(19) DANMARK

Patent- og
Varemærkestyrelsen

(10) **DK/EP 3642169 T3**

(12) Oversættelse af europæisk patentskrift

(51) Int.Cl.: *C 03 C 25/32 (2018.01)* *C 03 C 25/14 (2018.01)* *D 04 H 1/587 (2012.01)*
D 04 H 1/60 (2006.01) *D 04 H 1/64 (2012.01)*

(45) Oversættelsen bekendtgjort den: **2022-11-14**

(80) Dato for Den Europæiske Patentmyndigheds
bekendtgørelse om meddelelse af patentet: **2022-10-26**

(86) Europæisk ansøgning nr.: **18748955.4**

(86) Europæisk indleveringsdag: **2018-06-04**

(87) Den europæiske ansøgnings publiceringsdag: **2020-04-29**

(86) International ansøgning nr.: **FR2018051288**

(87) Internationalt publikationsnr.: **WO2018234652**

(30) Prioritet: **2017-06-23 FR 1755761**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **SAINT-GOBAIN ISOVER, Tour Saint-Gobain , 12 place de l'Iris, 92400 Courbevoie, Frankrig**

(72) Opfinder: **SALOMON, Pierre, 31 Rue Adam Ledoux, 92400 Courbevoie, Frankrig**
AZEVEDO, Joël, 6, Avenue Hoche, 91190 Gif sur Yvette, Frankrig
JAFFRENNOU, Boris, 33 rue des Alouettes, 75019 Paris, Frankrig

(74) Fuldmægtig i Danmark: **Novagraaf Brevets, Bâtiment O2, 2 rue Sarah Bernhardt CS90017, F-92665 Asnières-sur-Seine cedex, Frankrig**

(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF ET ISOLERINGSPRODUKT FREMSTILLET UD FRA MINERALFIBRE**

(56) Fremdragne publikationer:
GB-A- 565 340
US-A- 2 619 475
DATABASE WPI Week 198712 Thomson Scientific, London, GB; AN 1987-080375 XP002784872, & CS 8 509 803 A (PRIDAL J) 15 janvier 1987 (1987-01-15)

METHOD FOR MANUFACTURING AN INSULATION PRODUCT MADE FROM MINERAL FIBRES

The present invention relates to a process for the manufacture of an insulating product based on mineral fibers bonded by a biosourced organic binder. The process makes possible in particular the manufacture of an insulating product comprising mineral fibers which are sensitive to acids without said fibers being detrimentally affected by the acidity of the organic binder. The invention also relates to the products obtained by such a process.

The manufacture of insulating products based on mineral fibers generally comprises a stage of manufacture of the fibers and a stage of assembling said fibers using a sizing composition.

The fibers can be manufactured by different processes. The most widely known method is centrifugal fiberizing (FR 2 500 492, FR 2 579 196, WO9110626, FR 2 443 436, FR 2 529 878), in which the molten mineral material is projected onto centrifuging wheels (FR 2 500 492, FR 2 579 196, WO9110626) or onto the walls of a centrifuge provided with a multitude of orifices (FR 2 443 436, FR 2 529 878) in order to form filaments under the action of centrifugal force. The filaments formed are subsequently drawn and then transported towards a receiving member in order to be deposited in the form of a web or of a mat of mineral fibers (or mineral wool).

In order to provide the web of fibers with a degree of cohesion, the fibers are coated with a sizing composition containing a thermosetting resin. A heat treatment, at a temperature generally of greater than 100 °C, makes it possible to carry out the curing or the polycondensation of the resin and to thus obtain a thermal and/or acoustic insulating product having specific properties, in particular a dimensional stability, a tensile strength and a thickness recovery after compression. The sizing composition to be projected onto the mineral wool is generally provided in the form of an aqueous solution containing the thermosetting resin and additives, such as in particular a catalyst for the crosslinking of the resin, an adhesion-promoting silane and a dust-preventing mineral oil. The sizing composition is generally applied on the fibers by spraying.

Regulations relating to human health and the environment expressly require or encourage the resin or the compounds which it contains or generates to have a reduced impact on the environment and the mineral fibers to be described as non-carcinogenic.

The thermosetting resins most commonly used in the manufacture of insulating products based on mineral fibers are formaldehyde-based resins (urea/formaldehyde, phenol/formaldehyde, melamine/formaldehyde resins). These resins are relatively inexpensive, soluble in water and capable of crosslinking under the abovementioned thermal conditions. However, they may still contain a certain proportion of free formaldehyde, the harmful effects of which are established by toxicological studies. These resins then form the subject of a treatment with urea in order to fix this free formaldehyde in the form of nonvolatile condensates. In point of fact, these condensates are unstable under the temperature conditions to which the webs of glass fibers are subjected. They may decompose to give formaldehyde and ammonia (itself produced from the degradation of the urea) which are released into the treatment atmosphere and then have to form the subject of capturing procedures in order to reduce their impact on the environment. Solutions for replacing formaldehyde-based resins in sizing compositions have been developed. A large number of them are based on the use of polymers of carboxylic acids and/or of saccharides (WO2012168619, WO2012072938, WO2009080938, US2011260094), ideally prepared from natural compounds resulting from sources which are renewable in the short term, in particular plant sources, or produced by microbial fermentation.

