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- (54) Benævnelse: **Slettemiddelsammensætning til mineraluld indeholdende et ikke-reducerende sukker og et metalsalt af en uorganisk syre, og tilvejebragte isoleringsprodukter**
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5 The present invention relates to the field of thermal and/or acoustic insulating products based on mineral wool, in particular of glass or of rock, and on a formaldehyde-free binder.

The invention more particularly relates to a sizing composition capable of crosslinking to form said binder, which includes at least one non-reducing sugar and at least one inorganic acid metal salt, to the
10 process for the manufacture of thermal and/or acoustic insulating products and to the insulating products which result therefrom.

The manufacture of insulating products based on mineral wool generally comprises a stage of manufacture of the wool itself, which can be carried out by various processes, for example according to the known
15 technique of fiberizing by internal or external centrifugation.

Internal centrifugation consists in introducing the molten material (generally glass or a rock) into a centrifugal device comprising a multitude of small orifices, the material being projected toward the peripheral wall of the device under the action of the centrifugal force and escaping therefrom
20 in the form of filaments. On leaving the centrifugal device, the filaments are drawn and carried toward a receiving member by a gas stream having a high temperature and a high speed, in order to form a web of fibers (or mineral wool).

External centrifugation consists, for its part, in pouring out the
25 molten material at the external peripheral surface of rotating members, known as rotors, from where said material is ejected under the action of the centrifugal force. Means for drawing by gas stream and for collecting on a receiving member are also provided.

In order to provide for the assembly of the fibers together and to
30 make it possible for the web to have cohesion, a sizing composition comprising a thermosetting resin is projected onto the fibers, on the route between the outlet of the centrifugal device and the receiving member. The web of fibers coated with the size is subjected to a heat treatment, at a temperature generally of greater than 100°C, in order to bring about the
35 polycondensation of the resin and to thus obtain a thermal and/or acoustic insulating product having specific properties, in particular dimensional stability, tensile strength, thickness recovery after compression and homogeneous color.

The sizing composition to be projected onto the mineral wool is generally provided in the form of an aqueous solution including the thermosetting resin and additives, such as a catalyst for the crosslinking of the resin, an adhesion-promoting silane, a dust-preventing mineral oil, and the like. The sizing composition is generally applied to the fibers by spraying.

The properties of the sizing composition depend largely on the characteristics of the resin. From the viewpoint of the application, it is necessary for the sizing composition to exhibit good sprayability and to be able to be deposited at the surface of the fibers in order to efficiently bind them.

The resin has to be stable for a given period of time before being used to form the sizing composition, which composition is generally prepared at the time of use by mixing the resin and the additives mentioned above.

At the regulatory level, it is necessary for the resin to be regarded as non-polluting, that is to say for it to comprise - and for it to generate during the sizing stage or subsequently - as little as possible in the way of compounds which may be harmful to human health or to the environment.

The thermosetting resins most commonly used are phenolic resins belonging to the family of the resols. In addition to their good crosslinkability under the abovementioned thermal conditions, these resins are soluble in water, have a good affinity for mineral fibers, in particular glass fibers, and are relatively inexpensive.

These resols are obtained by condensation of phenol and formaldehyde, in the presence of a basic catalyst, in a formaldehyde/phenol molar ratio of greater than 1, so as to promote the reaction between the phenol and the formaldehyde and to reduce the level of residual phenol in the resin. The condensation reaction between the phenol and the formaldehyde is carried out while limiting the degree of condensation of the monomers, in order to avoid the formation of long, relatively water-insoluble, chains which reduce the dilutability. Consequently, the resin comprises a certain proportion of unreacted monomer, in particular formaldehyde, the presence of which is undesirable because of its known harmful effects.

