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Canadian Intellectual Property Office

CA 3063260 A1 2009/02/12

(21) 3 063 260

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(22) Date de dépôt/Filing Date: 2008/08/01
(41) Mise à la disp. pub./Open to Public Insp.: 2009/02/12
(62) Demande originale/Original Application: 2 695 407
(30) Priorités/Priorities: 2007/08/03 (GB0715100.4); 2008/04/29 (GB0807777.8); 2008/06/06 (GB0810297.2)

(51) Cl.Int./Int.Cl. *C03C 27/10* (2006.01), *C03C 13/06* (2006.01), *C08L 61/20* (2006.01)

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(54) Titre : LIANTS
(54) Title: BINDERS

(57) Abrégé/Abstract:
An un-reacted substantially formaldehyde free curable binder solution for binding loose matter consists essentially of a solution obtainable by dissolving - a reducing sugar, - an ammonium salt acid precursor - optionally a carboxylic acid or a precursor thereof and - optionally ammonia in water.

ABSTRACT

An un-reacted substantially formaldehyde free curable binder solution for binding loose matter consists essentially of a solution obtainable by dissolving

- a reducing sugar,
- an ammonium salt acid precursor
- optionally a carboxylic acid or a precursor thereof and
- optionally ammonia

in water.

BINDERS

This is a division of Canadian patent application no. 2,695,407 filed August 1, 2008.

This invention relates to binders, for example for glass wool or stone wool insulation.

WO 2007/014236 relates to binders, including binders comprising Maillard reactants. One particular binder disclosed is based on a triammonium citrate – dextrose system derived from mixing dextrose monohydrate, anhydrous citric acid, water and aqueous ammonia. One of the many advantages of this binder system is that it is formaldehyde free.

One aspect of the present invention provides a binder solution in accordance with claim 1; the dependent claims define alternative and/or preferred embodiments.

In another aspect, the present invention provides a binder solution comprising a solution obtainable by dissolving

- a carbohydrate,
- an acid precursor derivable form an inorganic salt,
- a source of nitrogen
- optionally an organic acid or a precursor thereof and
- optionally ammonia.

Binder solutions used in accordance with the present invention may be "substantially formaldehyde free", that is to say that they liberate less than 5 ppm formaldehyde as a result of drying and/or curing (or appropriate tests simulating drying and/or curing). Such binder solutions are preferably "formaldehyde free", that is the say they liberate less than 1 ppm formaldehyde in such conditions.

Products in accordance with the invention which incorporate binders (for example insulation materials or wood boards) may be "substantially formaldehyde free", that is to say that they comprise less than 5 ppm or less than detectable limits of free formaldehyde and/or consist of materials which together comprise less than these amounts of free formaldehyde and/or release levels of formaldehyde in standardised tests adapted to simulate their ordinary use which allows them to be classified as having no or undetectable levels of formaldehyde release. Preferably, such products release less than 10μg/m³, more preferably less than 5 μg/m³ of formaldehyde during the period of 24-48 hours from the start of testing in accordance with ISO 16000.

It has been found that binders according to the present invention may have at least equivalent and indeed improved properties compared to, for example, the tri-ammonium citrate – dextrose system of WO 2007/014236. WO 2007/014236 teaches binder systems based, inter alia, on a combination of a carbohydrate (for example a reducing sugar), ammonia and a carboxylic acid and suggests that a Maillard type reaction may form the basis of the curing chemistry. It would have been thought that the nature of the acid used would have a significant effect upon the properties of the cured binder, particularly if the acid precursor and/or a derivative therefrom is incorporated into the structure of the cured binder. It is thus surprising that an acid precursor derivable from an inorganic salt should provide a suitable acid precursor in an otherwise apparently similar binder system.

Use of an acid precursor derivable from an inorganic salt may have significant advantages in terms of cost, availability and ease of handling. The acid precursor derivable from an inorganic salt of the binder solution may comprise a species selected from the group consisting of sulphates, phosphates, nitrates and carbonates. A particular advantage can be achieved by use of one or more inorganic ammonium salts, for example, an ammonium sulphate, an ammonium phosphate or an ammonium carbonate. An ammonium salt may provide the or part of the acid precursor and/or the or part of the source of nitrogen and/or the or part of a pH control system. An ammonium nitrate may also work; however, ammonium nitrate may oxidise aldehyde groups of the carbohydrate (for example in the case of dextrose) and/or require precautions to avoid explosions.

An ammonium sulphate is particularly advantageous but ammonium phosphate may be used in addition to or instead of this. Ammonium phosphate may be mono ammonium phosphate, di ammonium phosphate or tri ammonium phosphate; it may be an ammonium hydrogen phosphate. An ammonium carbonate, alone or in combination with the other materials disclosed herein, may also provide good results. The ammonium carbonate may be an ammonium bicarbonate.

The acid precursor, particularly when this consists essentially of inorganic ammonium salt(s), may make up

- at least 5%, preferably at least 7%, more preferably at least 9% by dry weight of the uncured binder solution; and/or
- less than 25% or 20%, preferably less than 18%, more preferably less than 16% by dry weight of the uncured binder solution.

