ADHESIVE COMPOSITION, COMPOSITE AND FOAM MADE OF THIS ADHESIVE COMPOSITION

The present invention provides thermosetting adhesive/binder compositions comprising a maleated one or more triglycerides of ethylenically unsaturated fatty acids, and amine, imine or hydroxyamine hardener, the two components in a weight ratio of from 30:70 to 98:2. As formulated, the compositions may comprise from 30 to 98 wt. % of the maleated one or more triglycerides of ethylenically unsaturated fatty acids component containing from 5 to 55 wt. % of maleic anhydride moiety, preferably 20-35 wt. %. Any of the compositions may be formulated with one or more components cure on heating and pressing. The adhesive enables the provision of mechanically sound and low cost ligninocellulosic composites chosen from chipboard, particleboard, fiberboard, glued laminated timber, laminated strand lumber, parallel strand lumber, plywood, laminated veneer lumber and oriented strand board. Composites with other fillers, also, can be made with the invented binder. The adhesive composition contains no solvent or water.
ADHESIVE COMPOSITION, COMPOSITE AND FOAM MADE OF THIS ADHESIVE COMPOSITION

DESCRIPTION OF THE INVENTION

This invention is closely related to RU201 1/000899

BACKGROUND OF THE INVENTION

Two binder materials, phenol formaldehyde (PF) and urea formaldehyde (UF) resins, currently are preferred in the building and industrial markets. These binders provide mechanical integrity to plywood, particle board, pressed wood products (called ligninocellulosic composites hereafter in the text), fiberglass insulation, roofing shingles, and composite products. Despite all made efforts to reduce emission of formaldehyde from these binders the emission is still a concern because of high toxicity of formaldehyde [California Air Resources Board, "Fact Sheet Proposed Airborne Toxic Control Measure (ATCM) to Reduce Formaldehyde Emission from Composite Wood Products" (http://www.ard.ca.gov/toxics/compwood/background.htm)]

PF results in 90% less formaldehyde emission than UF, but does not completely eliminate formaldehyde emissions altogether [US 6432254; US 8007698; US 5217665; California Air Resources Board, Staff Report: Initial Statement of Reasons for Proposed Rulemaking - Adoption of the Proposed Airborne Toxic Control Measure to Reduce Formaldehyde Emission from Composite Wood Products, April 2007 (http://www.arb.ca.gov/regact/2007/compwood2007/isor.pdf)].

Among noticeable replacements for formaldehyde binders are isocyanates [US 4376745, US 7361710] and soy protein binder [US 20100069533, US 7081159]. However, isocyanates themselves are a concern due to toxicity [US
EPA, Toxicological Review of MDI (February 1998)]. As to soy-based binders, their use is limited due to low moisture resistance. Even improved soy-based binder composition [US2004007156] showed 18% absorption of water in just 2 hours. Swelling in water is essential for ligninocellulosic composites as it reduces dimensional stability of the composites and their mechanical properties. Besides, high quality soy-based binders are more expensive than PF or UF ones.

The present invention have endeavored to solve the problem of providing essentially natural material binders for wood composites that enable one to make formaldehyde-free composites having acceptable mechanical properties and low cost.

Also, present invention provides essentially natural material for making packaging and insulation foams. Currently, such foams are made of a variety of synthetic resins. The most widely used method of making the foam is saturation of molten resin with carbon dioxide or other gas (blowing agent) under pressure followed by rapid relies of pressure with simultaneous chilling of the resin. Solidifying resin produces foam. Such foams are called extrusion foams.

In many cases cross-linked foams are required. Cross-linking is an additional step to improve properties of the extrusion foams. Isocyanates are used to make cross-linked foam at single step [WO 2008144224]. Besides, isocyanate foams have good adhesion to solid substrates eliminating necessity of another additional step of gluing of foam when solid bond between the foam and the substrate is required. The disadvantage of isocyanates is their high toxicity and high cost.

