A method of reducing the formaldehyde emission of a mineral fibre product bonded with a urea-modified phenol-formaldehyde resin-type binder comprises the step of adding dextrose to the binder composition during and/or after preparation of the binder composition but before curing of the binder composition applied to the mineral fibres.
METHOD OF REDUCING THE FORMALDEHYDE EMISSION OF A MINERAL FIBER PRODUCT, AND MINERAL FIBER PRODUCT WITH REDUCED FORMALDEHYDE EMISSION

FIELD OF THE INVENTION

[0001] The present invention relates to a method of reducing formaldehyde emission of a mineral fibre product, and to bonded mineral fibre products having low formaldehyde emission.

BACKGROUND OF THE INVENTION

[0002] Mineral fibre products generally comprise man-made vitreous fibres (MMVF) such as, e.g., glass fibres, ceramic fibres, basalt fibres, slag wool, mineral wool and stone wool, which are bonded together by a cured thermoset polymeric binder material. For use as thermal and/or acoustical insulation products, bonded mineral fibre mats are generally produced by converting a melt made of suitable raw materials to fibres in conventional manner, for instance by a spinning cup process or by a cascade rotor process. The fibres are blown into a forming chamber and, while airborne and while still hot, are sprayed with a binder solution and randomly deposited as a mat or web onto a travelling conveyor. The fibre mat is then transferred to a curing oven where heated air is blown through the mat to cure the binder and rigidly bond the mineral fibres together.

[0003] Phenolic binders, in particular phenol-formaldehyde resole resins are frequently used in the manufacture of mineral fibre insulation materials, such as insulative batts for walls, roof boards, ceiling tiles, insulative coverings for pipes, and the like.

[0004] Typically, when a phenol-formaldehyde resole resin is used as a binder, a significant amount of formaldehyde is released into the environment during cure. Formaldehyde also can be released subsequently from the cured resin. Such formaldehyde emission is undesirable, particularly in enclosed spaces, because it is hazardous to human health and to the environment. Formaldehyde has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO); see the IARC Monograph on Formaldehyde, Volume 88 (2006). It is therefore desirable to reduce the release of formaldehyde into the environment.

[0005] Various techniques have been used to reduce formaldehyde emission from formaldehyde-based resins. In particular, various formaldehyde scavengers have been used for that purpose. For instance, urea acts as a formaldehyde scavenger both at, and subsequent to, the manufacture of bonded mineral fibre products. Urea is typically added directly to the phenol-formaldehyde resin to produce a urea-modified phenol-formaldehyde resole resin. To obtain a typical urea-modified resole binder resin, a mixture of phenol and formaldehyde is reacted with a suitable basic catalyst in one or more steps. The reaction conditions, temperature, amount of catalyst, etc., are adjusted to favour phenol methyloation reactions over condensation reactions. Urea is then added before or after inactivating the resin just prior to use of the resin. Such a resin is typically referred to as a PUF resin, or PUF binder.

[0006] Another commonly used formaldehyde scavenger is ammonia which binds formaldehyde with formation of amine compounds such as hexamethylene tetramine.

[0007] For instance, WO 96/26164 describes a phenol-formaldehyde resin composition for use as a binder in mineral wool products wherein the emission of phenol is reduced by using a stoichiometric excess of formaldehyde over phenol, wherein the emission of the excess formaldehyde is reduced by adding ammonia as a formaldehyde scavenger and wherein the emission of ammonia is reduced by reacting the ammonia with a sugar compound.

[0008] Other thermosetting phenol-formaldehyde resole resin-type mineral wool binder systems that contain a sugar component are known in the art. For instance, WO 2006/1136614 discloses a binder system similar to that of WO 96/26164 but substituting hydroxylamine or an amino alcohol for ammonia.

[0009] U.S. Pat. No. 4,339,361 discloses phenol-formaldehyde resole resins which are suitable for use in binder systems for bonding mineral fibre products and which are extended with an amide or amine such as urea and a sugar as inexpensive extenders. The sugar component may be selected from mono- and oligosaccharides and water-soluble polysaccharides.