The term "consist or consisting essentially of" is intended to limit the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention.

The acid may comprise: a sulphuric acid, a phosphoric acid, a nitric acid or a weak acid.

The binder may comprise between 5% and 25%, preferably 10% to 20 %, more preferably 15% to 20% by dry weight of acid precursor (particularly where this is an inorganic ammonium salt) to carbohydrate (particularly when this is a sugar).

Where the binder comprises both an acid precursor derivable from an inorganic salt and an organic acid, these may be present in the following amounts by dry weight with respect to the carbohydrate (particularly where this is a sugar):

	Preferred	More preferred	Most preferred
acid precursor derivable from an inorganic salt	At least 2.5%	At least 5%	

organic acid	At least 2.5%	At least 5%	
Combination of organic acid and acid precursor derivable from an inorganic salt	5-25%	10-20%	15-20%

Where an organic acid is used, this is preferably derived from an ammonium salt. For example, an ammonium citrate, particularly tri-ammonium citrate may be used as a source of citric acid.

Prior art phenol formaldehyde binder systems for mineral wool insulation have been used with the addition of about 2% by weight ammonium sulphate as a curing agent. However, the chemistry of such phenol formaldehyde binder systems is not comparable to the binder systems of the present invention which are not based on phenol and/or formaldehyde and/or on other phenolics.

A carbohydrate may be used in the binder solution rather than specifically a reducing sugar and may comprise a monosaccharide, for example in its aldose or ketose form. Preferably, the carbohydrate comprises a sugar, more preferably a reducing sugar or a reactant that yields a reducing sugar in situ under thermal curing condition; it may comprise glucose (ie dextrose). The carbohydrate may comprise a carbohydrate having a reducing aldehyde. It is believed that the use of a reducing sugar and particularly dextrose gives good binder strengths, particularly for the manufacture of mineral wool insulation products. The dextrose need not be 100% pure but use of a material having a dextrose equivalent value of at least 0.85, preferably at least 0.9 and more preferably at least 0.95 is thought to be advantageous. The dextrose equivalent value DE can be thought of as i) a measure of de-polymerization and is roughly: DE= 100/dp where dp stands for degree of polymerization or ii) the total amount of reducing sugars calculated as D-glucose (dextrose) on a dry basis.

Preferably, the binder solution and/or the binder is free or substantially free of starch; the presence of substantial quantities of starch is thought to increase the curing time and/or reduce the strength of the cured binder. The binder solution and/or the binder may be free or substantially free of proteins.

Industrial, non-food grade dextrose may be used as the reducing sugar; products such as Sirodex331 which is a 75% solids sugar solution obtainable from Tate and Lyle with a DE value of 94.5 may be used.

The reducing sugar may consist essentially of dextrose. Particularly in this case and more particularly where, in addition, the acid precursor consists essentially of an ammonium salt, for example an ammonium sulphate, the ratio by dry weight of the amount of reducing sugar/ the amount of acid precursor may be greater than or equal to 2.5 and/or less than or equal to 13.

The source of nitrogen may be an amine or an amine reactant; it may be derivable from the same source as the acid precursor, for example, from an inorganic ammonium salt. It is preferably ammonia in solution.

Precursors for and/or reactants which give the materials referred to may be used.

In one embodiment, the binder is derived essentially from a reducing sugar and an inorganic ammonium salt in aqueous solution.

In another embodiment, the binder may also comprise an organic acid, particularly a carboxylic acid; this may be a polycarboxylic acid, particularly a bi-carboxylic acid or tri-carboxylic acid, preferably citric acid; it is preferably monomeric. The combination of an organic acid (or a precursor a salt or an anhydride thereof) with an acid precursor derivable from an inorganic salt may present various advantages. Firstly, such a combination may reduce the risk of punking (which has been observed with such binders based solely on organic acids) whilst providing acceptable strength. Punking is a term of art in the mineral fibre insulation area

which generally denotes a comparatively rapid oxidation of a binder with a concomitant generation of heat in a finished and generally packaged insulation product. Punking generally causes generation of fumes and discolouring of the insulation material. It may be associated with exothermic reactions which increase the temperatures through the thickness of the insulation material; this may destroy the integrity of the insulation product and/or present a fire hazard.
Alternatively or additionally, the combination of an organic acid (or a precursor, a salt or an anhydride thereof) with an acid precursor derivable from an inorganic salt may moderate acid conditions occurring during curing and thus reduce the risk or tendency of such conditions to cause significant damage to the material being bound. Such a combination may be particularly advantageous as a binder for stone wool insulation whose fibres may be more susceptible to potential damage by acid than, for example, glass wool insulation.

In a further embodiment, the binder is derived essentially from: a carbohydrate; an inorganic ammonium salt; and an organic acid and/or organic acid precursor; in aqueous solution.

Binders which comprise or consist essentially of the components described herein may include additives, for example, additives selected from: silanes, mineral oils, coupling agents, silicones or siloxanes (particularly for water repellency), silicon containing compounds, surfactants, hydrophilic additives, hydrophobic additives, waxes, substances useful for controlling the pH (e.g. ammonium hydroxide) and ammonia. Ammonium hydroxide when used, and indeed other additives, may provide the and/or an additional source of nitrogen.
Preferably, the total quantity of additives (excluding ammonia) is less than 5 % by weight (excluding the weight of water present), more preferably less than 3% or less than 2% by weight.