The carcinogenicity of mineral fibers depends on their biopersistence in the respiratory system of a living being, that is to say their ability to be removed and/or degraded naturally by the body. This biopersistence of mineral fibers is characterized in particular by their solubility in a pulmonary fluid. According to Regulation No. 1272/2008 of the European Parliament and of the Council, mineral fibers are not categorized as carcinogenic if, during in vivo tests, the mineral fibers with a length of greater than 20 µm have a biopersistence such that their half life is less than 10 days for a test by inhalation or less than 40 days for a test by intratracheal instillation.

Article 7 of the same regulation clearly encourages the replacement of the tests on animals by in vitro tests. Thus, in vitro tests which simulate the two pulmonary environments which an inhaled mineral fiber is liable to encounter have thus been developed. They have the objective of measuring the rate of dissolution of the fibers in physiological solutions at pH 7.4 (for example, a Gamble's solution which simulates the pulmonary fluid) and at pH 4.5 (for example, a solution which simulates the environment inside the phagolysosomes of macrophages and at the surface of activated macrophages). Examples of compositions of these physiological solutions are described in the following papers: Sebastian et al., Glass Science Technologies, 75(5): 263-270, 2002; Marques et al., Dissolution Technologies, 18(3): 15-28, 2011. The abstract WPI with the accession number (AN) 1987-080375 (see also the document CS 8 509 803 A) discloses an insulating element made of aluminosilicate fibers bound by an organic binder.

The document US 2 619 475-A discloses a process for manufacturing an insulation product based on mineral fibers with a sizing composition comprising a polymer based on furfuryl alcohol.

In the context of research studies targeted at developing more durable binders for mineral wools, that is to say binders based on compounds originating from natural resources which are renewable in the short term, problems of degradation of some mineral fibers soluble in an acidic physiological medium were encountered for some sizing compositions which contain acids, in particular polycarboxylic acids, or which release acids during the phase of crosslinking of the binder. This is in particular the case with acidic sizing compositions, which generally have a pH of between 1 and 5, during the contact thereof with the fibers, and which at least partially dissolve some fibers. Consequently, the mechanical properties of the final product may become mediocre.

The present invention solves these problems. It turns out that a specific biosourced resin makes it possible to advantageously replace the known binders for binding mineral fibers biosoluble at acidic pH. This resin is based on poly(furfuryl alcohol), a furfural derivative obtained by treatment of biomass. It makes it possible to efficiently bind mineral fibers biosoluble at pH 4.5 without dissolving them and to thus obtain mineral wool insulating products which observe the criteria of non-toxicity and which exhibit excellent mechanical properties. This result is also obtained with a neutralized resin based on poly(furfuryl alcohol).

The present invention more particularly relates to a process for the manufacture of an insulating product based on mineral fibers bonded by an organic binder, comprising the following stages:

a. the application of a sizing composition to said mineral fibers,

b. the formation of an assembly of said mineral fibers,

c. the heating of said assembly of mineral fibers until said sizing composition has cured (that is to say, crosslinked), so as to form an insoluble binder.

said process being characterized in that:

- said sizing composition comprises the following constituents within the limits defined below, expressed as fractions by weight with respect to the total weight of the composition:

○ from 80 % to 98 % of water,

○ from 2 % to 20 % of water-soluble poly(furfuryl alcohol),

○ less than 0.5 % of furfuryl alcohol, and

- said mineral fibers are fibers of aluminosilicate glass comprising aluminum oxide, Al_2O_3, in a fraction by weight of between 14 % and 28 %.

The resins used in the sizing composition which can be used according to the invention are furfuryl alcohol oligomers. They are water-soluble, that is to say miscible in any proportion with water. They are obtained by polycondensation of furfuryl alcohol in the presence of an acid catalyst. They generally exhibit an acidic pH between approximately 4.5 and 5.5, a low content of furfuryl alcohol (fraction by weight of less than 1 %) and a viscosity at 25 °C of less than 1000 mPa.s at a solids content of 75 % according to the Brookfield method described in Standard ASTM D2983. For the requirements of the invention, the resin can be diluted and/or additivated with pH-correcting agents.

The sizing composition which can be used according to the present invention thus essentially comprises:

- water,
- furfuryl alcohol oligomers, hereinafter known as poly(furfuryl alcohol),
- generally, but in a low proportion, residual unreacted furfuryl alcohol,
- and, optionally, a salt resulting from the neutralization of the organic or inorganic acid which has been used as polycondensation catalyst.