[0010] WO 2009/1136106 discloses mineral wool binders comprising a liquid phenolic resin having a free formaldehyde content of less than or equal to 0.1% and an extender. The extender may be chosen from carbohydrates, including monosaccharides, oligosaccharides and polysaccharides.

[0011] U.S. Pat. No. 7,959,934 discloses a urea-modified phenol-formaldehyde resole resin composition which comprises an alkanolamine alone or preferably in combination with a monosaccharide or disaccharide in an amount sufficient to improve the storage stability of the urea-modified phenolic resole resin.

[0012] WO 2008/127936 discloses composite Maillard-resole binder compositions comprising a phenol-formaldehyde resole resin or urea-modified phenol-formaldehyde resole resin and so-called Maillard reactants which comprise a mixture of a monosaccharide and an ammonium salt of a polycarboxylic acid.

SUMMARY OF THE INVENTION

[0013] The present invention is based on the discovery that dextrose acts as a formaldehyde scavenger in the manufacture of mineral fibre products bonded with a urea-modified phenol-formaldehyde resole resin-type binder.

[0014] Accordingly, in one aspect, the present invention relates to a method of reducing the formaldehyde emission of a mineral fibre product bonded with a urea-modified phenol-formaldehyde resole resin-type binder, said method comprising the step of adding dextrose to the binder composition during and/or after preparation of the binder composition but before curing of the binder composition applied to the mineral fibres. Preferably, the dextrose is added to the binder composition after the preparation of the binder composition but before curing of the binder composition applied to the mineral fibres.

[0015] In another aspect, the present invention relates to a mineral fibre product having reduced formaldehyde emission and bonded with a cured urea-modified phenol-formaldehyde resole resin-type binder composition, the non-cured binder composition comprising dextrose in an amount of 15 wt % or
more, and up to 70 wt %, based on total dry solids of phenol-formaldehyde resol resin and dextrose.

[0016] In a further aspect, the present invention relates to the use of dextrose as a formaldehyde scavenger in a urea-modified phenol-formaldehyde resol resin-type binder composition for mineral fibre products. The dextrose used may be pure dextrose or in the form of a dextrose preparation having a DE equivalent of about 70 to 100, preferably about 90 to 100. The phenol may be reacted with molar excess formaldehyde in aqueous solution in a molar ratio of from 1:2.5 to 1:6, preferably from 1:3 to 1:5, in the presence of a base catalyst. The urea used may be in an amount of from 20 to 60 wt %, preferably 30 to 50 wt %, based on total dry solids of the phenol-formaldehyde resol resin and urea. The dextrose used may be in an amount of 15 to 70 wt %, preferably 20 to 50 wt %, based on total dry solids of a binder comprising a 43/57 (wt %) mixture of urea-modified phenol-formaldehyde resol resin and dextrose, a formaldehyde emission of 13 µg/m² was determined instead of an expected value (assuming a pure dilution effect) of 40 µg/m². Likewise, with a mineral wool product bonded with 3.59% of a binder comprising a 54/46 (wt %) mixture of urea-modified phenol-formaldehyde resol resin and dextrose, a formaldehyde emission of 7 µg/m² was measured instead of an expected value of 43 µg/m².

[0019] The notion of “reduced formaldehyde” is herein construed as a reduction in the formaldehyde emission, compared with an otherwise identical product in terms of binder content, urea content, ammonia content and product density.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

[0030] Urea-Modified Phenol-Formaldehyde Resol Resin

[0031] In accordance with the present invention, the nature of the urea-modified phenol-formaldehyde resol resin is not critical, and any urea-modified phenol-formaldehyde resol resin known in the art may be used.

[0032] However, in accordance with the invention, preferably no substantive urea-formaldehyde (UF) resin formation is taking place, i.e. a dedicated UF formation giving the resin the character of a UF resin is preferably not aimed at.


[0034] The proportion of phenol to aldehyde is selected to yield a resol-type resin (stoichiometric excess of aldehyde), when phenol and formaldehyde are used, the molar ratio of phenol to formaldehyde preferably being from about 1:2.5 to 1:6, and more preferably from about 1:3 to 1:5.