Particularly for mineral fibre products, it is preferred to include a silane as an additive. The binder and/or binder solution may comprise at least 0.1 % and/or less than 1% of a silane by dry weight. The silane may be amino substituted; it may be a silyl ether and it is believed that its presence may significantly improve the long term strength of the binder, particularly after weathering.

Preferences for the pH of the binder are:

	Preferred	More preferred	Most preferred
pH of binder	≥7	≥8	≥9

at least in the state in which the binder is applied to a material to be bound and/or recovered in a waste water recuperation system. Such a neutral or alkaline pH of the binder may alleviate problems of corrosion of manufacturing equipment which have been encountered with some essentially acidic prior art binder systems. Such prior art binders include binders consisting essentially of polyacrylic acids or polymer polycarboxylic acids. One particular advantage of the present invention is thus the use of a binder system that can operate in such neutral or alkaline conditions. When cured, the binder may become acidic during the curing process. However, equipment corrosion considerations are less significant in this case due to the minimal contact between the manufacturing equipment and the binder when in this state. The pH of the binder may be less than or equal to 13, preferably less than or equal to 12, 11 or 10. A preferred pH may be in the range of 7.5 to 9.5, particularly 8 to 9. Binder which has been applied to the material to be bound and is subsequently dissolved in water may have a pH of greater than 6.

It is preferred to arrange the pH of the binder solution at an appropriate level to prevent precipitation of its constituents and particularly to ensure that the acid precursor derivable from an inorganic salt remains in solution. This is particularly the case where ammonium phosphate provides the acid precursor. Better dry and/or weathered strengths and/or more homogeneous products may be achieved by using homogeneous binder solutions comprising ammonium salt acid precursors which are free from precipitates, particularly when ammonium phosphate is used and the binder solution is free from phosphate precipitates.

The binder composition may be provided in the form of an aqueous solution; it may contain free ammonia or excess ammonia in solution. A neutral or alkaline pH of the binder may be generated by an excess of alkaline groups compared with acid groups present in the binder solution, for example, due partially or substantially to the presence of ammonia in the solution. Additional ammonia may be added to the binder solution, for example 0.2% - 1% by weight, or indeed more; this may help to keep a wash water system alkaline over the long term, particularly for the manufacture of mineral wool insulation.

In the case or mineral wool fibres particularly for thermal insulation products, when binder solution is sprayed on to hot mineral wool fibres just after they have been formed, the residual heat of the mineral wool fibres may cause a significant portion of any water in the binder solution to evaporate. Consequently, the mineral wool fibres which are then collected to form a batt may have binder present on them in the form of a sticky, viscous or tacky liquid. This may facilitate bonding between individual fibres via the binder.

One of the many advantages of this binder system is that it is applied, for example sprayed onto mineral wool fibers, in a substantially unreacted state. The ability to apply the binder solution in a substantially unreacted state may alleviate problems associated with pre-reacting the binder components in solution which have been encountered with some prior art binder systems in which the components are pre-reacted. Such prior art binders include binders consisting essentially of pre-reacted polymers or resins which are applied to the materials to be bound. With substantially unreacted binder present in the form of a sticky, viscous or tacky liquid on the material to be bound, the reaction between the binder components may occur in a substantially dry state. One may describe the reaction as a bulk polymerization because it is occurring without the benefit of a solvent. A particular advantage of the present invention is thus the use of a binder system that can polymerise in a substantially dry state or through a bulk polymerisation.

Mineral fibres used in the context of the invention may be formed by internal or external spinning. They may have a temperature in the range 20 °C to 200 °C , generally 30 °C to 100 °C or 150 °C, when sprayed with the binder solution. The

quantity of binder solution sprayed may be used with or without additional water sprays to assist in cooling the mineral fibres to a desired temperature between their formation and their collection to form a batt.
A particular advantage of using ammonia in solution to control the pH of the binder solution applied to the mineral fibres is that at least part of the ammonia of binder solution that sticks to the fibres may flash off due to the residual heat of the mineral wool fibres. Consequently, the binder solution that coats the fibres may have a lower pH than the binder solution sprayed.

The invention extends to a method of manufacturing a mineral fibre thermal insulation product comprising the sequential steps of:

- Forming mineral fibres from a molten mineral mixture;
- spraying a substantially formaldehyde free binder solution on to the mineral fibres, the binder solution comprising: a carbohydrate (particularly a reducing sugar), an acid precursor derivable from an inorganic salt and a source of nitrogen;
- Collecting the mineral fibres to which the binder solution has been applied to form a batt of mineral fibres; and
- Curing the batt comprising the mineral fibres and the binder by passing the batt through a curing oven so as to provide a batt of mineral fibres held together by a substantially water insoluble cured binder.