Maleated triglycerides can be used for making cross-linked foams. For this purpose maleated triglyceride reacted with acrylates and the obtained copolymer
was used for making extrusion foam. Curing of the foam was achieved by UV-irradiation of it. [Wool R. P.; Sun X. S. "Bio-based polymers and composites", Academic Press, 2005 p.137]. Thus, aforementioned three steps, reaction with acrylate, extrusion and irradiation, are required to obtain cross-linked foam from maleated triglyceride. Special equipment, high pressure extrusion apparatus and UV-lamp, are, also, required. Present invention requires only one step of heating of maleated triglycerides with a curing agent for making cross-linked foam and no any complicated apparatus.

A. Gridnev in RU201 1/000899 describes new binder and composites made using inexpensive maleated triglycerides. The binder comprises mixture of maleated triglyceride and polyols. It can be used for composites with a number of fillers, including wood particles of different shape and size. The binder has no formaldehyde and provides sound mechanical properties for composites offering economical replacement for PF binders.

STATEMENT OF THE INVENTION

In accordance with the present invention, thermosetting adhesive compositions comprise a component of maleated one or more maleated ethylenically unsaturated triglyceride of fatty acids and a component of one or more polyamines or aminoalcohols (cross-linker).

Term fiber in the present invention means solid material with one dimension substantially larger than the other two. Sheet or flake means solid material two dimensions of which are comparable but substantially larger that the third dimension. Particle means solid material all three dimensions of which are comparable! Mineral fiber is fiber made from inorganic material. Term "wt. %" represents weight percent.
Under synthetic hardener this invention determines such chemical compound that cannot be isolated from natural sources only by physical methods, such as dissolution, crystallization, evaporation, chromatography, distillation or other methods where chemical reaction is not involved.

Ethlenically unsaturated triglycerides of fatty acids are, usually, naturally occurring triglycerides containing oleic, linoleic, linolenic and other unsaturated acids together with saturated fatty acids. Exact content of fatty acids in naturally occurring triglycerides depends on natural source and may vary in broad range.

Triglycerides of ethylenically unsaturated fatty acids can be made by esterification of glycerol but such triglycerides are more expensive than naturally occurring triglycerides. There is no reason to believe that synthetic ethylenically unsaturated triglyceride of fatty acids could not be used in the present invention instead of naturally occurring triglycerides of unsaturated fatty acids.

Triglycerides of ethyllycally unsaturated fatty acids are commonly known as vegetable oils.

Maleated ethylenically unsaturated naturally occurring oils, which include, but not limited to, olive oil, linseed oil, cottonseed oil, canola oil, sunflower oil, tung oil, tall oil, safflower oil and soybean oil, are widely used in chemical industry, especially sunflower, soybean, canola (rapeseed) and sufflower oils due to their low cost. Among their applications are packaging foams, sheet molding compounds (SMC), paints and emulsifiers. [Wool R. P.; X. S. Sun X. S. "Bio-based polymers and composites "Academic Press, 2005.], [Smith J. R. "Safflower", The American Oil Chemists Society, 1996]; [Wallenberger F. T.; Weston N. E. "Natural fibers, plastics and composites". Springer, 2004.]
For the most applications maleated triglycerides of ethylenically unsaturated fatty acids are further chemically modified with hydrogen peroxide, magnesium oxide, isocyanates, acrylates, etc.

Copolymerization of maleated triglycerides of ethylenically unsaturated fatty acids with styrene, methacrylates and other monomers are widely used with significant amount of such monomers, up to 60%.

The main reason for the additional modification of maleated triglycerides of ethylenically unsaturated fatty acids is to achieve higher glass-transition temperature or cross-linking. Thus, reaction of maleated soybeen oil with polyols resulted in "soft-rubbers". [Eren T.; Kusefoglu S. H.; Wool, R. ] "Polymerization of maleic anhydride-modified plant oils with polyols". J. Appl. Polymer Sci. 90 (2003) 197-202]. To make something useful of this "soft-rubbers" the authors mixed them with calcium carbonate. At level of 60% of calcium carbonate in the composition a material suitable as linoleum was obtained. The other method of making a useful polymer out of a product of reaction of maleinated soybeen oil with polyol was copolymerization with styrene [Can E.; Kusefoglu C. E.; Wool R. P. J. Appl. Polymer Sci., 83 (2002)(5)972-980; US 66460858 ].