[0035] The catalyst used in the process of preparing the resol resin can include at least one basic alkali metal or alkaline earth metal compound or amine catalyst, such as triethyl amine (TEA). Examples of alkali metal bases which can be used include the hydroxides of sodium, potassium and lithium. Examples of alkaline earth metal bases which can be used include the oxides and hydroxides of calcium, barium and strontium, such as calcium oxide and calcium hydroxide.

[0036] The exothermic condensation reaction of the phenol and the aldehyde is initiated after mixing the phenol and the aldehyde by addition of the catalyst. In a preferred embodiment, an aqueous mixture of phenol and formaldehyde is maintained at a first temperature of, for instance, 40 to 50 °C., as the basic catalyst is added. The temperature is then permitted to rise to a second reaction temperature of, for instance, 60 to 90 °C. Preferably, the reaction is carried out for a sufficient reaction time and at a suitable temperature to provide a resol resin having an acid tolerance of ≥8, preferably within the range of 0.5 to 7, more preferably 3 to 5. The degree of conversion of phenol is preferably ≥95%, more preferably ≥97%.

[0037] Acid tolerance is a measure of the reaction degree and is determined as follows: As acid is used a diluted solution of sulphuric acid (2.5 ml of concentrated sulphuric acid is added to 1 litre of ion-exchanged water). 5.0 ml of binder is transferred into an Erlenmeyer flask. Diluted acid is then added from a burette while keeping the binder in motion. The
titration is continued until a slight cloud appears in the binder, which does not disappear when the binder is shaken. The acid tolerance is calculated by dividing the amount of acid in ml used for the titration with the amount of ml of the sample.

0038 The reaction mixture may be inactivated by addition of a latent acid such as ammonium sulphate or an acid such as sulfuric acid.

0039 For modification of the phenol-formaldehyde resol resin with urea, urea is preferably added and/or reacted in an amount of from about 20 to 60 wt %, preferably 20 to 50 wt %, based on total dry solids of phenol-formaldehyde resol resin and urea. The urea may be added to the resol resin during its preparation or in a post-reaction step.

0040 Dextrose

0041 In accordance with the present invention, dextrose is added to the binder composition during and/or after preparation of the binder composition but before curing of the binder composition applied to the mineral fibres.

0042 For use as a formaldehyde scavenger, dextrose may be used as pure dextrose (glucose) or in the form of a dextrose preparation having a DE equivalent of about 70 to 100, preferably about 90 to 100.

0043 Dextrose is normally produced by subjecting an aqueous slurry of starch to hydrolysis by means of heat, acid or enzymes. Depending on the reaction conditions employed in the hydrolysis of starch, a variety of mixtures of glucose and intermediates is obtained which may be characterized by their DE number. DE is an abbreviation for Dextrose Equivalent and is defined as the content of reducing sugars, expressed as the number of grams of anhydrous D-glucose per 100 g of the dry matter in the sample, when determined by the method specified in International Standard ISO 5377:1981 (E). This method measures reducing end groups and attaches a DE of 100 to pure glucose (=dextrose) and a DE of 0 to pure starch.

0044 In accordance with the present invention, pure dextrose or high DE glucose syrup are preferably used as formaldehyde scavengers.

0045 Binder Composition

0046 The non-cured binder composition according to the present invention generally contains dextrose in an amount of from 15 to 70 wt %, preferably 20 to 50 wt %, based on total dry solids of phenol-formaldehyde resol resin and dextrose. Preferred lower concentrations of dextrose are 15 wt %, 20 wt %, 25 wt %, 30 wt %, 35 wt %, 40 wt % and 45 wt %. Preferred higher concentrations of dextrose are 50 wt %, 55 wt %, 60 wt %, 65 wt % and 70 wt %. Depending on the properties desired and on the type and amount of formaldehyde generators present, the skilled person will employ dextrose in appropriate concentration ranges between these values.