The sizing composition can contain a certain number of additives conventionally present in dilute sizing compositions intended to be applied to fibers. These additives can be added at the time of the dilution of the composition or to the concentrated composition before dilution with water. These additives must be chemically stable and must not react with the components of the sizing composition which can be used according to the present invention, when this sizing composition is stored under storage conditions similar to those used for the furfuryl alcohol resin which it contains. Examples of additives are:

- coupling agents chosen from functional silanes; a functional silane generally comprises at least one, preferably two or three, hydrolysable alkoxysilyl functional groups and at least one reactive functional group (oxirane, amine, hydroxyl, halide functional group) carried by a non-hydrolysable organic group bonded to the silicon atom by an Si-C bond;
- hydrophobic agents, for example silicones;
- dust-preventing agents, in particular mineral oils generally added in the form of an aqueous emulsion, optionally in the presence of one or more surface-active agents;
- flame retardants, for example of phosphate or organophosphate type;
- antistatic, softening or conditioning, or coloring agents;

- soluble or dispersible organic fillers (extenders) and also particulate solid additives, such as opacifying agents.

The fraction by weight of adjuvants and additives of the solid part of the sizing composition generally does not exceed 20 % to 25 %.

In the sizing composition of the present invention, the sum of the fractions by weight of the poly(furfuryl alcohol) and of the water is at least 95 %, preferably at least 96 %, in particular at least 97 % and ideally at least 98 %.

The fraction by weight of poly(furfuryl alcohol) in the sizing composition is between 2 % and 20 %, preferably between 5 % and 15 %.

These values for fractions by weight of water and poly(furfuryl alcohol) are necessary in order for the sizing composition to have a suitable viscosity, generally of less than a few tens of mPa.s at 25 °C according to the Brookfield method described in Standard ASTM D2983, in order to be able to be applied to the mineral fibers by spraying.

The residual content of furfuryl alcohol monomer of the solution of the present invention is preferably as low as possible. This is because furfuryl alcohol (CAS number 98-00-0) is a volatile organic compound (VOC) regarded as harmful by skin contact, inhalation and ingestion. The fraction by weight of furfuryl alcohol in the sizing composition is less than 0.5 %, preferably less than 0.1 %.

At high temperature, the resin included in the sizing composition crosslinks by polycondensation in the presence of an acid catalyst and forms an insoluble binder. Consequently, the sizing composition is generally acidic. However, it can be neutralized by the addition of a base in order to increase the stability on storage thereof, that is to say to reduce the rate at which the resin spontaneously reacts at the storage temperature so that its viscosity increases. Such a neutralization can be advantageous for the transportation or the storage of the sizing solution.

The sizing composition according to the invention thus has a pH of between 3.0 and 10.0, preferably between 4.0 and 9.0, in particular within the range from 5.0 to 8.5 and ideally within the range from 6.0 to 8.0.

The sensitivity of the fibers of aluminosilicate glass to acids depends on the content of aluminum oxide which they contain. In aluminosilicate glasses, the aluminum is in the Al^{3+} ionic form. The aluminum ions are "network formers" as they participate in the structure of the glass by forming coordination tetrahedra with the oxygen ions, one or more of said oxygen atoms being shared with coordination tetrahedra formed by the silicon in the Si^{4+} ionic form. In point of fact, aluminum oxide is an amphoteric compound, that is to say that it behaves both as a base and as an acid. This property has the consequence of rendering it particularly reactive, even when it is present in a glass. When a fiber of aluminosilicate glass comprising aluminum oxide is in contact with an acidic medium, said medium reacts preferentially with the aluminum ions, thus destroying the network which the Al^{3+} ions form with the silicon ions, and dissolving the glass. The aluminum oxide content of the fibers of aluminosilicate glass is thus an essential and determining characteristic of their degree of solubility in acidic media.

Fibers of aluminosilicate glass become soluble in acidic media when the fraction by weight of aluminum oxide which they contain is at least 14 %, in particular at least 16 %, indeed even at least 18 %. The maximum fraction by weight of aluminum oxide generally does not exceed a certain limit beyond which the manufacture of the fibers become particularly difficult. It is at most 28 %, preferably at most 26 %, indeed even at most 24 %.

In embodiments of the invention, it is advantageous for the mineral fibers of aluminosilicates to be more sensitive to acids in order to reduce their biopersistence such that their half life is less than certain values established by specific regulatory requirements or public health policies or also according to the manufacturer's own wish.

Some of these embodiments consist in adding other oxides to said mineral fibers or also in changing the fractions by weight of the oxides which they comprise.

