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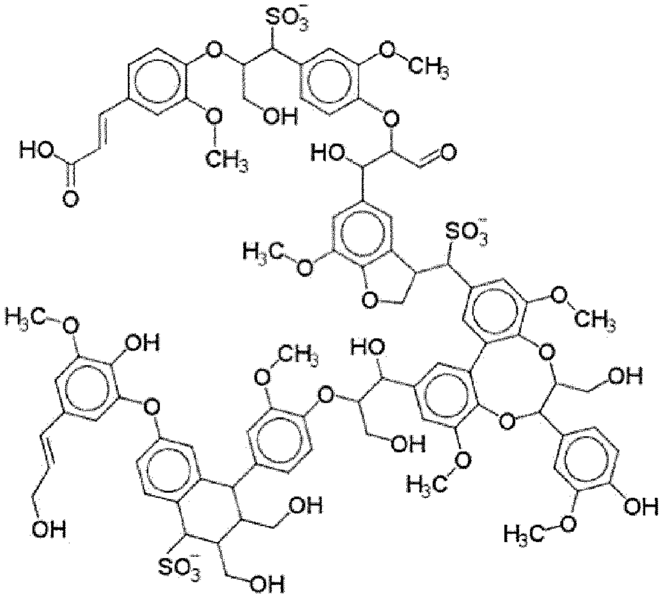
(54) Title: LOW CHLORIDE MINERAL WOOL PRODUCT

Fig. 1



(57) Abstract: The invention is directed to a mineral fibre product having a low water leachable chloride content which is suitable as non-corrosive thermal and/or acoustic insulation.

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Low chloride mineral wool product

Field of the Invention

The present invention relates to a mineral fibre product, and a use of a mineral fibre product.

Background of the Invention

Mineral fibre products (also termed mineral wool products) generally comprise mineral fibres (also termed as man-made vitreous fibres (MMVF)) such as, e.g., glass fibres, ceramic fibres, basalt fibres, slag fibres, and stone fibres (rock fibres), which are bonded together by a cured thermoset polymeric binder material. For use as thermal 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.

In the past, the binder resins of choice have been phenol-formaldehyde resins which can be economically produced and can be extended with urea prior to use as a binder. However, the existing and proposed legislation directed to the lowering or elimination of formaldehyde emissions have led to the development of formaldehyde-free binders such as, for instance, the binder compositions based on polycarboxy polymers and polyols or polyamines, such as disclosed in EP-A-583086, EP-A-990727, EP-A-1741726, US-A-5,318,990 and US-A-2007/0173588.

Another group of non-phenol-formaldehyde binders are the addition/-elimination reaction products of aliphatic and/or aromatic anhydrides with alkanolamines, e.g., as disclosed in WO 99/36368, WO 01/05725, WO 01/96460, WO 02/06178, WO 2004/007615 and WO 2006/061249. These binder compositions are water soluble and exhibit excellent binding properties in terms of curing speed and curing density. WO 2008/023032 discloses urea-modified binders of that type which provide mineral wool products having reduced moisture take-up.

Since some of the starting materials used in the production of these binders are rather expensive chemicals, there is an ongoing need to provide formaldehyde-free binders which are economically produced.

A further effect in connection with previously known aqueous binder compositions from mineral fibres is that at least the majority of the starting materials used for the productions of these binders stem from fossil fuels. There is an ongoing trend of consumers to prefer products that are fully or at least partly produced from renewable materials and there is therefore a need to provide binders for mineral wool which are, at least partly, produced from renewable materials.

A major problem of the use of mineral fibre products as thermal or acoustical insulation for industrial equipment or piping is corrosion. Thus, Corrosion Under Insulation (CUI) refers to the external corrosion of piping or equipment that occurs underneath externally cladded insulation due to water or moisture penetration. The corroded surface is mostly hidden by the insulation system and will not be observed until the insulation is removed for inspection or in the event of metal failure and/or leakage leading to health and safety incidents. CUI occurs in particular under insulation for steel structures which undergo cyclic temperature changes like e.g. pipelines in the oil and gas industry.

Corrosion occurs in the presence of water and oxygen. If the equipment or piping such as steelwork under insulation remains dry there is no corrosion problem. However, keeping insulation dry can be difficult. A certain type of corrosion can be caused or supported by water-soluble chlorides. Prior art binder compositions for mineral fibres can include significant amounts of water-soluble chlorides. Accordingly, the mineral fibre product itself can contribute to the corrosion of the insulated parts.

The risk of corrosion under insulation of carbon steel is considered high in the temperature range of 50 to 175°C and extreme in cyclic temperature service between -20 and 320°C. The most frequently occurring types of CUI are general and pitting corrosion of carbon steel which may occur if wet insulation comes in contact with carbon steel, and external stress corrosion tracking (ESCT) of austenitic stainless steel, which is a specific type of corrosion mainly caused by the action of water-soluble chloride

Summary of the Invention

Accordingly, it was an object of the present invention to provide a mineral fibre product for insulation which has a reduced corrosiveness towards the insulated objects, is economically produced and is using renewable materials as starting products for the preparation of the aqueous binder composition used to produce the mineral fibre product.

A further object of the present invention was to provide a use of such mineral fibre product.

In accordance with a first aspect of the present invention, there is provided a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins , wherein the mineral fibre product has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

In accordance with a second aspect of the present invention, there is provided a use of a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, as a thermal and/or acoustic insulation, in particular a non-corrosive thermal and/or acoustic insulation, wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

In accordance with a third aspect of the present invention, there is provided a method for the manufacture of a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001,
the method comprising the steps of

a) providing a non-cured aqueous binder composition comprising one or more lignosulfonate lignins and water,
b) contacting mineral fibres with the non-cured aqueous binder composition, and
c) curing the binder composition in contact with the mineral fibers,

wherein at least part of the water or the total water contained in the non-cured aqueous binder composition is non-purified water added, wherein the non-purified water is preferably selected from tap water, rain water, process water or a combination thereof.

Preferably, the lignosulfonate lignin has a carboxylic acid group content of 0.03 to 1.4 mmol/g based on the dry weight of the lignosulfonate lignings.

In accordance with a forth aspect of the present invention, there is provided a hollow object covered with a mineral fibre product as a thermal and/or acoustic insulation, wherein the mineral fibre product comprises mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

The inventors have found that it is possible to use a mineral fibre product as a low corrosive or even non-corrosive thermal and/or acoustic insulation, when a binder composition based on lignosulfonate lignins is used for the mineral fibre product. This binder composition has a surprisingly low water leachable chloride content.

Description of the Preferred Embodiments

The mineral fibre product of the invention comprises mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, wherein the mineral fibre product has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001, wherein the water leachable chloride content is preferably less than 6 mg/kg in accordance with EN 13468:2001.

For the purpose of the present application, the water leachable chloride content of the mineral fibre product is measured according to EN 13468:2001. The standard EN 13468:2001 inter alia relates to the determination of trace quantities of water soluble chloride in thermal insulating products for building equipment and industrial installations. The standard specifies the equipment and procedures for determining trace quantities of the water soluble chloride in an aqueous extract of the product. Reference is made to this standard for the details.

The water leachable chloride content is given in mg chloride per kg mineral fibre product. Referring to table 1 in the EN standard, 100°C and 0,5h for leaching is used. Sample preparation according to 7.2.1 of EN 13468. Analysis according to 7.2.2.2 of EN 13468 (ion chromatography determination).

The inventors found that the mineral fibre products of the present invention have a surprisingly low water leachable chloride content. This is even true when non- purified water such as tap water or process water is used for preparing the non- cured binder composition. As known by the skilled person, non-purified water can contain considerable amounts of chloride.

Without wanting to be bound by any particular theory, the present inventors believe that that the low water leachable chloride content of the mineral fibre products of the invention, even if tap water or process water is used for preparing the binder composition, is at least partly based on a capture of chloride ions within the binder matrix based on lignosulfonate lignins. This capture foreclose leaching of the chloride so that it is not available for corrosive activity.

In general, the uncured binder composition is an aqueous binder composition. The water contained in the aqueous binder composition may be purified water, non-purified water or a combination of purified water and non-purified water added.

In a preferred embodiment, the non-cured binder composition is an aqueous binder composition, wherein at least part of the water or the total water contained in the aqueous binder composition is non-purified water, the other part of the water, if any, being purified water. This is surprising since in common prior art binders purified water is usually used to avoid considerable chloride contents. Examples of purified water are osmosis water, deionized water or distilled water and further are mentioned below.

Purified water is generally water that has been mechanically filtered or processed to remove impurities and make it suitable for use. Distilled water has been the most common form of purified water, but, in recent years, water is more frequently purified by other processes including capacitive deionization, reverse osmosis, carbon filtering, microfiltration, ultrafiltration, ultraviolet oxidation, or electrodeionization. It is preferred that the purified water used in the non-cured binder composition has a chloride content of less than 10 mg/L, preferably less than 5 mg/L.

Examples of suitable non-purified water is tap water, rain water, process water or a combination thereof. The chloride content of tap water and rain water is generally in the range of 10-200 mg/L. The chloride content of process water is generally in the range of 25-200 mg/L chloride. It is preferred that the non-purified water used in the non-cured binder composition can have a chloride content of at least 10 mg/L, such as a chloride content in the range of 10-200 mg/L.

The proportion of non-purified water added can be in the range of 0 to 100 wt.-%, preferably 30 to 100 wt.-%, most preferred 50 to 100 wt.-%, based on the total weight of water contained in the non-cured binder composition, the other proportion, if any, being purified water.

In a production plant, the binder composition is usually produced in a concentrated form, i.e. the water content is kept low. After delivery, the concentrated binder composition is diluted by addition of water on site of the mineral fibre production to a suitable viscosity. The diluted binder composition is contacted with the mineral fibres and is cured to produce the mineral fibre product. It is a benefit of the present invention that non-purified water such as tap water, rain water or process water can be used for diluting the concentrated binder composition and nevertheless products with low water leachable chloride content are achieved.

The mineral wool product according to the present invention comprises mineral fibres in contact with a binder resulting from the curing of an aqueous binder composition free of phenol and formaldehyde comprising:

- a component (i) in form of one or more

  lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,

- a component (ii) in form of one or more cross-linkers;

- optionally a component (iii) in form of one or more plasticizers.

In particular, in accordance with a first aspect of the present invention, there is provided a mineral fibre product, comprising mineral fibres in contact with a binder resulting from the curing of an aqueous binder composition free of phenol and formaldehyde comprising:

- a component (i) in form of one or more

  lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,

- a component (ii) in form of one or more cross-linkers;
- optionally a component (iii) in form of one or more plasticizers,

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- epoxy compounds having a molecular weight M_W of 500 or less.

