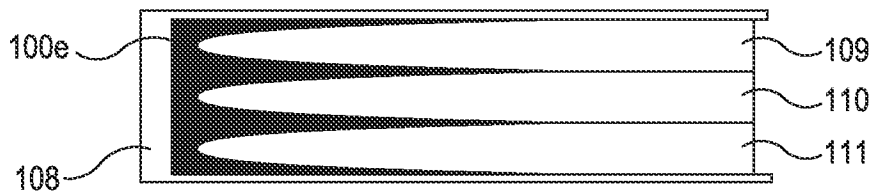


FIG. 1D

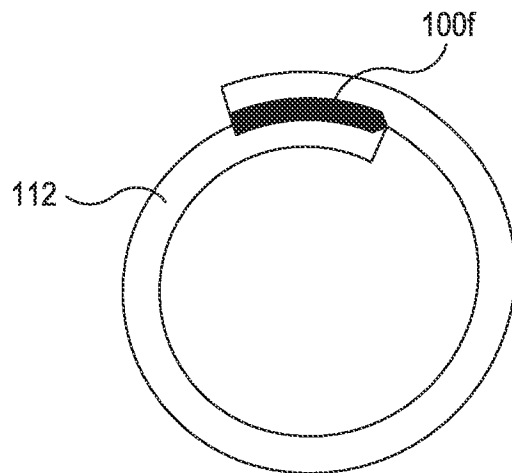


FIG. 1E

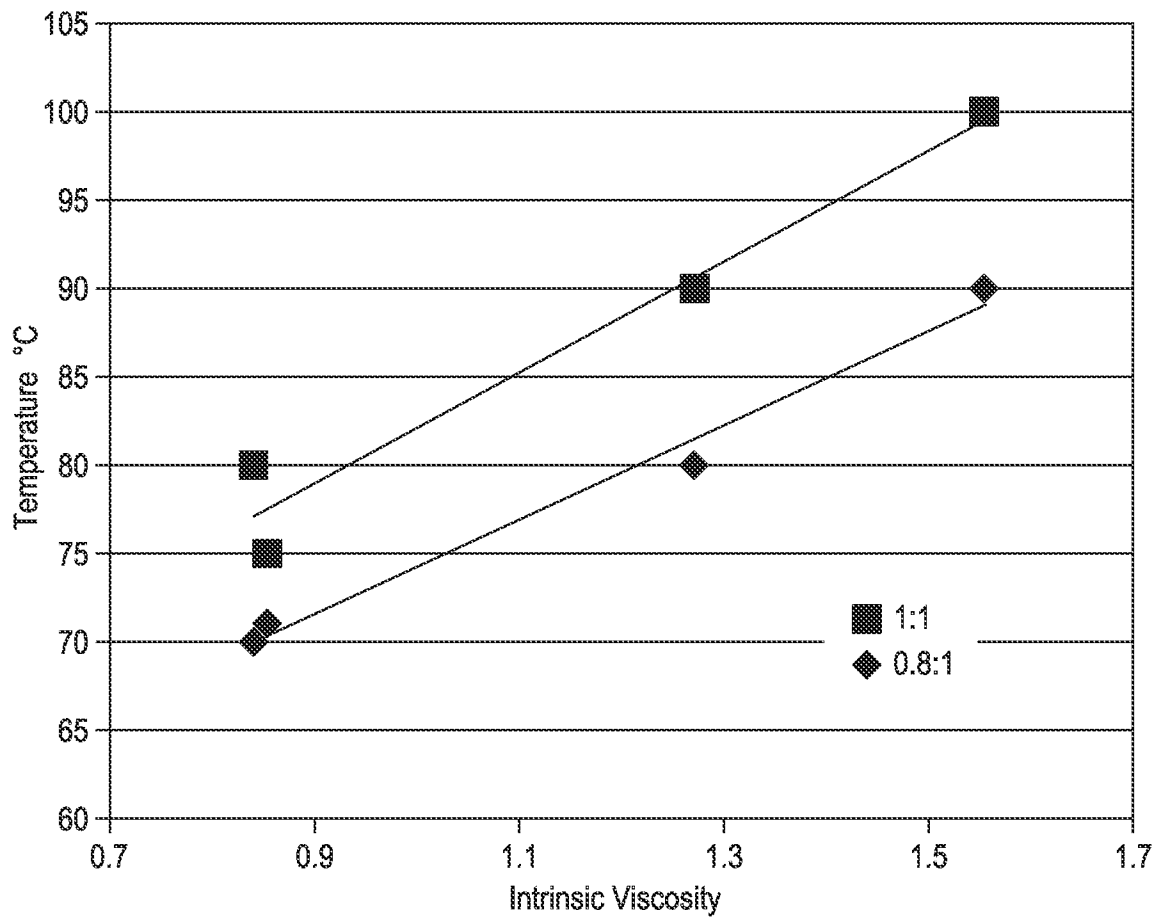


FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2014/018875****A. CLASSIFICATION OF SUBJECT MATTER****C09J 7/00(2006.01)i, C09J 7/02(2006.01)i, C09J 101/26(2006.01)i, C08J 5/18(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)

C09J 7/00; C08L 1/10; B44C 3/02; C08L 1/08; B29C 39/00; C09K 19/00; B44C 1/20; B28B 1/14; C09J 7/02; C09J 101/26; C08J 5/18

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) &amp; Keywords: hot melt adhesive, cellulose ester, plasticizer, biodegradable, triacetin, acetate butyrate

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2423823 A (BAKER, WILLIAM O.) 15 July 1947 See columns 1, 2 and 9.	21-27, 29-31
A		1-20, 28
A	WO 2013-019766 A2 (3M INNOVATIVE PROPERTIES COMPANY) 07 February 2013 See claims 1-10.	1-31
A	US 5478386 A (ITOH, MASANORI et al.) 26 December 1995 See abstract; and claims 1-9.	1-31
A	US 4600552 A (SELS, FRANCIS J. et al.) 15 July 1986 See column 4, lines 41-50; column 6, lines 1-9; and table 4.	1-31
A	US 2006-0127607 A1 (OKUBO, YASUSHI et al.) 15 June 2006 See paragraphs [0002], [0008], [0034] and [0162].	1-31

 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

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"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

26 June 2014 (26.06.2014)

Date of mailing of the international search report

**26 June 2014 (26.06.2014)**

Name and mailing address of the ISA/KR

International Application Division  
Korean Intellectual Property Office  
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,  
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

HONG, Sung Ran

Telephone No. +82-42-481-5405



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2014/018875**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2423823 A	15/07/1947	None	
WO 2013-019766 A2	07/02/2013	CA 2844368 A1 KR 10-2014-0043829 A WO 2013-019766 A3	07/02/2013 10/04/2014 25/04/2013
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