For this reason, resol-based resins are generally treated with urea, which reacts with the free formaldehyde by trapping it in the form of nonvolatile urea-formaldehyde condensates. The presence of urea in the

resin in addition brings a certain economic advantage as a result of its low cost because it is possible to introduce it in a relatively large amount without affecting the operating qualities of the resin, in particular without harming the mechanical properties of the final product, which significantly
5 lowers the total cost of the resin.

Nevertheless, it has been observed that, under the temperature conditions to which the web is subjected in order to obtain crosslinking of the resin, the urea-formaldehyde condensates are not stable; they decompose with restoration of the formaldehyde and urea, in its turn at
10 least partially decomposed to give ammonia, which are released into the atmosphere of the factory.

Regulations with regard to environmental protection, which are becoming more restrictive, are forcing manufacturers of insulating products to look for solutions which make it possible to further lower the levels of
15 undesirable emissions, in particular of formaldehyde.

Solutions in which resols are replaced in sizing compositions are known.

A first solution is based on the use of a carboxylic acid polymer, in particular an acrylic acid polymer.

20 In US 5 340 868, the size comprises a polycarboxylic polymer, a β -hydroxyamide and an at least trifunctional monomeric carboxylic acid.

Other sizing compositions have been provided which comprise a polycarboxylic polymer, a polyol and a catalyst, this catalyst being able to be a phosphorus-comprising compound (US 5 318 990, US 5 661 213,
25 US 6 331 350, US 2003/0008978), a fluoroborate (US 5 977 232) or else a cyanamide, a dicyanamide or a cyanoguanidine (US 5 932 689).

The sizing compositions based on a polycarboxylic polymer and on a polyol can additionally comprise a cationic, amphoteric or nonionic surfactant (US 2002/0188055), a coupling agent of silane type (US
30 2004/0002567) or a dextrin as cobinder (US 2005/0215153).

A description has also been given of sizing compositions comprising an alkanolamine including at least two hydroxyl groups and a polycarboxylic polymer (US 6 071 994, US 6 099 773, US 6 146 746) in combination with a copolymer (US 6 299 936).

35 A second solution in which resols are replaced is based on the combination of a saccharide and a polycarboxylic acid.

In US 5 895 804, a description is given of an adhesive composition based on heat-crosslinkable polysaccharides which can be used as size for

mineral wool. The combination includes a polycarboxylic polymer having at least two carboxylic acid functional groups and a molecular weight at least equal to 1000, and a polysaccharide having a molecular weight at least equal to 10 000.

5 In WO 2009/080938, the sizing composition comprises a monosaccharide and/or a polysaccharide and an organic polycarboxylic acid with a molar mass of less than 1000.

A formaldehyde-free aqueous sizing composition which comprises a Maillard reaction product, in particular combining a reducing sugar, a
10 carboxylic acid and ammonia (WO 2007/014236), is also known. In WO 2009/019232 and WO 2009/019235, the proposal is made to substitute, for the carboxylic acid, an acid precursor derived from an inorganic salt, in particular an ammonium salt, which exhibits the additional advantage of being able to replace all or part of the ammonia.

15 The latter sizing compositions nevertheless comprise nitrogen-including compounds which are capable of decomposing, in particular to give ammonia, during the heat treatment employed in order for the mineral fibers to be able to be bonded to one another and to form the final insulating product.

20 An aim of the present invention is to provide a sizing composition for insulating products based on mineral wool, in particular of glass or of rock, which is devoid of formaldehyde and other nitrogenous compounds. In addition, said sizing composition does not comprise any organic polycarboxylic acid with a molar mass of less than 1000 and preferably is
25 completely devoid of organic polycarboxylic acid.

In order to achieve this aim, the present invention provides a sizing composition which comprises:

- at least one non-reducing sugar, and
- at least one inorganic acid metal salt chosen from inorganic
30 acid alkali metal, alkaline earth metal, transition metal or poor metal salts.

The expression "non-reducing sugar" should be understood in the conventional sense, namely a sugar composed of several saccharide units, the carbon 1 of which carrying the hemiacetal OH group is the participant in a bond.

