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(54) Title: FORMALDEHYDE-FREE BINDER AND USE FOR MINERAL WOOL INSULATION PRODUCTS

(57) Abstract: The present invention relates to a new formaldehyde - free binder composition for mineral wool products., wherein the binder composition is an aqueous composition containing starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, and an acrylic component. The present invention also relates to the use of this formaldehyde-free binder composition in the manufacturing of mineral wool insulation products. Finally, the present invention relates to a process for manufacturing the formaldehyde-free binder composition wherein a dispersion of starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, is brought in contact with the acrylic component at a temperature of not higher than 40 °C.



Formaldehyde -free binder and use for mineral wool insulation products

Field of the Invention

The present invention relates to formaldehyde -free resins and their use in the manufacture of mineral wool insulation products of zero formaldehyde emissions .

State of the Art

The mineral wool products have traditionally being manufactured by adhering mineral fibers by means of phenol-formaldehyde resins, profiting from relatively low costs and good mechanical properties, stability and water resistance granted to the finished products. Most common phenol-formaldehyde resins for mineral wool production are resols manufactured by condensation of formaldehyde and phenol catalyzed by alkalis and using a large molar excess of the formaldehyde .

The main drawback of the used phenol-formaldehyde resins is the slow release of formaldehyde in finished products to the environment, contributing to worsen the indoor air quality; hence the interest of formaldehyde-free resins for mineral wool products. Different alternative resins have been described in the art,

One alternative to the use of phenol-formaldehyde resins in mineral wool production are the polyester resins based on carboxylated polymers . Most common ones contain a combination

of one **acrylic** (co)polymer and one **low** molecular weight **polyol**. The resin cures at high temperatures under acidic conditions **via** the formation of ester-bonds. **For** instance **EP 583 086** (US 5,763,524), **EP 0 990 729 A1** (US 6,331,350), **US 6,136,916** and **US 6,221,973** [**Rohm&Haas**] describe the use of **polyacrylic acid** and either **hydroxylamines** (such as triethanolamine) or **glycerol** as cross-linkers. **US 5,318,990** [**Owens Corning**] teaches the use of polycarboxylic polymer and **glycerol** or trimethylolpropane. **US 6,331,350** [**Johns Manville**] describes a binder consisting of **polycarboxylic** polymer and **polyol** such as triethanolamine, at a pH not greater than 3.5. Another group of binders contain resins based on co-polymers of acrylic acid. **For** instance, **US 6,071,994** [**BASF**] describes the use of co-polymers based on **acrylic** and maleic acids, and **polyols** as cross-linkers at a pH lower than 3.5. **US 2010/0029160** [**Georgia Pacific**] teaches the use of hydrolyzed copolymer of maleic anhydride and a vinyl compound such as styrene and a monomeric polyol as cross-linker, at a pH of more than 7. The acrylic resins above confer excellent mechanical properties to the mineral wool products. Unfortunately, the costs of these resins are about two to three-fold higher than the conventional phenolic-based resins, this being a significant draw-back for their use in industry. Additionally, acrylic resins normally have the processing disadvantage of a relatively high viscosity which limits the use for manufacturing high density mineral wool products.

Another important group of formaldehyde-free resins found in the art refers to bio-resins based on carbohydrates and low molecular weight poly-acid, such as citric acid, as cross-linker. The resins cure at high temperatures under acidic conditions **via**, in most cases, the formation of ester-bonds. In general, it is preferred the use of carbohydrates soluble in water to facilitate the processing and the curing of the

resins . One representative group is based on sugars . **For** instance **WO** 2009/19232 **and US** 2011/260094 [**Knauf**] describe a binder **based on** the MaiHard type **reaction composed** of a reducing sugar, acid precursor derivable from an inorganic salt and a source of nitrogen. **WO** 2012/028810 [**Isover**] describes a binder composition consisting of non-reducing sugar such as glucose and one inorganic acid metal salt . **WO** 2010/1398 99 [**Isover**] describes a binder composition consisting of saccharide **such as glucose and polycarboxylic acid** . A second representative **group** consists of a combination of dextrans derived upon chemical or enzymatic treatment of native starches. **For** instance, **US** 2005/0215153 A1 [**Ovens Corning**] teaches **the use of dextrin in combination with cross-linkers** . **WO** 2011/044490 A1 teaches the **use** of water soluble carbohydrates having a Dextrose Equivalent (**DE**) between 2 and 20 in combination with cross-linkers . **WO** 2011/002730 A1 describes the use of modified starches with a degree of polymerization between 20 and 4000 units, in combination with cross-linkers . **In** this group of patent applications, **it** is claimed that the dextrination to obtain water soluble modified starches favors the processability of the binder, because of **the** lowering of the viscosity, and an increase of the curing **rate** in **the** presence of cross-linkers . **US** 2008/108741 **and WO** 2008/053332 [**Dynea**] describe mixtures **of** water-soluble starches containing more **than 80** weight % of amylopectin and a polycarboxylic acid as cross-linker. The bio-resins based on renewable **polyols** offer important advantages over the **synthetic -resins**, particularly their lower costs and better sustainability profile. Yet, these bio-resins shall be **used** in higher dosage on mineral fibers compared to the phenolic or acrylic resins because the mechanical properties, particularly upon aging, delivered to mineral wool are normally lower, and because of the greater mass losses due **to** thermal degradation during the process of curing. **Indeed**, the process of curing of

these bio-resins requires a strict control of **the** temperature between narrow ranges. This is needed to achieve the suitable mechanical properties and to **avoid** unwanted thermal degradation.

It is **an** object of **the** present invention to provide a formaldehyde-free binder **which** is particularly valuable for the use in mineral wool production due to excellent binding strength, easy manufacture and low costs.

It **is a** further object **of** the present invention to provide a process for the preparation **of** the new formaldehyde-free binder.

