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

(72) Inventors: **CHEN, Xue**; 2301 N. Brazosport Blvd,
Freeport, TX 77541 (US). **KING, Stephen W.**; 2301 N.
Brazosport Blvd, Freeport, TX 77541 (US). **SEKHARAN,**
Manesh Nadupparambil; 1712 Building, Midland, MI
48667 (US).

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

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(54) Title: TREATED POROUS MATERIAL

(57) Abstract: A method for preparing a treated cellulosic material comprising: providing a cellulosic material; a treatment protocol comprising impregnating the cellulosic material with an aqueous dispersion comprising a polybutene and a stabilizing agent.



TREATED POROUS MATERIAL

BACKGROUND

Porous materials, such as cellulosic materials, need to be protected from insect
5 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.

Modern preservation methods typically involve pressure treating the cellulosic
material with a treating agent. Pressure treatment typically allows the treating agent to
10 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 increase hardness, 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
15 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. Treating agents that repel insects, or minimize the formation of fungi, or
20 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, fire resistance and other issues which might affect the
physical properties of the cellulosic material.

An improved treating agent for cellulosic materials is desired.
25

SUMMARY

A method for preparing a treated cellulosic material comprising: providing a
cellulosic material; a treatment protocol comprising impregnating the cellulosic material
with an aqueous dispersion comprising a polybutene and a stabilizing agent.
30

DETAILED DESCRIPTION

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.

As used herein, unless otherwise indicated, the phrase “molecular weight” refers to the weight average molecular weight. In some instance, the molecular weight is measured by GPC (Gel permeation chromatography).

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, 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.

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 an aqueous dispersion comprising a polybutene and a stabilizing 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, spraying, dipping, soaking and extrusion. Once applied, the treating agent will permeate at least a portion of the pores of the cellulosic material.

In one instance, the polybutene comprises an olefinic polymer formed from butene monomers, including 1-butene, 2-butene and isobutylene. In one instance, the polybutene is selected with a molecular weight of less than 3000. In one instance, the polybutene is selected with a molecular weight of less than 2000. In one instance, the polybutene is selected with a molecular weight of less than 1500. In one instance, the polybutene is selected with a molecular weight of less than 1000. In one instance, the polybutene is selected with a molecular weight of greater than 300.

In one instance, the polybutene is a constituent part of an aqueous dispersion. In one instance, the dispersion is a medium that comprises the polymer, water and a stabilizing agent. 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
5 through the cellulosic material. In one instance, the average particle size of the solids in the aqueous dispersion is greater than 0.01 microns. In one instance, the average particle size of the solids in the aqueous dispersion is less than 50 microns. In one instance, the average particle size of the solids in the aqueous dispersion is less than 4.0 microns. In one instance, the average particle size of the solids in the aqueous dispersion is less than 3.0 microns. In
10 one instance, the average particle size of the solids in the aqueous dispersion is less than 2.0 microns. The aqueous dispersion is prepared such that the viscosity of the aqueous dispersion is suitable for penetrating the pores of the cellulosic material for distribution through the cellulosic material. In one instance the viscosity of the aqueous dispersion is less than 100,000 cP at ambient temperature. In one instance the viscosity of the aqueous
15 dispersion is less than 1,000 cP at ambient temperature. In one instance, the viscosity of the aqueous dispersion is less than 500 cP at ambient temperature. 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. In one instance, the polybutene content of the
20 dispersion is 1 to 75 weight percent. In one instance, the solid content of the dispersion is 5 to 75 weight percent. In one instance, the solid content of the dispersion is 5 to 55 weight percent. In one instance, the solid content of the dispersion is 10 to 50 weight percent. In one instance, the solid content of the dispersion is 15 to 45 weight percent. In one instance, the solid content of the dispersion is 20 to 40 weight percent.

25 The stabilizing agent is a substance that stabilizes the aqueous dispersion. In one instance, the stabilizing agent is a surfactant. For example, suitable surfactants may be nonionic or anionic. 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
30 polyols. For example, a nonionic surfactant is TERGITOL™ 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 DOWFAX™ C10L, commercially available from the Dow Chemical Company. In one

instance, the stabilizing agent is suitable for being processed at temperatures up to 200 °C. In one instance the concentration of the surfactant is 0.1 to 20 % in the dispersion. In one instance the concentration of the surfactant is 1 to 10 % in the dispersion. The stabilizing agent is a nonionic surfactant, an anionic surfactant, or a mixture of both.

5 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, dipping, soaking, spraying, and extrusion. The treating agent becomes impregnated in at least a portion of the pores of the
10 cellulosic material, and thereby increases the weight of the cellulosic material. In one instance, the treating agent – the combination of the polybutene and the stabilizing agent – increases the weight of the cellulosic material by 5 to greater than 100 percent (as calculated after drying the cellulosic material).

 In one instance, the treating agent comprises one or more additives. The additive
15 may be included as part of the dispersion containing the polymer, 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
20 polymer into the wood, for example, solvents 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, optical brighteners, coalescence agents, biocides and anti-foaming agents. Such fillers may include
25 silica, $\text{Ca}(\text{OH})_2$ or CaCO_3 . 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
30 technologies which use zinc salts or boron containing compounds. Optionally, other additives such as insecticides, termiticides, and fungicides 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, 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
5 in the art are suitable for impregnating the cellulosic material with the treating agent. The temperature for the pressure treatment may be performed at a range of temperatures, for example, from ambient to 150 °C.

In one instance, the treated cellulosic material is prepared according to a treatment protocol. In one instance, the treatment protocol comprises impregnating the cellulosic
10 material with the aqueous dispersion comprising the polybutene and the stabilizing agent. The 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 aqueous dispersion comprising the polybutene and the stabilizing agent to the vessel; (d) pressurizing the vessel to 1.03 MPa for 5 to 60 minutes; (e) draining the
15 excess aqueous dispersion; (f) optionally removing excess aqueous dispersion by vacuum and (g) air drying the cellulosic material at 20 to 60 °C for 24 to 48 hours.