In particular, in accordance with a first aspect of the present invention, there is provided mineral fibre product, comprising mineral fibres in contact with a binder resulting from the curing of an aqueous binder composition free of phenol and formaldehyde comprising:

- a component (i) in form of one or more

  lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,

- a component (ii) in form of one or more cross-linkers;
- optionally a component (iii) in form of one or more plasticizers,

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

  in which:

  R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and

x varies from 1 to 10.

In particular, in accordance with a first aspect of the present invention, there is provided mineral fibre product, comprising mineral fibres in contact with a binder resulting from the curing of an aqueous binder composition free of phenol and formaldehyde comprising:

- a component (i) in form of one or more

  lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,

- a component (ii) in form of one or more cross-linkers;

- optionally a component (iii) in form of one or more plasticizers,

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines.

In particular, in accordance with a first aspect of the present invention, there is provided mineral fibre product, comprising mineral fibres in contact with a binder resulting from the curing of an aqueous binder composition free of phenol and formaldehyde comprising:

- a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,

- a component (ii) in form of one or more cross-linkers;
- optionally a component (iii) in form of one or more plasticizers,

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

In one embodiment, the mineral wool product according to the present invention comprises mineral fibres in contact with a binder resulting from the curing of an aqueous binder composition free of phenol and formaldehyde comprising:

- a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,
- a component (ii) in form of one or more cross-linkers selected from
    - β-hydroxyalkylamide-cross-linkers, and/or
    - epoxy compounds having a molecular weight of more than 500, such as an epoxidised oil based on fatty acid triglyceride or one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups, and/or
    - one or more cross-linkers in form of multifunctional carbodiimides, such as aliphatic multifunctional carbodiimides; and/or

  - Primid XL-552;

- optionally a component (iii) in form of one or more plasticizers,

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- epoxy compounds having a molecular weight M_W of 500 or less
- carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

  in which:

  R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

  R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and

  x varies from 1 to 10,

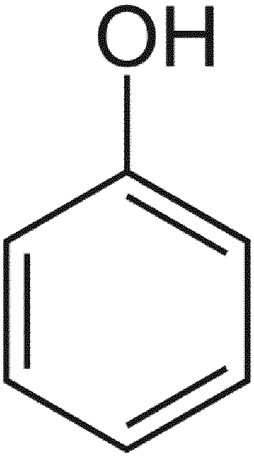
- polyamines.

In a preferred embodiment, the binders according to the present invention are formaldehyde free.

For the purpose of the present application, the term "formaldehyde free" is defined to characterize a mineral wool product where the emission is below 5 µg/m²/h of formaldehyde from the mineral wool product, preferably below 3 µg/m²/h. Preferably, the test is carried out in accordance with ISO 16000 for testing aldehyde emissions.

In a preferred embodiment, the binders are phenol free.

For the purpose of the present application, the term "phenol free" is defined in such a way that the aqueous binder composition does contain phenol



in an amount of ≤ 0.25 wt.-%, such as ≤ 0.1 wt.-%, such as ≤ 0.05 wt.-%, based on the total weight of an aqueous composition having a dry solids binder content of 15 wt.%.

In one embodiment, the binder composition does not contain added formaldehyde.

In one embodiment, the binder composition does not contain added phenol.

For the purpose of the present invention, the term "mono- and oligosaccharides" is defined to comprise monosaccharides and oligosaccharides having 10 or less saccharide units.

For the purpose of the present invention, the term "sugar" is defined to comprise monosaccharides and oligosaccharides having 10 or less saccharide units.

The non-cured binder composition for preparing of the mineral fibre product according to the present invention comprises one or more lignosulfonate lignins as a component (i).

Component (i)

Component (i) is in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins.

Lignin, cellulose and hemicellulose are the three main organic compounds in a plant cell wall. Lignin can be thought of as the glue, that holds the cellulose fibres together. Lignin contains both hydrophilic and hydrophobic groups. It is the second most abundant natural polymer in the world, second only to cellulose, and is estimated to represent as much as 20-30% of the total carbon contained in the biomass, which is more than 1 billion tons globally.

The lignosulfonate process introduces large amount of sulfonate groups making the lignin soluble in water but also in acidic water solutions. Lignosulfonates has up to 8% sulfur as sulfonate, whereas kraft lignin has 1-2% sulfur, mostly bonded to the lignin. The molecular weight of lignosulfonate is 15.000-50.000 g/mol. The typical hydrophobic core of lignin together with large number of ionized sulfonate groups make this lignin attractive as a surfactant and it often finds application in dispersing cement etc.

To produce lignin-based value-added products, lignin should be first separated from biomass, for which several methods can be employed. Kraft and sulfite pulping processes are known for their effective lignin separation from wood, and hence, are used worldwide. Kraft lignin is separated from wood with the help of NaOH and Na_2S. Lignins from sulfite pulping processes are denoted as lignosulfonates, and are produced by using sulfurous acid and/or a sulfite salt containing magnesium, calcium, sodium, or ammonium at varying pH levels. Currently, lignosulfonates account for 90 % of the total market of commercial lignin, and the total annual worldwide production of lignosulfonates is approximately 1.8 million tons. Lignosulfonates have generally abundance of sulfonic groups, and thus, a higher amount of sulfur than kraft lignin. Due to the presence of the sulfonated group, lignosulfonates are anionically charged and water soluble. The molecular weights (Mw) of lignosulfonates can be similar to or larger than that of kraft lignin. Due to their unique properties, lignosulfonates have a wide range of uses, such as animal feed, pesticides, surfactants, additives in oil drilling, stabilizers in colloidal suspensions, and as plasticizers in concrete admixtures. However, the majority of new pulp mills employ kraft technology for pulp production, and thus, kraft lignin is more readily available for value-added production.

However, lignosulfonates and kraft lignin have different properties coming from different isolation processes and thus distribution of functional groups. High level of sulfonic groups in lignosulfonates, generally at least one for every four C9 units, makes lignosulfonates strongly charged at all pH levels in water. This abundance of ionisable functional groups can explain most of the differences compared to other technical lignins. Higher charge density allows easier water solubility and higher solid content in solution possible compared to kraft lignin. Also, for the same reason, lignosulfonates will have lower solution viscosity compared to kraft lignin at the same solid content which can facilitate handling and processing. Commonly used model structure of lignosulfonates is shown on Figure 1.

In one embodiment, component (i) is having a carboxylic acid group content of 0.05 to 0.6 mmol/g, such as 0.1 to 0.4 mmol/g, based on the dry weight of lignosulfonate lignins.

In one embodiment, component (i) is in form of one or more lignosulfonate lignins having an average carboxylic acid group content of less than 1.8 groups per macromolecule considering the M_n wt. average of component (i), such as less than 1.4 such as less than 1.1 such as less than 0.7 such as less than 0.4.

In one embodiment, component (i) is having a content of phenolic OH groups of 0.3 to 2.5 mmol/g, such as 0.5 to 2.0 mmol/g, such as 0.5 to 1.5 mmol/g. based on the dry weight of lignosulfonate lignins.

In one embodiment, component (i) is having a content of aliphatic OH groups of 1.0 to 8.0 mmol/g, such as 1.5 to 6.0 mmol/g, such as 2.0 to 5.0 mmol/g, based on the dry weight of lignosulfonate lignins.

In one embodiment, component (i) comprises ammoniumlignosulfonates and/or calciumlignosulfonates, and/or magnesiumlignosulfonates, and any combinations thereof.

In one embodiment, component (i) comprises ammoniumlignosulfonates and calciumlignosulfonates, wherein the molar ratio of NH_4^+ to Ca^{2+} is in the range of 5:1 to 1:5, in particular 3:1 to 1:3.

For the purpose of the present invention, the term lignosulfonates encompasses sulfonated kraft lignins.

In one embodiment, component (i) is a sulfonated kraft lignins.

In one embodiment, the aqueous binder composition contains added sugar in an amount of 0 to 5 wt.-%, such as less than 5 wt.-%, such as 0 to 4.9 wt.-%, such as 0.1 to 4.9 wt.-%, based on the weight of lignosulfonate and sugar.

In one embodiment, the aqueous binder composition comprises component (i), i.e. the lignosulfonate, in an amount of 50 to 98 wt.-%, such as 65 to 98 wt.-%, such as 80 to 98 wt.-%, based on the total weight of components (i) and (ii).

In one embodiment, the aqueous binder composition comprises component (i), i.e. the lignosulfonate, in an amount of 50 to 88 wt.-%, such as 50 to 87 wt.-%, such as 65 to 88 wt.-%, such as 65 to 87 wt.-%, such as 80 to 88 wt.-%, such as 80 to 87 wt.-%, based on the total weight of components (i) and (ii).

In one embodiment, the aqueous binder composition comprises component (i) in an amount of 50 to 98 wt.-%, such as 65 to 98 wt.-%, such as 80 to 98 wt.-%, based on the dry weight of components (i), (ii), and (iii).

In one embodiment, the aqueous binder composition comprises component (i), i.e. the lignosulfonate, in an amount of 50 to 88 wt.-%, such as 50 to 87 wt.-%, such as 65 to 88 wt.-%, such as 65 to 87 wt.-%, such as 80 to 88 wt.-%, such as 80 to 87 wt.-%, based on the total weight of components (i), (ii) and (iii).

For the purpose of the present invention, content of lignin functional groups is determined by using ^{31}P NMR as characterization method.

Sample preparation for ^{31}P NMR is performed by using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) as phosphitylation reagent and cholesterol as internal standard. Integration is according to the work of Granata and Argyropoulos (J. Agric. Food Chem. 43:1538–1544).

Component (ii)

Component (ii) is in form of one or more cross-linkers.

In one embodiment, component (ii) is in form of one or more cross-linkers selected from

a) β-hydroxyalkylamide-cross-linkers and/or oxazoline-cross-linkers, and/or

b) the group consisting of multifunctional organic amines such as an alkanolamine, diamines, such as hexamethyldiamine, triamines, and/or

c) epoxy compounds having a molecular weight of more than 500, such as one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups, and/or

d) one or more cross-linkers selected from the group consisting of polyethylene imine, polyvinyl amine, fatty amines; and/or

e) one more cross-linkers in form of fatty amides; and/or

f) one or more cross-linkers selected from the group consisting of aromatic aldehydes such as hydroxybenzaldehyde, such as aminobenzaldehyde, such as hydroxy-methoxy benzaldehyde and/or from the group of aliphatic aldehydes such as decanal and/or

g) one or more cross-linkers selected from polyester polyols, such as polycaprolactone; and/or

h) one or more cross-linkers selected from the group consisting of starch, modified starch, CMC; and/or

i) one or more cross-linkers in form of aliphatic multifunctional carbodiimides; and/or

j) one or more cross-linkers selected from melamine based cross- linkers, such as a hexakis(methylmethoxy)melamine (HMMM) based cross-linkers.