0047 In addition to the urea-modified phenol-formaldehyde resole resin and dextrose, the aqueous binder compositions according to the present invention may comprise one or more conventional binder additives. These include, for instance, curing accelerators such as the free acid and salt forms of strong acids such as boric acid, sulphuric acid, nitric acid and p-toluene sulphonic acid which may be used either alone or in combination with guanidine carbonate. Other suitable binder additives are, for example, silane coupling agents such as γ-aminopropyltriethoxysilane; thermal stabilizers; UV stabilizers; emulsifiers; surface active agents, particularly nonionic surfactants; biocides; plasticizers; anti-migration aids; coalescents; fillers and extenders such as starch, clay, silicates and magnesium hydroxide; pigments such as titanium dioxide; hydrophobizing agents such as fluorinated compounds, mineral oils and silicone oils; flame retardants; corrosion inhibitors such as thionoor; antifoaming agents; antioxidants; and others.

0048 These binder additives and adjuvants may be used in conventional amounts generally not exceeding 20 wt % of the binder solids. The amount of curing accelerator in the binder composition is generally between 0.05 and 5 wt %, based on solids.

0049 The final aqueous binder composition generally has a solids content of from 1 to 20 wt %, and a pH of 6 or higher.

0050 The binder composition according to the present invention preferably does not contain any one of the following components:

0051 hydroxylamine; amino alcohols; alkanol amines; polycarboxylic acids and ammonium salts of polycarboxylic acids; sugar alcohols.

0052 Mineral Fibre Product

0053 The mineral fibres employed may be any of man-made vitreous fibres (MMVF), glass fibres, ceramic fibres, basalt fibres, slag fibres, rock fibres, stone fibres and others. These fibres may be present as a wool product, e.g. like a rock wool product.

0054 Suitable fibre formation methods and subsequent production steps for manufacturing the mineral fibre product are those conventional in the art. Generally, the binder is sprayed immediately after fibrillation of the mineral melt on to the airborne mineral fibres. The aqueous binder composition is normally applied in an amount of 0.1 to 10%, preferably 0.2 to 8% by weight, of the bonded mineral fibre product on a dry basis.

0055 The spray-coated mineral fibre web is generally cured in a curing oven by means of a hot air stream. The hot air stream may be introduced into the mineral fibre web from below, or above or from alternating directions in distinctive zones in the length direction of the curing oven.

0056 Typically, the curing oven is operated at a temperature of from about 150 to 350°C. Preferably, the curing temperature ranges from about 200 to about 300°C. Generally, the curing oven residence time is from 30 seconds to 20 minutes, depending on, for instance, the product density.

0057 If desired, the mineral wool web may be subjected to a shaping process before curing. The bonded mineral fibre products emerging from the curing oven may be cut to a desired format, e.g., in the form of a batt. Thus, the mineral fibre products produced may, for instance, have the form of mats, batts, slabs, sheets, plates, strips, rolls, pipe sections, granulates, and other shaped articles.

0058 A specific type of bonded mineral fibre product is a horticultural growth substrate product. Such horticultural growth substrate products may be in any of the known forms for growth substrate products, such as those usually known as plugs, blocks, slabs and mats. In particular the invention is beneficial in the case where the product is in a form generally known for use as a substrate for the propagation stage.

0059 The horticultural growth substrate product has a greater uniformity of environment across the set of seeds being grown, leading to greater uniformity of the end-product plants; this leads to generally improved plant quality.

0060 The growth substrate product may further comprise a wetting agent. This can be a conventional non-ionic surfactant but preferably the wetting agent is an ionic surfactant, more preferably an anionic surfactant. Particularly preferred wetting agents are anionic surfactants such as linear alkyl
benzene sulphonates wherein the alkyl chain has from 5 to 20 carbon atoms. Preferably the amount (by weight) of ionic surfactant based on the weight of binder (dry matter) is in the range 0.01 to 5%, preferably 0.1 to 4%.

[0061] This type of surfactant provides particularly beneficial water distribution properties for growth substrates of relatively large height and also provides excellent re-saturation properties and does not lead to foaming problems in the irrigation water.