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

In one instance, the product of the treatment protocol is surface coated with a water repellant coating. An example of a suitable surface coating is polyurethane.

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
25 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 a cellulosic material treated according to the first treatment protocol described herein except that the dispersion is replaced by distilled water; second, measuring the tangential
30 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 ± 3 °C until a constant weight is achieved; fourth, immersing both the treated wafer and the control wafer

in distilled water at 24 ± 3 °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).

DoN refers to the degree of neutralization of the carboxylic acid functionality in the polymer.

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

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

In each of the Examples herein, the percent swelling of the control wafer is 4.7% for initial test, and 6.75% after wood wafers was leached following the leaching test procedure in experimental session.

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:

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

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

Example1: Dispersion of Polybutene 24 using Tergitol™ 15-S-12

200g of Polybutene 24 obtained from Soltex Inc. (weight average molecular weight 950, as determined by gel permeation chromatography (GPC)) and 10g of Tergitol 15-S-12 from The Dow Chemical Company are weighed into a polyethylene beaker. The content of the beaker is stirred at room temperature using a cowles blade at RPM of ~2000 for 1-2 minutes to obtain uniform mixing. To this mixture water is added approximately at the rate of 3ml/minute for 10 minutes while maintaining the stirring. Another 170ml of water is added at a rate of ~20ml/minute to obtain the dispersion.

The dispersion particle size measured using a Coulter LS 320 is 1.09 micrometers, and the dispersion solid percentage is 56.8%. The synthesized dispersion is diluted using water to 30% concentration which was used for the wood treatment.

Example 2: Polybutene 24 with Empicol ESB70

100g of Polybutene 24 obtained from Soltex Inc. and 7g of Empicol ESB70 (a sodium laureth sulfate + 2EO) manufactured by Huntsman are weighed into a polyethylene beaker. The contents of the beaker are stirred at room temperature using a cowles blade at an rpm of ~1800 for 1-2 minutes to obtain uniform mixing. To this mixture water is added approximately at the rate of 3ml/minute for 6 minutes while maintaining the stirring. Another 42 ml of water is added at rate of ~10ml/minute to obtain the final dispersion.

The dispersion particle size measured using a Coulter LS 320 is 700nm and the dispersion solid percentage is 57%. The synthesized dispersion was diluted using water to 30% concentration, which is used for the wood treatment.

10 Treatment procedures

The dispersions prepared in Examples 1 and 2 are each used to pressure-treat southern yellow pine wafers. The wood pieces (4cm*2cm* 0.5cm) are each pressed down by a ring in an evacuated Parr reactor for half an hour followed by drawing in 80 ml of the respective dispersion. The reactor is pressurized to 150 psi under nitrogen and maintained for 60 min. Each wood piece is then placed in an oven with air drying at 60 °C for 48 h.

A leaching test is performed by washing each treated wood block with deionized water at 60 °C for 8 hours. The leached wood wafers are dried in an oven in air at 60 °C overnight. The dimensional stability of the dried wood is then conducted following the AWPAS E4-11 procedure, with results listed in Table 1.

20

Example	Aqueous Dispersion	Percentage of swelling (Initial)	WRE, Initial leaching	Percentage of swelling (after leaching)	WRE, after leaching
Control	none	4.69%	0%	6.75%	0%
1	Polybutene 24 using Tergitol 15-S-12	1.6%	66.47%	2.4%	64.04%
2	Polybutene 24 with Empicol ESB70	1.7%	63.14%	2.2%	67.40%

As the table above shows, and without being limited by theory, the use of an aqueous dispersion comprising a polybutene and a stabilizing agent forms a protective layer around the pores of the wood, which minimizes the absorption of water by the wood thus

providing a significantly longer period of dimensional stability compared to wood which has not been treated with an aqueous dispersion comprising a polybutene and a stabilizing agent. Furthermore, the treating agent is not leached significantly by water.

CLAIMS

1. A method for preparing a treated cellulosic material comprising:
 - (a) providing a cellulosic material;
 - (b) a treatment protocol comprising impregnating the cellulosic material with an aqueous dispersion comprising a polybutene and a stabilizing agent.
2. The method of claim 1, wherein the polybutene has a molecular weight of less than 3000.
3. The method of claim 1, wherein the stabilizing agent is a non-ionic or an anionic surfactant or a mixture of both.
4. The method of claim 1, wherein the impregnating step of the treatment protocol is conducted under pressure greater than or lower than ambient.
5. The method of claim 1, further comprising impregnating the cellulosic material with an additive.
6. The method of claim 1, wherein the aqueous dispersion contains from 5 to 75 weight percent solids.
7. The method of claim 1, further comprising drying the treated cellulosic material.
8. The method of claim 1, wherein the average particle size of the solids in the aqueous dispersion is less than 50 microns.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

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ADD.

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 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)

EPO-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	WO 2016/003999 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 7 January 2016 (2016-01-07) page 2: [0007]; page 3: [0011]; page 4: [0016]; page 7, 8: [0025]; page 8, 9: [0027]; page 9, 10: [0031]; page 10: [0032]; page 11-14: [0041-0047]	1-8
X	EP 0 846 668 A1 (DOW CORNING [US]) 10 June 1998 (1998-06-10) page 2: line 20-24, line 31-36; page 3: line 18-23; page 7: line 30-56; page 8: line 1-6; page 4: line 35-36; page 5: line 36-44	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

Authorized officer

Nania, Manuela

INTERNATIONAL SEARCH REPORT

Information on patent family members

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