In one embodiment, the component (ii) comprises in one embodiment one or more cross-linkers selected from β-hydroxyalkylamide-cross-linkers and/or oxazoline-cross-linkers.

β-hydroxyalkylamide-cross-linkers is a curing agent for the acid-functional macromolecules. It provides a hard, durable, corrosion resistant and solvent resistant cross-linked polymer network. It is believed the β-hydroxyalkylamide cross-linkers cure through esterification reaction to form multiple ester linkages. The hydroxy functionality of the β-hydroxyalkylamide-cross-linkers should be an average of at least 2, preferably greater than 2 and more preferably 2-4 in order to obtain optimum curing response.

Oxazoline group containing cross-linkers are polymers containing one of more oxazoline groups in each molecule and generally, oxazoline containing cross-linkers can easily be obtained by polymerizing an oxazoline derivative. The patent US 6 818 699 B2 provides a disclosure for such a process.

In one embodiment, the component (ii) is one or more epoxy compounds having a molecular weight of more than 500, such as an epoxidised oil based on fatty acid triglyceride or one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups, such as β-hydroxyalkylamide groups.

In one embodiment, component (ii) is one or more cross-linkers selected from the group consisting of fatty amines.

In one embodiment, component (ii) is one or more cross-linkers in form of fatty amides.

In one embodiment, component (ii) is one or more cross-linkers selected from polyester polyols, such as polycaprolactone.

In one embodiment, component (ii) is one or more cross-linkers selected from the group consisting of starch, modified starch, CMC.

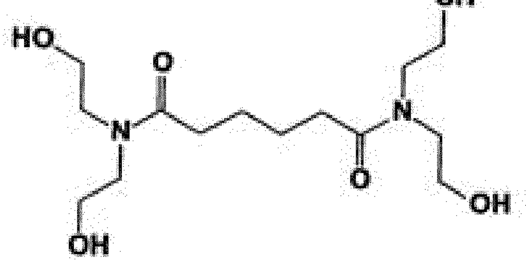
In one embodiment, component (ii) is one or more cross-linkers in form of multifunctional carbodiimides, such as aliphatic multifunctional carbodiimides.

In one embodiment, the component (ii) is one or more cross-linkers in form of aziridines, such as CX100, NeoAdd-Pax 521/523.

In one embodiment, component (ii) is one or more cross-linkers selected from melamine based cross-linkers, such as a hexakis(methylmethoxy)melamine (HMMM) based cross-linkers.

Examples of such compounds are Picassian XL 701, 702, 725 (Stahl Polymers), such as ZOLDINE® XL-29SE (Angus Chemical Company), such as CX300 (DSM), such as Carbodilite V-02-L2 (Nisshinbo Chemical Inc.).

In one embodiment, component (ii) is Primid XL552, which has the following structure:



Primid XL-552

Component (ii) can also be any mixture of the above mentioned compounds.

In one embodiment, the binder composition according to the present invention comprises component (ii) in an amount of 1 to 50 wt.-%, such as 4 to 20 wt.-%, such as 6 to 12 wt.-%, based on the dry weight of component (i).

In one embodiment, the component (ii) is in form of one or more cross-linkers selected from

- β-hydroxyalkylamide-cross-linkers, such as N-(2-hydroxyisopropyl)amide-cross-linkers, such as N-(2-hydroxyethyl)amide-cross-linkers, such as N-(2-hydroxyethyl)adipamide-cross-linkers, such as N,N,N′,N′-tetrakis(2-hydroxyethyl)adipamide and/or

- the group consisting of multifunctional organic amines such as an alkanolamine, diamines, such as hexamethyldiamine, and/or

- epoxy compounds having a molecular weight of more than 500, such as an epoxidised oil based on fatty acid triglyceride or one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups, and/or

- one or more cross-linkers in form of multifunctional carbodiimides, such as aliphatic multifunctional carbodiimides.

In one embodiment, the component (ii) comprises one or more cross-linkers selected from

- β-hydroxyalkylamide-cross-linkers, such as N-(2-hydroxyisopropyl)amide-cross-linkers, such as N-(2-hydroxyethyl)amide-cross-linkers, such as N-(2-hydroxyethyl)adipamide-cross-linkers, such as N,N,N′,N′-tetrakis(2-hydroxyethyl)adipamide.

In one embodiment, the component (ii) in an amount of 2 to 90 wt.-%, such as 6 to 60 wt.-%, such as 10 to 40 wt.-%, such as 25 to 40 wt.-%, based on the dry weight of component (i).

Component (iii) of the binder composition

Optionally and preferably, the binder composition may comprise a component (iii). Component (iii) is in form of one or more plasticizers.

In one embodiment, component (iii) is in form of one or more plasticizers selected from the group consisting of polyols, such as carbohydrates, hydrogenated sugars, such as sorbitol, erythriol, glycerol, monoethylene glycol, polyethylene glycols, polyethylene glycol ethers, polyethers, phthalates and/or acids, such as adipic acid, vanillic acid, lactic acid and/or ferullic acid, acrylic polymers, polyvinyl alcohol, polyurethane dispersions, ethylene carbonate, propylene carbonate, lactones, lactams, lactides, acrylic based polymers with free carboxy groups and/or polyurethane dispersions with free carboxy groups, polyamides, amides such as carbamide/urea, or any mixtures thereof.

In one embodiment, component (iii) is in form of one or more plasticizers selected from the group consisting of carbonates, such as ethylene carbonate, propylene carbonate, lactones, lactams, lactides, compounds with a structure similar to lignin like vanillin, acetosyringone, solvents used as coalescing agents like alcohol ethers, polyvinyl alcohol.

In one embodiment, component (iii) is in form of one or more non-reactive plasticizer selected from the group consisting of polyethylene glycols, polyethylene glycol ethers, polyethers, hydrogenated sugars, phthalates and/or other esters, solvents used as coalescing agents like alcohol ethers, acrylic polymers, polyvinyl alcohol.

In one embodiment, component (iii) is one or more reactive plasticizers selected from the group consisting of carbonates, such as ethylene carbonate, propylene carbonate, lactones, lactams, lactides, di- or tricarboxylic acids, such as adipic acid, or lactic acid, and/or vanillic acid and/or ferullic acid, polyurethane dispersions, acrylic based polymers with free carboxy groups, compounds with a structure similar to lignin like vanillin, acetosyringone.

In one embodiment, component (iii) is in form of one or more plasticizers selected from the group consisting of fatty alcohols, monohydroxy alcohols such as pentanol, stearyl alcohol.

In one embodiment, component (iii) comprises one or more plasticizers selected from the group consisting of polyethylene glycols, polyethylene glycol ethers, and/or one or more plasticizers in form of polyols, such as 1,1,1-Tris(hydroxymethyl)propane, and/or triethanolamine.

Another particular surprising aspect of the present invention is that the use of plasticizers having a boiling point of more than 100 °C, in particular 140 to 250 °C, strongly improves the mechanical properties of the mineral fibre products according to the present invention although, in view of their boiling point, it is likely that these plasticizers will at least in part evaporate during the curing of the binders in contact with the mineral fibres.

In one embodiment, component (iii) comprises one or more plasticizers having a boiling point of more than 100 °C, such as 110 to 380 °C, more preferred 120 to 300 °C, more preferred 140 to 250 °C.

It is believed that the effectiveness of these plasticizers in the binder composition according to the present invention is associated with the effect of increasing the mobility of the lignins during the curing process. It is believed that the increased mobility of the lignins during the curing process facilitates the effective cross-linking.

In one embodiment, component (iii) comprises one or more polyethylene glycols having an average molecular weight of 150 to 50000 g/mol, in particular 150 to 4000 g/mol, more particular 150 to 1000 g/mol, preferably 150 to 500 g/mol, more preferably 200 to 400 g/mol.

In one embodiment, component (iii) comprises one or more polyethylene glycols having an average molecular weight of 4000 to 25000 g/mol, in particular 4000 to 15000 g/mol, more particular 8000 to 12000 g/mol.

In one embodiment component (iii) is capable of forming covalent bonds with component (i) and/or component (ii) during the curing process. Such a component would not evaporate and remain as part of the composition but will be effectively altered to not introduce unwanted side effects e.g. water absorption in the cured product. Non-limiting examples of such a component are caprolactone and acrylic based polymers with free carboxyl groups.

In one embodiment, component (iii) is selected from the group consisting of fatty alcohols, monohydroxy alcohols, such as pentanol, stearyl alcohol.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of alkoxylates such as ethoxylates such as butanol ethoxylates, such as butoxytriglycol.

In one embodiment, component (iii) is selected from one or more propylene glycols.

In one embodiment, component (iii) is selected from one or more glycol esters.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of adipates, acetates, benzoates, cyclobenzoates, citrates, stearates, sorbates, sebacates, azelates, butyrates, valerates.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of phenol derivatives such as alkyl or aryl substituted phenols.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of silanols, siloxanes.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of sulfates such as alkyl sulfates, sulfonates such as alkyl aryl sulfonates such as alkyl sulfonates, phosphates such as tripolyphosphates; such as tributylphosphates.

In one embodiment, component (iii) is selected from one or more hydroxy acids.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of monomeric amides such as acetamides, benzamide, fatty acid amides such as tall oil amides.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of quaternary ammonium compounds such as trimethylglycine, distearyldimethylammoniumchloride.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of vegetable oils such as castor oil, palm oil, linseed oil, tall oil, soybean oil.

In one embodiment, component (iii) is in form of tall oil.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of hydrogenated oils, acetylated oils.

In one embodiment, component (iii) is selected from one or more fatty acid methyl esters.

In one embodiment, component (iii) is selected from one or more plasticizers selected from the group consisting of alkyl polyglucosides, gluconamides, aminoglucoseamides, sucrose esters, sorbitan esters.

In one embodiment, component (iii) is selected from the group consisting of polyethylene glycols, polyethylene glycol ethers.

In one embodiment, component (iii) is selected from the group consisting of triethanolamine.

In one embodiment, component (iii) is in form of propylene glycols, phenol derivatives, silanols, siloxanes, hydroxy acids, vegetable oils, polyethylene glycols, polyethylene glycol ethers, and/or one or more plasticizers in form of polyols, such as 1,1,1-Tris(hydroxymethyl)propane, triethanolamine, or any mixtures thereof.