[0062] In accordance with the present invention, it is also possible to produce composite materials by combining the bonded mineral fibre product with suitable composite layers or laminate layers such as, e.g., metal, glass surface mats and other woven or non-woven materials.

[0063] The mineral fibre products according to the present invention generally have a density within the range of from 5 to 250 kg/m³, preferably 20 to 200 kg/m³.

[0064] A particular group of mineral fibre products according to the present invention are ceiling tiles having a density of from 50 to 220 kg/m³ and manufactured using a non-cured binder composition comprising dextrose in an amount of 20 to 70 wt %, preferably 40 to 70 wt %, based on total dry solids of phenol-formaldehyde resol resin and dextrose.

[0065] Another group of mineral fibre products according to the present invention are roof boards having a density of from 100 to 250 kg/m³ and manufactured using a non-cured binder composition comprising dextrose in an amount of 20 to 50 wt %, preferably 20 to 40 wt %, based on total dry solids of phenol-formaldehyde resol resin and dextrose.

[0066] There are essentially two types of roof boards: mono density and dual density roof boards such as disclosed, e.g., in EP-A-889981 and EP-A-1456444, the disclosure of which is incorporated herein by reference.

[0067] In preferred dual density roof boards, the mineral fibre baits include an upper layer having a density of around 100 to 250 kg/m³ and a lower layer with a density which is usually not more than 80% but usually more than 30% of the density of the upper layer, often around 40 to 70% of the density of the upper layer. Usually, the upper and lower layers in the final product have a total thickness of 30 to 300 mm. The lower layer is usually 25 to 275 mm thick and is usually at least 75 mm thick. Generally, it is at least 50%, and often 75 to 95%, of the combined thickness of the upper and lower layers.

[0068] The mineral fibre products according to the present invention are light-coloured and often brownish to a varying degree, depending on the amount of dextrose.

[0069] The mineral fibre products according to the present invention satisfy the formaldehyde emission requirements of international building industry standards.

[0070] For instance, tests with mineral fibre products according to the invention showed that the formaldehyde emission requirements of Finnish Standard RTS-M1 (limit 50 g/m² h) for a roof board can be met by using >20 wt % of dextrose. The Finnish Standard RTS-M1 standard determines the emission of the sample after 4 weeks in a testing chamber according to ISO-16000-9, first edition, corrected version 2006 Jun. 15.

[0071] Similarly, the formaldehyde emission requirements of U.S. Standard CDHS (version 15 Jul. 2004; limit 16.5 g/m²) for a roof board can be met by using >30 wt % of dextrose, and the formaldehyde emission requirements of Japanese Standard JIS-A 1901-2003 (E) (limit 12 g/m², the F*** limit) can be met by using about 47 wt % of dextrose.

[0072] Another standard that is met by the product according to the present invention is the Greenguard Children and Schools standard limit, which corresponds to a specific emission rate of approximately 35 g/m² h. Preferably, this standard is met for a building insulation product board or roll having a density of from 5 to 70 kg/m³ and manufactured using a non-cured binder composition comprising dextrose in an amount of 10 to 50 wt %, preferably 20 to 40 wt %, based on total dry solids of phenol-formaldehyde resol resin and dextrose.

[0073] The following examples are intended to illustrate the invention without limiting its scope. Unless indicated otherwise, the solids content (dry matter) is herein determined at 200 °C, 1 hour and expressed as wt. %.

EXAMPLE 1

[0074] A phenol-formaldehyde resin is prepared by reacting formaldehyde and phenol in a molar ratio of 3.7 to 1 in the presence of a catalyst (6 wt % KOH, relative to the amount of phenol) at a reaction temperature of 84 °C. The reaction is continued until the acid tolerance of the resin is 4 and most of the phenol is converted. Urea is then added in an amount corresponding to 52 parts by weight of phenol-formaldehyde resin and 48 parts by weight of urea.