Wash water may be sprayed on to mineral fibres between their formation and their collection to form a batt, at least a part of the wash water having been sprayed on mineral fibres and subsequently returned to a wash water system to be reused as wash water. The binder solution may comprise wash water.

The binder may be curable; it may be cured, for example in a curing oven; it may form a thermoset binder. In its cured form, the binder may: comprise melanoidins; and/or be thermoset; and/or be water insoluble or substantially water insoluble.
The binder solution may be substantially colourless or white to off-white; upon curing, the binder may take on a dark colour, particularly a dark brown colour. The cured product may be dark in colour, particularly dark brown in colour. The binder

may be free of proteins; it may be free of cellulosic feedstock. One of the many advantages of this binder system is that the extent of curing can be determined by the colour. Substantially dehydrated binder appears white or off-white. Progressively cured to a greater extent, the binder appears progressively darker in colour (a darker shade of brown). When applied to mineral fibers, the extent to which the mineral wool insulation has cured can be determined by its colour.

When applied to the material to be bound and/or prior to curing, the binder may be free or substantially free of melanoidins and/or other reaction products derived from curing. Curing of the binder may produce glucosylamine, particularly as an intermediate product. Consequently, a cured or particularly a partially cured product may comprise glucosylamine.

The reaction of the binder upon curing may be essentially a Maillard type reaction as described for example in US Patent Application 20070027283 or WO2007/14236. The binder may comprise polymerisation products of a mixture that comprises a reducing sugar and a material selected from the group consisting of ammonium sulphate, ammonium phosphate, ammonium nitrate and ammonium carbonate.

The binder solution may be formulated by combining:

- A carbohydrate, preferably a reducing sugar;
- An acid precursor derivable from an inorganic salt, preferably an ammonium sulphate or ammonium phosphate;
- A source of nitrogen; and
- water.

The formulation may comprise optional or additional ammonia provided in the form of an aqueous ammonia solution. The water may comprise wash water or recycled process water.

Forming the binder solution from a carbohydrate and an acid precursor comprising an inorganic ammonium salt provides one particular advantageous preparation method. This may be achieved in a simple mixing chamber which may be open and/or at atmospheric pressure. The carbohydrate and/or the acid precursor may be added in powder or liquid form. The preparation is preferably carried out at room temperature. Preferably it is not necessary to supply heat to prepare the binder solution; nevertheless, the binder solution may be heated during its preparation, for example to a temperature with the range 20°C to 80°C, particularly where this facilitates dissolving and/or mixing of its ingredients.

The binder solution, particularly in the state applied to the material to be bound, may comprise:

- at least 5% 10%, 15% or 18% solids and/or
- less than 70% or 60% (particularly in the case of wood board applications) or less than 50%, 40% or 20% solids (particularly in the case of mineral fibre insulation applications)

particularly determined as bake out solids by weight after drying at 140 °C for 2 hours.

The collection of loose matter bound together by means of the binder solution may comprise materials selected from: fibres, fibrous materials, mineral fibres, glass fibres, stone wool fibres, cellulosic fibres (including wood fibres, wood shavings, wood particles and sawdust), wood veneers, facings, wood facings, particles, woven or non-woven materials, loosely assembled materials, woven or non-woven materials.

The binder solution and/or the binder are preferably organic.

The loose matter may be shaped and/or dimensioned and/or moulded with the aid of the binder. The material produced may be selected from: a thermal insulation material, a mineral fibre product, a wood board product (including chip board, orientated strand board, particle board, medium density fibre board, wood facing products), foundry sands.

The matter to be bound may be at a temperature in the range 20 °C to 100 °C when the binder is applied. Particularly in the case of wood boards products, the binder and the loose matter may be mechanically mixed, for example by tumbling.

The binder solution, particularly when applied to the loose matter, may have a viscosity appropriate for application by spraying or pouring. Its viscosity at 20°C may be:

- Less than about 1.5 Pa.s, preferably less than about 1 x 10^{-2} Pa.s; and/or
- Greater that about 2 x 10^{-4} Pa.s, preferably greater than about 5 x 10^{-4} Pa.s

Curing of the binder may occur in a curing oven, for example using forced hot air circulation; it may occur in a press. Curing may comprise a dehydration of the binder; it may comprise a polymerisation; it may comprise a bulk polymerisation reaction. Curing may be carried out for duration of 20 minutes or less, preferably 10 minutes or less; it may be carried out by passing the product (for example a mineral fibre batt) through at least one zone of a curing oven at a temperature within the range 230 °C – 300 °C with an oven residence time in the range 30 seconds to 20 minutes. Curing of the binder preferably occurs when the binder solution (from which water may have been evaporated) is in contact with the loose matter; it may occur at substantially atmospheric pressure. The curing may be a substantially dry curing, that is to say by application of dry heat and/or substantially dry or heated atmospheric air rather than using steam or heated water vapour.

Particularly in the case of mineral fibre insulation products, the curing temperature and time may be selected as a function of the product density and/or thickness. The curing oven in such cases may have a plurality of heating zones having temperatures within the range 200 °C to 350 °C (typically 230°C to 300 °C). A thin, low density product (12 kg/m³ or less) may be cured by passing through the curing oven in as little as 20 seconds; a thick, high density product (80 kg/m³ or more) may require a passage of 15 minutes or more in the curing oven. The product may reach a temperature in the range 180 °C – 220 °C during the curing process.