It has surprisingly been found that the inclusion of plasticizers in the binder compositions according to the present invention strongly improves the mechanical properties of the mineral fibre products according to the present invention.

The term plasticizer refers to a substance that is added to a material in order to make the material softer, more flexible (by decreasing the glass-transition temperature Tg) and easier to process.

Component (iii) can also be any mixture of the above mentioned compounds.

In one embodiment, component (iii) is present in an amount of 0.5 to 60, preferably 2.5 to 25, more preferably 3 to 15 wt.-%, based on the dry weight of component (i).

In one embodiment, component (iii) is present in an amount of 0.5 to 60, preferably 2.5 to 25, more preferably 3 to 15 wt.-%, based on the dry weight of components (i), (ii), and (iii).

Mineral fibre product comprising mineral fibres in contact with a binder resulting from the curing of a binder composition comprising components (i) and (iia)

In one embodiment the present invention is directed to a mineral fibre product comprising mineral fibres in contact with a binder resulting from the curing of a binder composition for mineral fibres comprising:

- a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins.
- a component (iia) in form of one or more modifiers, preferably with the proviso that the aqueous binder composition does not comprise a cross-linker selected from
    - epoxy compounds having a molecular weight M_W of 500 or less,

    and/or with the proviso that the aqueous binder composition does not comprise a cross-linker selected from
    - carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

      in which:

      R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and

x varies from 1 to 10,

and/or with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines,

and/or with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

The present inventors have found that the excellent binder properties can also be achieved by a two-component system which comprises component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins and a component (iia) in form of one or more modifiers, and optionally any of the other components mentioned above and below.

In one embodiment, component (iia) is a modifier in form of one or more compounds selected from the group consisting of epoxy compounds having a molecular weight of more than 500, such as an epoxidised oil based on fatty acid triglyceride or one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups such as β-hydroxyalkylamide groups.

In one embodiment, component (iia) is one or more modifiers selected from the group consisting of polyethylene imine, polyvinyl amine, fatty amines.

In one embodiment, the component (iia) is one or more modifiers selected from multifunctional carbodiimides, such as aliphatic multifunctional carbodiimides.

Component (iia) can also be any mixture of the above mentioned compounds.

Without wanting to be bound by any particular theory, the present inventors believe that the excellent binder properties achieved by the binder composition for mineral fibres comprising components (i) and (iia), and optional further components, are at least partly due to the effect that the modifiers used as components (iia) at least partly serve the function of a plasticizer and a cross-linker.

In one embodiment, the binder composition comprises component (iia) in an amount of 1 to 40 wt.-%, such as 4 to 20 wt.-%, such as 6 to 12 wt.-%, based on the dry weight of the component (i).

Further components

In some embodiments, the mineral fibre product according to the present invention comprises mineral fibres in contact with a binder composition resulting from the curing of a binder which comprises further components.

In one embodiment, the binder composition comprises a catalyst selected from inorganic acids, such as sulfuric acid, sulfamic acid, nitric acid, boric acid, hypophosphorous acid, and/or phosphoric acid, and/or any salts thereof such as sodium hypophosphite, and/or ammonium salts, such as ammonium salts of sulfuric acid, sulfamic acid, nitric acid, boric acid, hypophosphorous acid, and/or phosphoric acid, and/or sodium polyphosphate (STTP), and/or sodium metaphosphate (STMP), and/or phosphorous oxychloride. The presence of such a catalyst can improve the curing properties of the binder compositions according to the present invention.

In one embodiment, the binder composition comprises a catalyst selected from Lewis acids, which can accept an electron pair from a donor compound forming a Lewis adduct, such as $ZnCl_2$, Mg $(ClO_4)_2$, Sn $[N(SO_2\text{-n-}C_8F_{17})_2]_4$.

In one embodiment, the binder composition comprises a catalyst selected from metal chlorides, such as KCl, $MgCl_2$, $ZnCl_2$, $FeCl_3$ and $SnCl_2$ or their adducts such as $AlCl_3$ adducts, such as BF_3 adducts, such as BF_3 ethylamine complex.

In one embodiment, the binder composition comprises a catalyst selected from organometallic compounds, such as titanate-based catalysts and stannum based catalysts.

In one embodiment, the binder composition comprises a catalyst selected from chelating agents, such as transition metals, such as iron ions, chromium ions, manganese ions, copper ions and/or from peroxides such as organic peroxides such as dicumyl peroxide.

In one embodiment, the binder composition according to the present invention comprises a catalyst selected from phosphites such as alkyl phosphites, such as aryl phosphites such as triphenyl phosphite.

In one embodiment, the binder composition according to the present invention comprises a catalyst selected from the group of ternary amines such as tris-2,4,6-dimethylaminomethyl phenol.

In one embodiment, the binder composition further comprises a further component (iv) in form of one or more silanes.

In one embodiment, the binder composition comprises a further component (iv) in form of one or more coupling agents, such as organofunctional silanes.

In one embodiment, component (iv) is selected from group consisting of organofunctional silanes, such as primary or secondary amino functionalized silanes, epoxy functionalized silanes, such as polymeric or oligomeric epoxy functionalized silanes, methacrylate functionalized silanes, alkyl and aryl functionalized silanes, urea funtionalised silanes or vinyl functionalized silanes.

In one embodiment, the binder composition further comprises a component (v) in form of one or more components selected from the group of bases, such as ammonia, such as alkali metal hydroxides, such as KOH, such as earth alkaline metal hydroxides, such as $Ca(OH)_2$, such as $Mg(OH)_2$, such as amines or any salts thereof.

In one embodiment, the binder composition further comprises a further component in form of urea, in particular in an amount of 5 to 40 wt.-%, such as 10 to 30 wt.-%, 15 to 25 wt.-%, based on the dry weight of component (i).

In one embodiment, the binder composition further comprises a further component in form of one or more carbohydrates selected from the group consisting of sucrose, reducing sugars, in particular dextrose, polycarbohydrates, and mixtures thereof, preferably dextrins and maltodextrins, more preferably glucose syrups, and more preferably glucose syrups with a dextrose equivalent value of DE = 30 to less than 100, such as DE = 60 to less than 100, such as DE = 60-99, such as DE = 85-99, such as DE = 95-99.

In one embodiment, the binder composition further comprises a further component in form of one or more carbohydrates selected from the group consisting of sucrose and reducing sugars in an amount of 5 to 50 wt.-%, such as 5 to less than 50 wt.-%, such as 10 to 40 wt.-%, such as 15 to 30 wt.-% based on the dry weight of component (i).

In one embodiment, the mineral fibre product according to the present invention comprises mineral fibres in contact with the binder composition comprising a further component in form of one or more silicone resins.

In one embodiment, the binder composition according to the present invention comprises a further component (vi) in the form of one or more reactive or nonreactive silicones.

In one embodiment, the component (vi) is selected from the group consisting of silicone constituted of a main chain composed of organosiloxane residues, especially diphenylsiloxane residues, alkylsiloxane residues, preferably dimethylsiloxane residues, bearing at least one hydroxyl, carboxyl or anhydride, amine, epoxy or vinyl functional group capable of reacting with at least one of the constituents of the binder composition and is preferably present in an amount of 0.025-15 weight-%, preferably from 0.1-10 weight-%, more preferably 0.3-8 weight-%, based on the binder solids.

In one embodiment, the mineral fibre product according to the present invention comprises mineral fibres in contact with the binder composition comprising a further component in form of one or more mineral oils.

In the context of the present invention, a binder composition having a sugar content of 50 wt.-% or more, based on the total dry weight of the binder components, is considered to be a sugar based binder. In the context of the present invention, a binder composition having a sugar content of less than 50 wt.-%, based on the total dry weight of the binder components, is considered a non-sugar based binder.

In one embodiment, the binder composition further comprises a further component in form of one or more surface active agents that are in the form of non-ionic and/or ionic emulsifiers such as polyoxyethylenes (4) lauryl ether, such as soy lecithin, such as sodium dodecyl sulfate.

The use of lignin-based sulfonated products in binders may result in an increase in the hydrophilicity of some binders and final products, meaning one or more hydrophobic agents are to be added, such as one or more mineral oils, such as one or more silicone oil, such as one or more silicone resin.

In one embodiment, the aqueous binder composition consists essentially of

- a component (i) in form of one or more lignins selected from the group of:
    - lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,

      and/or
- a component (ii) in form of one or more cross-linkers;
- a component (iii) in form of one or more plasticizers;
- a component (iv) in form of one or more coupling agents, such as organofunctional silanes;
- optionally a component in form of one or more compounds selected from the group of bases, such as ammonia, such as alkali metal hydroxides, such as KOH, such as earth alkaline metal hydroxides, such as $Ca(OH)_2$, such as $Mg(OH)_2$, such as amines or any salts thereof;
- optionally a component in form of urea;
- optionally a component in form of a more reactive or non-reactive silicones;
- optionally a hydrocarbon oil;
- optionally one or more surface active agents;

- water,

preferably with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- epoxy compounds having a molecular weight M_W of 500 or less

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

    in which:

    R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

    R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and x varies from 1 to 10

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

In one embodiment, the aqueous binder composition consists essentially of

- a component (i) in form of one or more lignins selected from the group of:
    - lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins,
- a component (ii) in form of one or more cross-linkers;
- a component (iii) in form of one or more plasticizers;

- a component (iv) in form of one or more coupling agents, such as organofunctional silanes;
- optionally a component in form of one or more compounds selected from the group of bases, such as ammonia, such as alkali metal hydroxides, such as KOH, such as earth alkaline metal hydroxides, such as $Ca(OH)_2$, such as $Mg(OH)_2$, such as amines or any salts thereof;
- optionally a component in form of urea;
- optionally a component in form of a more reactive or non-reactive silicones;
- optionally a hydrocarbon oil;
- optionally one or more surface active agents;
- water,

preferably with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- epoxy compounds having a molecular weight M_W of 500 or less

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

  in which:

  R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

  R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and x varies from 1 to 10

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

In one embodiment, the aqueous binder composition according to the present invention consists essentially of

- a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins;
- and/or
- a component (ii) in form of one or more cross-linkers;
- a component (iv) in form of one or more coupling agents, such as organofunctional silanes;
- optionally a component in form of one or more compounds selected from the group of ammonia, amines or any salts thereof;
- optionally a component in form of urea;
- optionally a component in form of a more reactive or non-reactive silicones;
- optionally a hydrocarbon oil;
- optionally one or more surface active agents,

preferably with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- epoxy compounds having a molecular weight M_W of 500 or less

  and/or

  with the proviso that the aqueous binder composition does not comprise a cross-linker selected from
- carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

  in which:

  R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and x varies from 1 to 10

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

In one embodiment, the aqueous binder composition according to the present invention consists essentially of

- a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins;
- a component (ii) in form of one or more cross-linkers;
- a component (iv) in form of one or more coupling agents, such as organofunctional silanes;
- optionally a component in form of one or more compounds selected from the group of ammonia, amines or any salts thereof;
- optionally a component in form of urea;
- optionally a component in form of a more reactive or non-reactive silicones;
- optionally a hydrocarbon oil;
- optionally one or more surface active agents,

preferably with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- epoxy compounds having a molecular weight M_W of 500 or less

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$

in which:

R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical to contain other functional groups,

R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and x varies from 1 to 10

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines

and/or

with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

The present inventors have surprisingly found that mineral fiber products comprising mineral fibers in contact with a binder resulting in the curing of an aqueous binder composition as it is described above have at a very high stability, both when freshly produced and after aging conditions.

