



(51) International Patent Classification:

B27K 3/15 (2006.01) *C08K 5/17* (2006.01)
C08H 8/00 (2010.01) *C08L 33/08* (2006.01)
C08K 3/10 (2006.01) *C08L 33/10* (2006.01)
C08K 5/00 (2006.01) *C08L 33/12* (2006.01)
C08K 5/1515 (2006.01) *C08L 33/14* (2006.01)

(21) International Application Number:

PCT/US2015/038479

(22) International Filing Date:

30 June 2015 (30.06.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/096,042 23 December 2014 (23.12.2014) US

(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC**
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: **KING, Stephen W.**; 2301 N. Brazosport Blvd,
Freeport, TX 77541 (US). **CHEN, Xue**; 2301 N. Brazos-
port Blvd, Freeport, TX 77541 (US). **MALOTKY, David**
L.; Building 1714, Washington Street, Midland, MI 48674
(US).

(74) Agent: **JOHNSON, Christopher A.**; The Dow Chemical
Company, Intellectual Property, PO Box 1967, Midland,
Michigan 48641-1967 (US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: TREATED POROUS MATERIAL

(57) Abstract: A treated cellulosic material comprising a cellulosic material having a porous structure defining a plurality of pores, at least a portion of the pores containing a treating agent comprising a polymer comprising a poly(meth)acrylate polymer. The present further describes a method for preparing a treated cellulosic material comprising (a) providing a cellulosic material; and (b) a first treatment protocol comprising impregnating the cellulosic material with an aqueous dispersion comprising a polymer, the polymer comprising a poly(meth)acrylate polymer.



TREATED POROUS MATERIAL

BACKGROUND OF THE INVENTION

[0001] Porous materials, such as cellulosic materials, need to be protected from mold growth, insect attack, rot and water impregnation to help preserve the physical properties of the cellulosic material. One example of such a cellulosic material is wood. A variety of treatment agents and preservation methods are known to preserve cellulosic materials.

[0002] Modern preservation methods typically involve pressure treating the cellulosic material with a treating agent. Pressure treatment typically allows the treating agent to penetrate throughout the porous structure of the cellulosic material. The treating agent is typically a chemical compound selected to impart the desired physical properties to the cellulosic material. For example, treating agents that add water resistance and improve the dimensional stability of the cellulosic material are of interest. Wood is capable of absorbing as much as 100% of its weight in water which causes the wood to swell, which, after loss of water through evaporation causes the wood to shrink. This process of water absorption/evaporation is non-uniform and creates internal stresses in the wood leading to splitting, warping, bowing, crooking, twisting, cupping, etc. Also, water can serve as a pathway for organisms that degrade the cellulosic material, such as insects or fungus.

[0003] Termites are one of the most significant insect groups responsible for wood damage. In order to mitigate termite damage, the use of naturally durable wood species, preservative treatments, and engineered wood products have been employed. However, the need for improved technologies for termite resistance are desirable due to the limited availability of durable woods, the high percentage weight gains required for preservatives to provide efficacy, and the “unnatural” look of engineered wood. A technology which provides termite resistance and dimensional stability to wood is highly desirable.

[0004] Treating agents that repel insects, or minimize the formation of fungi/molds, or improve the overall durability of the cellulosic material are of interest. Further, treating agents can improve wind resistance, ultraviolet radiation resistance, stability at high and low temperatures, pest resistance, mold resistance, fire resistance and other issues which might affect the physical properties of the cellulosic material.

[0005] An improved treating agent for cellulosic materials is desired.

SUMMARY OF THE INVENTION

[0006] The present disclosure describes a treated cellulosic material comprising a cellulosic material having a porous structure defining a plurality of pores, at least a portion of the pores containing a treating agent comprising a polymer comprising a poly(meth)acrylate polymer.

[0007] The present disclosure further describes a method for preparing a treated cellulosic material comprising (a) providing a cellulosic material; and (b) a first treatment protocol comprising impregnating the cellulosic material with an aqueous dispersion comprising a polymer, the polymer comprising a poly(meth)acrylate polymer.

DETAILED DESCRIPTION OF THE INVENTION

[0008] As used herein, the term “porous material” refers to a material which is permeable such that fluids are movable therethrough by way of pores or other passages. An example of a porous material is a cellulosic material. Other examples of porous materials include stone, concrete, ceramics, and derivatives thereof. As used herein, the term “cellulosic material” refers to a material that includes cellulose as a structural component. Examples of cellulosic materials include wood, paper, textiles, rope, particleboard and other biologic and synthetic materials. As used herein, wood includes solid wood and all wood composite materials (e.g., chipboard, engineered wood products, etc.). Cellulosic materials generally have a porous structure that defines a plurality of pores.

[0009] A “treated cellulosic material” is a cellulosic material that has been treated with a treating agent to modify the properties of the cellulosic material. The properties modified by the treating agent include, but are not limited to, increased hydrophobicity, dimensional stability, fungi resistance, mold resistance, insect resistance, hardness, surface appearance, UV stability, fire resistance, and coatability. Increasing the hydrophobicity of a cellulosic material can provide other ancillary benefits, such as dimensional stability, by reducing the rate of water adsorption and evaporation, thus reducing the internal stresses of expanding and contracting.