35 The non-reducing sugar in accordance with the present invention is a non-reducing oligosaccharide including at most 10 saccharide units.

Mention may be made, as examples of such non-reducing sugars, of disaccharides, such as trehalose, isotrehaloses, sucrose and

isosucroses, trisaccharides, such as melezitose, gentianose, raffinose, erlose and umbelliferose, tetrasaccharides, such as stachyose, and pentasaccharides, such as verbascose.

5 Preference is given to sucrose and trehalose and better still to sucrose.

The inorganic acid metal salt reacts with the non-reducing sugar under the effect of the heat to form a polymeric network constituting the final binder. The polymeric network thus formed makes it possible to establish bonds at the junction points of the fibers in the mineral wool.

10 As already indicated, the inorganic acid metal salt is chosen from inorganic acid alkali metal, alkaline earth metal, transition metal or poor metal salts. Preferably, it is a sodium, magnesium, iron, cobalt, nickel, copper, zinc or aluminum salt, advantageously an aluminum or copper salt.

15 The inorganic acid metal salt is advantageously chosen from sulfates, chlorides, nitrates, phosphates and carbonates and better still from sulfates and chlorides.

Preference is given to aluminum sulfate, copper sulfate, potassium aluminum sulfate (or potassium alum) and aluminum chloride, in particular to aluminum sulfate and copper sulfate.

20 In the sizing composition, the inorganic acid metal salt represents from 1 to 30% by weight of the total weight of the mixture composed of the non-reducing sugar and the inorganic acid metal salt, preferably from 3 to 20% and advantageously from 5 to 15%.

25 The sizing composition in accordance with the invention can also comprise the conventional additives below in the following proportions, calculated on the basis of 100 parts by weight of non-reducing sugar and of inorganic acid metal salt:

- from 0 to 2 parts of silane, in particular an aminosilane,
- from 0 to 20 parts of oil, preferably from 4 to 15 parts,
- 30 - from 0 to 20 parts of glycerol, preferably from 0 to 10 parts,
- from 0 to 5 parts of a silicone,
- from 0 to 30 parts of an "extender".

35 The role of the additives is known and is briefly restated: the silane is an agent for coupling between the fibers and the binder, and also acts as antiaging agent; the oils are dust-preventing and hydrophobic agents; the glycerol acts as plasticizer and makes it possible to prevent pregelling of the sizing composition; the silicone is a hydrophobic agent having the role of reducing the absorption of water by the insulating product; the "extender"

is an organic or inorganic filler, soluble or dispersible in the aqueous sizing composition, which makes it possible in particular to reduce the cost of the sizing composition.

5 The sizing composition exhibits a pH which varies to a large extent according to the nature of the inorganic acid metal salt used, generally from 2 to 10, advantageously acidic, in particular of less than or equal to 6.

The sizing composition is intended to be applied to mineral fibers,, in particular glass or rock fibers.

10 Conventionally, the sizing composition is projected onto the mineral fibers at the outlet of the centrifugal device and before they are collected on the receiving member in the form of a web of fibers which is subsequently treated at a temperature which makes possible the crosslinking of the size and the formation of an infusible binder. The crosslinking of the size according to the invention takes place at a
15 temperature of the order of from 100 to 200°C, generally at a temperature comparable to that of a conventional formaldehyde-phenol resin, in particular of greater than or equal to 110°C, preferably of less than or equal to 170°C.

20 The acoustic and/or thermal insulating products obtained from these sized fibers also constitute a subject matter of the present invention.

These products are generally provided in the form of a mat or felt of mineral wool, of glass or of rock, or of a veil of mineral fibers, also of glass or of rock, intended in particular to form a surface coating on said mat or said felt.