Further, the present inventors have found that even higher product stability can be obtained by using a curing temperature of >230 °C.

In one embodiment, the present invention is therefore directed to a mineral fiber product comprising mineral fibers in contact with a binder resulting from the curing of an aqueous binder composition as it is described above, where the curing temperature of >230 °C is used.

The present inventors have further found that the stability of the mineral fiber product can be further increased by the following measures:

- Lower line capacity, meaning longer curing time

- Addition of silicone resins

- Addition of high amounts of crosslinker

- Addition of a combination of two or more different crosslinkers

- Addition of small amounts of cationic species such as multivalent metal ions such as calcium and/or organic cationic species such as amines and/or organically modified inorganic compounds such as amine modified montmorillonite clays.

Mineral fibre product comprising mineral fibres in contact with a binder resulting from the curing of a binder composition comprising components (i) and (iia)

In one embodiment the present invention is directed to a mineral fibre product comprising mineral fibres in contact with a binder resulting from the curing of a binder composition for mineral fibres comprising:

- a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins.
- a component (iia) in form of one or more modifiers, preferably with the proviso that the aqueous binder composition does not comprise a cross-linker selected from
    - epoxy compounds having a molecular weight M_W of 500 or less,
    and/or with the proviso that the aqueous binder composition does not comprise a cross-linker selected from
    - carbonyl compounds selected from aldehydes, carbonyl compounds of the formula $R—[C(O)R_1]_x$
      in which:
      R represents a saturated or unsaturated and linear, branched or cyclic hydrocarbon radical, a radical including one or more aromatic nuclei which consist of 5 or 6 carbon atoms, a radical including one or more aromatic heterocycles containing 4 or 5 carbon atoms and an oxygen, nitrogen or sulfur atom, it being possible for the R radical

to contain other functional groups,

R_1 represents a hydrogen atom or a C_1-C_{10} alkyl radical, and

x varies from 1 to 10,

and/or with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- polyamines,

and/or with the proviso that the aqueous binder composition does not comprise a cross-linker selected from

- mono- and oligosaccharides.

The present inventors have found that the excellent binder properties can also be achieved by a two-component system which comprises component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 2.0 mmol/g, such as 0.03 to 1.4 mmol/g, such as 0.075 to 2.0 mmol/g, such as 0.075 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins and a component (iia) in form of one or more modifiers, and optionally any of the other components mentioned above and below.

In one embodiment, component (iia) is a modifier in form of one or more compounds selected from the group consisting of epoxy compounds having a molecular weight of more than 500, such as an epoxidised oil based on fatty acid triglyceride or one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups such as β-hydroxyalkylamide groups.

In one embodiment, component (iia) is one or more modifiers selected from the group consisting of polyethylene imine, polyvinyl amine, fatty amines.

In one embodiment, the component (iia) is one or more modifiers selected from multifunctional carbodiimides, such as aliphatic multifunctional carbodiimides.

Component (iia) can also be any mixture of the above mentioned compounds.

Without wanting to be bound by any particular theory, the present inventors believe that the excellent binder properties achieved by the binder composition for mineral fibres comprising components (i) and (iia), and optional further components, are at least partly due to the effect that the modifiers used as components (iia) at least partly serve the function of a plasticizer and a cross-linker.

In one embodiment, the binder composition comprises component (iia) in an amount of 1 to 40 wt.-%, such as 4 to 20 wt.-%, such as 6 to 12 wt.-%, based on the dry weight of the component (i).

A Method for Producing a Mineral Fibre Product

The mineral fibre product of the present invention can be prepared by a common method for producing a mineral fibre product by binding mineral fibres with the binder composition. Accordingly, the mineral fibre product of the present invention is preferably prepared by a method which comprises the steps of contacting mineral fibres with an uncured and preferably aqueous binder composition comprising one or more lignosulfonate lignins.

Preferably, the lignosulfonate lignin has a carboxylic acid group content of 0.03 to 1.4 mmol/g based on the dry weight of the lignosulfonate lignins.

In particular, the present invention also relates to a method for the manufacture of a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins, wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001, the method comprising the steps of

a) providing a non-cured aqueous binder composition comprising one or more lignosulfonate lignins and water,

b) contacting mineral fibres with the non-cured aqueous binder composition, and

c) curing the binder composition in contact with the mineral fibers,

wherein at least part of the water or the total water contained in the non-cured aqueous binder composition is non-purified water added, wherein the non-purified water is preferably selected from tap water, rain water, process water or a combination thereof.

Preferably, the lignosulfonate lignin has a carboxylic acid group content of 0.03 to 1.4 mmol/g based on the dry weight of the lignosulfonate lignins.

In a preferred embodiment of the method of the invention, the proportion of non-purified water added is in the range of 30 to 100 wt.-%, more preferably 50 to 100 wt.-%, based on the total weight of water contained in the non-cured binder composition.

In a further preferred embodiment of the method of the invention, the water content in the non-cured aqueous binder composition is in the range of 40 to 90 wt.-%, preferably 60 to 85 wt.-%, based on the total weight of the non-cured aqueous binder composition.

The mineral fibre product obtained in the method according to the invention can have all features which are described herein for the inventive mineral fibre product so that reference is made thereto.

In a preferred embodiment, the non-cured aqueous binder composition comprises

- a component (i) in form of one or more lignosulfonate lignins;
- a component (ii) in form of one or more cross-linkers;
- optionally a component (iii) in form of one or more plasticizers.

Preferably, the lignosulfonate lignin has a carboxylic acid group content of 0.03 to 1.4 mmol/g based on the dry weight of the lignosulfonate lignins.

As mentioned above, in a preferred embodiment the non-cured binder composition for use is prepared by diluting a concentrated form of the binder composition by addition of non-purified water.

Curing

The uncured binder composition in mineral fibre product precursor such as a web where the mineral fibres are in contact with the binder composition is cured by a chemical and/or physical reaction of the binder components.

In one embodiment, the curing takes place in a curing device.

In one embodiment, the curing is carried out at temperatures from 100 to 300°C, such as 170 to 270°C, such as 180 to 250°C, such as 190 to 230°C.

In one embodiment, the curing takes place in a conventional curing oven for mineral wool production operating at a temperature of from 150 to 300°C, such as 170 to 270°C, such as 180 to 250°C, such as 190 to 230°C.

In one embodiment, the curing takes place for a time of 30 seconds to 20 minutes, such as 1 to 15 minutes, such as 2 to 10 minutes.

In a typical embodiment, curing takes place at a temperature of 150 to 250 °C for a time of 30 seconds to 20 minutes.

The curing process may commence immediately after application of the binder to the fibres. The curing is defined as a process whereby the binder composition undergoes a physical and/or chemical reaction which in case of a chemical reaction usually increases the molecular weight of the compounds in the binder composition and thereby increases the viscosity of the binder composition, usually until the binder composition reaches a solid state.

In one embodiment the curing process comprises drying by pressure. The pressure may be applied by blowing air or gas through/over the mixture of mineral fibres and binder.

Mineral Fibre Product according to the Present Invention

The present invention is directed to a mineral fibre product comprising mineral fibres in contact with a cured binder composition as described above, i.e. in contact with a cured binder resulting from the curing of the binder composition, preferably aqueous binder composition, described above.

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 stone wool product. In a preferred embodiment, the mineral fibres are stone fibres or stone wool, respectively.

Fibre/melt composition

The man-made vitreous fibres (MMVF) can have any suitable oxide composition. The fibres can be glass fibres, ceramic fibres, basalt fibres, slag fibres or rock or stone fibres. The fibres are preferably of the types generally known as rock, stone or slag fibres, most preferably stone fibres.

Stone fibres commonly comprise the following oxides, in percent by weight:

SiO_2: 30 to 51

Al_2O_3: 12 to 30

CaO: 8 to 30

MgO: 2 to 25

FeO (including Fe_2O_3): 2 to 15

Na_2O+K_2O: not more than 10

CaO+MgO: 10 to 30

In preferred embodiments the MMVF have the following levels of elements, calculated as oxides in wt%:

SiO_2: at least 30, 32, 35 or 37; not more than 51, 48, 45 or 43

Al_2O_3: at least 12, 16 or 17; not more than 30, 27 or 25

CaO: at least 8 or 10; not more than 30, 25 or 20

MgO: at least 2 or 5; not more than 25, 20 or 15

FeO (including Fe_2O_3): at least 4 or 5; not more than 15, 12 or 10

FeO+MgO: at least 10, 12 or 15; not more than 30, 25 or 20

Na_2O+K_2O: zero or at least 1; not more than 10

CaO+MgO: at least 10 or 15; not more than 30 or 25

TiO_2: zero or at least 1; not more than 6, 4 or 2

TiO_2+FeO: at least 4 or 6; not more than 18 or 12

B_2O_3: zero or at least 1; not more than 5 or 3

P_2O_5: zero or at least 1; not more than 8 or 5

Others: zero or at least 1; not more than 8 or 5

The MMVF made by the method of the invention preferably have the composition in wt%:

SiO_2	35 to 50
Al_2O_3	12 to 30
TiO_2	up to 2
Fe_2O_3	3 to 12

CaO	5 to 30
MgO	up to 15
Na_2O	0 to 15
K_2O	0 to 15
P_2O_5	up to 3
MnO	up to 3
B_2O_3	up to 3

Another preferred composition for the MMVF is as follows in wt%:

SiO_2	39-55% preferably 39-52%
Al_2O_3	16-27% preferably 16-26%
CaO	6-20% preferably 8-18%
MgO	1-5% preferably 1-4.9%
Na_2O	0-15% preferably 2-12%
K_2O	0-15% preferably 2-12%
R_2O (Na_2O + K_2O)	10-14.7% preferably 10-13.5%
P_2O_5	0-3% preferably 0-2%
Fe_2O_3 (iron total)	3-15% preferably 3.2-8%
B_2O_3	0-2% preferably 0-1%

TiO_2	0-2% preferably 0.4-1%
Others	0-2.0%

Glass fibres commonly comprise the following oxides, in percent by weight:

SiO_2: 50 to 70

Al_2O_3: 10 to 30

CaO: not more than 27

MgO: not more than 12

Glass fibres can also contain the following oxides, in percent by weight:

Na_2O+K_2O: 8 to 18, in particular Na_2O+K_2O greater than $CaO+MgO$ B_2O_3: 3 to 12

Some glass fibre compositions can contain Al_2O_3: less than 2%.