The cured binder may comprise greater than 2% and/or less than 8% nitrogen by mass as determined by elemental analysis.

The binder in its uncured state may comprise the following levels of sulphates, phosphates carbonates and/or nitrates by dry weight:

- Greater than 2.5%, 3% or 5%; and/or
- Less than 25%, 22%, or 20%

Finished materials manufactured using binder systems according to the present invention may have residual levels of sulphates, phosphates, carbonates and/or nitrates derived notably from the inorganic salt serving as the acid precursor. Such species may be present in the following quantities:

- Greater than 500, 750, 1000 or 1500 mg/kg ; and/or
- Less than 5000, 4000 or 3000 mg/kg .

The presence of such species may be assessed in a leach test and provide an indication in the final product of the binder system used.

The quantity of binder in the finished product, particularly in the case of mineral wool insulation, may be:

- Greater than: 1%, 2%, 2.5%, 3%, 3.5% or 4%; and/or
- Less than: 20%, 15%, 10 % or 8%

measured by dry weight of the finished product.

Particularly in the case of mineral fibre insulation, the products may have one or more of the following parting strengths:

Ordinary Parting Strength of

- At least 120 g/g, preferably at least 150 g/g; and/or
- Less than 400 g/g

Weathered Parting Strength of

- At least 120 g/g, preferably at least 150 g/g; and/or
- Less than 400 g/g

% loss between Ordinary and Weathered Parting Strength of

- Less than 10%, preferably less than 5%

Where the product is mineral wool insulation may have one or more of the following characteristics:

- A density greater than 5, 8 or 10 kg/m^3;
- A density less than 200, 180 or 150 km/m^3
- Comprise glass wool fibres and have a density greater than 5, 8 or 10 kg/m^3 and/or less than 80, 60 or 50 kg/m^3;
- Comprise stone wool fibres and have a density greater than 15, 20 or 25 kg/m^3 and/or less than 220, 200 or 180 kg/m^3;
- A thermal conductivity λ of less than 0.05 W/mK and/or greater than 0.02 W/mK
- Comprise less than 99% by weight and/or more than 80% by weight mineral fibres.
- A thickness of greater than 10 mm, 15mm or 20 mm and/or less than 400mm, 350 mm or 300 mm.

Where the product is wood board product, it may have one or more of the following characteristics:

- Dimensions of at least 50cm x 80 cm, preferably at least 1 m x 2m
- Thickness of at least 11mm, 12mm or 15 mm
- A curing time of less than 25, 15, 12 or 10 minutes
- An internal bond strength measured in accordance with EN319 of at least: 0.4 N/mm^2 or 0.45 N/mm^2 (particularly for particle board or fibre boards) or measured in accordance with EN300 of at least 0.28 N/mm^2 (particularly for orientated strand board)
- A thickness swelling after 24 hours in water at 20°C according to EN317 of less than 12%, preferably less than 10%
- A water absorption after 24 hours in water at 20°C of less than 40%, preferably less than 30%

- A modulus of elasticity according to EN310 of at least: 1800 N/mm² (particularly for particle board or fibre boards) or 2500 N/mm² (particularly for orientated strand board) or 3500 N/mm² or 4800 N/mm²
- A bending strength (MOR) of at least: 14 N/m² (particularly for particle board or fibre boards) or 18 N/mm² (particularly for orientated strand board) or 20 N/mm² or 28 N/mm²
- Wax as an additive, for example in the range 0.1 to 2 % by weight, preferably 0.5 to 1% by weight
- A resin content (weight of dry resin to weight of dry wood particles) in the range 8 to 18% by weight, preferably 10 to 16% by weight, more preferably 12 to 14% by weight.
- Be cured in a press, particularly between platens have a temperature of greater than 180 °c or 200 °C and/or less than 280 °C or 260 °C.

Embodiments of the invention will now be described by way of example with reference to Fig 1 which is a plan view of a mineral fibre test sample.

<u>Shell bone testing:</u>

Binders were prepared as aqueous solutions by

- combining the ingredients of a desired binder formulation in an open, unheated reaction vessel
- adding distilled water
- subsequently adding a silane solution
- agitating during addition of liquids and afterwards for several minutes to achieve complete dissolution of solids

such that the binder solution contained approximately 45% dissolved solids as a percentage of total weight of solution. A 2-g sample of this solution, upon thermal curing at about 200 °C to 210 °C for 8 minutes, would yield 30% solids (the weight loss being attributed to dehydration during thermoset binder formation).

An evaluation of dry and "weathered" tensile strength of glass bead-containing shell bones provided an indication of the likely tensile strength and the likely durability of fibreglass insulation or other materials prepared with that particular binder. Predicted durability is based on the ratio of a shell bone's weathered tensile strength to its dry tensile strength.