25 The following examples make it possible to illustrate the invention without, however, limiting it.

In these examples, the following are measured:

- the crosslinking start temperature (T_C) and the densification temperature (T_D) by the Dynamic Mechanical Analysis (DMA) method,
30 which makes it possible to characterize the viscoelastic behavior of a polymeric material. The procedure is as follows: a sample of Whatman paper is impregnated with the sizing composition (content of organic solids of the order of 40%) and is then fixed horizontally between two jaws. An oscillating component equipped with a device for measuring the stress as a
35 function of the strain applied is positioned on the upper face of the sample. The device makes it possible to calculate the modulus of elasticity E' . The sample is heated to a temperature varying from 20 to 250°C at the rate of 4°C/min. The curve of variation in the modulus of elasticity E' (in MPa) as a

function of the temperature (in °C) is plotted from the measurements, the general appearance of the curve being given in figure 1. The temperature values, in °C, for the start of crosslinking (T_C), corresponding to the first increase in the modulus of elasticity E' , and for the densification of the polymeric network (T_D), corresponding to the second increase in the modulus of elasticity E' , if this increase exists, are determined on the curve.

- the viscosity, expressed in mPa.s, using a rheometer of plate/plate rotational type with shearing of 100 s^{-1} at 25°C. The sample has a solids content of 30% by weight.

- the contact angle of the sizing composition, comprising 30% by weight of solids, on a glass substrate.

- the tensile strength according to the standard ASTM C 686-71T on a sample cut out by stamping from the insulating product. The sample has the shape of a torus with a length of 122 mm, a width of 46 mm, a radius of curvature of the cut-out of the outer edge equal to 38 mm and a radius of curvature of the cut-out of the inner edge equal to 12.5 mm.

The sample is positioned between two cylindrical mandrels of a test machine, one of which is movable and is moved at a constant rate. The breaking force F (in newtons) of the sample is measured and the tensile strength TS, defined by the ratio of the breaking force F to the weight of the sample, is calculated.

The tensile strength is measured after manufacture (initial tensile strength) and after accelerated aging in an autoclave at a temperature of 105°C under 100% relative humidity for 15 minutes (TS 15).

- the initial thickness of the insulating product and the thickness after compressing for 1 hour, 24 hours and 30 days with a degree of compression (defined as being the ratio of the nominal thickness to the thickness under compression) equal to 4.8/1. The thickness measurements make it possible to evaluate the good dimensional behavior of the product.

- the thermal conductivity coefficient λ according to the standard EN 13162, expressed in $\text{W}/(\text{m} \times ^\circ\text{K})$.

EXAMPLES 1 TO 6

Sizing compositions are prepared which comprise the constituents appearing in table 1, the amounts being expressed as parts by weight.

The sizing compositions are prepared by successively introducing, into a vessel containing water, the non-reducing or reducing sugar and the inorganic acid metal salt with vigorous stirring until the constituents have completely dissolved.

The properties of the sizing compositions which appear in table 1 are also evaluated in comparison with a conventional sizing composition including a formaldehyde-phenol resin and urea (Reference) prepared in accordance with example 2, test 1, of WO 01/96254 A1.

5 The sizing compositions of examples 1 and 2 in accordance with the invention exhibit a lower densification temperature (T_D) for the polymeric network than that of comparative examples 3 and 4 including glucose: the difference in temperature is 26°C in the case of aluminum sulfate (examples 1 and 3) and 13°C in the case of copper sulfate
10 (examples 2 and 4).

The other properties of examples 1 and 2 are similar to those of comparative examples 3 and 4; in particular, the viscosity and the contact angle retain low values, which allows good application to the mineral fibers, in particular by spraying.

15 The crosslinking start temperature (T_C) of examples 1 and 2 is markedly lower than that of comparative examples 5 and 6 which do not include inorganic acid metal salt. This temperature is also lower than that of the phenolic resin (Reference).