Summary of the invention

The above object **is** solved **by a** formaldehyde-free aqueous binder composition comprising

- starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native **starch**, and
- one or more acrylic component **<s)** .

According **to** a preferred embodiment, the **object** is solved by **a** formaldehyde-free aqueous binder composition in the form of a dispersion, comprising starch, wherein an amount **of** 95 weight % or more of the starch is water-insoluble native starch, and one **or** more acrylic component {s), wherein the acrylic component {s) is/are selected from the group consisting of polyacrylic **acid**, copolymers of acrylic **and** maleic acids, **copolymers of** ethylene-unsaturated moieties containing at least 10 mol % of acrylic acid, maleic acid or maleic anhydride; salts of any preceding (co)polymers, **curable** resins based on any preceding (co)polymers, and mixtures thereof.

Another object of the present invention is to provide a mineral wool product comprising a cured formaldehyde-free binder obtainable by the following process steps;

- impregnating mineral fibers of a **binder--free** mineral wool product with an aqueous binder composition in the form of a dispersion **comprising** a) starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch; and b) one or more acrylic component (s), selected from the group consisting of **polyacrylic** acid, **copolymers** of acrylic and maleic acids, copolymers of ethylene-unsaturated moieties containing **at least** 10 mol % of acrylic acid, maleic acid or maleic anhydride; salts of any preceding **{co}polymers**, curable resins based on any preceding **(co) polymers**, and mixtures thereof, wherein the mineral fibers are impregnated via spraying the aqueous binder composition **with** a solid content of **4 to 10 weight %**, and
- **curing** the aqueous binder composition **at** a temperature above 100°C.

The inventors have **surprisingly found** three synergic effects **between** native starch being water insoluble **and** the acrylic component, such **as** acrylic resin **or** acrylic (co)polymers, which makes **the** new formaldehyde-free binder **of the present invention most** suitable **as** a binder **for** mineral wool;

- Firstly, the binding strength granted **to** mineral fibers by the mixture is maintained or even enhanced **in** comparison **to acrylic binders**. The later is particularly **seen** under stress 'wet' conditions, **which are** predictable **of the** behavior of the new binders upon aging. **Hence** the mixture of these two components exceptionally improves the "cost per job" and the sustainability of the new binder.

- Secondly, **the** viscosity and stability of the new binder **is** very suitable despite **of the** insolubility of the native starch component, due to the dispersing and stabilizing effect **that** the acrylic component exerts on the native **starch**. **This** enables the production of binder dispersions **of low** viscosity very suitable for further application to mineral fibers by spray-on process.

- Thirdly, the curing of the new binder can be done at reduced temperatures in comparison **to** other bio-resins **based on high DE** carbohydrates **like** dextrans or sugars, **what** results **in** a considerable energy saving. An additional advantage over the bio-resins based on high DE carbohydrates like dextrans or sugars, is that the curing process of the new binder **does not require a** strict control **of the** temperature. **This is because the mass** loss by thermal degradation of the **new** resin during **the** curing **is** negligible. Indeed, the **mineral** wool product made with the new binder has **a** characteristic whitish color instead **of brownish color** of products **made** with **above** mentioned **bio-resins**.

Brief Description of the Drawings

Figure 1 **shows** the bonding properties **of** binders **A to D** according to the **present** invention, native starch Meritena 120 and acrylic resin **Aquaset BI700**.

Figure 2 shows **the** viscosity **of** binders **A to D** according to the **present** invention, **and acrylic resin Aquaset BI700 alone**. The viscosity **has** been measured **on** aqueous compositions **containing a solid** content **of 50 weight %**.

Figure 3 shows the sedimentation time of binders A to D according to the present invention, and a dispersion of native starch Meritena 120. The sedimentation time has been measured on aqueous compositions containing a solid content of 45 weight %.

Figure 4 shows the Young moduli under wet conditions for binders B and D according to the present invention, and bio-resin based on dextrose described in WO 2008/08 9851 A1 at page 6.

Figure 5 shows the mass loss (TGA, 10 °C/min, % solid losses at 200 °C) for binders B and D according to the present invention, acrylic resin Aquaset B1700, and for bio-resin based on dextrose described in WO 2008/08 9851 A1 at page 6.

Composition of the new binder

According to the present invention, the new formaldehyde-free binder is an aqueous composition containing at least one starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, and one or more acrylic component (s). This means that the new formaldehyde-free binder of the present invention contains at least one starch wherein 95 to 100 weight % of the starch is water-insoluble native starch, and one or more acrylic component (s). Preferentially the formaldehyde-free binder is an aqueous composition comprising at least one starch, wherein 99 or 100 weight % or an amount ranging between these two values of the starch is water-insoluble native starch, and one or more acrylic component (s).

The binder composition of the present invention is 'formaldehyde-free'. The term 'formaldehyde-free' in the sense

of the present application indicates that essentially no formaldehyde is contained in nor released from the binder composition of the present invention.

95 weight % or more of the starch used as first component of the new binder of the present invention is a native starch with no chemical modification. It may be obtained from vegetable sources such as corn, potatoes, wheat, rice, cassava, soybean or other plants containing high starch content. The native starches are usually available as white powders, which still contain small amounts of non-carbohydrate components such as proteins and salts. They also contain about 10 to 15 weight % humidity, which can be measured according to the method in ISO 1666. In the present application, the native starch weight % values refer to the 'dry' native starch excluding the humidity content.

95 to 100 weight % of the starch used in the binder of the present invention is insoluble in water. It is particularly preferred that all of the starch used in the binder composition of the present invention is water-insoluble. The term 'insoluble in water' as used herein means a solubility of the starch lower than 0.15 g per 100 g of water at 20 °C. The solubility can be measured as follows; prepare a homogeneous dispersion of starch in water at 20 °C, filter it through a standard laboratory filter paper to get a clear solution, and evaporate 100 g of said clear solution at 135 °C for 120 minutes to obtain a solid residue. The solubility is reported as per the weight of the solid residue in grams contained in the 100 g clear starch solution.