To prepare the shell bones, an electric mixer was used for about two minutes to mix approximately 75 g of binder with 727.5g of glass beads (equivalent to Quality Ballotini Impact Beads, Spec. AD, US Sieve 70-140, 106-212 micron-#7, from Potters Industries, Inc.). Any clumps from the sides of the mixer whisk and from the sides and bottom of the mixing bowl were mixed in manually using a spatula about half way through the mixing and also at the end of the mixing.

The prepared glass beads/binder mixture was added to the mould cavities of a shell bone mould (Dietert Foundry Testing Equipment; Heated Shell Curing Accessory, Model 366) which had been pre-heated to about 218 °C (425°F). The surface of the mixture in each cavity was flattened out, while scraping off the excess mixture to give a uniform surface area to the shell bone. Any inconsistencies or gaps that existed in any of the cavities were filled in with additional glass beads/binder mixture and then flattened out. The top platen was quickly placed onto the bottom platen (to avoid producing shell bones with two differentially cured layers). The cured shell bones were removed after seven minutes, cooled to room temperature on a wire rack, labelled and placed individually in plastic storage bags. If shell bones could not be tested on the day they were prepared, the shell bone-containing plastic bags were placed in a dessiccator unit. During curing the temperature of the bottom platen ranged from about 204 °C to about 221 °C (about 400°F to about 430°F), while the temperature of the top platen ranged from about 227 °C to about 243 °C (about 440°F to about 470 °F).

Procedure for testing breaking strength:

- Equipment: 5500 R Instron machine

- Immediately prior to testing, each shell bone was removed from is plastic bag and its weight and thickness recorded.

Weathering Procedure for Shell Bones:

- 16 hours weathering in a pre-heated humidity chamber (65 °C , 95% relative humidity)
- upon removal shell bones were sealed in individual plastic storage bags and taken immediately for testing.

Procedure for measuring gel time:

A small amount of binder (2.0ml) is added to the centre of a hot plate set to 150°C and a stop watch is started .The binder is worked with a spatula until it is possible to draw the sample into a long string. The time taken from the addition of the binder to the string formation is the gel time.

Binder formulations tested – inorganic acid precursors compared with citric acid:

Test ref:	Binder formulation (by dry weight)
A	85% DMH + 15% CA + 4.8% NH4OH + 0.3% ISI0200
B	90% DMH + 10% AmSO4 + 4.8% NH4OH + 0.3% ISI0200
C	85% DMH + 15% AmSO4 + 4.8% NH4OH + 0.3% ISI0200
D	80% DMH + 20% AmSO4 + 4.8% NH4OH + 0.3% ISI0200
E	90% DMH + 10% AmPO4 + 4.8% NH4OH + 0.3% ISI0200
F	85% DMH + 15% AmPO4 + 4.8% NH4OH + 0.3% ISI0200
G	80% DMH + 20% AmPO4 + 4.8% NH4OH + 0.3% ISI0200

Binder formulations tested – combined inorganic acid precursor and citric acid compared with citric acid alone and inorganic acid precursor alone:

Test ref:	Binder formulation (by dry weight)
H	85% DMH + 15% CA + 4.8% NH4OH + 0.3% ISI0200
I	85% DMH + 10% CA + 5% AmSO4 + 4.8% NH4OH + 0.3% ISI0200

J	85% DMH + 5% CA + 10% AmSO4 + 4.8% NH4OH + 0.3% ISI0200
K	85% DMH + 15% AmSO4 + 4.8% NH4OH + 0.3% ISI0200

Key:
DMH=Dextrose monohydrate
CA= citric acid
NH4OH= ammonium hydroxide
ISIO200= silane
AmSO4= ammonium sulphate
AmPO4= ammonium phosphate

Test results – inorganic acid precursors compared with citric acid:

Test ref	Dry breaking strength (MN/m²)	Weathered breaking strength (MN/m²)	Loss in breaking strength from weathering/ %	Gel time of binder solution (s)	pH of binder solution just before mixing with beads
A	1,455	1,567	-7,70	343	9,54
B	1,271	0,895	29,57	280	10,28
C	1,550	0,856	44,79	362	10,24
D	1,877	1,156	38,39	327	10,13
E	1,499	1,069	28,68	356	10,18
F	1,281	0,848	33,82	334	9,99
G	1,123	0,801	28,74	287	9,73

Test results - combined inorganic acid precursor and citric acid compared with citric acid alone and inorganic acid precursor alone:

Test ref	Dry breaking strength (MN/m^2)	Weathered breaking strength (MN/m^2)	Loss in breaking strength from weathering/ %	Gel time of binder solution (s)	pH of binder solution just before mixing with beads
H	1.69	1.50	11.32	363	9.39
I	1.50	1.18	21.37	341	9.71
J	1.21	1.05	13.19	375	9.99
K	1.47	1.02	30.33	376	9.97

Results from tests carried out together (test A to G were carried out in one session and tests H to K carried out during another session) provide a useful indication of results relative to other results obtained during the same test session. It may not be reliable to compare tests results from different test sessions.