[0010] A “treating agent” is a substance that, when combined with the cellulosic material, modifies the properties of the cellulosic material. In one instance, the treating agent comprises a polymer. In one instance, the treating agent comprises both a polymer and a modifying agent. The treating agent is applied to the cellulosic material. One method of applying the treating agent to the cellulosic material is through impregnation using pressure

treatment. In one instance, the polymer is applied to the cellulosic material as part of a dispersion. Other methods of applying the treating agent are known, such as brushing, coating, spraying, dipping, soaking and extrusion. Once applied, the treating agent will permeate at least a portion of the pores of the cellulosic material.

[0011] As used herein, the term “polymer” refers to a molecule that is formed from one or more types of monomers. The polymer may be a polymer or a copolymer. As used herein, the term “copolymer” may refer to an alternating copolymer, a periodic copolymer, a statistical copolymer, a random copolymer, a block copolymer, a graft copolymer, or other copolymer as is known. As used herein, copolymer refers to a polymer formed by uniting two or more monomers. Examples of copolymers include bipolymers, terpolymers, tetrapolymers, and other higher-ordered copolymers. In one instance, the polymer comprises a (meth)acrylate polymer (also referred to herein as poly(meth)acrylate). In one instance, the poly(meth)acrylate polymer is formed using one or more monomers, for example, acrylic acid and its derivatives, including methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, and hydroxyethyl methacrylate. Additional unsaturated monomers such as styrene and styrene derivative monomers may be added to form poly(meth)acrylate/styrene copolymers.

[0012] As used herein, the use of the term “(meth)” followed by another term such as acrylate refers to both acrylates and methacrylates. For example, the term “(meth)acrylate” refers to either an acrylate or methacrylate; the term “(meth)acrylic” refers to either acrylic or methacrylic acid.

[0013] In one instance, the polymer comprises a copolymer wherein one of the monomers is hydrophobic. In one instance, the polymer comprises a copolymer wherein one of the monomers is hydrophilic. In one instance, the polymer comprises a copolymer containing one or more hydrophobic monomers and one or more hydrophilic monomers. In one instance the hydrophobic monomer is a (meth)acrylate monomer, for example, butyl acrylate, 2-ethylhexyl acrylate, or butyl methacrylate. In one instance the hydrophobic monomer is a styrene monomer. In one instance the hydrophilic monomer is a (meth)acrylic acid monomer. In one instance the polymer comprises a (meth)acrylic acid/styrene copolymer. In one instance, the polymer comprises a (meth)acrylic acid/(meth)acrylate copolymer. In one instance the polymer comprises a (meth)acrylate/styrene/(meth)acrylic acid copolymer. In one instance the copolymer

comprises 10 weight percent or more of acrylic acid. In one instance the polymer is formed from one or more monomers which are derivatives of acrylic acid. In one instance the polymer is formed from one or more monomers which are derivatives of styrene. Examples of styrene and styrene derivative monomers suitable for use in the poly(meth)acrylate/styrene copolymer include 2-methylstyrene, 4-methylstyrene, 4-t-butylstyrene, divinyl benzene, styrene, 4-t-butoxystyrene, 4-nitrostyrene, and 4-vinylbenzoic acid.

[0014] In one instance, the polymer is a constituent part of an aqueous dispersion. In one instance, the dispersion is a medium that comprises the polymer and a neutralizing agent. The neutralizing agent, as described in greater detail herein, is selected to neutralize at least a portion of the carboxylic acid substituents of the poly(meth)acrylic polymer. In one instance, the dispersion includes a surfactant. The aqueous dispersion is prepared such that the suspended particle size in the dispersion is suitable for penetrating the pores of the cellulosic material for distribution through the cellulosic material, for example having a particle size of 5-50,000 nm, more preferably 5-500 nm. In one instance, the dispersion also comprises one or more additives. In one instance, any solids present in the aqueous dispersion are held in a stable suspension and are transportable by the dispersion into the pores of the cellulosic material. A stable dispersion is a dispersion that, once formed, resists change in its properties over time and is therefore suitable for penetrating the pores of the cellulosic material. In one instance, the solid content of the dispersion is 1 to 75 weight percent.

[0015] In one instance the dispersion includes a solvent. In one instance the solvent contains water. In one instance the solvent is an organic solvent. In one instance the organic solvent is an oxygenated solvent, a hydrocarbon solvent, a halogenated solvent, or a combination thereof.

[0016] The carboxylic acid portion of the polymer is neutralized with a neutralizing agent at least in part to form a stable aqueous dispersion. As used herein, a neutralizing agent is any material in which the reaction with the carboxylic acid can potentially result in the formation of a salt. In one instance the neutralizing agent is selected from the hydroxides of alkali metals, ammonia or organic derivatives thereof (including amines). In one instance the neutralizing agent is a base. For example, the neutralizing agent may be sodium hydroxide, potassium hydroxide, or ammonia or an amine, such as monoethanolamine (MEA), triethanolamine (TEA), phenethylamine (PEA), dimethylaminoethanol (DMEA), or

polyamine such as polyethylenimine (PEI). The neutralizing agent neutralizes at least a portion of the carboxylic acid groups of the polymer. As used herein, neutralization of the carboxylic acid groups refers to any reaction in which the hydrogen of the carboxylic acid group is transferred. In one instance, 5 to 100 mole percent of the carboxylic acid groups of the polymer are neutralized by the neutralizing agent. In another instance 50 to 100 mole percent of the carboxylic acid groups are neutralized by the neutralizing agent. In still another instance 90 to 100 mole percent of the carboxylic acid groups are neutralized by the neutralizing agent.