It is preferred that the native starches contained in the binder according to the present invention have a Dextrose Equivalent (DE) lower than 2, more preferable lower than 1.

Non-limiting examples of native starches useful for the binder of the present **invention** are Meritena **120**, **Amyzet** 150, Meritena 400 or **Amyzet** 500 from Syral, Maize Starch from Roquette or **C*Gel** series from Cargill.

The **one or** more acrylic component (s) used **as** second component of the new formaldehyde-free binder **in** the present invention is a curable acrylic resin, an acrylic (co)polymer or a mixture thereof.

In one embodiment of **the present** invention, the acrylic component used as a component of the formaldehyde-free **binder** according to **the present** invention is a curable acrylic resin described **in** the art. Preferably, **the** curable acrylic resin comprises at **least one acrylic** (co)polymer and a polyol. Optionally **they can** contain esterification **catalysts** and/or, **pH** modifiers. **The** acrylic (co)polymer is a copolymer of ethylene-unsaturated moieties containing at least 10 mol % of acrylic **acid**, maleic acid or maleic anhydride, and mixtures thereof; preferably **polyacrylic acid** or copolymers of acrylic and maleic **acids**. The polyol is an **alkane-polyol** or **alkanolamines** of molecular weight lower than 1000 g/mol described **in** the art, like **triethanolamine**, glycerol, **trimethylolpropane** and the like. Non-limiting examples of curable acrylic resin suitable **for** the new formaldehyde-free binder **in the present** invention are **Aquaset BI700** from Dow Chemicals, **Acrodur DS3530** from BASF, or Leaf **Free** series from **Georgia Pacific**,

In another embodiment of **the present** invention, the **acrylic** component **used** as second component of the new **formaldehyde-free** binder **in** the present invention is **an** acrylic (co)polymer. Preferably, **the** acrylic (co)polymer is a

copolymer of ethylene-unsaturated moieties containing at least 10 mol % of acrylic acid, maleic acid or maleic anhydride, and mixtures thereof. More preferably the acrylic (co)polymer is polyacrylic acid or copolymers of acrylic and maleic acids. The acrylic (co)polymers are normally available as water solutions, dispersion or powders, which can be dissolved or dispersed in water by mechanical means at temperatures from about 10 to 50 °C. Non-limiting examples of acrylic (co)polymers useful for the new binder in the present invention are Syntran 8220 from **Interpolymer**, Craymul 2154 from Cray Valley, or Acumer 1000 from Dow Chemicals.

In the case that the acrylic component used as second component of the new formaldehyde-free binder in the present invention is an acrylic (co)polymer, it is a more preferred embodiment to combine said acrylic (co)polymer with at least one cross-linker, such as **alkane-polyol** or alkanolamines of molecular weight lower than 1000 g/mol described in the art, like triethanolamine, glycerol, trimethylolpropane and the like.

The term "aqueous **binder composition**" as used in the present application means a binder composition that is composed of a solid content and water. Due to the water-insolubility of the water-insoluble native starch, the formaldehyde-free aqueous binder composition of the invention is a dispersion.

The solid content of the aqueous binder compositions is not particularly limited, and depends on its intended application. So, for example, for application of the binder composition in the form of a dispersion to the mineral fibers via spraying it is preferred that the formaldehyde-free binder composition according to the present invention contains a solid content of **4 to 10 weight %**. **Particularly** preferred in this case is a

solid content of 5 to 8 weight %. Other application methods of the aqueous binder composition according to the present invention are also possible, for example spreading or immersion. In those cases, other solid content ranges might be more appropriate. Thus, for example, a solid content of 15 to 30 weight %, e.g. 20 weight %, may be more suitable if the binder composition is applied by immersion of the substrate in the aqueous binder composition according to the present invention. Merely for comparison purposes of the properties of the binder compositions through this description and in the examples, a reference solid content of 50 weight % is selected.

The amount of native starch and the amount of acrylic component to be used in the binder of the present invention are not specifically limited. However it is suitable that the amount of native starch is 10 to 35 weight % based on the total solid content of the binder composition, the amount of acrylic component is 5 to 90 weight % based on the total solid content of the binder composition, and the sum of the amount of native starch and the amount of acrylic component is at least 70 weight % based on the total solid content of the binder composition.

According to a another preferred embodiment, very useful binder compositions in form of low viscosity dispersions are obtained when the amount of native starch is 25 to 80 weight % based on the total solid content, the amount of acrylic component is 75 to 20 weight % based on the total solid content, and and the sum of the amount of native starch and acrylic component of at least 80% with respect to the total solid content of the binder composition.

According to a more preferred embodiment, **the** amount of native starch is from about 60 to about 90 weight % with respect to the total solid content **of** the binder composition, the amount **of** acrylic component **is** from about 10 to **about** 40 weight % with respect **to** the total solid content **of** the binder composition, **and** the **sum** of the amount **of** native starch **and** acrylic component **is** at least 70 weight % with respect to the total **solid** content of the binder composition.

This above embodiment **covers** binder compositions that are economically attractive (the acrylic component **is** normally more expensive than the native starch) and, **at the** same time, after they are applied and cured on the substrates show good binding strength in dry and wet conditions, and good ageing behavior .

According to another preferred embodiment, the binder composition in the form of a dispersion **according** to the present invention comprises an amount of native starch of 25 to 50 weight % based on the total **solid** content, **an** amount of **acrylic** component **of** 75 to 50 weight % based on the total solid content, and the native starch and **the acrylic** component amounts add **at** least 90 weight % with respect to **the** total solid content of the binder composition. Such **binder** compositions, after being applied **and** cured on **the** substrates, result **in** improved binding strength in wet conditions and improved ageing behavior **of the** bonded products in humid conditions .