First comparative testing on insulation product:

Comparative testing of binder systems on a mineral fibre insulation product gave the following results:

Binder tested	Description	Formulation
PF1	Comparative example – standard phenol formaldehyde binder	Resin, Urea, Lignin, Ammonia, Silane
AC1	Comparative example – ammonium citrate based binder	Dextrose 85% Citric Acid 15% Ammonia 4.8% Silane 0.3%
Ex1	Example 1 of the present	Dextrose 85% Ammonium

	invention	Sulphate 15% Ammonia 4.8% Silane 0.3%

Product used for test:	glass wool fibre insulation product, nominal density 16 kg/m³, nominal thickness 75mm, nominal width 455mm

Binder content of test product LOI (Loss on ignition) %weight:

Binder	Mean LOI
PF1	6,22%
AC1	6,91%
Ex1	6,78%

Drape test (mean average in mm measured after the periods specified):

Binder	Day 1	Week 1	Week 3	Week 6
PF1	55	68	60	71
AC1	83	99	80	72
Ex1	66	76	66	75

Thickness (mean average in mm measured after the periods specified in accordance with British Standard BS EN 823:1995)

Binder	Day 1	Week 1	Week 3	Week 6
PF1	76,4	75,1	75,1	75,2
AC1	75,3	73,6	72,5	74
Ex1	76	76,7	74,9	74,3

Density (mean average in kg/m³ measured after the periods specified)

Binder	Day 1	Week 1	Week 3	Week 6
PF1	16,44	16,7	16,35	16,44
AC1	16,68	16,41	16,33	16,48
Ex1	16,5	16,9	16,5	16,5

Quantity of sulphates present mg/kg

Binder	Sample 1	Sample 2
AC1	240	240
Ex1	2000	2200

Parting strength (g/g)

Binder	Ordinary	Weathered	%loss
PF1	248	107	56.85
AC1	230	199	13.47
Ex1	196	189	3.57

Test procedures:

Binder content LOI (Loss on ignition)

A weighed sample of wool plus binder is placed in a muffle furnace set to 550°C. After a set time the wool is removed from the furnace, placed in a desiccator to cool and re-weighed. The weight loss is expressed as a percentage of the original sample weight and is known as the binder content or Loss On Ignition (LOI).

Drape test

A single batt (or slab) is placed across two poles (each 500mm long , 20mm diameter) set into a wall 1 metre apart. The degree of sag in the centre of the batt is recorded. This is repeated for all of the batts in a pack and for several packs. Packs are measured at set points over a period of time to determine the long term effects of compression on the batts.

Density: measured for the samples subjected to the drape test

Quantity of sulphates present: leaching test for granular wastes in water with eluate analysis according to British standard BS EN 12457-2 at L/S10

Parting Strength

The parting strength is expressed in grams/gram being the total breaking load of six test specimens divided by their total weight.

The test is carried out on mineral fibre mats as received for testing (Ordinary Parting Strength) and after an accelerated weathering test as explained below (Weathered Parting Strength).

A first set of six samples of the form and dimensions shown in Fig 1 are cut from the mineral fibre mat to be tested. The dimensions are:

r: radius 12.7mm;

DC: distance between centres 44.5mm;

a: 25.4 mm;

b: 121 mm.

The long axis of the samples should be parallel to the conveyor direction and the samples should be taken across the full width of the mineral mat. A second set of six samples is then taken in the same way.

The total weight of the first group of six samples W1 in grams is recorded.

The total weight of the second group of six samples W2 in grams is recorded; these samples are then placed in a preheated autoclave and conditioned on a wire mesh shelf away from the bottom of the chamber under wet steam at 35kN/m² for one hour. They are then removed, dried in an oven at 100°C for five minutes and tested immediately for parting strength.

To test the parting strength, each sample is mounted in turn on the jaws of a 5500 Instron tensile strength machine and the maximum breaking load in grams or Newtons is recorded. If the breaking load is measured in Newtons it is converted to grams by multiplying it by 101.9. Six results in grams are obtained for each set of samples: G1 G2 G3 G4 G5 and G6 for the first set of samples and G7 G8 G9 G10 G11 and G12 for the second set of samples.

The Ordinary Parting Strength is calculated from the first set of samples using the formula Ordinary Parting Strength = (G1+G2+G3+G4+G5+G6)/W1.

The Weathered Parting Strength is calculated from the second set of samples using the formula Weathered Parting Strength = (G7+G8+G9+G10+G11+G12)/W2.

Second comparative testing on insulation product:

Product used for test:	glass wool fibre insulation product, nominal density 7.2 kg/m^3, nominal thickness 159 mm

SAMPLES: The following samples of fibreglass batts were tested:

Example	Binder Description	Target binder content (LOI) for product
PF2	standard phenol formaldehyde binder of Resin, Urea, Ammonia, Silane	4.5%
2.1	Dextrose 85% Ammonium Sulphate 15% Silane 0.3% (10.6% solids in binder solution)	4.5%
2.2	Dextrose 85% Ammonium Sulphate 15% Silane 0.3% Norjohn oil (11.4% solids in binder solution)	4.5%
2.3	Dextrose 85% Ammonium Sulphate 15% Silane 0.3%, 2.4%NH3 (10.6% solids in binder solution)	4.5%
2.4	Dextrose 85% Ammonium Sulphate 15% Silane 0.3% , 2.4%NH3 (10.6% solids in binder solution)	6.0%