According to a first embodiment, because silicon, in its ionic form, participates in the formation of the structure of said fibers, the fraction by weight of silicon oxide, SiO_2, which said fibers contain is adjusted. Thus, the sensitivity to acids increases when this fraction by weight is within the range extending from 32 % to 50 %, in particular from 33 % to 48 %, indeed even from 34 % to 46 %.

As aluminum and silicon both participate in the formation of the structure of the aluminosilicate glass, it is also possible to add silicon oxide so that the sum of the fractions by weight of the aluminum oxide Al_2O_3 and of said silicon oxide SiO_2 are within a certain interval of values. The sum of the Al_2O_3 and SiO_2 fractions by weight of said mineral fibers is preferably between 46 % and 78 %, in particular between 47 % and 76 %, indeed even between 48 % and 74 %.

In another embodiment of the invention, the composition of the mineral fibers can be such that the $Al^{3+}/(Al^{3+} + Si^{4+})$ molar ratio is greater than 0.25, in particular greater than 0.30, preferably greater than 0.35.

The fibers of aluminosilicate glass can additionally comprise other oxides, such as oxides of alkali metals and of alkaline earth metals. The alkali metals or alkaline earth metals have a role of modifying the network formed by the coordination tetrahedra around Si^{4+} and Al^{3+} ions. The sensitivity of the mineral fibers to acids can be affected by the nature and the amount of alkali metal and alkaline earth metal oxides.

The mineral fibers according to one embodiment of the present invention can thus comprise the oxides CaO and MgO, the sum of the fractions by weight of said oxides preferably being between 7 % and 32 %. They can also comprise the oxides Na_2O and K_2O in amounts such that the sum of the fractions by weight of said oxides is between 1 % and 15 %, preferably between 2 % and 15 %.

The aluminosilicate mineral fibers used in the present invention preferably exhibit a dissolution coefficient calculated from the amount of SiO_2 of said mineral fibers which is dissolved in a synthetic pulmonary fluid of pH 4.5, thermally regulated at 37 °C, after immersion in said fluid for 14 days. An experimental protocol which makes possible the calculation of such a dissolution coefficient is described in a very precise manner by Sebastian K. et al. in EURIMA test guideline: In-vitro acellular dissolution of man-made vitreous silicate fibers. Glass science and technology, 2002. 75(5): p. 263-270.

Fibers of aluminosilicate glass having a dissolution coefficient of greater than 100 $ng.cm^{-2}.h^{-1}$, in particular of greater than 200 $ng.cm^{-2}.h^{-1}$, preferably of greater than 400 $ng.cm^{-2}.h^{-1}$, satisfy the requirements of Regulation No. 1272/2008 of the European Parliament and of the Council. During *in vivo* tests, their half life is less than 10 days for a test by inhalation or less than 40 days for a test by intratracheal instillation.

In a preferred embodiment of the process of the invention, stage (a) of application of the sizing solution to the mineral fibers can be carried out by spraying by means of spray nozzles. The application of the sizing composition preferably precedes the assembling stage (b), during which the sized fibers are gathered together, for example in a mold or on a conveyor, before being heated, consecutively or extemporaneously, in order to crosslink and cure the binder. The fibers can be assembled:

- into flexible mats which can be rolled up and can be compressed or can be folded,

- into blocks or panels of fibers which are denser and more rigid than the mats which can be rolled up,

- into molded products based on fibers, for example linings of conduits or pipes,

- into nonwoven textiles, such as nonwoven mats of glass fibers.

Stage (c) of heating the assembly of fibers is preferably carried out at a temperature of between 100 °C and 250 °C for a period of time of between 1 minute and 10 minutes, preferably in a thermally regulated atmosphere.

Another subject-matter of the present invention is a product capable of being obtained by any one of the embodiments of the process of the invention. The product obtained, which will comprise a furfuryl alcohol polymer, will exhibit a dimensional stability, a tensile strength and a thickness recovery after compression which are superior to those of a product obtained according to the state of the art and comprising a binder based on polymers of carboxylic acids and/or saccharides, this being the case for one and the same type of mineral fibers having a fraction by weight of aluminum oxide between 14 % and 28 %.

The contribution of the present invention is clearly illustrated by the two examples described below and the figures to which these two examples refer.

Figure 1 is an electron micrograph of the interface between a flat mineral substrate having the composition Glass 1 and an organic coating obtained by crosslinking the sizing composition 1 (comparative).

Figure 2 is an electron micrograph of the interface between a flat mineral substrate having the composition Glass 1 and an organic coating obtained by crosslinking the sizing composition 2 (comparative).

Figure 3 is an electron micrograph of the interface between a flat mineral substrate having the composition Glass 1 and an organic coating obtained by crosslinking the sizing composition 3 (which can be used according to the invention).