According to a **yet** more preferred embodiment, the binder composition **of** the present invention **also** comprises additives described in the art to enhance the performance for its use **for** mineral wool. Non-limiting examples **of** additives are esterification catalysts **such as** sodium **hypophosphite**, pH

control agent such as ammonium sulfate, **hydrophobizing agent** such as silicones, **de**-dusting agent such as paraffin oils, adhesion promoter agent such as alkoxy silanes, fiber softeners, preservatives, dyes **and corrosion** inhibitors. It is also preferred that the **new** binder additionally comprises at **least** one filler or chain extender such as, but not limited to, urea, sugars, molasses, lignosulfonates or tannins.

There is no limitation about the **pH** of the new binder composition. Nevertheless it is preferred that the pH of the new binder **is above 2**.

In view of its suitability as a binder composition for mineral fibers, **it is** particularly preferred that binder composition of the present invention has the following characteristic: when the binder composition has a solid content of 50 weight-%, **the** viscosity of the binder composition **is less** than 200 mPa.s at 20 °C, and preferably less **than 50 mPa.s** at 20 °C.

Manufacturing of the new binder

The process for manufacturing the formaldehyde-free binder composition according to the present invention comprises the steps of:

- (a) preparation **of a** dispersion of starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, in water at **a** temperature of 10 to 40 °C;
- (b) contacting the dispersion obtained in step (a) with one **or** more acrylic component (s) and, optionally, further additives, at **a** temperature of 10 to 40 °C.

Preferably, the dispersion step (a) is done with mechanical stirring until obtaining a homogenous mixture. It is important to carry out this step at a temperature between 10 to 40 °c, and preferably from about 20 to 30 °c. This range of temperature is suitable to disperse the starch in water and low enough to avoiding 'gelatinization' of the starch granules what otherwise would increase the viscosity and difficult the processing. The time of dispersing is not particularly limited because depends on the specific dispersion equipment.

Preferably, the contacting in step (b) is done with mechanical stirring until obtaining a homogenous mixture. It is important to carry out said contacting process at a temperature between 10 to 40 °c, and preferably from about 20 to 30 °c, for the reasons mentioned above. Additionally, this range of temperature is also suitable to avoid unwanted hydrolysis and solubilization of the native starch. The time of contacting step (b) is not particularly limited. Nevertheless it is preferred to carry out this step in less than 60 minutes. Under these conditions it is possible, for example, to obtain a binder composition having a viscosity below 50 mPa.s at a solid content of 50 weight % solids.

In order to avoid premature reaction and/or gelatinization of the starch and to maintain the binder composition in the form of a dispersion with low viscosity, the temperature during the preparation of the binder composition according to the present invention should be kept below 65 °c, preferably below 50 °c, and most preferably below 40 °c. According to a particularly preferred embodiment of the present invention, the temperature during the process of preparing the binder composition of the present invention is not raised above room temperature. In other words, the un-modified insoluble native starch is applied as such to the fibers as part of the binder

composition. The binder composition on the fibers is subsequently dried and cured at temperatures above 100 °c.

Alternatively, the process for manufacturing of the new formaldehyde -free binder composition according to the present invention may comprise the step of dispersing starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, in an aqueous mixture containing the acrylic component and, optionally, further additives, at a temperature of 10 to 40 °C.

Use of the new binders for mineral wool

The new formaldehyde -free binders according to the present invention are to be used as binder for fibrous substrates, particularly mineral wool fibers. The new binder is applied to the mineral fibers so that they become impregnated. Preferably, the application is via spraying. For the application, the total solid content of the new binder composition is not particularly limited. Nevertheless it is particularly suitable to use an aqueous binder composition wherein the solid content is from between 4 to 10 weight %. The amount of new binder to be applied onto the mineral fibers is not particularly limited and is suitably adjusted depending on the type of mineral wool product. A typical amount of dried binder applied onto the fibers is in the range of 4 to 20 weight % of dried binder with respect to the weight of mineral wool fibers.

The impregnated fibers are then collected in a forming chamber and then conveyed to a curing oven where the new binder cures to set. The binder composition of the present invention cures at temperatures of above 100 °c, preferably at a temperature

of 140 °C to 180 °C, e.g. at 170 °C, which is lower than the curing temperatures required for sugar-based bio-binders described in the art. For instance, the bio-binder described in WO 2008/089851 A1 at page 6 has a curing temperature of 190 °C, as seen in Figure 4. Additionally, the new binder composition of the present invention loses a very low amount of mass during the process of curing, preferable less than 1 % at 200 °C. This is very suitable to increase the binder-efficiency, defined as the amount of binder solids after curing compared to the amount of binder solids applied on mineral fibers. In contrast, sugar-based bio-binders described in the art lose significantly more mass. This deteriorates the binder efficiency. For instance, the bio-binder described in WO 2008/089851 A1 at page 6 loses about 25 % mass at 200 °C.

The mineral wool mat is afterwards cut and shaped into its final dimensions and packaged. The mineral wool product manufactured with the new binder may comprise at least one additional facing made of paper, aluminum, glass veil or mixtures thereof. The mineral wool product obtained may be used for thermal or acoustic insulation purposes in buildings, conducts, particularly air-conditioning conducts, electrical appliances, ships, aircrafts and spaceships.

Examples

One example of the first embodiment of the present invention is a binder composed by a mixture of native starch Meritena 120 supplied by Syral and acrylic resin Aquaset BI 700 supplied by Dow Chemicals, at 50 weight % each with respect to the total solid %. Meritena 120 is a native starch derived from corn, with DE close to zero, supplied as a whitish powder containing 12% humidity. Aquaset BI 700 is an acrylic resin

based on polyacrylic acid and triethanolamine, supplied as a 55 weight % solids water solution.