In a preferred embodiment, the mineral fibres are hydrophobically treated mineral fibres, preferably hydrophobically treated stone wool. The hydrophobic treatment is a common treatment and may be effected e.g. by adding at least one hydrophobic agent such as a mineral oil, a siloxane or reactive or nonreactive silicone during the mineral fibre manufacturing process, forming a hydrophobic film around the fibres. Accordingly, hydrophobically treated mineral fibres preferably have a hydrophobic film on the surface thereof.

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 air- borne mineral fibres. The non-cured and preferably aqueous binder composition is normally applied in an amount of 0.1 to 18%, preferably 0.2 to 8 % by weight, of the bonded mineral fibre product on a dry basis.

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.

Typically, the curing oven is operated at a temperature of from about 150°C to about 300°C, such as 170 to 270°C, such as 180 to 250°C, such as 190 to 230°C. Generally, the curing oven residence time is from 30 seconds to 20 minutes, such as 1 to 15 minutes, such as 2 to 10 minutes, depending on, for instance, the product density.

In a typical embodiment, the mineral fibre product according to the present invention is cured at a temperature of 150°C to 250°C for a time of 30 seconds to 20 minutes.

If desired, the mineral fibre web may be subjected to a shaping process before curing. The bonded mineral fibre product emerging from the curing oven may be cut to a desired format e.g., in the form of a batt.

In a preferred embodiment, the mineral fibre product according to the present invention is a thermal and/or acoustic insulation product, preferably a thermal insulation product.

The mineral fibre products can have the form of a preformed pipe section, a wired mat or a slab.

The preformed pipe section may be a in the form of a hollow cylinder or a part thereof. The dimensions of the preformed pipe section shall fit to the pipe to be insulated. Wired mats are lightly bonded mineral fibre mats stitched on galvanized wired mesh with galvanized wire.

In a preferred embodiment, the mineral fibre product according to the present invention is a thermal and/or acoustic insulation for a pipe, a storage tank, a boiler, a vessel or a column, preferably a pipe.

In a preferred embodiment, the mineral fibre product according to the present invention has a thickness in the range of 20 mm to 500 mm or 25 mm to 300 mm, preferably 30 mm to 300 mm, such as 50 mm to 150 mm, wherein in general the mineral fibre product is in form of a sheet.

The mineral fibre products according to the present invention generally have a density within the range of from 6 to 250 kg/m^3, preferably 20 to 200 kg/m^3. The mineral fibre products generally have a loss on ignition (LOI) within the range of 0.3 to 18.0 %, preferably 0.5 to 8.0 %.

Use of the Mineral Fibre Product according to the Present Invention

A use according to the present invention of a mineral fibre product is directed to a use as a thermal and/or acoustic insulation, in particular as non-corrosive thermal and/or acoustic insulation.

The term "non-corrosive" here means that the thermal and/or acoustical insulation material does not contribute to increased corrosion. "Non-corrosive" does not imply that corrosion cannot appear, but then it is caused by other factors than the thermal and/or acoustical insulation material itself.

Accordingly, the invention also relates to a use of a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins, as a thermal and/or acoustic insulation, in particular a non-corrosive thermal and/or acoustic insulation. It is generally preferred that the mineral fibre product has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

Preferably, the lignosulfonate lignin has a carboxylic acid group content of 0.03 to 1.4 mmol/g based on the dry weight of the lignosulfonate lignins.

In a preferred embodiment of the use according to the invention, the mineral fibre product is used as a thermal and/or acoustic insulation, in particular a non- corrosive thermal and/or acoustic insulation, for an object selected from a pipe, a storage tank, a boiler, a vessel or a column, preferably a pipe. A pipe or pipework, respectively, also includes exhaust ducts.

In a preferred embodiment of the use according to the invention, the mineral fibre product is used as a termal and/or acoustic insulation for an object made of metal, wherein the object is generally a hollow object, for which examples are given above. The metal is preferably selected from copper or steel, wherein steel is preferred. The steel is preferably carbon steel, stainless steel, austenitic stainless steel, non-alloy steel or low alloy steel. In a particular preferred embodiment, the object is a steel pipe.

In a preferred embodiment of the use according to the invention, the use is preferably at temperatures in the range of -20 °C to 320 °C, more preferably 0 °C to 200 °C, such as 50 °C to 175 °C. The temperature refers to the temperature of the object insulated by the mineral fibre product, i.e. the operating temperature. The operation may be continuous or cyclic with respect to the temperature. In case of cyclic operation, the above temperature range generally refers to the maximum temperature of the operation.

The object covered by the mineral fibre product as a thermal and/or acoustic insulation, in particular a non-corrosive thermal and/or acoustic insulation, generally includes a medium which may be selected from a gas, steam or a fluid. The mineral fibre product for the use according to the invention can have all features which have been described above for the inventive mineral fibre product so that reference is made thereto.

Hollow Object with Thermal and/or Acoustic Insulation according to the Present Invention

The invention also relates to a hollow object covered with a mineral fibre product as a thermal and/or acoustic insulation, wherein the mineral fibre product comprises mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins.

Preferably, the lignosulfonate lignin has a carboxylic acid group content of 0.03 to 1.4 mmol/g based on the dry weight of the lignosulfonate lignins.

It is preferred that the mineral fibre product has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

In a preferred embodiment, the hollow object is selected from a pipe, a storage tank, a boiler, a vessel or a column, preferably a pipe. A pipe or pipework, respectively, also includes exhaust ducts.

In a preferred embodiment, the hollow object is made of metal. The metal is preferably selected from copper or steel, wherein steel is preferred. The steel is preferably carbon steel, stainless steel, austenitic stainless steel, non-alloy steel or low alloy steel. In a particular preferred embodiment, the object is a steel pipe.

The mineral fibre product covering the hollow object according to the invention can have all features which have been described above for the inventive mineral fibre product so that reference is made thereto.

Examples

In the following examples, several binders which fall under the definition of the present invention were prepared and compared to binders according to the prior art.

Lignosulfonates were supplied by Borregaard, Norway and LignoTech, Florida as liquids with approximately 50 % solid content. Primid XL552 was supplied by EMS-CHEMIE AG. PEG 200 was supplied by Sigma-Aldrich and was assumed anhydrous for simplicity and used as such. Silane (Momentive VS-142 40% activity), was supplied by Momentive and was calculated as 100% for simplicity. Silicone resin BS 1052 was supplied by Wacker Chemie AG. NH4OH 24.7% was supplied by Univar and used in supplied form.

The following properties were determined for the binders according to the present invention and the binders according to the prior art, respectively:

Determination of the water leachable chloride content of mineral fibre products

The water leachable chloride content of the mineral fibre product is measured according to EN 13468:2001. The standard specifies the equipment and procedures for determining trace quantities of the water soluble chloride in an aqueous extract of the product. Reference is made thereto. The water leachable chloride content is given in mg chloride per kg mineral fibre product.

Determination of the loss of ignition (LOI) of mineral fibre products

The quantity of organic material (loss of ignition) is determined as the loss of weight of the specimen obtained by burning away of organic material. This is done as specified in EN 13820. The binder content is taken as the LOI. The binder includes oil and other binder additives, if present.

Determination of binder dry solid matter

The content of binder after curing is termed "binder solids".

Disc-shaped stone wool samples (diameter: 5 cm; height 1 cm) were cut out of stone wool and heat-treated at 580 °C for at least 30 minutes to remove all organics. The solids of the binder mixture was measured by distributing a sample of the binder mixture (approx. 2 g) onto a heat treated stone wool disc in a tin foil container. The weight of the tin foil container containing the stone wool disc was weighed before and directly after addition of the binder mixture. Two such binder mixture loaded stone wool discs in tin foil containers were produced and they were then heated at 200 °C for 1 hour. After cooling and storing at room temperature for 10 minutes, the samples were weighed and the binder solids was calculated as an average of the two results.

Unless stated otherwise, the following reagents were used as received:

PEG 200: supplied by Sigma-Aldrich and assumed anhydrous for simplicity and used as such.

Primid XL552: hydroxyalkylamide crosslinker supplied by EMS-CHEMIE AG

Binder example, reference binder A3 (Phenol-formaldehyde resin modified with urea and dextrose, a PUF-resol)

This binder is a phenol-formaldehyde resin modified with urea, a PUF-resol.

A phenol-formaldehyde resin is prepared by reacting 37% aq. formaldehyde (606 g) and phenol (189 g) in the presence of 46% aq. potassium hydroxide (25.5 g) at a reaction temperature of 84°C preceded by a heating rate of approximately 1°C per minute. The reaction is continued at 84 °C until the acid tolerance of the resin is 4 and most of the phenol is converted. Urea (241 g) is then added and the mixture is cooled.

The acid tolerance (AT) expresses the number of times a given volume of a binder can be diluted with acid without the mixture becoming cloudy (the binder precipitates). Sulfuric acid is used to determine the stop criterion in a binder production and an acid tolerance lower than 4 indicates the end of the binder reaction.

To measure the AT, a titrant is produced from diluting 2.5 ml conc. sulfuric acid (>99 %) with 1 L ion exchanged water. 5 mL of the binder to be investigated is then titrated at room temperature with this titrant while keeping the binder in motion by manually shaking it; if preferred, use a magnetic stirrer and a magnetic stick. Titration is continued until a slight cloud appears in the binder, which does not disappear when the binder is shaken.

The acid tolerance (AT) is calculated by dividing the amount of acid used for the titration (mL) with the amount of sample (mL):

AT = (Used titration volume (mL)) / (Sample volume (mL))

Using the urea-modified phenol-formaldehyde resin obtained, a binder is made by addition of 25% aq. ammonia (90 mL) and ammonium sulfate (13.2 g) followed by water (1.30 kg).

To the above mix is added 18% Dextrose (127.5 g) based upon the dry matter of the above binder and the dextrose. The binder solids were then measured as described above and the mixture was diluted with the required amount of water and silane (15 % binder solids solution, 0.5% silane of binder solids) for production of an insulation product.

Dilution water used for reference binder A3 was process water.