Figure 4 is an electron micrograph of the interface between a flat mineral substrate having the composition Glass 2 and an organic coating obtained by crosslinking the sizing composition 1 (comparative).

Figure 5 is an electron micrograph of the interface between a flat mineral substrate having the composition Glass 2 and an organic coating obtained by crosslinking the sizing composition 2 (comparative).

Figure 6 is an electron micrograph of the interface between a flat mineral substrate having the composition Glass 2 and an organic coating obtained by crosslinking the sizing composition 3 (which can be used according to the invention).

In the examples, a sizing composition which can be used according to the invention is compared with two sizing compositions which are according to the state of the art and which do not make it possible to solve the technical problem. The sizing composition which can be used according to the invention was used on two glass compositions for mineral fibers sensitive to acids. For comparison purposes, the two sizing compositions according to the state of the art were used on the same two glass compositions for mineral fibers sensitive to acids.

The quality of the effect of the acidity of the sizing compositions was determined by comparing the quality of the interfaces formed between said sizing compositions, once cured or crosslinked, and the two glass compositions for mineral fibers put into the form of flat substrates. The use of flat substrates, instead of fibers, is preferred for practical reasons. This is because they make it possible to simulate the interface between the fibers and said sizing compositions and to make easier the observation thereof using a microscope. The quality of the interface provides qualitative information on the level of adhesion between the substrate and the fiber, in particular after an ageing test. In particular, the presence of cracks or of detachments will be the manifestation of a deterioration in the surface of the substrate by the sizing composition which has been deposited thereon.

The two glass compositions biosoluble at pH 4.5 used for the flat substrates are those presented in Table 1. The substrates were manufactured according to the usual methods of the glass industry. This table also shows the values of the sums of the fractions by weight, $Al_2O_3 + SiO_2$, $CaO + MgO$ and $Na_2O + K_2O$, of the $Al^{3+}/(Al^{3+} + Si^{4+})$ molar ratio and of the dissolution coefficient, k, calculated from the amount of SiO_2 of said glass fibers which is dissolved in a synthetic pulmonary fluid of pH 4.5, thermally regulated at 37 °C, after 14 days, according to the protocol which was referred to above.

The three sizing compositions, and also their pH values, are described in Table 2. The sizing compositions 1 and 2 correspond to sizing compositions according to the state of the art. The sizing composition 3 is a sizing composition which can be used according to the invention.

The sizing composition 1 is prepared in two stages:

a) maleic anhydride and tetraethylenepentamine are mixed in a first container and then the mixture is put in reserve at a temperature of between 20 °C and 25 °C for 15 minutes;

b) the mixture obtained in stage a), the sucrose, the ammonium sulfate and the silane are mixed with stirring until the constituents have completely dissolved.

The sizing compositions 2 and 3 are prepared by mixing all of the constituents in a single stage.

For the purposes of the tests, the sizing compositions have a greater concentration of resin than the sizing compositions used for the application to the mineral fibers. The concentration of each composition is chosen in order for the viscosity to be suitable for application to a flat substrate, and the conditions of the heat treatment are chosen in order for the kinetics of the possible reactions between said sizing compositions and said substrates to be accelerated. The same results can be obtained with sizing compositions exhibiting a greater degree of dilution of resin by allowing the water which they contain to further evaporate. The test is thus representative of the formation of a film of binder at the surface of the glass under the conditions of manufacture of the mineral wool.

The protocol used for the test of determining the quality of the effect of the acidity is as follows:

- cleaning the surfaces of the flat substrates with deionized water and with ethanol;

- flame treating said surface using a laboratory burner, so as to remove any contamination of organic nature;

- cooling the surfaces to ambient temperature;

- depositing the sizing compositions on the flat substrates by screen printing in order to form a cured or crosslinked coating having a thickness of approximately 20 µm;

- curing the samples thus manufactured at 210 °C for 20 min in a suitable oven, the oven having been preheated to 550 °C and then cooled in order to prevent any contamination of organic nature;

- accelerated ageing of the samples in an autoclave at 105 °C, 1.2 bars for 15 min;

- cutting the samples in cross section so as to be able to observe the interface between the organic coating and the flat substrate;

- observing the sections thus obtained using a scanning electron microscope, the acceleration voltage of which is set at 15 kV, the magnification of which is set at x10 000 and the detection mode of which is the secondary electron detection mode.

Table 1. Compositions of the glass fibers, expressed in fractions by weight of oxides.

	Glass 1	**Glass 2**
SiO_2	43	41.5
Al_2O_3	24.2	15.4
Na_2O	6.6	1.7
K_2O	4	1.5
CaO	14.5	25.6
MgO	1.5	6.4
Fe_2O_3	5.5	5.5
B_2O_3	-	-
P_2O_1	0.7	0.4
$Al_2O_3 + SiO_2$	67.2	56.9
CaO + MgO	16	32
$Na_2O + K_2O$	10.6	3.2
k ($ng.cm^{-2}.h^{-1}$)	~600	~250
$Al^{3+}/(Al^{3+} + Si^{4+})$	0.40	0.30

Table 2. Compositions of the sizing solutions, expressed in fractions by weight of the dry constituents.