A 2.5 liter round-bottom flask is charged with 489 mL of water and a mechanical stirring bar. Then, 511 grams of Meritena 120 powder are added and the mixture vigorously stirred for 30 minutes at 20 °C, obtaining a homogenous white dispersion of approximately 45 weight % solids. Afterwards, 818 grams of Aquaset BI 700 were added and the mixture stirred for additional 10 minutes at 20 °C. The resulting binder C is a milky dispersion of approximately 50 weight % solids, consisting of a 50:50 solids mixture of starch and acrylic component.

A series of new binders based on mixtures of Meritena 120 and Aquaset BI 700 are provided in Table 1. All of them can be similarly prepared following the method above, by varying the mixing ratio between both components.

Table 1 - New binders based on mixtures of native starch Meritena 120 and acrylic resin Aquaset BI700. Composition is given in weight % with respect to the total solid %.

Composition	A	B	C	D
Meritena 120	20%	35%	50%	70%
Aquaset BI700	80%	65%	50%	30%

The bonding strength on mineral fibers of the new binders A to D was measured in a strain-strength test, as per the Young modulus of a glass paper treated with the binder. The treatment of the glass paper consists of impregnating the glass paper with 20 weight % solids of the new binder, and curing for 3 min at 170 °C. The modulus measured under these

conditions is referred **as** under 'dry' conditions. The effect of ageing on the bonding properties of the new binders was also evaluated in a consecutive experiment, consisting of immersing the **cured** treated glass paper specimens in water at **85 °C for 10 minutes**, drying and measuring again **the** Young modulus value in a **strain-strength** test. The **Young modulus** measured **under** these **conditions** is referred **as** under 'wet' **conditions**. The Fig. 1 shows the Young moduli measured **under** 'dry' and 'wet' conditions for binders **A to D**, **composed** of mixtures of **native starch** Meritena **120** and **acrylic resin** Aquaset **BI 700**. **As a** reference **the** Young **modulus values** for native **starch** Meritena **120** and acrylic resin Aquaset **BI 700** on their own measured **under** **the** same conditions are also provided. Remarkably, the bonding strength of the new binders under **wet** conditions is improved in comparison to that of the acrylic resin alone or the native starch alone. The best performing under wet conditions is **binder B**; i.e. **a** composition of about 35 weight % of native starch and 65% of acrylic component. The bonding properties under 'dry' conditions for binders **A to D** are very suitable.

Young modulus is measured on **25x75mm** strips of glass paper type Borosilicate **GF/A** from Whatman International, impregnated with binder and cured **as** described above, by using a tensile strength tester set at a constant extension rate of 6 mm/min.

The viscosity of the new binders was measured **with** a Brookfield viscometer with spindle 1 **at** 20 °C at a solid content of 50 weight %. The Fig. 2 shows the viscosity for binder **A to D**, based on mixtures of native starch Meritena **120** and acrylic resin Aquaset **BI700**, **at** 50 weight % solids. As a reference, the viscosity **of** acrylic resin Aquaset **BI700** is also provided also at 50 weight % solids. It can be seen that all the binders **A to D** have a viscosity below 50 mPa.s at 20

°C which is very favorable for their use in mineral wool manufacturing. The starch component has a significant viscosity reduction effect on the high viscous acrylic component .

The stability of the new binder dispersions was measured visually via sedimentation tests, as the time for a homogeneous mixture to start phase splitting at 20 °C . Fig. 3 shows the sedimentation time for binders A to D according to the present invention, based on mixtures of native starch Meritena 120 and acrylic resin Aquaset BI7 00 at 45% weight % solids . As a reference, the sedimentation time of a homogeneous dispersion of native starch Meritena 120 alone in water is provided. It can be seen that all binder dispersions A to D according to the present invention have an increased stability, with sedimentation time above 5 minutes, in comparison to the low stability of the dispersion of insoluble native starch in water. This is also very suitable for the use of the new binders in mineral wool manufacturing.

The curing temperature of the new binders was compared to other bio-resins using the respective values of the Young modulus under wet conditions . The Figure 4 shows the Young modulus under wet conditions for the binders B and D according to the present invention, based on mixtures of native starch Meritena 120 and acrylic resin Aquaset BI700, cured for 3 minutes at 170 °C . As a reference it has been also measured the Young modulus under wet conditions of a bio-resin composed of dextrose (82%), citric acid (15%) and ammonia (3.1%) (see WO 2008/089851 A1; page 6) . In this later case, the bio-resin was cured at 170 °C and 190 °C, in both cases for 3 minutes. It can be seen that the binders B and D according to the present invention already achieve mechanical strength curing

at 170 °C, whereas the bio-resin needs curing at 190 °C to provide sufficient mechanical strength.

The mass loss % upon curing for the new binders was measured by TGA (Thermal Gravimetric Analysis) , as the relative solids content weight diminution at 200 °C using a ramp of 10 °C/min in a nitrogen atmosphere. This is representative of the maximum temperatures at which resins are normally exposed during the curing process. The Figure 5 shows the mass loss of binders B and D according to the present invention. As a comparison, it also shows the mass loss % for the acrylic resin Aguaset BI700 and a bio-resin composed of dextrose (82%), citric acid (15%) and ammonia (3.1%) (described in patent application WO 2008/08 9851 A1 at page 8). It can be seen that the mass loss, referred as relative solids content weight diminution, for the new binders B and D is less 0.3%, similar to the acrylic resin but significantly lower than the bio-resin based on dextrose, which loses up to 25% mass.

Other new binders according to the present invention are provided in the Table 2, along with the main characteristics. All of them can be produced according to a similar method to the one described above for the Binder c.

Table 2 -- New binders based on mixtures of native starch and acrylic component. Composition is given in weight % with **respect** to the total solid %.