[0017] In one instance the treating agent comprises a poly(meth)acrylate/styrene copolymer and a modifying agent. In one instance the treating agent comprises a poly(meth)acrylate/styrene copolymer without a modifying agent. The “modifying agent” is a substance that, when combined with the polymer modifies at least a portion of the carboxylic acid groups of the polymer. The modifying agent may modify the polymer in a variety of ways, for example, by crosslinking the polymer, by neutralizing the carboxylic acid portion of the polymer, or by adding hydrophobic properties to the polymer. In one instance, the modifying agent is a hydrophobic amine, for example, a primary, a secondary or a tertiary amine. In one instance, the modifying agent is a hydrophobic amine salt. In one instance the hydrophobic amine contains only one amino group. The hydrophobic amine may be any suitable amine, such as a linear amine, a branched aliphatic amine, a cyclic amine, an aromatic amine, or a mixture thereof. The amine is selected such that the viscosity is low enough to penetrate the pores of the cellulosic material and contains six or more carbon atoms to provide sufficient hydrophobicity. In the case of highly viscous amines or solid amines, a solvent may be used, for example, water, oxygenated solvents, halogenated solvents, aromatic solvents, hydrocarbons, or a mixture thereof. Examples of hydrophobic amines include N-methyl N-hexyl amine, N,N-diethyl n-hexylamine, n-octyl amine, n-decyl amine, n-dodecyl amine, N-methyl cyclohexylamine, N,N,-diethyl cyclohexylamine, dicyclohexylamine, benzyl amine, coco amine, oleyl amine, stearyl amine, and the N, N-dimethyl substituted fatty amines. In one example, the modifying agent is phenethylamine or tallow amine.

[0018] In one instance, the modifying agent comprises a polyamine having greater than or equal to 2 amine groups. In one instance, the modifying agent crosslinks at least a portion of the polymer. In one instance, the modifying agent is a diamine, a triamine, a higher-order polyamine or a mixture thereof. Suitable modifying agents include polyamines formed

from the reductive amination of monoethanolamine (commonly known as ethyleneamines) or monoisopropanolamine (commonly known as propyleneamines). Other examples of suitable modifying agents include triaminononane (4-aminomethyl – 1,8 – octanediamine), hexamethylenediamine, 1,3-diaminopropane, 1,4 diaminobutane, 1,5 diaminopentane, bis(3-aminopropyl)amine, 1,3-pentanediamine, 2-methylpentamethylenediamine, bis(hexamethylene)triamine, 1,2-diaminocyclohexane, polyethyleneimines (PEIs) or a mixture thereof.

[0019] In one instance, the modifying agent comprises a bivalent, trivalent, or tetravalent metal ion, or a mixture thereof. In one instance, the modifying agent interacts with at least a portion of the polymer such that, without being limited by theory, the modifying agent at least partially impedes the polymer from leaching out of the cellulosic material. In one instance, the modifying agent is capable of forming a stable dispersion in water. In one instance, the modifying agent is capable of crosslinking the polymer. Examples of suitable bivalent metal ions include Ca^{2+} , Zn^{2+} , Mg^{2+} , Ba^{2+} , Fe^{2+} , Cu^{2+} , Sn^{2+} , S^{2+} , and Ni^{2+} , or a mixture thereof. Example of suitable trivalent metal ions include Fe^{3+} , B^{3+} , P^{3+} , Al^{3+} , Cu^{3+} , La^{3+} , Y^{3+} , and Ga^{3+} , or a mixture thereof. Examples of suitable tetravalent metal ions include Si^{4+} , S^{4+} , Ti^{4+} , Zr^{4+} , Sn^{4+} , Ce^{4+} , and Hf^{4+} , or a mixture thereof.

[0020] In one instance, the modifying agent is a quaternary ammonium compound comprising a quaternary ammonium cation and an anion, and is referred to herein as a “quat.” Examples of suitable quaternary ammonium compounds include but are not limited to, those having the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}$ where R^1 , R^2 , R^3 , and R^4 independently are saturated or unsaturated carbon substituents which are linear, branched, cyclic or any combination thereof and X is an anion. The sum of the number of carbon atoms in R^1 , R^2 , R^3 , and R^4 broadly ranges from about 8 to 50. R^1 , R^2 , R^3 , and R^4 may be, for example, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, or any combination of these, and the anion X may be, for example, chloride, bromide, iodide, borate, carbonate, bicarbonate, nitrite, or a carboxylate such as acetate, laurate or stearate. Examples of suitable modifying agents include trimethyl soya alkyl ammonium chloride, or an alkyl trimethyl ammonium chloride/bromide (where the alkyl can be C12, C16, C18, C12, Coco, palmacyl), or a dialkyl dimethyl ammonium chloride/bromide (where the alkyl can be -C8, C10, C12, C16, C18, Hydrogenated Tallow), or an alkyl dimethyl benzyl ammonium chloride/bromide (where the alkyl can be C12, C14, C16, C18, Coco), or a mixture thereof.