	Composition 1 (comparative)	**Composition 2 (comparative)**	**Composition 3 (invention)**
Sucrose	34		
Tetraethylenepentamine	4.9		
Maleic anhydride	5.1		

Ammonium sulfate	6		
Maltitol		30.3	
Citric acid		24.6	
Poly(furfuryl alcohol)			66.3
Sodium hypophosphite		2.4	
Silane	2.5	2.4	2.5
Water	47.5	40.3	31.2
pH	6	1-2	5

Example 1

In the first example, the three sizing compositions of Table 2 were deposited on a flat substrate with the composition Glass 1 of Table 1 according to the protocol described above. Figures 1, 2 and 3 exhibit the electron micrographs of the interfaces obtained between said substrate and the three organic coatings respectively. The substrate is located at the bottom of the micrographs and the coating at the top. In Figures 1 and 2, which are obtained with sizing compositions according to the state of the art, the interfaces are degraded. In Figure 1, the interface is cracked and fractured. In Figure 2, the interface exhibits microcracks which propagate in the substrate and the organic coating. On the other hand, in Figure 3, which corresponds to a product obtained with a sizing composition which can be used according to the invention, the interface is smooth and flat and does not exhibit any cracking or detachment defect.

Example 2

In the second example, the three sizing compositions of Table 2 were deposited on a flat substrate with the composition Glass 2 of Table 1 according to the protocol described above. Figures 4, 5 and 6 exhibit the electron micrographs of the interfaces obtained between said substrate and the three organic coatings respectively. The substrate is located at the bottom of the micrographs and the organic coating at the top. In Figures 4 and 5, which are obtained with sizing compositions according to the state of the art, the interfaces are degraded. They are cracked and fractured with a pronounced separation of the material. On the other hand, in Figure 6, obtained with a sizing composition which can be used according to the invention, the interface is smooth and flat and does not exhibit any cracking or detachment defect.

Example 3

In the third example, two industrial insulating products were manufactured using two sizing compositions, one according to the state of the art and the other which can be used according to the invention. These two sizing compositions respectively correspond to the sizing compositions 1 and 3 with a greater dilution. The fractions by weight of their constituents are shown in Table 3. The composition of the mineral fibers on which these two sizing compositions were applied is that of Glass 1 of Table 1. The mineral fibers were coated with sizing composition before being assembled and heated at 200 °C. The density of the industrial products obtained is approximately 16 $kg.m^{-3}$. The fraction by weight of binder in the final product, obtained following the drying and the curing of the sizing compositions, is approximately 5 %.

The mechanical strength of the insulating products depends on the quality of the interfaces between the binder and the fibers. This quality can change over time with the ageing of the product. It can in particular degrade. This degradation increases as the degree of degradation of the mineral fibers by the binder or the degree of degradation of the binder itself increases. The measurement of the variations in the mechanical strength before and after ageing thus provides a qualitative and quantitative indication of the degree of degradation of the mineral fibers by the binder or of the degree of degradation of the binder itself.

For the purposes of demonstrating the advantages of the invention, the two insulating products were subjected to a climatic treatment for 15 minutes in a chamber thermally regulated at 105 °C with a relative humidity of 100 % in order to simulate their ageing in accelerated fashion. The tensile strength of the industrial insulating products, before and after climatic treatment, was measured using a mechanical test according to Standard ASTM C686-71T. Before and after climatic treatment, a series of samples was cut out from each product by stamping. The sample has the shape of a torus 122 mm long, 46 mm wide, with a radius of curvature of the cut of the outer edge equal to 38 mm and a radius of curvature of the cut 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 tensile strength is the ratio of the breaking force F, measured in newtons, to the weight W of the sample. The unit of the tensile strength is the newton/gram or N.g^{-1}.

The values of the mechanical strengths of the two products before and after climatic treatment are shown in Table 4. Before climatic treatment, the two insulating products have comparable tensile strength values. This is remarkable and all the more surprising as the size according to invention is 10 times more acidic than the size of the comparative example. After climatic treatment, the value of the tensile strength of the product 1, manufactured using a sizing composition according to the state of the art, decreases by 53 %, whereas that of the product 2, manufactured using a sizing composition which can be used according to the invention, only decreases by 14 %. After ageing, the loss in tensile mechanical strength is thus nearly four times smaller for a product capable of being obtained according to the invention than for a product capable of being obtained according to the state of the art.

Table 3. Compositions of the sizing solutions, expressed in fractions by weight of the dry constituents.