Binder example A1 and A2:

Made as described in example A3, but without addition of dextrose. For binder example A1 process water is used, and for A2 osmosis water.

Binder example, reference binder B1 and B2

A mixture of 75.1% aq. glucose syrup (19.98 kg; thus efficiently 15.0 kg glucose syrup), 50% aq. hypophosphorous acid (0.60 kg; thus efficiently 0.30 kg, 4.55 mol hypophosphorous acid) and sulfamic acid (0.45 kg, 4.63 mol) in water (30.0 kg) was stirred at room temperature until a clear solution was obtained. 28% aq. ammonia (0.80 kg; thus efficiently 0.22 kg, 13.15 mol ammonia) was then added dropwise until pH = 7.9.

The binder solids was then measured (21.2%). For mechanical strength studies (15 % binder solids solution, 0.5% silane of binder solids), the binder mixture was diluted with water (0.403 kg / kg binder mixture) and 10% aq. silane (0.011 kg / kg binder mixture, Momentive VS-142). The final binder mixture for had pH = 7.9 and was used for production of an insulation product.

For binder B1 rain water was used and for B2 process water.

Examples 1, 2 and 3 – mineral wool products according to the invention:

The stonewool products according to examples 1, 2, and 3 have been produced with the following binders:

Example 1

1163.0 kg of ammonium lignosulfonate was placed in a mixing vessel to which 14 l NH_4OH (24,7 %) was added and stirred. Afterwards, 240 kg Primid XL552 solution (pre-made 31 wt% solution in water) and 68 kg PEG 200 (100 % solids) were added and mixed followed by addition of 21 kg Silane (Momentive VS-142 40% activity, 10% in water).

Example 2

1910.0 kg of ammonium lignosulfonate was placed in a mixing vessel to which 22 l NH_4OH (24,7 %) was added and stirred. Afterwards, 395 kg Primid XL552 solution (pre-made 31 wt% solution in water) and 112 kg PEG 200 (100 % solids) were added and mixed followed by addition of 34 kg Silane (Momentive VS-142 40% activity, 10% in water).

Example 3

1395.0 kg of ammonium lignosulfonate was placed in a mixing vessel to which 16 l NH_4OH (24,7 %) was added and stirred. Afterwards, 289 kg Primid XL552 solution (pre-made 31 wt% solution in water) and 82 kg PEG 200 (100 % solids) were added and mixed followed by addition of 25 kg Silane (Momentive VS-142 40% activity, 10% in water) and 76 kg silicone (Wacker BS 1052, 12% in water).

This binder was used to produce the stonewool products according to examples 1, 2, and 3 as shown in table 1. Curing oven temperature was set to 255 °C for examples 1 and 2 and to 275 °C for example 3.

Stonewool products with Reference binders A1 to A3, reference binders B1 and B2 and binder examples 1 to 3 (inventive products) were made in a standard stonewool factory using the specified water type in table 1.

The stonewool products obtained were tested with respect to binder dry solid matter, loss of ignition and chloride content according to the methods described above as well as pH value. The results are also shown in Table 1.

Table 1

Material	Ref A1	Ref A2	Ref A3	Ref B1	Ref B2	1	2	3
water type for stone wool production	process water	Osmosis water	process water	rain water	Process water	Process water	Process water	Process water
water dosed L/h	2682	2750	4883	3300	3500	3442	2500	6000
Binder formulation:								
Ammonium lignosulfonate (kg) (50%)	-	-	-	-	-	1163	1910	1395
PEG 200 (kg) (100%)	-	-	-	-	-	68	112	82
Primid XL 552 (kg) (31%)	-	-	-	-	-	240	395	289
Results:								
Binder dry solid matter, 200C, 1h	42,5	42,5	42,5	20,0	20,0	38,7	39,0	39
Loss of ignition, stone wool product	3,5	3,5	3,5	3,8	3,5	3,5	3,5	3,5
Cl, mg/kg (EN 13468)	44,5	5,2	39,3	16	12,4	4,2	3,1	4,3
pH	9,5	9,9	9,7	6,8	7,1	6,5	7,1	7,1

Claims

1. A mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising
   - a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins

   wherein the mineral fibre product has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

2. The mineral fibre product according to claim 1, wherein the mineral fibre product has a water leachable chloride content of less than 6 mg/kg in accordance with EN 13468:2001.

3. The mineral fibre product according to claim 1 or claim 2, which is a thermal and/or acoustic insulation product.

4. The mineral fibre product according to any of the preceding claims, wherein the mineral fibre product is a thermal and/or acoustic insulation for a pipe, a storage tank, a boiler, a vessel or a column, and/or

   wherein the mineral fibre product is in the form of a preformed pipe section, a wired mat or a slab, and/or

   wherein the mineral fibre product has a thickness in the range of 20 mm to 500 mm, preferably 30 mm to 300 mm, such as 50 mm to 150 mm.

5. The mineral fibre product according to any of the preceding claims, wherein the non-cured binder composition is an aqueous binder composition, wherein preferably at least part of the water or the total water contained in the aqueous binder composition is non-purified water, wherein the non-purified water is preferably selected from tap water, rain water, process water or a combination thereof.

6. The mineral fibre product according to any of the preceding claims, wherein the non-cured binder composition comprises:

   - a component (i) in form of one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins;

   - a component (ii) in form of one or more cross-linkers;

   - optionally a component (iii) in form of one or more plasticizers.

7. The mineral fibre product according to any of the preceding claims, wherein component (i) is having a carboxylic acid group content of 0.05 to 0.6 mmol/g, based on the dry weight of lignosulfonate lignins.

8. The mineral fibre product according to any of the preceding claims, wherein component (i) is in form of one or more lignosulfonate lignins having an average carboxylic acid group content of less than 1.8 groups per macromolecule considering the M_n wt. average of component (i), such as less than 1.4 such as less than 1.1 such as less than 0.7 such as less than 0.4.

9. The mineral fibre product according to any of the preceding claims, wherein component (i) is having a content of phenolic OH groups of 0.3 to 2.5 mmol/g, such as 0.5 to 2.0 mmol/g, such as 0.5 to 1.5 mmol/g. based on the dry weight of lignosulfonate lignins.

10. The mineral fibre product according to any of the preceding claims, wherein component (i) is having a content of aliphatic OH groups of 1.0 to 8.0 mmol/g, such as 1.5 to 6.0 mmol/g, such as 2.0 to 5.0 mmol/g, based on the dry weight of lignosulfonate lignins.

11. The mineral fibre product according to any of the preceding claims, wherein the component (i) comprises ammoniumlignosulfonates and/or calcium-lignosulfonates, and/or magnesiumlignosulfonates, and any combinations thereof.

12. The mineral fibre product according to any of the preceding claims, wherein component (i) comprises ammoniumlignosulfonates and calciumlignosulfonates, wherein the molar ratio of NH_4+ to Ca_2+ is in the range of 5:1 to 1:5, in particular 3:1 to 1:3.

13. The mineral fibre product according to any of the preceding claims, wherein the aqueous binder composition contains added sugar in an amount of 0 to less than 5 wt.-%, based on the weight of lignosulfonate and sugar.

14. The mineral fibre product according to any of the preceding claims, wherein the binder composition comprises component (i) in an amount of 50 to 98 wt.-%, such as 65 to 98 wt.-%, such as 80 to 98 wt.-%, based on the dry weight of components (i) and (ii).

15. The mineral fibre product according to any of the preceding claims, wherein the binder composition comprises component (i) in an amount of 50 to 88 wt.-%, such as 50 to 87 wt.-%, such as 65 to 88 wt.-%, such as 65 to 87 wt.-%, such as 80 to 88 wt.-%, such as 80 to 87 wt.-%, based on the dry weight of components (i) and (ii).

16. The mineral fibre product according to any of the preceding claims, wherein the aqueous binder composition comprises component (i) in an amount of 50 to 98 wt.-%, such as 65 to 98 wt.-%, such as 80 to 98 wt.-%, based on the dry weight of components (i) and (ii).

17. The mineral fibre product according to any of claims 6 to 14, wherein the component (ii) is in form of one or more cross-linkers selected from

    a) β-hydroxyalkylamide-cross-linkers and/or oxazoline-cross-linkers, and/or

    b) multifunctional organic amines such as an alkanolamine, diamines, such as hexamethyldiamine, triamines, and/or

    c) epoxy compounds having a molecular weight of more than 500, such as one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups, and/or

d) one or more cross-linkers selected from the group consisting of polyethylene imine, polyvinyl amine, fatty amines; and/or

e) one more cross-linkers in form of fatty amides; and/or

f) one or more cross-linkers selected from polyester polyols, such as polycaprolactone; and/or

g) one or more cross-linkers selected from the group consisting of starch, modified starch, CMC; and/or

h) one or more cross-linkers in form of aliphatic multifunctional carbodiimides; and/or

i) one or more cross-linkers selected from melamine based cross-linkers, such as a hexakis(methylmethoxy)melamine (HMMM) based cross- linkers.

18. The mineral fibre product according to claim 17, wherein the component (ii) comprises one or more cross-linkers selected from β-hydroxyalkylamide-cross-linkers and/or oxazoline-cross-linkers.

19. The mineral fibre product according to any of the preceding claims, comprising component (ii) in an amount of 1 to 50 wt.-%, such as 4 to 20 wt.-%, such as 6 to 12 wt.-%, based on the dry weight of component (i).

20. The mineral fibre product according to any of the preceding claims, comprising component (ii) in an amount of 1 to 50 wt.-%, such as 4 to 20 wt.-%, such as 6 to 12 wt.-%, based on the dry weight of component (i).

21. The mineral fibre product according to any of the preceding claims, wherein the component (ii) is in form of one or more cross-linkers selected from

- β-hydroxyalkylamide-cross-linkers, such as N-(2-hydroxyisopropyl)amide-cross-linkers, such as N-(2-hydroxyethyl)amide-cross-linkers, such as N-(2-hydroxyethyl)adipamide-cross-linkers, such as N,N,N′,N′-tetrakis(2-hydroxyethyl)adipamide and/or

- the group consisting of multifunctional organic amines such as an alkanolamine, diamines, such as hexamethyldiamine, and/or

- epoxy compounds having a molecular weight of more than 500, such as an epoxidised oil based on fatty acid triglyceride or one or more flexible oligomer or polymer, such as a low Tg acrylic based polymer, such as a low Tg vinyl based polymer, such as low Tg polyether, which contains reactive functional groups such as carbodiimide groups, such as anhydride groups, such as oxazoline groups, such as amino groups, such as epoxy groups, and/or

- one or more cross-linkers in form of multifunctional carbodiimides, such as aliphatic multifunctional carbodiimides.