[0021] In one instance, the modifying agent is an epoxy resin. In one instance, the epoxy resin is provided as a liquid in a solution with one or more solvents. In another instance the epoxy resin is provided as a solid suspended in a dispersion (referred to herein as an epoxy dispersion). Epoxy resins are those compounds containing at least one vicinal epoxy group. The epoxy resin may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic. The epoxy resin may be substituted. The epoxy resin may also be monomeric or polymeric. The epoxy resin useful in the present invention may be selected from any known epoxy resins in the art. Examples of suitable epoxy resins include, but are not limited to, polyglycidyl ethers of polyhydric alcohols, polyglycidyl ethers of polyhydric phenols, polyglycidyl amines, polyglycidyl amides, polyglycidyl imides, polyglycidyl hydantoins, polyglycidyl thioethers, epoxidized fatty acids, epoxidized drying oils, epoxidized polyolefins, epoxidized di-unsaturated acid esters, epoxidized unsaturated polyesters, and mixtures thereof. Particularly suitable epoxy resins are based on reaction products of polyfunctional alcohols, phenols, cycloaliphatic carboxylic acids, aromatic amines, or aminophenols with epichlorohydrin. A few non-limiting embodiments include, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, resorcinol diglycidyl ether, and triglycidyl ethers of para-aminophenols. Other suitable epoxy resins include reaction products of epichlorohydrin with o-cresol and, respectively, phenol novolacs. It is also possible to use a mixture of two or more epoxy resins. The epoxy resins, used in embodiments disclosed herein, may vary and include conventional and commercially available epoxy resins, which may be used alone or in combinations of two or more. For example, D.E.R. 330, D.E.R. 331, D.E.R.332, D.E.R. 334, D.E.R. 354, D.E.R. 383, D.E.R. 580, D.E.N. 431, D.E.N. 438, D.E.R. 736, or D.E.R. 732 epoxy resins available from The Dow Chemical Company may be used. In addition, waterborne dispersions of solid or liquid epoxy resins such as those available under the trademark OUDRASperse™, commercially available from The Dow Chemical Company, e.g., OUDRASperse™ WB 3001, OUDRASperse™ WB 4001, OUDRASperse™ WB 6001, may be used. Mixtures of epoxy resins may also be used. In one instance, the epoxy resin comprises any aromatic or aliphatic glycidyl ether or glycidyl amine or a cycloaliphatic epoxy resin. However, diglycidyl ether of bisphenol A and derivatives thereof are particularly preferred. Other epoxy resins can be selected from, but limited to, the groups of: bisphenol F epoxy resins, novolac epoxy resins, glycidylamine-based epoxy resins, alicyclic epoxy resins, linear aliphatic epoxy resins, tetrabromobisphenol A epoxy resins, and combinations thereof.

Suitable modifying agents include 2,2-Bis(p-(2,3-epoxypropoxy)phenyl)propane. Suitable epoxy dispersions include water and Bisphenol A diglycidyl ether. The epoxy dispersion is prepared such that the suspended particle size in the dispersion is suitable for penetrating the pores of the cellulosic material for distribution through the cellulosic material.

[0022] The treating agent is combined with the cellulosic material. In one instance, the treating agent is introduced to the cellulosic material by pressure treatment, as described herein. In another instance, the treating agent is introduced to the cellulosic material by other techniques known in the art, for example, brushing, coating, dipping, soaking, spraying, and extrusion. The treating agent becomes impregnated in at least a portion of the pores of the cellulosic material, and thereby increases the weight of the cellulosic material. In one instance, the polymer increases the weight of the cellulosic material by 1 to 80 percent (as calculated after drying the cellulosic material for at least 2 hours at or above 60 °C). In one instance, the treating agent increases the weight of the cellulosic material by 5 to greater than 100 percent (as calculated after drying the cellulosic material for at least 2 hours at or above 60 °C).

[0023] In one instance, the treating agent comprises one or more additives. The additive may be included as part of the dispersion, as part of the modifying agent, or may be included separately therefrom. Additives which are known to add properties to treated cellulosic materials are suitable, such as, flame retardants, dispersants and/or dyes. For example, the additives may be organic compounds, metallic compounds, or organometallic compounds. In one instance, the additive is a material which improves the wetting or penetration of the polymer into the wood, for example, solvents or surfactants (anionic, cationic or nonionic) that are stable in the dispersion. Examples of additives include solvents, fillers, thickeners, emulsifiers, dispersing agents, buffers, pigments, penetrants, antistatic agents, odor substances, corrosion inhibitors, preservatives, siliconizing agents, rheology modifiers, anti-settling agents, anti-oxidants, other crosslinkers (e.g. diols and polyols), optical brighteners, waxes, coalescence agents, biocides and anti-foaming agents. Such waxes may include petroleum waxes, paraffin waxes, a natural wax, or a synthetic wax such as polyethylene wax or oxidized polyethylene wax, beeswax, or slack wax. In addition, the treating agent may be used in conjunction with wood preservatives containing, for example, cupric-ammonia, cupric-amine, cupric-ammonia-amine complexes, quaternary ammonium compounds, or other systems. For example, the treating agent may be used with Alkaline Copper-Quaternary ammonium (ACQ) preservative systems. The treating agent