As mentioned in the original article [Eren T.; Kusefoglu S. H.; Wool, R. ] "Polymerization of maleic anhydride-modified plant oils with polyols". J. Appl. Polymer Sci. 90 (2003) 197-202 ], all of reaction products of maleated soybeen oil with polyols were "soft tacky solids that could not be used as a structural polymer". Also, nothing was said in the article about formation of foam.

In the present invention polyamines are used as cross-linkers for curing maleated triglycerides of ethylenically unsaturated fatty acids. As compared to polyols,
polyamines and polyimines react faster with maleated triglycerides and provide
cross-linked polymers with higher glass-transition temperature eliminating
necessity of adding co-monomers like styrene or methacrylates.

Maleinization of triglycerides of ethylenically unsaturated fatty acids is well
known process. It can be conducted either by heating of triglycerides with maleic
or at lower temperatures in the presence of peroxide initiators of radical
Chem. Soc. 82(2005)169].

The present invention provides ligninocellulosic composites without usage of
formaldehyde or phenol. It, also, reduces amount of heat required for making
wood composite materials as no water to evaporate is added to the binder
composition as compared to the currently used PF compositions.
Ligninocellulosic composites obtained with adhesive composition of the present
invention are proven to have sound mechanical properties.

Primary amine is amine that is chemically linked to a single substituent and have
general formula C(R)₃NH₂, where R is, independently, H, alkyl or substituted
alkyl that may comprise heteroatoms, like N, S, O, Cl, Br and P and aromatic
rings. Secondary amine is amine that is chemically linked to two substituents and
have general formula [C(R)₃]₂NH. Imines have the following formula,
C(R)₃N=C[C(R)₃]₂.

Aromatic amines, Ar-NH₂, (Ar)₂NH and Ar[C(R)₃]NH (where Ar is an aromatic
ring, like phenyl, pyridyl, thiazolyl, naphtalyl, triazinyl, etc.), also, can be used
as cross-linkers. Ar may comprise substituents R.
Two and more amine, hydroxyl or imine functional groups combined per molecule of synthetic hardener are required for achieving formation of high polymers and cross-linked polymers in reaction with maleated triglyceride of ethylenically unsaturated fatty acids that are suitable as adhesives and binders for making composite materials. In contrast, monoamines react with maleated triglyceride of ethylenically unsaturated fatty acids without formation of polymers with good mechanical properties. Hydroxyls or imino groups react with said triglycerides so that hydroxyl or imino group can replace an amino group in cross-linking reaction. Thus, monoethanolamine provides formation of high polymer in reaction with maleated triglyceride as diaminoethane does.

Composites with sound mechanical properties require high polymeric binder. For making high polymers amount of amino and hydroxyl groups together in synthetic hardener, ideally, should corresponds to the amount of anhydride groups in maleated triglyceride of ethylenically unsaturated fatty acids. Some deviations are tolerable. Also, the best mechanical properties in composites require certain amount of reactive groups per molecule of each component. Amount of these groups, anhydride in the maleated triglycerides, and amino or hydroxyl groups in the synthetic hardener, should not be much less than two groups per molecule. Reactant molecules with single reactive group reduce molecular weight of cured adhesive composition. This effect can be diminished at some extent by increasing amount of reactive groups in the other component of the adhesive composition. Hence, synthetic hardener can contain some amount of molecules with single amino or hydroxy group if maleated triglyceride contains higher content of maleic anhydride moiety. However, synthetic hardener with substantial amount of monoamino or hydroxy reagent, -30% wt/wt or more, provides only sticky, waxy gum even with highly maleinized triglycerides.
The curing of the invented adhesive compositions can be conducted in a broad range of temperatures. At temperatures below 140 °C the rate of curing is noticeably slower than at the higher temperatures. Temperatures above 180 °C were not applied as reasonable curing time and physical properties were obtained at the temperatures of 140-180 °C. However, by no means temperatures beyond 140-180 °C range cannot be applied for curing compositions of this invention. Temperatures below 140 °C and higher than 180 °C can be applied if there should be special technological need for that.