EXAMPLES 7 AND 8

20 These examples illustrate the manufacture of insulating products on a pilot scale line.

Use is made of the sizing compositions of example 2 and comparative example 4, to which the following additives are added, per 100 parts by weight of sugar and copper sulfate: 1 part of
25 γ -aminopropyltriethoxysilane and 8 parts of a mineral oil. These sizing compositions constitute examples 7 and 8 (comparative) respectively.

Glass wool is manufactured by the internal centrifugation technique in which the molten glass composition is converted into fibers by means of a tool, referred to as centrifuging disk, comprising a basket
30 forming a chamber for receiving the molten composition and a peripheral band pierced by a multitude of orifices: the disk is rotated about its vertically positioned axis of symmetry, the composition is ejected through the orifices under the effect of the centrifugal force and the material escaping from the orifices is drawn into fibers with the assistance of a
35 drawing gas stream.

Conventionally, a size spraying ring is positioned beneath the fiberizing disk so as to uniformly distribute the sizing composition over the glass wool which has just been formed.

The mineral wool, thus sized, is collected on a belt conveyor with a width of 2.4 m equipped with internal extraction boxes which hold the mineral wool in the form of a web at the surface of the conveyor. The web passes continuously through an oven maintained at 270°C, where the constituents of the size polymerize to form a binder. The final insulating product has a nominal density of 17.5 kg/m³.

During the manufacture of the insulating product, the nitrogen emissions in the chimney remained at a minimal level.

The insulating product exhibits the following properties:

	Ex. 7	Ex. 8 (comp.)
Tensile strength (N)		
before aging	3.0	2.3
after aging	2.8	2.2
Thickness (mm)		
after 1 hour	108	110
after 24 hours	105	104
after 30 days	105	104
Loss on ignition (%)	5.6	5.1
λ (W/(m × K))	0.035	0.035

The insulating product according to example 7 is stable in thickness and it exhibits a better tensile strength than the product of example 8 including glucose: the gain is 30% before aging and 27% after aging.

EXAMPLES 9 TO 12

Sizing compositions are prepared under the conditions of examples 1 to 6 which include the constituents appearing in table 2, the amounts being expressed as parts by weight.

Table 1

Example	1	2	3 (Comp.)	4 (Comp.)	5 (Comp.)	6 (Comp.)	Reference
Sizing composition							
Sucrose	85	85	-	-	100	-	-
Glucose	-	-	85	85	-	100	-
Aluminum sulfate	15	-	15	-	-	-	-
Copper sulfate	-	15	-	15	-	-	-
Properties							
Crosslinking start temp. T _c (°C)	104	110	102	111	233	228	151
Densification temp. T _D (°C)	177	187	203	200	-	-	-
Viscosity (mPa.s)	6.1	5.1	5.6	6.1	5.1	5.2	8.0
Contact angle (°)	27	27	28	31	22	27	10
pH ⁽¹⁾	2.9	3.2	3.0	3.3	7.5	6.9	6.0

⁽¹⁾ solids content: 30%

Table 2

Example	9	10	11	12
Sizing composition				
Trehalose	85	85	-	-
Melezitose	-	-	85	85
Aluminum sulfate	15	-	15	-
Copper sulfate	-	15	-	15
Properties				
Crosslinking start temp. T_C (°C)	99	83	102	82
Densification temp. T_D (°C)	172	153	190	123
Viscosity (mPa.s)	7.6	7.3	7.2	7.4
Contact angle (°)	26	31	18	19
pH ⁽¹⁾	3.0	4.0	3.1	4.3