may also be used with wood preservative technologies which use zinc salts or boron containing compounds. Optionally, other additives such as insecticides, termiticides, fungicides, and moldicides may be added to the treating agent. In one instance, the additive is included as part of the dispersion and forms a stable suspension therewith. In one instance, one or more surfactant is added to the dispersion. In one instance, a surfactant is selected which reduces gelling of the polymer at the surface of the cellulosic material. In one instance, a surfactant is selected which increases the amount of polymer impregnated in the cellulosic material. For example, suitable surfactants may be nonionic, anionic, or cationic. Examples of nonionic surfactants include: alkoxyated alcohols, alkoxyated alkyl phenols, fatty acid esters, amine and amide derivatives, alkylpolyglucosides, ethylene oxide/propylene oxide copolymers, polyols and alkoxyated polyols. For example, a nonionic surfactant is TERGITOLTM L-62, commercially available from The Dow Chemical Company. Examples of anionic surfactants include: alkyl sulfates, alkyether sulfates, sulfated alkanolamides, alpha olefin sulfonates, lignosulfonates, sulfosuccinates, fatty acid salts, and phosphate esters. For example, an anionic surfactant is DOWFAXTM C10L, commercially available from The Dow Chemical Company. Examples of cationic surfactants include alkyltrimethylammonium salts.

[0024] In one instance, the cellulosic material is prepared as a treated cellulosic material by pressure treatment. The pressure used to pressure treat the cellulosic material may be either higher or lower than atmospheric pressure. In one instance, the pressure is lower than ambient pressure, for example, 0.0001 to 0.09 MPa (0.75 to 675 mmHg). In another instance, the pressure is greater than ambient pressure, for example, 0.1 to 1.7 MPa (750 to 12750 mmHg). It is envisioned that pressure treatment processes known in the art are suitable for impregnating the cellulosic material with the treating agent.

[0025] In one instance, the treated cellulosic material is prepared according to at least a first treatment protocol and a second treatment protocol. In one instance, the first treatment protocol comprises impregnating the cellulosic material with the polymer. The first treatment protocol comprises one or more of the following steps: (a) depositing the cellulosic material in a vessel; (b) holding the vessel at vacuum for 5 to 60 minutes; (c) introducing the polymer to the vessel; (d) pressurizing the vessel to 1.03 MPa for 5 to 60 minutes; (e) draining the excess polymer; (f) optionally removing excess polymer by vacuum and (g) drying the cellulosic material at 20 to 60 °C for 24 to 48 hours. In one instance, the polymer is part of the aqueous dispersion.

[0026] In one instance, the product of the first treatment protocol is subsequently prepared according to a second treatment protocol that impregnates the cellulosic material with the modifying agent. The second treatment protocol comprises one or more of the following steps: (a) depositing the cellulosic material prepared according to the first treatment protocol in a vessel; (b) introducing the modifying agent to the vessel; (c) holding the vessel at either vacuum or increased pressure for 5 to 60 minutes; (d) optionally removing excess modifying agent by vacuum; and (e) drying the cellulosic material at 60 °C for 24 to 48 hours.

[0027] In one instance, the product of the second treatment protocol is subsequently neutralized according to a neutralization protocol that neutralizes any residual modifying agent from the second treatment protocol by the use of a modifying agent neutralizer. In one instance, the modifying agent neutralizer is any material suitable for reacting with the modifying agent to reduce its basicity, for example, the dispersion. The neutralization protocol comprises one or more of the following steps: (a) depositing the cellulosic material prepared according to the second treatment protocol in a vessel; (b) introducing the modifying agent neutralizer to the vessel for 30 minutes; and (c) drying the cellulosic material at 60 °C for 24 to 48 hours.

[0028] The designations “first treatment protocol” and “second treatment protocol” are not meant to be read as defining a treatment order. It is envisioned that the cellulosic material may be treated first with the dispersion and second treated with the modifying agent, whereby the second treatment follows the first treatment in time. It is also envisioned that the cellulosic material may be treated first with the modifying agent and second treated with the dispersion, whereby the second treatment protocol precedes the first treatment protocol in time. In the preferred embodiment, the first treatment protocol precedes the second treatment protocol.

[0029] The several drying steps may be performed at a range of temperatures, whereby the duration of the drying step is proportional to the temperature. Suitable drying temperatures are between room temperature (roughly 20 °C) and 180 °C. The drying may be performed in air, in nitrogen, or other suitable atmosphere.

[0030] A water immersion test is used to determine the water repellency of the treated cellulosic material according to the American Wood Protection Association Standard E4-11 procedure (Standard Method of Testing Water Repellency of Pressure Treated Wood). The water immersion test involves first, providing both a treated wafer, comprising a treated

cellulosic material prepared as described herein, and a control wafer, comprising an untreated cellulosic material; second, measuring the tangential dimension of both the treated wafer and the control wafer to provide an initial tangential dimension (T_1) (where the tangential dimension is perpendicular to the direction of the grain of the cellulosic material); third, placing both the treated wafer and the control wafer in a conditioning chamber maintained at $65 \pm 3\%$ relative humidity and $21 \pm 3^\circ\text{C}$ until a constant weight is achieved; fourth, immersing both the treated wafer and the control wafer in distilled water at $24 \pm 3^\circ\text{C}$ for 30 minutes; and fourth, measuring the tangential dimension of both the treated wafer and the control wafer following removal from the water to provide a post tangential dimension (T_2).