Several composites were tested and reasonable tensile strength, from 6 to 20 kg/cm², was determined for each composition (Examples 1-5 and 8) after curing. These values of tensile strength are similar to tensile strength of standard MDF (http://www.spanogroup.be/upload/docs/MDF-manual%20ENG%20LO%20RES.pdf)

In a separate experiment given in the Example 6 tensile strength of the adhesive bond between two pieces of wood was measured. Obtained value, 20 kg/cm², is similar to the tensile strength of the best currently used adhesives (http://expert.urc.ac.ru/home_work/625_48_196.html).

During experiments with present adhesive composition good adhesion properties of the cured adhesive to glass, rubber, aluminum, brass, steel, sand, concrete, tile, polyvinylchloride and fabric were recognized. In the Experiments 9 a composite with basalt fiber having sound mechanical properties was obtained.

Thus, invented adhesive composition can be used for bonding together materials of different shapes (particles, sheet, flake, and fiber) and different chemical origin.
Formation of foam is described in the Experiment 7. The foam is cross-linked as it cannot be melt and hold its geometrical form at temperatures, at least, up to 210°C.

Curing rate depends on chemical origin of the hardener and temperature. The higher the molecular weight of the hardener, the more is the rigidity of the cured composition.

EXAMPLES
Maleic anhydride, polyethyleneimine (average molecular weight -423, a mixture of linear and branched chains), monoethanolamine, m-phenylenediamine, diethylenetriamine, ethylenediamine and hexamethylenediamine (Aldrich, USA) were used as received. All oils were purchased in local grocery stores. Maleinization was performed according to US7361710. Basalt fiber was purchased in a local hardware store.

Example 1. Ligninocellulosic particle board
9 g of saw dust, 0.6 g of maleated sunflower oil with 25 wt. % content of maleic anhydride moiety 0.1 g hexamethylenediamine were mixed and the mixture was compressed at 40 kg/cm² pressure at 150°C. A ligninocellulosic composite formed of 0.91 g/cm³ specific density and tensile strength of 9 kg/cm².

Example 2. Ligninocellulosic particle board with different amount of binder.
9 g of saw dust, 0.3 g of maleated sunflower oil with 25 wt. % content of maleic anhydride moiety 0.033 g hexamethylenediamine were mixed and the mixture was compressed at 30 kg/cm² pressure at 150°C. A ligninocellulosic composite formed of 0.84 g/cm³ specific density and tensile strength of 6 kg/cm².
Example 3. Ligninocellulosic particle board with aminoalcohol.
9 g of saw dust, 0.9 g of maleated sunflower oil with 37 wt. % content of maleic anhydride moiety 0.075 g monoethanolamine were mixed and the mixture was compressed at 40 kg/cm² pressure at 160°C. A ligninocellulosic composite formed of 0.9 g/cm³ specific density and tensile strength of 11 kg/cm².

Example 4. Ligninocellulosic particle board with different amine and triglyceride
9 g of saw dust, 0.6 g of maleated soybeen oil with 15 wt. % content of maleic anhydride moiety 0.15 g polyethyleneimine were mixed and the mixture was compressed at 40 kg/cm² pressure at 140°C. A ligninocellulosic composite formed of 0.9 g/cm³ specific density and tensile strength of 9 kg/cm².

Example 5. Ligninocellulosic particle board with different amine
9 g of saw dust, 0.9 g of maleated sunflower oil with 37 wt. % content of maleic anhydride moiety 0.075 g ethylenediamine were mixed and the mixture was compressed at 40 kg/cm² pressure at 160°C. A ligninocellulosic composite formed of 0.9 g/cm³ specific density and tensile strength of 14 kg/cm².