⁽¹⁾ solids content: 30%

P A T E N T K R A V

1. Slettemiddelsammensætning fri for formaldehyd, nitrogenforbindelser og organiske polycarboxylsyrer, til isoleringsprodukter på basis af mineraluld, især af sten eller af glas, k e n d e t e g n e t ved, at den omfatter
- 5 - mindst et ikke-reducerende sukker og
- mindst et metalsalt af en uorganisk syre valgt blandt alkalimetalsalte, jordalkalimetalsalte, overgangsmetalsalte eller hovedgruppemetalsalte (FR: métal pauvre) af en uorganisk syre.
2. Sammensætning ifølge krav 1, k e n d e t e g n e t ved, at det ikke-reducerende
- 10 sukker er et oligosaccharid indeholdende højst 10 saccharidgrupper.
3. Sammensætning ifølge krav 2, k e n d e t e g n e t ved, at det ikke-reducerende sukker er et di-, tri-, tetra- eller pentasaccharid.
4. Sammensætning ifølge et af kravene 1 til 3, k e n d e t e g n e t ved, at det ikke-reducerende sukker er trehalose, en isotrehalose, saccharose, melezitose, gentianose, raf-
- 15 finose, erlose, umbelliferose, stachyose eller verbascose.
5. Sammensætning ifølge et af kravene 1 til 4, k e n d e t e g n e t ved, at metalsaltet af en uorganisk syre er et salt af natrium, af magnesium, af jern, af cobalt, af nikkel, af kobber, af zink eller af aluminium, fortrinsvis af aluminium eller af kobber.
6. Sammensætning ifølge krav 5, k e n d e t e g n e t ved, at metalsaltet af en uor-
- 20 ganisk syre er valgt blandt sulfater, chlorider, nitrater, phosphater og carbonater, fortrinsvis sulfater og chlorider.
7. Sammensætning ifølge krav 5 eller 6, k e n d e t e g n e t ved, at metalsaltet af en uorganisk syre er sulfat af aluminium, sulfat af kobber, dobbeltsulfat af aluminium og af kalium (eller kaliumalun) og chlorid af aluminium, fortrinsvis sulfat af aluminium og sulfat
- 25 af kobber.
8. Sammensætning ifølge et af kravene 1 til 7, k e n d e t e g n e t ved, at metalsaltet af en uorganisk syre udgør 1 til 30 vægt% på basis af den samlede vægt af blandingen bestående af det ikke-reducerende sukker og metalsaltet af en uorganisk syre, fortrinsvis 3 til 20 % og mere fortrinsvis 5 til 15 %.
- 30 9. Sammensætning ifølge et af kravene 1 til 8, k e n d e t e g n e t ved, at den yderligere omfatter følgende additiver i de følgende forhold beregnet på basis af 100 vægtandele af ikke-reducerende sukker og af metalsalt af en uorganisk syre :
- 0 til 2 dele af silan,
- 0 til 20 dele af olie, fortrinsvis 4 til 15 dele,
- 35 - 0 til 20 dele af glycerol, fortrinsvis 0 til 10 dele,
- 0 til 5 dele af en silicone,
- 0 til 30 dele af et "udstrækningsmiddel" (FR: extendeur).
10. Akustisk og/eller termisk isoleringsprodukt på basis af mineraluld, især af glas eller af sten, slettet ved hjælp af slettemiddelsammensætningen ifølge et af kravene 1 til 9.
- 40 11. Filt af mineralfibre, især af glas eller af sten, slettet ved hjælp af slettemiddelsammensætningen ifølge et af kravene 1 til 9.

12. Fremgangsmåde til fremstilling af et akustisk og/eller termisk isoleringsprodukt på basis af mineraluld ifølge krav 10 eller af en filt af mineralfibre ifølge krav 11, hvor mineraluld eller mineralfibre fremstilles, ulden eller fibrene påføres en slettemiddelsammensætning, og ulden eller fibrene behandles ved en temperatur, der tillader krydsbinding af
- 5 slettemidlet og dannelse af varmebestandigt (FR: infusible) bindemiddel, k e n d e t e g n e t ved, at slettemiddelsammensætningen omfatter
- mindst et ikke-reducerende sukker og
 - mindst et metalsalt af en uorganisk syre valgt blandt alkalimetalsalte, jordalkalimetalsalte, overgangsmetalsalte eller hovedgruppemetalsalte af en uorganisk syre.

Fig. 1