Composition	A	B	C	D	E	F	G	H	I	J
Meritena 120 ⁽¹⁾	20%	35%	50%	70%	46.5%				64%	60.5%
Maize Starch ⁽²⁾						35%	50%	70%		
Aquaset BI700 ⁽³⁾	80%	65%	50%	30%	47%	65%	50%	30%		
Polyacrylic acid ⁽⁴⁾									30%	27%
Triethanolamine									5%	4%
Sodium hypophosphite									1%	1%
Mineral Oil emulsion Hydrowax 296 ⁽⁵⁾					6%					7%
Epoxy-trimethylsilane					0.5%					0.5%
Properties										
Modulus 'dry' conditions (N/mm ²) ⁽⁶⁾	564	517	519	383	464	506	443	381	492	474
Modulus 'wet' conditions (N/mm ²) ⁽⁷⁾	279	314	242	194	210	92	72	153	26	151
Viscosity (mPa.s) ⁽⁸⁾	47	32	25	17	28	40	31	24	150	195

(1) Supplied by Syral

(2) Supplied by Roquette

(3) Supplied by Dow Chemicals

(4) Supplied by Sigma Aldrich . molecular weight 8000 g/mol, at pH 2.5

(5) Supplied by Sasol

- (6) Glass paper impregnated with 20 weight % solids of binder, and cured for 3 min at 170 °C.
- (7) Glass paper impregnated with 20 weight % solids of binder, and cured **for** 3 min at 170 °C, then submerged in water at 85 °C for 10 minutes, and dried.
- (8) Brookfield spindle 1 at 20 °C. At 50 weight % solid.
- (9) **TGA**, 10 °C/min. Weight loss % at 200 °C vs. initial solids weight % content.

Patent Claims

1. **A** formaldehyde-free aqueous binder composition comprising
 - starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, and
 - one or more acrylic component (s).
2. The formaldehyde-free binder composition according to claim 1, wherein the native starch has a DE (Dextrose Equivalent) lower than 2.
3. The formaldehyde-free binder composition according to claims 1 or 2, wherein the amount of native starch is 10 to 95 weight % based on the total solid content of the binder composition, the amount of acrylic component is 5 to 90 weight % based on the total solid content of the binder composition, and the sum of the amount of native starch and the amount of acrylic component is at least 70 weight % based on the total solid content of the **binder** composition.
4. The formaldehyde-free binder composition according to any preceding claim, wherein the acrylic component is selected from the group consisting of **polyacrylic** acid, copolymers of acrylic and maleic acids, copolymers of ethylene-unsaturated moieties containing at least 10 mol % of acrylic acid, maleic acid or maleic anhydride; salts of any preceding (co)polymers, curable resins based on any preceding (co)polymers, and mixtures thereof.

5. The formaldehyde-free binder composition according to claim 4, wherein the acrylic component is a curable aqueous resin comprising at least one acrylic (co)polymer and one polyol, wherein
 - the acrylic (co)polymer is polyacrylic acid or a copolymer of acrylic and maleic acids, and
 - the polyol is a polyalkanol or alkanolamines of M.W. lower than 1000 g/mol.
6. The formaldehyde-free binder composition according to claim 4, wherein the acrylic component is polyacrylic acid or copolymers of acrylic and maleic acids.
7. The formaldehyde-free binder composition according to claim 6, further comprising a cross-linker such as polyols of M.W. lower than 1000 g/mol.
8. The formaldehyde-free binder composition according to any preceding claim, further comprising additives such as esterification catalysts, pH control agents, hydrophobizing agents, de-dusting agents, adhesion promoters, fiber softeners, preservatives, dyes, corrosion inhibitors, fillers or chain extenders.
9. Use of the formaldehyde-free binder composition according to any one of claims 1-8 in the manufacturing of mineral wool insulation products.
10. A mineral wool product comprising a formaldehyde-free binder composition according to any of the preceding claims.

11. The use of mineral wool product of claim 10 for thermal or acoustic insulation purposes in buildings, conducts, electrical appliances, ships, aircrafts and spaceships.

12. Process for manufacturing the formaldehyde-free binder composition according to any one of claims 1-8 comprising the steps of:
 - (a) preparation of a dispersion of starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, in water at a temperature of 10 to 40 °C;
 - (b) contacting the dispersion obtained in step (a) with the acrylic component and, optionally, further additives at a temperature of 10 to 40 °C.

13. Process for manufacturing the formaldehyde-free binder composition according to any one of claims 1-8 comprising dispersing starch, wherein an amount of 95 weight % or more of the starch is water-insoluble native starch, in an aqueous mixture containing the acrylic component and, optionally, further additives, at a temperature of 10 to 40 °C.