	Composition 1, diluted (comparative)	**Composition 3, diluted (invention)**
Sucrose	3.9	
Tetraethylenepentamine	0.5	
Maleic anhydride	0.6	
Ammonium sulfate	0.7	
Poly(furfuryl alcohol)		5.8
Furfuryl alcohol		< 0.02
Silane	0.3	0.2
Water	94	94

Table 4. Tensile strengths (N.g^{-1}) of the industrial insulating products manufactured using the sizing compositions of Table 3.

	Product 1 (comparative)	**Product 3 (invention)**
Composition of the mineral fibers	Glass 1	Glass 1
Sizing composition	Composition 1, diluted	Composition 3, diluted
Tensile strength		
Before climatic treatment	3.8 $N.g^{-1}$	3.6 $N.g^{-1}$
After climatic treatment	1.8 $N.g^{-1}$	3.1 $N.g^{-1}$

PATENTKRAV

1. Fremgangsmåde til fremstilling af et isoleringsprodukt på basis af mineralfibre, der er sammenklæbet med et organisk bindemiddel, hvilken fremgangsmåde omfatter følgende trin:

a. påføring af en limningssammensætning på mineralfibrene,

b. dannelse af en samling af mineralfibrene,

c. opvarmning af samlingen af mineralfibre, indtil limningssammensætningen er hærdet, **kendetegnet ved, at:**

– limningssammensætningen omfatter følgende bestanddele inden for de nedenfor definerede grænser, udtrykt som vægtfraktioner i forhold til sammensætningens samlede vægt:

○ fra 80 % til 98 % vand,

○ fra 2 % til 20 % vandopløselig poly(furfurylalkohol) og

○ mindre end 0,5 % furfurylalkohol, og

– summen af vægtfraktionerne af poly(furfurylalkohol) og af vand er med fordel mindst 95 %, og

– mineralfibrene er fibre af aluminiumsilicatglas, der omfatter aluminiumoxid, Al_2O_3, i en vægtfraktion på mellem 14 % og 28 %.

2. Fremgangsmåde ifølge krav 1, således at mineralfibrene har en vægtfraktion af SiO_2 på mellem 32 % og 50 %.

3. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at summen af Al_2O_3- og SiO_2-vægtfraktionerne af mineralfibrene er mellem 46 % og 78 %.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at mineralfibrene har et $Al^{3+}/(Al^{3+} + Si^{4+})$-molforhold på mere end 0,25, især på mere end 0,30, fortrinsvis på mere end 0,35.

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at mineralfibrene desuden omfatter oxiderne CaO og MgO, idet summen af vægtfraktionerne af oxiderne er mellem 7 % og 32 %.

6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at mineralfibrene desuden omfatter oxiderne Na_2O og K_2O, idet summen af vægtfraktionerne af oxiderne er mellem 1 % og 15 %.

7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at mineralfibrene har en opløsningskoefficient på mere end 100 $ng.cm^{-2}.h^{-1}$, især på mere end 200 $ng.cm^{-2}.h^{-1}$, fortrinsvis på mere end 400 $ng.cm^{-2}.h^{-1}$, idet opløsningskoefficienten beregnes ud fra den mængde af SiO_2 i mineralfibrene, der er opløst i en syntetisk lungevæske med en pH-værdi på 4,5, termisk reguleret ved 37 °C, efter 14 dage.

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at summen af vægtfraktionerne af poly(furfurylalkohol) og af vand er mindst 95 %, fortrinsvis mindst 96 %, især mindst 97 % og ideelt mindst 98 %.

9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at indholdet af furfurylalkohol i limningssammensætningen er mindre end 0,1 %.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at limningssammensætningen yderligere omfatter én eller flere adjuvanser, der fortrinsvis er valgt blandt koblingsmidler, støvforebyggelsesmidler, hydrofobe midler, retardanter, antistatiske midler, blødgøringsmidler, konditionerende midler, farvegivende midler eller opakiseringsmidler.

11. Fremgangsmåde ifølge krav 10, således at vægtfraktionen af adjuvanser og tilsætningsstoffer i faststofdelen af limningssammensætningen ikke overstiger 25 %, fortrinsvis 20 %.

12. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at limningssammensætningen udviser en pH-værdi på mellem 3,0 og 10, fortrinsvis mellem 4,0 og 9,0, især mellem 5,0 og 8,5 og ideelt mellem 6,0 og 8,0.

13. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at påføringen af limningssammensætningen ifølge trin a) på mineralfibrene udføres ved påsprøjtning ved hjælp af sprøjtedyser.

14. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, således at trin c) omfatter opvarmning af samlingen af mineralfibre ved en temperatur på mellem 100 °C og 250 °C i et tidsrum på mellem 1 minut og 10 minutter, fortrinsvis i en termisk reguleret atmosfære.