Example 6. Gluing pieces of wood with imine hardener.
10.3 g of diethylenetriamine was slowly added into 11.6 g of propyonaldehyde upon cooling with ice-water bath to maintain temperature < 40°C. After 20 min stirring the reaction mixture was heated to 80°C under vacuum of water vacuum aspirator to remove all volatile compounds. 0.66 g of obtained slightly yellow diimine compound was mixed 4g of maleated linseed oil with 25 wt. % content of maleic anhydride moiety. This mixture was applied onto two 1x2x2 cm pieces of ash tree along grain and pressure of 125 g/cm² was applied. The assembly was cured at 160°C for 30 min. Tensile strength of the cured assembly was 20 kg/cm².
Example 7. Formation of foam.
12.8 g of 2-ethylhexanal was slowly added to 5.8 g of hexaethylenediamine at 50-60°C. After 20 min stirring the reaction mixture was heated to 100°C under vacuum of water vacuum aspirator to remove all volatile compounds. 2.1 g of obtained diimine compound was mixed 4g of maleated linseed oil with 30 wt. % content of maleic anhydride moiety. The mixture was heated at 180°C for 20 min. A cross-linked foam formed with closed cells, specific density ~ 0.42 g/cm³.

Example 8. Ligninocellulosic particle board with aromatic amine.
9 g of saw dust, 0.9 g of maleated linseed oil with 30 wt. % content of maleic anhydride moiety and 0.15 g m-phenylenediamine were mixed and the mixture was compressed at 40 kg/cm² pressure at 160°C. A ligninocellulosic composite formed with tensile strength of 12 kg/cm².

18 g of shredded basalt fiber, 0.6 g of maleated sunflower oil with 25 wt. % content of maleic anhydride moiety 0.1 g hexamethylediamine were mixed and the mixture was compressed at 40 kg/cm² pressure at 150°C. A basalt composite formed with tensile strength of 24 kg/cm².

Example 10. Water swelling.
5 mm thick slice of cured at 160°C adhesive composition from Experiment 8 was kept 7 days immersed into water at ambient temperature. The gain in its weight after such water treatment indicated 1.9% water swelling.

While the invention has been described with respect to the presently preferred embodiments, it will be appreciated that changes and modifications can be made without departing from the spirit and of the invention. Accordingly, the scope of the invention is to be determined by the following claims.
1. An adhesive composition comprising a component of maleated one or more triglyceride of ethylenically unsaturated fatty acids, a component of one or more of synthetic hardener at concentration from 2 to 70 wt. % of the final adhesive composition.

2. Adhesive composition of claim 1, wherein maleated ethylenically unsaturated triglyceride contains from 5 to 55 wt. % of maleic anhydride moiety.

3. Adhesive composition of claim 1, wherein ethylenically unsaturated triglyceride contains oleic, linoleic and linolenic acid moiety.

4. Adhesive composition of claim 1, wherein synthetic hardener comprises a polyamine with combined amount of primary amino group, secondary amino group and imino groups per molecule equal or more than 2.

5. Adhesive composition of claim 1, wherein synthetic hardener comprises aminoalcohol with amount of combined amino and hydroxy group per molecule equal or more than 2.

6. A composite formed from the adhesive composition of claim 1 and one or more filler, wherein the weight ratio of the filler and the adhesive ranges from 250: 1 to 1:250.
7. A composite of claim 6, wherein the filler is finely divided ligninocellulosic material, mineral fiber, finely divided mineral material or metal particles.

8. A composite of claim 7, wherein the composite is chipboard, particleboard, and fiberboard.

9. A composite of claim 7 wherein the filler is one or more sheet or flake material by applying the adhesive composition between sheets or flakes.

10. A composite of claim 9, wherein the composite is plywood, strand board, flakeboard, and laminated veneer lumber.

11. A composite of claim 9, wherein the composite is glued laminated timber, laminated strand lumber, parallel strand lumber.

12. Foam formed by curing of the adhesive composition of claim 1.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2012/000056

A. CLASSIFICATION OF SUBJECT MATTER

C09J 191/00 (2006.01)
B32B 21/02 (2006.01)

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 19 l00., B32B 21/02

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 database and, where practicable, search terms used)

PatSearch (RUPTO internal), Esp@cenet, PAJ, USPTO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
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<td>US 39445 12 A (HOECHST AKTIENGESELLSCHAFT) 16.03.1976, abstract, col. 1, lines 39-42, col. 4, lines 45-48, col. 7, lines 22-27, claims 1, 1a, 6, 8</td>
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<td>GB 1279939 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 28.06.1972, claims 1, 5, 6, 7, 8</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

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