[0031] The percent swelling (S) for each individual wafer (both the treated wafer and the control wafer) is calculated as:

$$S (\%) = \frac{T_2 - T_1}{T_1} \times 100$$

[0032] In each of the Examples herein, the percent swelling of the control wafer is 4.7%.

[0033] Water-repellency efficiency (WRE) is used to determine the effectiveness of the treating agent in adding water repellant properties to the treated cellulosic material. WRE is calculated as:

$$WRE (\%) = \frac{S_1 - S_2}{S_1} \times 100$$

[0034] S_1 refers to the percent swelling of the untreated wafer; S_2 refers to the percent swelling of the treated wafer. According to E4-11, for most outdoor applications a minimum WRE of 75% is preferred. The WRE of the control untreated wood is 0%.

[0035] The hardness of the treated cellulosic material is determined according to the Shore (Durometer) test using a Type D Durometer (30° cone, 1.40 mm diameter, 2.54mm extension, 44.48N spring force). Hardness is determined using the Type D Durometer by placing the cellulosic material on a hard flat surface, and the foot of the durometer is pressed with the given spring force against the cellulosic material. The hardness value is recorded from the gauge on the Durometer within one second of contact with the cellulosic material. At least five hardness tests were performed per sample of cellulosic material. Hardness values reported herein are averages of the tests performed for a given cellulosic material. The hardness value of an untreated southern yellow pine control wafer is approximately 40.

[0036] The following Examples illustrate certain aspects of the present disclosure, but the scope of the present disclosure is not limited to the following Examples.

[0037] All the vacuum operations in the examples are in the range of -0.00399MPa to -0.00267MPa.

Example 1

[0038] ACCUDYNE™ 1000 (an acrylate/hydroxyester acrylate copolymer manufactured by The Dow Chemical Company) is firstly modified by monoethanol amine to reduce the particle size. 1,930g of deionized water is loaded while the reactor is heating to 90C. This is followed by 1,912g of Acudyne 1000 and 158g of monoethanol amine. The reaction between ACCUDYNE 1000 and monoethanol amine is conducted for 2 hours at temperature 90C, and at 5 hours the system is cooled to 60C while mixing. The modified ACCUDYNE 1000 has a pH of 6.27 and particle size of 108 nm.

[0039] A pine wafer (southern yellow pine, 4 cm x 2 cm x 0.5 cm) is held at the bottom of a Parr reactor by a weight (here a ring is used). The reactor pressure is set to vacuum for 30 minutes. 80 ml of a dispersion comprising 24 percent by weight modified ACCUDYNE™ 1000 and 76 percent by weight water is introduced to the reactor. The reactor pressure is then set to 1.03 MPa for 60 minutes under nitrogen. The wafer is then placed in an oven and dried in air at 60 °C for 48 hours. The wafer is placed back into the reactor, and held in place by the weight. The reactor is filled with sufficient phenethylamine (PEA) to submerge the wafer. The reactor pressure is set to vacuum for 60 minutes. The wafer is then placed in an oven and dried in air at 60 °C for 48 hours, thereby providing a treated wafer. The treated wafer and a control wafer are each processed according to the E4-11 procedure. The percent swelling for the treated wafer is 0.45%; the WRE of the treated wafer is 92%. The hardness of the treated wafer is measured as 57 using a Type D Durometer.

Example 2

[0040] A pine wafer (southern yellow pine, 4 cm x 2 cm x 0.5 cm) is held at the bottom of a Parr reactor by a weight (here a ring is used). The reactor pressure is set to vacuum for 30 minutes. 80 ml of a dispersion comprising 20 percent by weight of a styrene/acrylic/acrylate copolymer (52.3% butyl acrylate/ 32.7% styrene/ 15% acrylic acid, Tg ~ 10 °C, 4.7 pH, particle size of 164 nm) and 80 percent by weight water is introduced to the reactor. The styrene/acrylic/acrylate aqueous dispersion is synthesized based on AQUASET LT™ technology. The reactor pressure is then set to 1.03 MPa for 60 minutes

under nitrogen. The wafer is then placed in an oven and dried in air at 60 °C for 48 hours, thereby providing a treated wafer. The treated wafer and a control wafer are each processed according to the E4-11 procedure. The percent swelling for the treated wafer is 1.86%; the WRE of the treated wafer is 60.4%. The hardness of the treated wafer is measured as 48.8 using a Type D Durometer.

Example 3

[0041] A pine wafer (southern yellow pine, 4 cm x 2 cm x 0.5 cm) is held at the bottom of a Parr reactor by a weight (here a ring is used). The reactor pressure is set to vacuum for 30 minutes. 80 ml of a dispersion comprising 20 percent by weight of a styrene/acrylic/acrylate copolymer (52.3% butyl acrylate/ 32.7% styrene/ 15% acrylic acid, $T_g \sim 10^\circ\text{C}$, with 0.5 equivalents of PEA based on acrylic acid content added to neutralize the styrene/acrylic/acrylate copolymer dispersion to a pH of 6.8, particle size of 181 nm) and 80 percent by weight water is introduced to the reactor. The styrene/acrylic latexes aqueous dispersions are synthesized based on AQUASET LTTM technology. The reactor pressure is then set to 1.03 MPa for 60 minutes under nitrogen. The wafer is then placed in an oven and dried in air at 60 °C for 48 hours, thereby providing a treated wafer. The treated wafer and a control wafer are each processed according to the E4-11 procedure. The percent swelling for the treated wafer is 1.5%; the WRE of the treated wafer is 64.5%. The hardness of the treated wafer is measured as 46.3 using a Type D Durometer.