15. Produkt, der kan opnås ved en fremgangsmåde ifølge et hvilket som helst af de foregående krav.

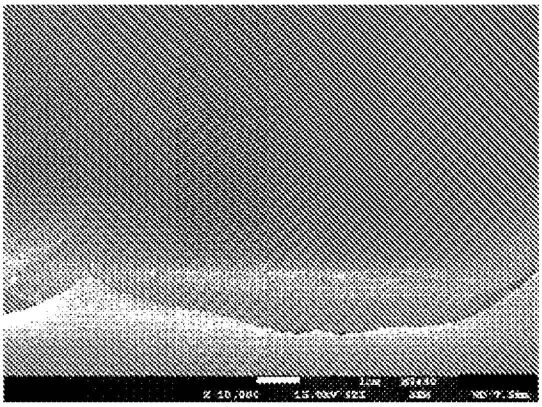

FIG. 1

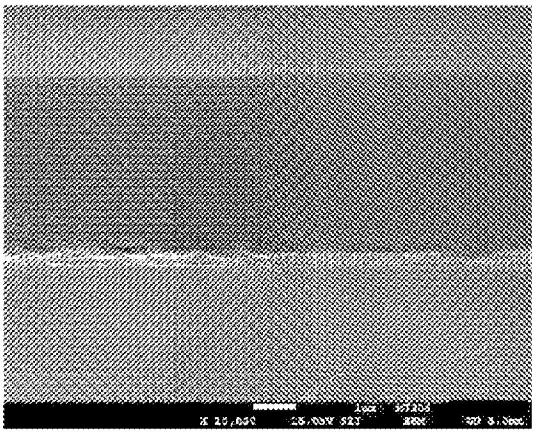

FIG. 2

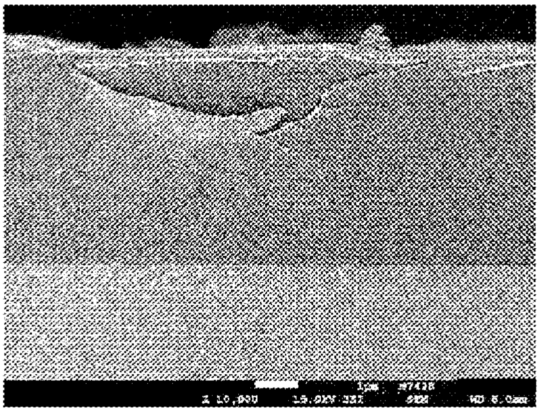

FIG. 3

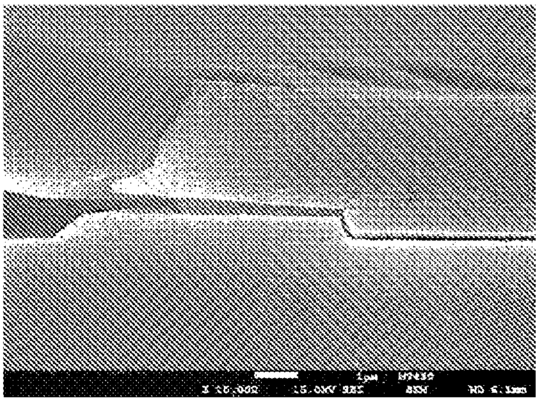

FIG. 4

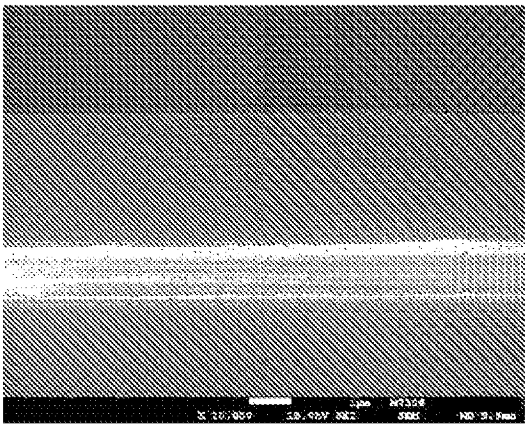

FIG. 5

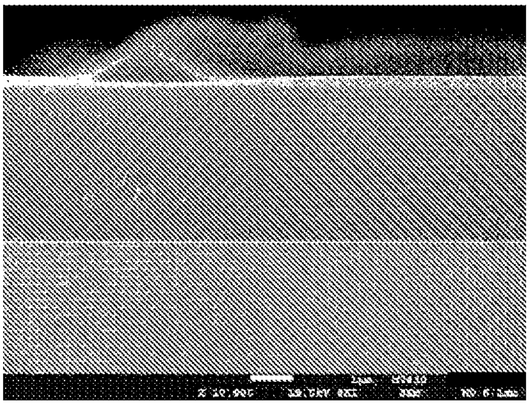

FIG. 6