22. The mineral fibre product according to any of the preceding claims, wherein the component (ii) comprises one or more cross-linkers selected from

    - β-hydroxyalkylamide-cross-linkers, such as N-(2-hydroxyisopropyl)amide-cross-linkers, such as N-(2-hydroxyethyl)amide-cross-linkers, such as N-(2-hydroxyethyl)adipamide-cross-linkers, such as N,N,N′,N′-tetrakis(2-hydroxyethyl)adipamide.

23. The mineral fibre product according to any of the preceding claims, comprising component (ii) in an amount of 2 to 90 wt.-%, such as 6 to 60 wt.-%, such as 10 to 40 wt.-%, such as 25 to 40 wt.-%, based on the dry weight of component (i).

24. The mineral fibre product according to any of the claims 6 to 23, wherein component (iii) is comprised in the non-cured binder composition in form of

    - one or more plasticizers selected from the group consisting of fatty alcohols, monohydroxy alcohols, such as pentanol, stearyl alcohol; and/or

- one or more plasticizers selected from the group consisting of alkoxylates such as ethoxylates, such as butanol ethoxylates, such as butoxytriglycol; and/or

- one or more plasticizers in form of propylene glycols; and/or

- one or more plasticizers in form of glycol esters; and/or

- one or more plasticizers selected from the group consisting of adipates, acetates, benzoates, cyclobenzoates, citrates, stearates, sorbates, sebacates, azelates, butyrates, valerates; and/or

- one or more plasticizers selected from the group consisting of phenol derivatives, such as alkyl or aryl substituted phenols; and/or

- one or more plasticizers selected from the group consisting of silanols, siloxanes; and/or

- one or more plasticizers selected from the group consisting of sulfates such as alkyl sulfates, sulfonates such as alkyl aryl sulfonates such as alkyl sulfonates, phosphates such as tripolyphosphates; and/or

- one or more plasticizers in form of hydroxy acids; and/or

- one or more plasticizers selected from the group consisting of monomeric amides, such as acetamides, benzamide, fatty acid amides such as tall oil amides; and/or

- one or more plasticizers selected from the group consisting of quaternary ammonium compounds such as trimethylglycine, distearyldimethylammoniumchloride; and/or

- one or more plasticizers selected from the group consisting of vegetable oils such as castor oil, palm oil, linseed oil, soybean oil; and/or

- tall oil, and/or

- one or more plasticizers selected from the group consisting of hydrogenated oils, acetylated oils; and/or

- one or more plasticizers selected from acid methyl esters; and/or

- one or more plasticizers selected from the group consisting of alkyl polyglucosides, gluconamides, aminoglucoseamides, sucrose esters, sorbitan esters; and/or

- one or more plasticizers selected from the group consisting of polyethylene glycols, polyethylene glycol ethers; and/or

- one or more plasticizers in form of polyols, such as glycerol, such as 1,1,1-Tris(hydroxymethyl)propane; and/or

- triethanolamine.

25. The mineral fibre product according to any of claims 6 to 24, wherein component (iii) is in form of propylene glycols, phenol derivatives, silanols, siloxanes, hydroxy acids, vegetable oils, polyethylene glycols, polyethylene glycol ethers, triethanolamine, or any mixtures thereof.

26. The mineral fibre product according to any of claims 6 to 24, wherein component (iii) comprises one or more plasticizers having a boiling point of 100 to 380 °C, more preferred 120 to 300 °C, more preferred 140 to 250 °C.

27. The mineral fibre product according to any of claims 6 to 24, wherein component (iii) comprises one or more polyethylene glycols having an average molecular weight of 150 to 50000 g/mol, in particular 150 to 4000 g/mol, more particular 150 to 1000 g/mol, preferably 150 to 500 g/mol, more preferably 200 to 400 g/mol.

28. The mineral fibre product according to any of claims 6 to 24, wherein the component (iii) is present in an amount of 0.5 to 60, preferably 2.5 to 25, more preferably 3 to 15 wt.-%, based on the dry weight of component (i).

29. The mineral fibre product according to any of the preceding claims, comprising a further component (iv) in form of one or more coupling agents, such as organofunctional silanes.

30. The mineral fibre product according to any of the preceding claims, further comprising a component (v) in form of one or more components selected from the group of bases, such as ammonia, such as alkali metal hydroxides, such as KOH, such as earth alkaline metal hydroxides, such as $Ca(OH)_2$, such as $Mg(OH)_2$, such as amines or any salts thereof.

31. The mineral fibre product according to any of the preceding claims, comprising a further component in form of urea, in particular in an amount 5 to 40 wt.-%, such as 10 to 30 wt.-%, such as 15 to 25 wt.-%, based on the dry weight of component (i).

32. The mineral fibre product according to any of the preceding claims, comprising a further component (vi) in the form of one or more reactive or nonreactive silicones.

33. A use of a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, as a thermal and/or acoustic insulation, in particular a non-corrosive thermal and/or acoustic insulation, wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

34. The use according to claim 33, wherein the mineral fibre product is used as a thermal and/or acoustic insulation, in particular a non-corrosive thermal and/or acoustic insulation, for an object selected from a pipe, a storage tank, a boiler, a vessel or a column, preferably a pipe.

35. The use according to claim 33 or claim 34, at temperatures in the range of -20 °C to 320 °C, preferably 0 °C to 200 °C, such as 50 °C to 175 °C.

36. The use according to any of claims 33 to 35, wherein the mineral fibre product

is used as a thermal and/or acoustic insulation, in particular a non- corrosive thermal and/or acoustic insulation, for an object made of metal, wherein the metal is preferably selected from copper or steel, in particular carbon steel, stainless steel, austenitic stainless steel, non-alloy steel or low alloy steel.

37. The use according to any of claims 33 to 36, wherein the mineral fibre product is as defined in any of claims 1 to 32.

38. A method for the manufacture of a mineral fibre product, comprising mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001,

    the method comprising the steps of

    a) providing a non-cured aqueous binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, and water,

    b) contacting mineral fibres with the non-cured aqueous binder composition, and

    c) curing the binder composition in contact with the mineral fibers, wherein at least part of the water or the total water contained in the non- cured aqueous binder composition is non-purified water added, wherein the non-purified water is preferably selected from tap water, rain water, process water or a combination thereof.

39. The method of claim 38, wherein the proportion of non-purified water added is in the range of 30 to 100 wt.-%, preferably 50 to 100 wt.-%, based on the total weight of water contained in the uncured binder composition, and/or

    the water content in the uncured aqueous binder composition is in the range of 40 to 90 wt.-%, preferably 60 to 85 wt.-%, based on the total weight of the uncured aqueous binder composition.

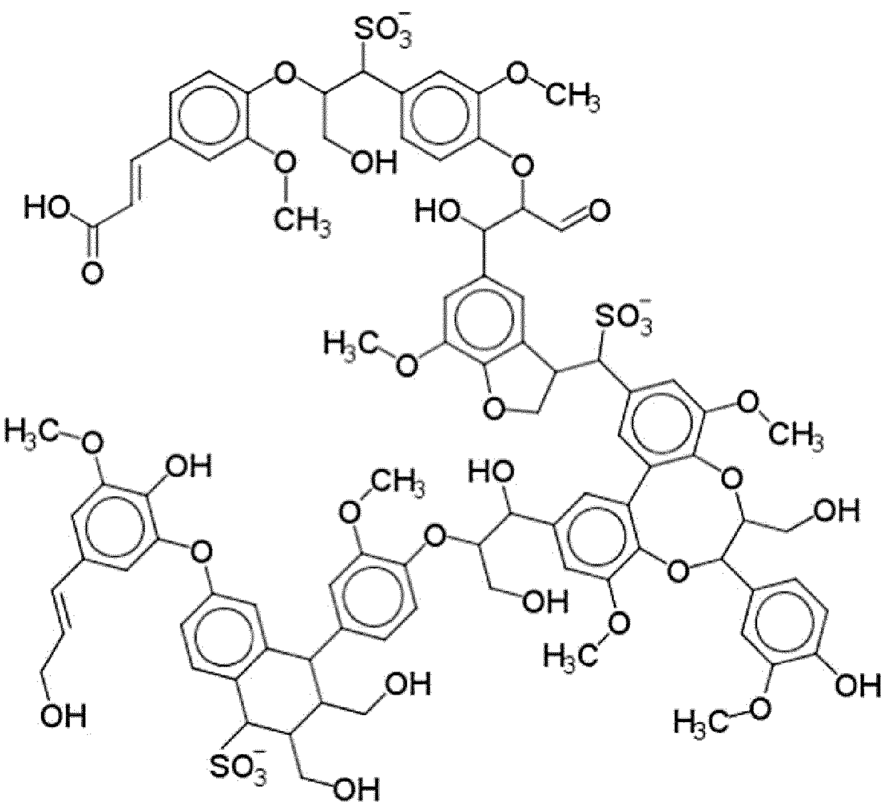
40. The method according to claim 38 or claim 39, wherein the mineral fibre product is as defined in any of claims 1 to 32.

41. A hollow object covered with a mineral fibre product as a thermal and/or acoustic insulation, wherein the mineral fibre product comprises mineral fibres bound by a cured binder composition, the non-cured binder composition comprising one or more lignosulfonate lignins having a carboxylic acid group content of 0.03 to 1.4 mmol/g, based on the dry weight of the lignosulfonate lignins, , wherein the mineral fibre product optionally has a water leachable chloride content of less than 10 mg/kg in accordance with EN 13468:2001.

42. The hollow object according to claim 41, wherein the hollow object is selected from a pipe, a storage tank, a boiler, a vessel or a column, preferably a pipe, and/or wherein the hollow object is made of metal, wherein the metal is preferably selected from copper or steel, in particular carbon steel, stainless steel, austenitic stainless steel, non-alloy steel or low alloy steel.

43. The hollow object according to claim 41 or claim 42, wherein the mineral fibre product is as defined in any of claims 1 to 32.

Fig. 1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O
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H_3C
OH
CH_3
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OH
OH
H_3C
OH
H_3C
OH
SO_3^-
OH

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2021/077180

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L97/00
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)
C08L D04H

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, BIOSIS, EMBASE, 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 Y	EP 3 632 866 A1 (ROCKWOOL INT A/S [DK]) 8 April 2020 (2020-04-08) paragraphs [0025] - [0033], [0119], [0126]; claims 1, 7, 9, 10,18-20	1-10, 13-43 1-43
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 6 January 2022	Date of mailing of the international search report 18/01/2022
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 Friedrich, Christof

INTERNATIONAL SEARCH REPORT

Information on patent family members

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