[0042] The Examples illustrate that when the cellulosic material is treated with the treating agent favorable WRE results are obtained compared to the cellulosic material which does not contain a treating agent. Example 2 shows favorable results by using a polymer synthesized using hydrophobic monomers butyl acrylate and styrene. Further, when this material is neutralized with a hydrophobic amine as in Example 3, the percent swelling and the WRE are improved compared to the same material which is not neutralized by a hydrophobic amine.

WHAT IS CLAIMED IS:

1. A treated cellulosic material comprising:
a cellulosic material having a porous structure defining a plurality of pores, at least a portion of the pores containing a treating agent comprising:
a polymer comprising a poly(meth)acrylate polymer.
2. The treated cellulosic material of claim 1, and the treating agent further comprises a modifying agent comprising a hydrophobic amine, a bivalent, trivalent, or tetravalent metal ion, a polyamine having greater than or equal to 2 amine groups, an epoxy or a quat.
3. The treated cellulosic material of claim 1, wherein at least a portion of the carboxylic acid groups of the polymer are neutralized.
4. The treated cellulosic material of any one of claims 1-3, wherein the poly(meth)acrylate polymer comprises, in polymerized form, at least one monomer selected from the group comprising acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, and hydroxyethyl methacrylate.
5. The treated cellulosic material of any one of claims 1-4, wherein the hydrophobic amine is a primary, secondary, or tertiary amine that contains six or more carbon atoms.
6. The treated cellulosic material of any one of claims 2-5, wherein the modifying agent comprises at least one of N-methyl N-hexyl amine; N,N-diethyl n-hexylamine; n-octyl amine; n-decyl amine n-dodecyl amine; N-methyl cyclohexylamine; N,N-diethyl cyclohexylamine; dicyclohexylamine; benzyl amine; coco amine; oleyl amine; stearyl amine; an N, N-dimethyl substituted fatty amine; phenethylamine; tallow amine; triaminononane (4-aminomethyl – 1,8 – octanediamine); hexamethylenediamine; 1,3-diaminopropane; 1,4 diaminobutane; 1,5 diaminopentane; bis(3-aminopropyl)amine; 1,3-pentanediamine; 2-methylpentamethylenediamine; bis(hexamethylene)triamine; 1,2-diaminocyclohexane; polyethyleneimine; Ca^{2+} ; Zn^{2+} ; Mg^{2+} ; Ba^{2+} ; Fe^{2+} ; Cu^{2+} ; Sn^{2+} ;

S^{2+} ; Ni^{2+} ; Fe^{3+} ; B^{3+} ; P^{3+} ; Al^{3+} ; Cu^{3+} ; La^{3+} ; Y^{3+} ; Ga^{3+} ; Si^{4+} ; S^{4+} ; Ti^{4+} ; Zr^{4+} ; Sn^{4+} ; Ce^{4+} ; Hf^{4+} ; trimethyl soya alkyl ammonium chloride; alkyl trimethyl ammonium chloride where the alkyl is C12, C16, C18, C12, Coco, or palmacyl; alkyl trimethyl ammonium bromide where the alkyl is C12, C16, C18, C12, Coco, or palmacyl; dialkyl dimethyl ammonium chloride where the alkyl is C8, C10, C12, C16, C18, or hydrogenated tallow; dialkyl dimethyl ammonium bromide where the alkyl is C8, C10, C12, C16, C18, or hydrogenated tallow; alkyl dimethyl benzyl ammonium chloride where the alkyl is C12, C14, C16, C18, or Coco; and alkyl dimethyl benzyl ammonium bromide where the alkyl is C12, C14, C16, C18, Coco; or saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic epoxy.

7. The treated cellulosic material of any one of claims 2-6, wherein the modifying agent modifies the polymer by crosslinking the polymer, by neutralizing the carboxylic acid portion of the polymer, or by adding hydrophobic properties to the polymer.
8. The treated cellulosic material of any one of claims 1-7, wherein the treated cellulosic material is prepared by (1) impregnating the cellulosic material with an aqueous dispersion comprising the polymer and (2) impregnating the cellulosic material with the modifying agent.
9. The treated cellulosic material of any one of claims 1-8, further comprising one or more additives.
10. The treated cellulosic material of claim 1, wherein the polymer comprises a poly(meth)acrylate/styrene copolymer.
11. The treated cellulosic material of claim 10, wherein the poly(meth)acrylate/styrene copolymer comprises, in polymerized form, at least one monomer selected from the group comprising acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, and at least one monomer selected from the group comprising styrene, 2-methylstyrene, 4-methylstyrene, 4-t-butylstyrene, divinyl benzene, 4-t-butoxystyrene, 4-nitrostyrene, and 4-vinylbenzoic acid.