Results

	PF2	2.1	2.2	2.3	2.4
Recovery	158mm	157 mm	163 mm	160 mm	166 mm
Recovery. % nominal	99.4 %	99.0 %	102.8 %	100.6 %	104.8 %
Parting Strength (ASTM C-686)	190.8 g/g	131.7 g/g	146.7 g/g	159.9 g/g	143.9 g/g
Parting strength after weathering (ASTM C-686 following conditioning for 7 days at 90 °F, 90% relative humidity)	145.9 g/g	100.0 g/g	110.3 g/g	124.9 g/g	114.3 g/g

CLAIMS:

1. A substantially formaldehyde free binder solution comprising
   - a carbohydrate comprising a reducing sugar or a carbohydrate reactant that yields a reducing sugar in situ under thermal curing conditions;
   - an acid precursor derivable from an inorganic salt; and
   - a source of nitrogen;

   and in which the binder solution comprises:
   - at least 5% by dry weight of the acid precursor with respect to the uncured binder solution, and
   - in which the ratio by dry weight of the amount of the reducing sugar/ the amount of the acid precursor is greater than or equal to 2.5 and less than or equal to 13.

2. A substantially formaldehyde free binder solution in accordance with claim 1, in which the binder solution further comprises an organic acid or a precursor, a salt or an anhydride thereof.

3. A substantially formaldehyde free binder solution in accordance with claim 2, in which the organic acid is provided in the form of an ammonium salt.

4. A substantially formaldehyde free binder solution in accordance with claim 2 or claim 3, in which the organic acid is a carboxylic acid.

5. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 4, in which the binder solution comprises ammonia.

6. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 5, in which the acid precursor is selected from the group consisting of ammonium sulphate salts, ammonium phosphate salts, ammonium nitrate salts and ammonium carbonate salts.

7. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 6, in which the binder solution comprises at least 7% by dry weight of said acid precursor with respect to the uncured binder solution.

8. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 7, wherein the acid precursor comprises an ammonium salt and in which the binder solution derived essentially from: a reducing sugar; and the inorganic ammonium salt in aqueous solution.

9. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 7, in which the binder is derived essentially from: a carbohydrate; an inorganic ammonium salt; and an organic acid and/or organic acid precursor in aqueous solution.

10. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 9, in which the binder comprises excess ammonia in solution.

11. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 10, in which the reducing sugar comprises dextrose.

12. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 11, in which the pH of the solution is greater than 7.

13. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 12, in which the binder solution has a pH which, in its conditions of use, prevents precipitation of sulphates, phosphates, nitrates or carbonates.

14. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 13, in which the binder solution comprises at least 5% solids and less than 50% solids.

15. A substantially formaldehyde free binder solution in accordance with any one of claims 1 to 14, in which the binder solution comprises one or more additives selected from: silanes, mineral oils, coupling agents, silicones, siloxanes, silicon containing compounds, surfactants, hydrophilic additives, hydrophobic additives, waxes and substances useful for controlling the pH; and in which the total quantity of the additives in the binder solution is less than 5% by dry weight.

16. A material comprising a collection of loose matter maintained together by a cured, substantially formaldehyde free, thermoset binder characterised in that the material comprises more than 500 mg/kg of species selected from the group consisting of sulphates, phosphates, nitrates and carbonates.

17. A material in accordance with claim 16 in which the material comprises a mineral fiber thermal insulation material, notably having a thermal conductivity λ of less than 0.05 W/mK.

18. A material in accordance with claim 16 or claim 17, in which the species selected from the group consisting of sulphates, phosphates, nitrates and carbonates is derived essentially from binder precursors.

19. A material in accordance with any one of claims 16 to 18 in which the binder is cured and comprises melanoidins.

20. A material in accordance with any of claims 16 to 19 in which the material comprises a mineral fiber thermal insulation material comprising a collection of non-woven mineral fibers maintained together by a cured, thermoset, substantially water insoluble, substantially formaldehyde-free, polymer-containing binder,

wherein the quantity of binder is greater than 2.5% by dry weight and less than 15% by dry weight, and
wherein the mineral fiber insulation material has
an ordinary parting strength of at least 120 g/g,
a weathered parting strength of at least 120 g/g,
a thermal conductivity λ of less than 0.05 W/mK., and
comprises less than 99% by weight and more than 80% by weight mineral fibers.

21. A material in accordance with claim 20, in which the material comprises glass wool fibres and has a density greater than 5 kg/m^3 and less than 80 kg/m^3.

22. A material in accordance with claim 20, in which the material comprises stone wool fibres and has a density greater than 15 kg/m^3 and less than 220 kg/m^3.

23. A material in accordance with any of claims 16 to 22, in which the cured binder comprises greater that 2% nitrogen by mass.

24. A material in accordance with any of claims 16 to 23, in which the cured binder comprises less than that 8% nitrogen by mass.

25. A material in accordance with any of claims 16 to 24, in which the cured, substantially formaldehyde free, thermoset binder is obtained by curing a binder solution as defined in any one of claims 1 to 15.

Fig 1