Figure 1

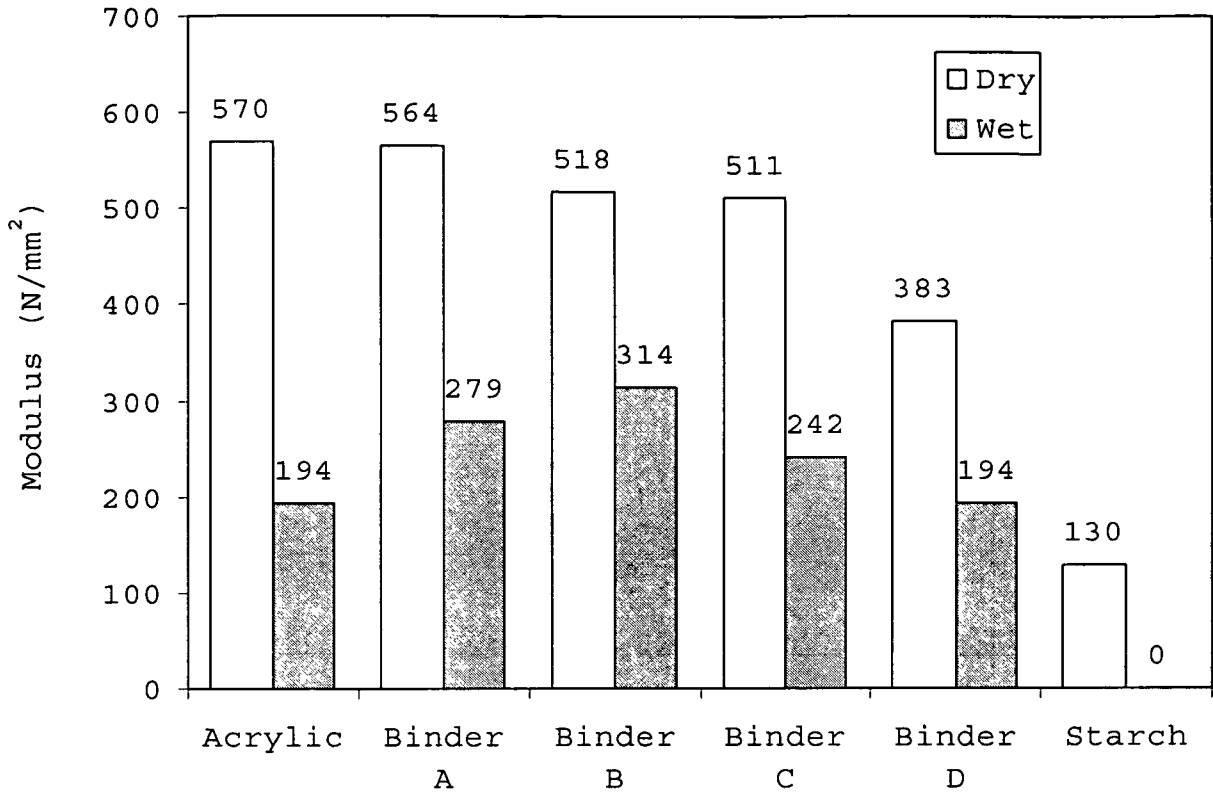


Figure 2

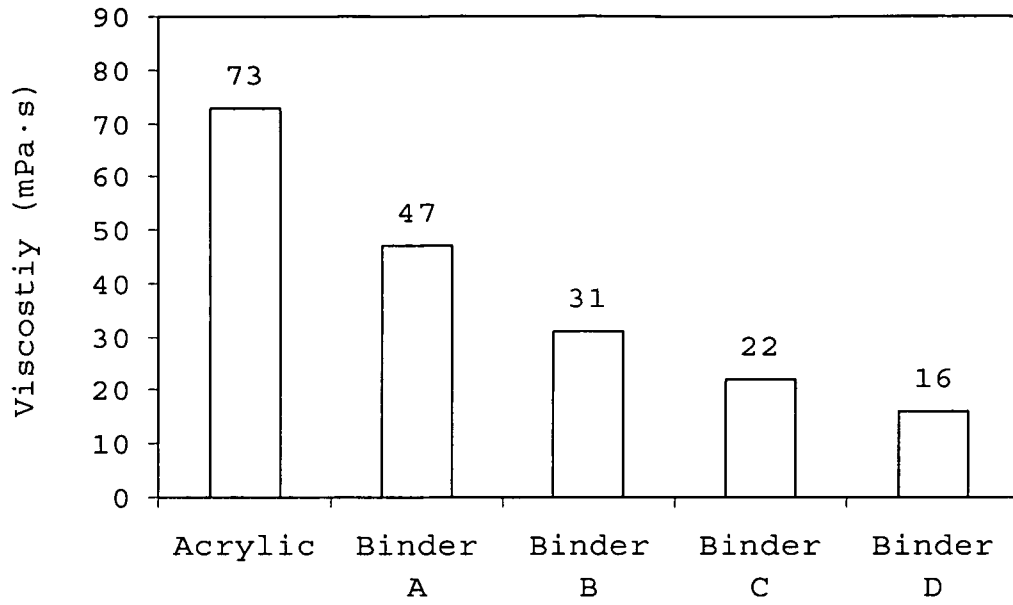


Figure 3

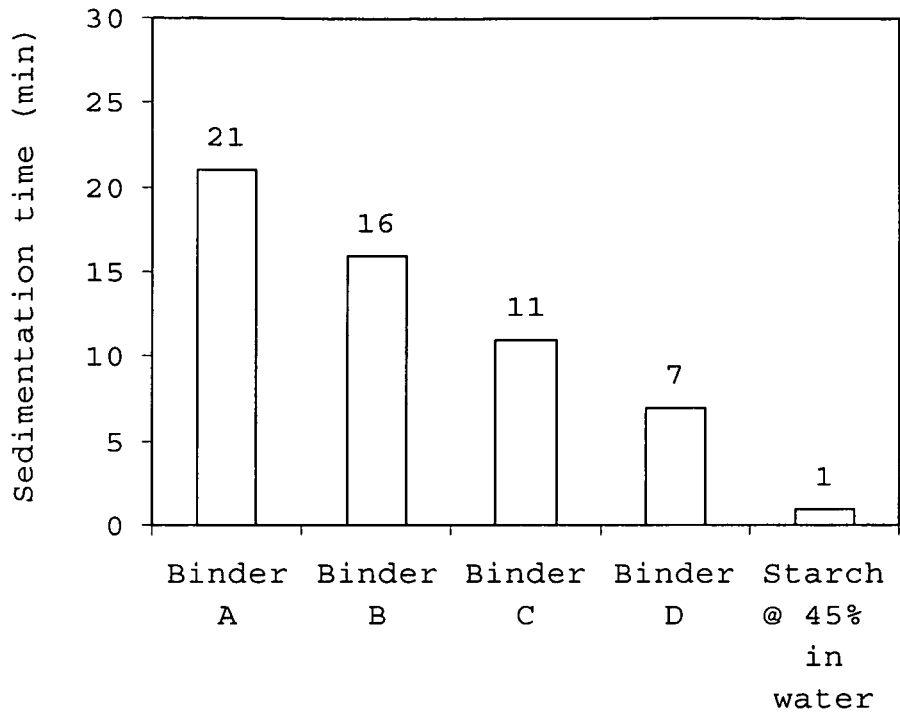


Figure 4

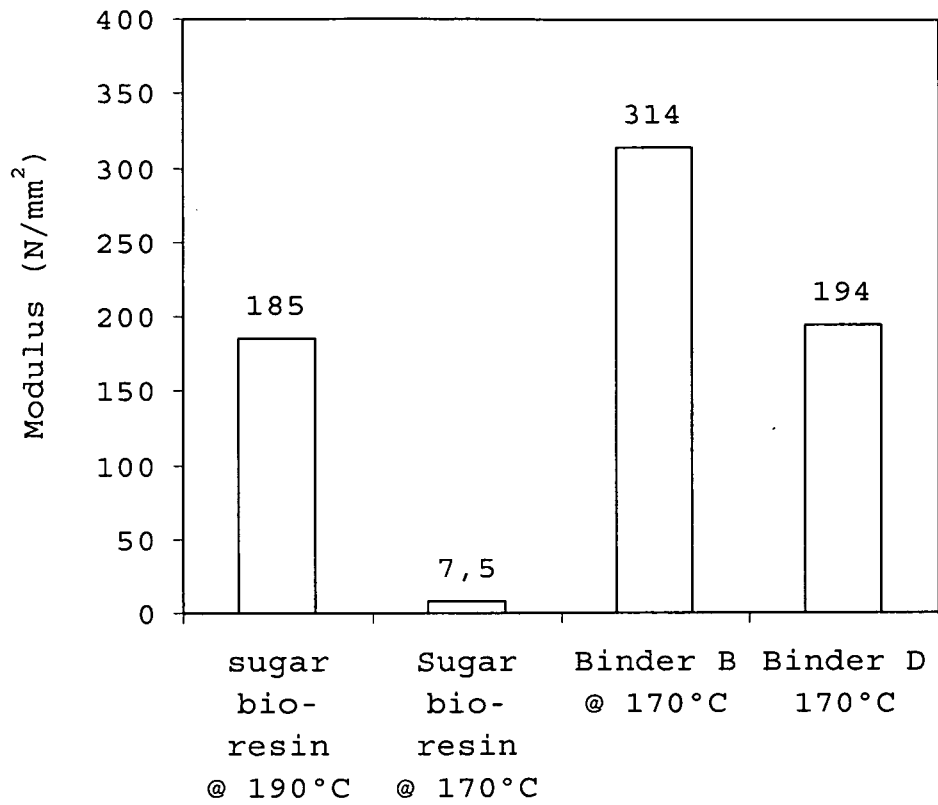
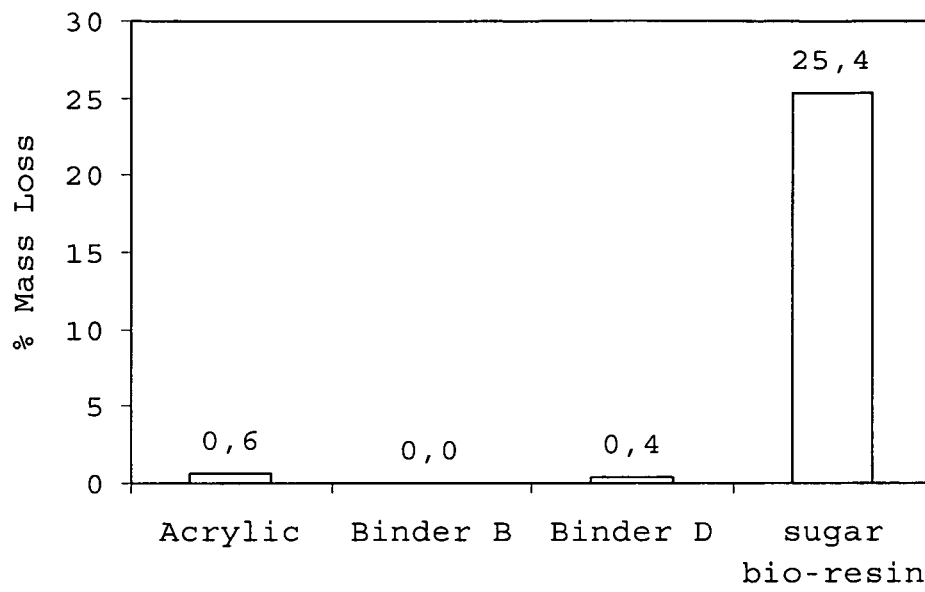


Figure 5



INTERNATIONAL SEARCH REPORT

International application No PCT/EP2013/063660

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L3/02 C08L33/08 C04B26/06 C04B26/28
 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 C04B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 016 105 A (WOOD CONVERSION CO) 5 January 1966 (1966-01-05) exampl e 1 -----	1-13
X	CN 101 081 742 A (SHANDONG LUYANG SHARE CO LTD [CN]) 5 December 2007 (2007-12-05) exampl e 3 page 1 -----	1-13
X	W0 02/088468 A2 (STOCKHAUSEN CHEM FAB GMBH [DE]; HUEPPERLING FRANK [DE]; WERRES JOACHIM) 7 November 2002 (2002-11-07) exampl e 1 -----	1-13
X	US 2010/326614 A1 (HUND RENE [FR] ET AL) 30 December 2010 (2010-12-30) paragraphs [0086] - [0087] ----- -/--	1-13

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 12 August 2013	Date of mailing of the international search report 03/09/2013
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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 Bergmei er, Marti n
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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/063660

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 44 670 A1 (BASF AG [DE]) 29 June 1995 (1995-06-29) claims 1-2; example 1 -----	1-13

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Information on patent family members

International application No PCT/EP2013/063660
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