12. A method for preparing a treated cellulosic material comprising:
 - (a) providing a cellulosic material; and
 - (b) a first treatment protocol comprising impregnating the cellulosic material with an aqueous dispersion comprising a polymer, the polymer comprising a poly(meth)acrylate polymer.
13. The method of claim 12 further comprising:
 - (c) a second treatment protocol comprising impregnating the cellulosic material with a modifying agent, the modifying agent comprising a hydrophobic amine.
14. The method of claim 12, wherein the impregnating of the first treatment protocol is conducted under pressure greater than or lower than ambient.
15. The method of any one of claims 12-14, wherein the modifying agent comprises N-methyl N-hexyl amine; N,N-diethyl n-hexylamine; n-octyl amine; n-decyl amine n-dodecyl amine; N-methyl cyclohexylamine; N,N,-diethyl cyclohexylamine; dicyclohexylamine; benzyl amine; coco amine; oleyl amine; stearyl amine; the N, N-dimethyl substituted fatty amine; phenethylamine; tallow amine; triaminononane (4-aminomethyl – 1,8 – octanediamine); hexamethylenediamine; 1,3-diaminopropane; 1,4 diaminobutane; 1,5 diaminopentane; bis(3-aminopropyl)amine; 1,3-pentanediamine; 2-methylpentamethylenediamine; bis(hexamethylene)triamine; 1,2-diaminocyclohexane; polyethyleneimine; Ca^{2+} ; Zn^{2+} ; Mg^{2+} ; Ba^{2+} ; Fe^{2+} ; Cu^{2+} ; Sn^{2+} ; S^{2+} ; Ni^{2+} ; Fe^{3+} ; B^{3+} ; P^{3+} ; Al^{3+} ; Cu^{3+} ; La^{3+} ; Y^{3+} ; Ga^{3+} ; Si^{4+} ; S^{4+} ; Ti^{4+} ; Zr^{4+} ; Sn^{4+} ; Ce^{4+} ; Hf^{4+} ; trimethyl soya alkyl ammonium chloride; alkyl trimethyl ammonium chloride where the alkyl is C12, C16, C18, C12, Coco, or palmacyl; alkyl trimethyl ammonium bromide where the alkyl is C12, C16, C18, C12, Coco, or palmacyl; dialkyl dimethyl ammonium chloride where the alkyl is C8, C10, C12, C16, C18, or hydrogenated tallow; dialkyl dimethyl ammonium bromide where the alkyl is C8, C10, C12, C16, C18, or hydrogenated tallow; alkyl dimethyl benzyl ammonium chloride where the alkyl is C12, C14, C16, C18, or Coco; alkyl dimethyl benzyl ammonium bromide where the alkyl is C12, C14, C16, C18, Coco; or saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic epoxy ; or a mixture thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/038479

A. CLASSIFICATION OF SUBJECT MATTER

INV. B27K3/15 C08H8/00
ADD. C08K3/10 C08K5/00 C08K5/1515 C08K5/17 C08L33/08
C08L33/10 C08L33/12 C08L33/14

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)

B27K C08H C08K C08L

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 188 466 A (DEGUSSA [DE]) 15 April 1970 (1970-04-15)	1-4,6-15
A	page 2, lines 6-19, 26-28, 39-43 -----	5
A	EP 1 216 801 A2 (MARMETSCHKE MICHAEL [DE]) 26 June 2002 (2002-06-26) paragraph [0013] -----	3,7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 September 2015

Date of mailing of the international search report

07/01/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bjola, Bogdan

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/038479

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

5, 13(completely); 1-4, 6-12, 14, 15(partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 5, 13(completely); 1-4, 6-12, 14, 15(partially)

wood material containing in at least a portion of its pores
a polymer comprising a poly(meth)acrylate and a hydrophobic
amine.

2. claims: 1-4, 6-12, 14, 15(all partially)

wood material containing in at least a portion of its pores
a polymer comprising a poly(meth)acrylate and a bivalent,
trivalent, or tetravalent metal ion

3. claims: 1-4, 6-12, 14, 15(all partially)

wood material containing in at least a portion of its pores
a polymer comprising a poly(meth)acrylate and a polyamine

4. claims: 1-4, 6-12, 14, 15(all partially)

wood material containing in at least a portion of its pores
a polymer comprising a poly(meth)acrylate and an epoxy
component

5. claims: 1-4, 6-12, 14, 15(all partially)

wood material containing in at least a portion of its pores
a polymer comprising a poly(meth)acrylate and a quat
component

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/038479

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1188466	A	15-04-1970	AT 284416 B	10-09-1970
			ES 353476 A1	01-10-1969
			FR 1567400 A	16-05-1969
			GB 1188466 A	15-04-1970
			SE 336658 B	12-07-1971

EP 1216801	A2	26-06-2002	AT 297303 T	15-06-2005
			CZ 20014429 A3	14-08-2002
			DE 10064381 A1	11-07-2002
			DE 50106443 D1	14-07-2005
			DK 1216801 T3	08-08-2005
			EP 1216801 A2	26-06-2002
			HR P20010938 A2	31-12-2002
			HU 0105386 A2	28-04-2004
			PL 351180 A1	01-07-2002
			SI 1216801 T1	31-10-2005
			SK 19022001 A3	02-07-2002