[0075] Using the urea-modified phenol-formaldehyde resin obtained, a binder is made by addition of ammonium sulphate in equimolar amounts to the catalyst so as to inactivate the catalyst. The final PUF resin has a free formaldehyde content of <0.5%, relative to the solids.

[0076] The thus obtained PUF binder is mixed with a dextrose preparation, Sirodex® 431 from Syral (DE value 95), in the amounts indicated in Table 1 below.

[0077] Further, the binder is diluted with water to a solids content equal to 22%, and a commercial prehydrolysed ammosilane is added in an amount corresponding to 0.5% of the solids.

[0078] The binder composition obtained is used for production of monolayer roof boards ("A-Taglade"). Further details are given in the following table.

<table>
<thead>
<tr>
<th>TABLE 1</th>
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<tr>
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<tr>
<td>A</td>
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<tr>
<td>B</td>
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<tr>
<td>C</td>
</tr>
</tbody>
</table>

*The binder content (%) and the dextrose content (%) are weight percentages based on total dry solids of phenol-formaldehyde resol resin and dextrose.

EXAMPLE 2

[0079] A commercial resin PF-0415M from Hexion is used for the test. The resin is a phenol-formaldehyde resin modified with urea and ammonia. Free formaldehyde is <0.3% based on the liquid resin. The amount of urea is 28% in relation to the solids content.

[0080] The resin is mixed with a dextrose preparation, Sirodex® 431 (DE value 95) from Syral, in the amounts indicated in Table 2 below. For comparison, a glucose syrup, i.e., C Sweet® 04103 (DE value 30) from Cargill, is used in the amount indicated in Table 2 (Sample II).
The composition is diluted to 15% with water to provide a binder composition and further added with 0.5% of a commercial silane of the type pre-hydrolysed amino silane.

The binder composition obtained is used for production of monolayer roof boards (DP-GF). Further details are given in the following table.

<p>| TABLE 2 |
|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>PUF Binder %</th>
<th>Dextrose %</th>
<th>Binder content of product* (%</th>
<th>Product density (kg/m³)</th>
</tr>
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<tr>
<td>D</td>
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<td>0</td>
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<tr>
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<tr>
<td>H</td>
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<td>20</td>
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</tr>
</tbody>
</table>

The PUF binder content (%) and the dextrose content (%) are weight percentages based on total dry solids of phenol-formaldehyde resol resin and dextrose.

*Binder content of product (%) = LOI (%) - impregnation oil (%)
an amount of from 10 to 50 wt %, based on total dry solids of phenol-formaldehyde resol resin and dextrose.

34. A method of scavenging formaldehyde in a urea-modified phenol-formaldehyde resol resin-type binder composition for a mineral fiber product, wherein the method comprises adding to the binder composition dextrose as a formaldehyde scavenger.

35. The method of claim 34, wherein the mineral fiber product is selected from
   a roof board having a density of from 100 to 250 kg/m³ and having been manufactured using a non-cured binder composition and dextrose in an amount of 20 to 50 wt %;
   a ceiling tile having a density of from 50 to 220 kg/m³ and having been manufactured using a non-cured binder composition and dextrose in an amount of from 20 to 70 wt %; and
   a building insulation product board having a density of from 5 to 70 kg/m³ and having been manufactured using a non-cured binder composition and dextrose in an amount of from 10 to 50 wt %;

the indicated weight percentages being based on total dry solids of phenol-formaldehyde resol resin and dextrose.

36. An apparatus for making a mineral fiber product having reduced formaldehyde emission and bonded with a cured dextrose-containing urea-modified phenol-formaldehyde resol resin-type binder composition, wherein the apparatus comprises
   a device for fiberizing a mineral melt into mineral fibers, separate tanks for the binder composition and dextrose; a device for mixing the binder composition and the dextrose, a device for applying a mixture of binder composition and dextrose to the mineral fibers,
   a collection chamber for the mineral fibers having the mixed binder composition and dextrose applied thereto, a curing oven for curing the mixed binder composition and dextrose applied to the mineral fibers to form a cured web, and
   a device for confectioning the cured web to a mineral fiber product.

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